Characterization of Novel Co-Anhydride cured Epoxy Resins

by

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Abstract

Epoxy resins are widely used as coatings, encapsulations, structural composites, castings, and adhesives in a number of electrical applications. Recently, novel uncatalyzed co-anhydride cured epoxy formulations that exhibit a high performance property profile, have been introduced. The objective of this thesis was to perform a comprehensive material characterization of these new resin/hardener combinations, which are potentially used as electrical insulation material in medium and high voltage engineering.

The thermal cure behaviour of commercial tetracyclidyl-diamino-diphenylmethane (TGDDM) and a co-anhydride mixture consisting of maleic anhydride (MA) and hexahydrophthalic anhydride (HHPA) was extensively studied. Different analytical real-time methods, such as FT-Raman spectroscopy, differential scanning calorimetry, and chemo-rheological methods were applied to investigate the principal polymerization mechanism and the related curing kinetics. It was demonstrated that kinetic parameters that were based on isothermal measurements provided consistent and reliable results. On the other hand the general limitations of different dynamic methods for kinetic parameter calculations were outlined and discussed. Temperature modulated differential scanning calorimetry provided a powerful technique to confirm a TGDDM/MA and TGDDM/HHPA sub-network structure of the co-anhydride cured epoxy. A generalized time-temperature-transformation-diagram was developed in order to predict the complex material transformations (e.g. gelation and vitrification) occurring during the entire isothermal curing process.

In the selected system, the mechanical deformation and fracture behaviour as a function of temperature, strain rate, inorganic filler fraction, particle size, and filler/matrix-adhesion were thoroughly studied by using compression-, tension- and double torsion fracture-tests. The potential of hyperbranched polymers (HBPs) as low viscosity toughening modifiers for highly crosslinked anhydride-cured epoxy networks was experimentally evaluated. The effects of the HBP molecular structure, in particular the specific shell chemistry, on thermo-mechanical properties, final morphology, and blend concentration, were assessed. For the neat investigated epoxy-system the most efficient toughening modifier was obtained for a molecular HBP-design that provided a pseudo-homogeneous blend morphology. Thus, by using suitable HBPs in a concentration of 20% w/w, the fracture toughness, expressed by the critical stress intensity factor ($K_{IC}$) of 0.58 MPam$^{0.5}$, was increased by over 50% to 0.88 MPam$^{0.5}$. The corresponding Young’s modulus and glass transition temperature were only affected to a limited extent by the addition of the HBP-additive. The
toughest epoxy blend (critical stress intensity factor of about 1.6 MPa m^0.5) was achieved by the incorporation of 60% w/w inorganic silica particles. The application of hybrid concepts by utilizing synergistic toughening mechanisms (HBP and silica), revealed only moderate benefits within the investigated highly crosslinked materials.

As the examined epoxy/anhydride formulations are generally considered for high temperature applications, it was essential to determine their long-term thermo-oxidative ageing performance. The long-term thermo-oxidative ageing behaviour has been investigated by means of thermo-gravimetric analysis (TGA), dynamic mechanical analysis (DMA) and vibrational infrared spectroscopy (FT-IR) methods with special emphasis on fundamental understanding of the ageing mechanism. Effects of the thermal ageing on the characteristic viscoelastic and flexural behaviour, weight-loss and oxidation susceptibility of the examined epoxy networks were assessed and discussed, thus providing an understanding of the principal material endurance properties.

The thermo-mechanical behaviour and the related structural changes with thermal ageing were examined by Cole-Cole plots in combination with a molecular theory previously developed by Perez. It was demonstrated that this new methodology provides a connection between conversion, glass transition temperature, and mechanical relaxation data and allows a fundamental molecular interpretation with respect to physical and chemical ageing phenomena.

A variety of thermo-gravimetric experiments were carried out in order to determine and model the specific weight-loss profile as a function of anhydride nature and ageing temperature. The influence of different inorganic fillers on the thermo-oxidative response was systematically studied. Different models were applied to extract meaningful kinetic parameters in order to describe the thermo-oxidative degradation and to facilitate an extrapolation of weight-loss data outside the experimental time- and temperature-scale.

FT-IR micro ATR-spectroscopy was used to identify, localize and quantify the complex oxidation behaviour. A thermo-oxidative degradation mechanism, that involved predominantly radical oxidation processes and C-N as well as C-O chain scissions, was proposed to account for the experimental observations. Specific oxidation-front profiles were constructed to describe the heterogeneous oxidation processes.

Finally, the comprehensive material characterization of these novel co-anhydride-cured amino-glycidyl resins in terms of curing mechanism and kinetic, deformation and fracture behaviour, and thermo-oxidative ageing performance, allows the
assessment of the potential of these materials for demanding applications in electrical and electronic industries.
## Contents

1 Introduction & scope of work .......................... 1  
1.1 Classification and history of epoxy thermosets ......................................................... 1  
1.2 Scope and survey of this thesis ........................................................................... 5  
1.3 References .......................................................................................................... 6  

2 Epoxy-anhydride crosslinking reaction ................. 8  
2.1 Introduction ......................................................................................................... 8  
2.1.1 The uncatalyzed epoxy/anhydride curing reaction ........................................... 9  
2.1.2 The base catalyzed epoxy/anhydride curing reaction ....................................... 10  
2.2 Experimental ....................................................................................................... 13  
2.2.1 Materials .......................................................................................................... 13  
2.2.2 Sample preparation .......................................................................................... 15  
2.2.3 Wide angle x-ray diffraction (WAXD) ........................................................... 15  
2.2.4 Differential scanning calorimetry (DSC) ........................................................... 15  
2.2.5 Gas chromatography (GC) ................................................................................. 15  
2.2.6 Temperature modulated differential scanning calorimetry (TMDSC) ............... 16  
2.2.7 Chemorheological analysis .............................................................................. 16  
2.2.8 Fourier-Transform Raman Spectroscopy (FT-Raman) ..................................... 17  
2.3 Results & discussion ........................................................................................... 17  
2.3.1 Phase behaviour of the binary MA-HHPA mixture ............................................ 17  
2.3.2 Curing reaction studied by differential scanning calorimetry (DSC) ............... 19  
2.3.2.1 Non isothermal DSC .................................................................................... 19  
2.3.2.2 Isothermal DSC ........................................................................................... 26  
2.3.2.3 Temperature modulated differential scanning calorimetry (TMDSC) ............ 32  
2.3.2.4 Relationship between glass transition temperature and conversion ........... 34  
2.3.3 Curing reaction studied by chemo-rheology ..................................................... 35  
2.3.4 Curing reaction studied by FT-Raman spectroscopy ....................................... 40  
2.3.4.1 Functional group analysis ............................................................................ 41  
2.3.4.2 Rate curves and kinetics analysis ................................................................... 51  
2.3.4.3 Cure mechanisms ....................................................................................... 54  
2.3.5 Time-Temperature-Transformation (TTT) ......................................................... 55  
2.4 Concluding remarks ............................................................................................ 58  
2.5 References .......................................................................................................... 60  

3 Deformation and fracture behaviour ....................... 63  
3.1 Introduction to fracture toughness ........................................................................... 63  
3.2 Linear elastic fracture mechanics (LEFM) ............................................................... 64  
3.2.1 Strain energy release rate criterion (G-Approach) ............................................ 64  
3.2.2 Stress intensity factor (K-Approach) .................................................................. 67  
3.2.3 Fracture toughness test modes .......................................................................... 68  
3.3 Toughening of epoxy thermosets ........................................................................... 69  
3.3.1 Epoxy toughening with soft particles (rubber toughening) ................................ 69  
3.3.2 Epoxy toughening with hard inorganic particles ............................................. 72  
3.3.2.1 Crack pinning mechanism of hard particles ................................................. 73  
3.3.3 Epoxy toughening with thermoplastics ............................................................. 75  
3.4 Experimental ........................................................................................................ 79  
3.4.1 Materials .......................................................................................................... 79
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.4.1.1 Hyperbranched polymers (HBP) modifier</td>
<td>79</td>
</tr>
<tr>
<td>3.4.1.2 Inorganic filler</td>
<td>81</td>
</tr>
<tr>
<td>3.4.2 Sample preparation</td>
<td>82</td>
</tr>
<tr>
<td>3.4.3 Double torsion test (DT)</td>
<td>83</td>
</tr>
<tr>
<td>3.4.4 Tensile test</td>
<td>85</td>
</tr>
<tr>
<td>3.4.5 Compression test</td>
<td>85</td>
</tr>
<tr>
<td>3.4.6 Dynamic mechanical analysis (DMA)</td>
<td>86</td>
</tr>
<tr>
<td>3.4.7 Microscopy</td>
<td>86</td>
</tr>
<tr>
<td>3.5 Results &amp; discussion</td>
<td>87</td>
</tr>
<tr>
<td>3.5.1 Effects of strain rate and temperature on the tensile deformation</td>
<td>87</td>
</tr>
<tr>
<td>3.5.2 Effect of the filler fraction on the tensile deformation</td>
<td>89</td>
</tr>
<tr>
<td>3.5.3 Effect of strain rate and temperature on the compressive deformation</td>
<td>91</td>
</tr>
<tr>
<td>3.5.4 Characterization of the fracture toughness behaviour</td>
<td>94</td>
</tr>
<tr>
<td>3.5.4.1 Effect of the test temperature</td>
<td>94</td>
</tr>
<tr>
<td>3.5.4.2 Effect of the strain rate</td>
<td>98</td>
</tr>
<tr>
<td>3.5.4.3 Effect of the inorganic filler fraction</td>
<td>99</td>
</tr>
<tr>
<td>3.5.4.4 Effect of the inorganic filler size</td>
<td>103</td>
</tr>
<tr>
<td>3.5.4.5 Effect of the filler/matrix adhesion</td>
<td>106</td>
</tr>
<tr>
<td>3.5.5 Hyperbranched polymer toughening</td>
<td>107</td>
</tr>
<tr>
<td>3.5.5.1 Effects of the hyperbranched polymer end-groups</td>
<td>107</td>
</tr>
<tr>
<td>3.5.5.2 Hyperbranched polymer modifier with a high epoxy functionality</td>
<td>109</td>
</tr>
<tr>
<td>3.5.5.3 Hyperbranched polymer modifier with a low epoxy functionality</td>
<td>114</td>
</tr>
<tr>
<td>3.6 Concluding remarks</td>
<td>120</td>
</tr>
<tr>
<td>3.7 References</td>
<td>122</td>
</tr>
<tr>
<td>4 Thermo-oxidative degradation behaviour</td>
<td>127</td>
</tr>
<tr>
<td>4.1 Introduction to thermo-oxidative degradation</td>
<td>127</td>
</tr>
<tr>
<td>4.1.1 Physical ageing of epoxy-networks</td>
<td>127</td>
</tr>
<tr>
<td>4.1.2 Thermo-oxidative degradation of epoxy-networks</td>
<td>128</td>
</tr>
<tr>
<td>4.2 Principals of dynamic mechanical analysis (DMA)</td>
<td>131</td>
</tr>
<tr>
<td>4.3 Experimental</td>
<td>135</td>
</tr>
<tr>
<td>4.3.1 Materials</td>
<td>135</td>
</tr>
<tr>
<td>4.3.2 Isothermal ageing experiments</td>
<td>136</td>
</tr>
<tr>
<td>4.3.3 Dynamic mechanical analysis (DMA)</td>
<td>136</td>
</tr>
<tr>
<td>4.3.4 Thermal gravimetric analysis (TGA)</td>
<td>136</td>
</tr>
<tr>
<td>4.3.5 Mechanical bending test</td>
<td>137</td>
</tr>
<tr>
<td>4.3.6 FT-IR micro attenuated total reflection (ATR) spectroscopy</td>
<td>137</td>
</tr>
<tr>
<td>4.4 Results and discussion</td>
<td>138</td>
</tr>
<tr>
<td>4.4.1 Mechanical endurance during thermo-oxidative ageing</td>
<td>138</td>
</tr>
<tr>
<td>4.4.1.1 Dynamic mechanical behaviour of the virgin state</td>
<td>138</td>
</tr>
<tr>
<td>4.4.1.2 Effects of thermo-oxidative ageing on the dynamic mechanical behaviour</td>
<td>141</td>
</tr>
<tr>
<td>4.4.1.3 Effects of thermo-oxidative ageing on the flexural behaviour</td>
<td>146</td>
</tr>
<tr>
<td>4.4.2 Short-term thermo-oxidative stability</td>
<td>149</td>
</tr>
<tr>
<td>4.4.2.1 Effects of the molar anhydride to epoxy ratio</td>
<td>153</td>
</tr>
<tr>
<td>4.4.3 Long-term thermo-oxidative stability</td>
<td>154</td>
</tr>
<tr>
<td>4.4.3.1 Effects of inorganic fillers</td>
<td>156</td>
</tr>
<tr>
<td>4.4.3.2 Modeling the isothermal weight-loss behaviour</td>
<td>159</td>
</tr>
<tr>
<td>4.4.3.3 The Double-Stage Mechanism (DSM)</td>
<td>159</td>
</tr>
<tr>
<td>4.4.3.4 The Fickian diffusion model</td>
<td>165</td>
</tr>
<tr>
<td>4.4.4 Thermo-oxidative degradation studied by FT-IR spectroscopy</td>
<td>168</td>
</tr>
<tr>
<td>4.4.4.1 Thermo-oxidation profiles</td>
<td>173</td>
</tr>
<tr>
<td>4.4.5 Thermo-oxidative degradation mechanism</td>
<td>176</td>
</tr>
</tbody>
</table>
4.5 Concluding remarks ................................................................. 179
4.6 References ............................................................................. 181

5 General conclusions and perspectives 185

6 Acknowledgments 188

7 Curriculum Vitae (CV) 189
Disclaimer

The work contained in this thesis has not been previously submitted for a degree or diploma at any higher education institute. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person except where due reference is made.

Signature: (Jens Rocks)

Date: 4. October 2004
Chapter 1

1 Introduction & scope of work

1.1 Classification and history of epoxy thermosets

Epoxy monomers are molecules that contain at least two or more epoxy groups. The prefix “epoxy” refers to a planar bridge consisting of an oxygen atom bonded to two carbon atoms in a way that a three membered ring is formed, see Figure 1. Such a chemical structure is also known as oxirane, ethoxyline or glycidyl group. Further specific information on the functional epoxy group can be found elsewhere [1, 2]. Most uncured epoxies are thermoplastic resins that have little value until they are reacted with crosslinking agents.

![Epoxy functional group](image)

Figure 1: Epoxy functional group

The epoxy group can undergo an extremely wide variety of chemical reactions and combine with a vast array of other materials to produce final products with wide ranging properties [3, 4]. One of the main features of the epoxy resin is that the ring opening reaction (cure) and the formation of an interconnected three-dimensional molecular network, takes place in the presence of many different bi- or multifunctional compounds, e.g., anhydrides, amines, polyphenols etc. that are able to react with the epoxy functional group. The choice of a curing agent depends on a variety of factors including cost, processing method, curing conditions, environmental limitations and the mechanical, chemical, electrical and thermal properties desired in the cured resin.

The reaction rate as well as the temperature at which an epoxy resin cures or hardens depends upon the curing agent selected. In general, polyfunctional aliphatic amines (e.g. diethylenetriamine or trimethylenetetramine), polysulfides and polyamido-amines are used when ambient-temperature cures (T<80°C) are desired. In contrast, aromatic amines, anhydrides, phenolics, ureas, imidazoles and other resinous hardeners generally require processing at elevated temperatures (T>80°C) to effect a cure. Certain hardeners allow a partial curing at room temperature, but require an elevated temperature to complete the cure. Catalytic curing agents, such as Lewis acids and bases, function as initiators for epoxy resin homopolymerization. A thorough explanation of the manifold epoxy resin chemistry can be found in standard textbooks [3-6] and thermoset handbooks [7, 8].
In their cured form, epoxy resins belong to the class of highly crosslinked polymers, also called thermosets or thermosetting polymers, which are an important group of synthetic polymers. The main difference between thermosets and other organic polymers such as thermoplastics and elastomers is in their three-dimensional densely crosslinked structures, i.e., an “infinite” molecular network with covalently bonded junction points having functionalities greater than two. Cured resins do not melt, but soften to a rubbery state at temperatures near and above the glass-transition temperature. In general, raising the crosslink density results in a higher glass-transition temperature and a higher continuous-use temperature; however, it reduces the flexibility of the cured resin.

Since their first commercial introduction in 1947, epoxy resins (EP) have experienced tremendous growth on a commercial sale. Rather than becoming a commodity item, epoxy resins have developed into engineering plastics, fulfilling the requirements in many different applications. Today, their global share in the world plastic market is about 0.5% corresponding to a consumption of roughly 1 billion metric tons per year [9] (Table 1).

The main areas of epoxy monomer consumption are in coatings, surface protection and electrical and electronics applications. Coatings are usually applied as liquid or solution type varnishes in severe corrosive environments, as powder coatings for sheet steels in consumer goods and by cathodic electro-deposition from aqueous bath onto car bodies. In the building industry, epoxies are becoming more and more important for the repair and conservation of concrete structures [10]. Electrical insulation is a traditional area for epoxy use [11]. High voltage insulators, impregnated coil insulation and electrical laminates are the most striking examples. Advanced structural composites based on glass, aramid or carbon fibers and epoxy matrixes as well as structural adhesives [12] are also very important. The market volume is, however, for the latter applications still very small. In Figure 2, the market shares for different application areas are given.
Today, the most frequently used epoxy resin is produced from epichlorohydrin and bisphenol-A. Known as conventional or DGEBA-type resins (see structure I in Figure 3), these diglycidyl ethers of bisphenol-A (and their higher molecular weight homologs) still account for about 80-85% of the total worldwide epoxy consumption. Although DGEBA-type resins comprise the majority of epoxy consumption, four other types of basic epoxies are of commercial importance. These include, as shown in Figure 3, (II) brominated resins, (III) novolac resins, (IV) cycloaliphatic resins and (V) phenoxy resins.

Figure 2: Epoxy resin consumption by end use in 1995 [13]

Figure 3: Commercial types of basic epoxies (I) diglycidyl ether of bisphenol-A (DGEBA), (II) brominated epoxy resins, (III) epoxy novolac (EN), (IV) cycloaliphatic epoxy resin (CEP), (V) phenoxy resin
Brominated epoxies are ignition-resistant compounds produced from epichlorohydrin (or low- molecular weight DGBPA resin) and halogenated bisphenol-A (e.g., tetrabromobisphenol-A). Brominated epoxies have grown in commercial importance over the past fifteen years and are now used extensively in the production of laminates for printed circuit boards.

Novolac epoxies include primarily polyglycidyl ethers of phenol-formaldehyde or cresol-formaldehyde resins. The diglycidyl ether of bisphenol-A is the simplest member of this family. When cured, epoxy novolacs have better high-temperature properties and chemical resistance than conventional epoxy resins. Epoxy novolacs are used in electrical laminates and encapsulations, moldings and castings and reinforced plastics requiring high chemical resistance.

Cycloaliphatic epoxy resins are usually non-glycidyl ethers that can be produced by the peracetic acid epoxidation of cyclic olefins. Advantages of these resins over conventional or novolac epoxies include lower viscosities, higher heat-distortion temperatures, lower dielectric constants and excellent weatherability. Cycloaliphatic epoxy resins are particularly useful for electrical applications (e.g., as replacements for porcelain in insulators) and for filament-wound structures. The flexibilized versions are also recommended for high-performance non-electrical applications.

Phenoxy resins are high-molecular-weight polymers (30'000-200'000 g/mole) derived from epichlorohydrin and bisphenol-A. Even if they use the same raw materials as conventional epoxies, they lack terminal epoxy groups. Although small relative to the total epoxy resin market, phenoxy resins are used in coatings and adhesives and in binders for magnetic tapes.

The remaining part of epoxy resins production comprises specialties. These include multifunctional epoxies (e.g. glycidyl amines), aliphatics, glycidyl imides and glycidyl esters. Together these types of epoxies are believed to comprise, at most, 5% of the epoxy market.

Research and development activities related to epoxy resins, however, by far exceed their purely quantitative significance on the market. The main reason is a unique combination of desirable properties, e.g. high glass transition temperature, high elastic modulus and mechanical strength, excellent resistance to corrosion and chemicals, good dielectric properties, high creep resistance and generally good performance at elevated temperatures, making epoxies suitable for use in applications with high mechanical, thermal and chemical demands. Recent developments in epoxy resin chemistry and applications have concentrated more on further improvement of existing products rather than looking for new syntheses.
1.2 Scope and survey of this thesis

For more than three decades, silica, dolomite, wollastonite and alumina filled, anhydride cured epoxy systems have been extensively used in the electrical power engineering industry. The main application areas include medium and high voltage insulation for gas insulated switchgears, generator circuit breakers, dry type distribution transformers, dry type bushings and high voltage cable accessories. Required material properties in the power electrical engineering industry include high electrical insulation resistance, high mechanical strength and modulus, low creep under thermo-mechanical loads, as well as high damage tolerance with reasonable toughness. Moreover, miniaturization and increased performance demands have led to higher operating temperatures over the years. Today, continuous operating temperature levels are at 105°C with guaranteed lifetimes up to 30 years.

Fierce competition on the electrical market has led to development of more compact power equipment with higher performance ratings. However, this substantially requires materials with continuous operating temperatures in the range of 150°C. Presently used insulation organic materials cannot withstand these relatively high thermo-mechanical requirements. Consequently, new insulating systems with higher glass transition temperatures ($T_g$) and hence higher continuous operating temperatures are needed.

In 1974, Graham and O’Conner have shown that a non-catalyzed epoxy resin formulation can be cured with a co-anhydride mixture at relatively low curing temperatures, while yielding a high thermo-mechanical property profile ($T_g>200°C$) [14]. Later Vohwinkel and co-workers extended the initial work of Graham and O’Conner and proposed a variety of further co-anhydride/epoxy systems [15] that show a potential for highly demanding electrical insulation applications. The high $T_g$ of these materials is here combined with high mechanical strength, high Young’s modulus ($E$), very good electrical insulation resistance and excellent processing and rheological properties. The ultimate $T_g$ of these systems can be well above 200°C demonstrating that continuous operating temperatures of 150°C are feasible. Furthermore, reduction in processing time and low temperatures for curing and post-curing make this new class of epoxy materials very attractive for a wide range of industrial applications.

The main objective of the thesis is to identify the potential and limitations of these co-anhydride/epoxy formulations for structural parts in the electro-technical industry. This required combining a wide range of material issues including polymer chemistry, polymerization mechanism and kinetics, rheology, thermodynamics, morphology and physical and mechanical properties in order to establish a comprehensive material characterization and more fundamental understanding of the material.
In Chapter 2, the general curing reactions between anhydride and epoxy are reviewed. A specific study of the liquid-solid transition occurring during the crosslinking reaction is discussed. In particular the chapter focuses on the analysis of the chemical and structural changes taking place during the in-situ polymerization by using real-time calorimetric, spectroscopic Raman scattering, and chemo-rheological analytical methods. Kinetic analysis from the conversion of the functional groups and the obtained empirical rate curves are discussed in the light of proposed reaction mechanisms for the thermal cure behaviour of the investigated uncatalyzed co-anhydride/epoxy-systems.

Chapter 3 discusses the thermo-mechanical deformation and fracture behaviour of the new materials. The possibility of overcoming the intrinsic brittleness of the current highly crosslinked networks by selecting alternative toughening additives is illustrated by using hyperbranched thermoplastics with functionalized end-groups. Furthermore, the influence of inorganic particles as externally added filler is elaborated in more detail. The obtained morphologies of the polymer composites and the effects on the deformation and toughening probability are outlined.

Chapter 4 presents a specific study on the long-term behaviour of the material during thermo-oxidative ageing. In particular, structural network changes occurring during ageing at elevated temperature are discussed by taking into account the changes of intrinsic chemical structures, as well as gravimetric, and viscoelastic alterations. On the basis of experimental observations a model allowing a reasonable prediction of an expected long-term property profile is created and verified.

1.3 References

Chapter 2

2 Epoxy-anhydride crosslinking reaction

2.1 Introduction

The curing of epoxy resins is an important reaction for the manufacture of structural parts, in particular for electrically insulating materials. A cure reaction can be described as initial chain formation, followed by linear growth and branching, gelation, and finally vitrification to a crosslinked, infinite network.

Presently, multifunctional aromatic or aliphatic amines are mainly used as curing agents for epoxy resins. Consequently, the curing behaviour and kinetics of amine-cured epoxy systems have been intensively studied by many different analytical methods such as differential scanning calorimetry (DSC) [1], gel permeation chromatography (GPC) [2], nuclear magnetic resonance (NMR) [3], and vibrational spectroscopy [4, 5], rheological analysis [6], and dielectric thermal analysis [7, 8], respectively, yielding an extensive knowledge of the reaction mechanisms involved. However, the use of amine curing agents has the general disadvantage that new polar functional groups are created and subsequently relatively high amounts of polar groups, e.g. water, can be absorbed. Hence, this behaviour can significantly influence the final property profile (i.e. mechanical and dielectric properties) of the glassy material and restricts the use of the materials in numerous technical applications such as medium and high voltage insulation.

The formation of polar groups does not occur when carboxylic acid anhydrides are used as the curing agent. Carboxylic acid anhydrides were among the first curing agents used with epoxy resins [9] and their generalized structure is given in Figure 4. Today the group of anhydrides has achieved a significant commercial importance due to a combination of their cure profiles and cured properties. Consequently, after amines, acid anhydrides constitute the next most commonly used class of curing agents.

![Figure 4: Anhydride functional group](image)

Figure 4: Anhydride functional group
In contrast to amine curing agents, anhydride reactions with epoxy are usually characterized by a low exothermal reaction, low shrinkage, low internal stresses, reduced water absorption, high glass transition temperatures and excellent electrical properties. Moreover, these properties are retained even under moderate to high operating temperatures due to the good thermal stability [9-11]. On the other hand most anhydride-epoxy curing reactions are less reactive and relatively high reaction temperatures (≥120°C) are required to initiate and propagate the curing reaction [12-14]. This results in very expensive processing and handling steps. Although the selection of anhydride/epoxy systems for many technical applications is essential, the formation and structure of the cured products is much less understood than in epoxy/amine-systems. Especially, information on the curing behaviour of multifunctional glycidyl resins in the presence of cyclic carboxylic acid anhydrides is rather limited.

The objective of this chapter is to study the curing kinetics and mechanism of a novel epoxy/co-anhydride-system by different analytical methods. Dynamic calorimetric experiments are performed and the obtained results are used for the extraction of the appropriate kinetic parameters for the analysis of cure. Isothermal calorimetry, chemorheometry, and FT-Raman spectroscopy are carried out, in order to compare the different analytical methods and outline underlying assumptions and limitations. Moreover, real-time vibrational FT-Raman spectroscopy, as a complementary method to DSC and rheometry, provides additional functional group information that is used to identify the curing mechanism of the epoxy/maleic anhydride/hexahydrophthalic anhydride-system.

Finally, the complex physical changes occurring during cure of the epoxy resin are visualized by means of a principal Time-Temperature-Transformation (TTT) diagram.

### 2.1.1 The uncatalyzed epoxy/anhydride curing reaction

The epoxy group is characterized by its reactivity towards nucleophilic and electrophilic species and thus it is reactive to a wide range of reagents. The formation of polyester from the uncatalyzed reactions of epoxy monomers and cyclic carboxylic acid anhydrides has been intensively studied during the last years [15]. The research resulted in a generally accepted stepwise reaction mechanism that occurs during the non-catalyzed polymerization [16-19] as schematically shown in Figure 5. The mechanism involves the presence of hydroxyl groups, which act as an initiator for the reaction. The hydroxyl groups are mostly present as substituents on a fraction of the epoxy resin molecules. An attack of these hydroxyl groups on the anhydride molecules forms a monoester having a free carboxyl group (reaction I). The monoester then reacts with the epoxide to yield a diester and a new secondary hydroxyl group (reaction II), thus starting the cascade of curing reactions.
(reaction III). The evidence that the quantities of mono- and diester produced are equal to
the amount of consumed anhydride confirmed these reaction sequences. Moreover, the fact
that no significant difference in the consumption of epoxy and anhydride groups [20] has
been observed at least up to gelation supports the proposed reaction scheme.
The observation that the number of epoxy groups at higher conversions decreases faster
than the increase in the diester groups can be attributed to the etherification reaction. This
reaction occurs between the epoxy and hydroxyl groups under the catalytic influence of
anhydride or carbonyl groups (reaction IV), and constitutes a significant side reaction. Other
side reactions, such as the epoxy homopolymerization, are also possible but these are
considered of little significance here as the curing temperatures are well below 180°C for the
studied TGDDM system [5].

\[
\begin{align*}
\text{COO} \quad & + \quad \text{R1} \quad \text{OH} \quad \rightarrow \quad \text{COO} \quad \text{R1} \\
\text{COOH} \quad & + \quad \text{CH}_{2} \quad \text{CH} \quad \text{CH} \quad \text{CH}_{2} \quad \text{R2} \quad \rightarrow \quad \text{COO} \quad \text{R1} \quad \text{CHCHCH}_{2} \quad \text{OH} \\
\text{COO} \quad & + \quad \text{CHCHCH}_{2} \quad \text{RO} \quad \rightarrow \quad \text{COO} \quad \text{R1} \quad \text{H}_{2} \quad \text{C} \quad \text{R2} \\
\text{H}_{2} \quad \text{OH} \quad & + \quad \text{R2} \quad \text{OH} \quad \rightarrow \quad \text{R2} \quad \text{CHCHCH}_{2} \quad \text{R1}
\end{align*}
\]

Figure 5: Schematic mechanism (reaction (I) to (III)) of uncatalyzed epoxy/acid-anhydride
addition reaction as suggested by Fisch and Hofmann [16, 21, 22]. The hydroxyl group is
present in the epoxy resin. The etherification reaction (reaction (IV)) occurs at higher
temperatures and is catalyzed by anhydride or carbonyl groups.

### 2.1.2 The base catalyzed epoxy/anhydride curing reaction

To accelerate the curing reaction for industrial processing, strong Lewis bases, such as
tertiary amines, imidazoles or ammonium salts are usually used to catalyze the cure of
epoxy resins with cyclic carboxylic acid anhydrides. A review of some of the postulated
reactions for the catalyzed epoxy/anhydride polymerization is given and discussed in this
section.
The initiation mechanism is still a matter of controversy and several reaction models are
available. Irrespective of the different proposed mechanisms three types of initiation have
been proposed so far [15, 23, 24]: (1) ionic mechanism according to Fischer, (2) initiation with the participation of pre-existing proton donor, and (3) Tanaka’s mechanism of initiation by the proton donor arising in the reaction.

According to Fischer [25] and several other workers, the reaction catalyzed by the presence of tertiary amines is initiated by the activation of the anhydride. It was proposed that the anhydride undergoes a nucleophilic attack by the lone electron pair of the tertiary amine, giving rise to a zwitterion containing a quaternary ammonium salt and a carboxylate anion as shown in Figure 6 in reaction (V). This activated tertiary amine complex may be considered as the real initiator of the chainwise co-polymerization. Further propagation occurs either through the reaction of the generated carboxylate with an epoxy group and the accompanied formation of new alkoxide anion (reaction VI) or with another anhydride under regeneration of a carboxylate (reaction VII), see Figure 6.

The generated alkoxide group is supposed to react at a very fast rate with another anhydride group and regenerate species containing carboxylate as active center. This suggests the initiation of an anionic strictly alternating copolymerization as later shown by Trappe et al. [26]. The fact that the presence of alkoxide anions could not be detected by NMR, was explained by their fast reaction rate with anhydrides [23, 27].

The presence of termination and chain transfer steps has been proposed in the literature [10, 15, 28] to account for the fact that molecular weights are lower than those expected for an ideal living polymerization. A possible mechanism involving the regeneration of the tertiary amine is shown in Figure 6, reaction (VIII). The regenerated tertiary amine becomes available to initiate a new chain.
Tanaka and Kakiuchi [20] proposed that the curing reaction requires the presence of proton donor (HA) as a catalyst, which forms a complex with the amine according to the reaction scheme illustrated by reaction (IX) to (XII) in Figure 7:

Additionally, Tanaka and Kakiuchi [29] stated, that the reaction might also be initiated in the absence of an external proton donor because of the formation of a proton donor during the isomerization of the epoxy to a derivative of alkyl alcohol as shown in reaction (XIII) in Figure 8.
Luston and Manasek [30, 31] also proposed the formation of allyl-alcohol derivatives by isomerization of epoxide. The hypothesis, which was based on conductivity measurements, presumed that the active site for the polymerization is a three-component complex that contains amine, epoxide, and anhydride as shown in reaction (XIV) and (XV) in Figure 9. However, in contradiction Antoon and Koenig [24, 32] did not confirm the formation of allyl-alcohol groups during the base-catalyzed reaction between an epoxy and anhydride by using different spectroscopic methods.

![This image is not available online. Please consult the hardcopy thesis available from the QUT Library.](image)

Figure 9: Initiation step of a catalyzed anhydride/epoxy co-reaction according to Luston and Manasek [30]

Although the various epoxy/anhydride/amine-systems in the above discussion are extremely similar, a generally accepted reaction mechanism of the complicated base catalyzed curing reaction between anhydrides of epoxies is not available at the present time. However, most authors agree that the reaction mechanism of the epoxy/anhydride catalyzed with tertiary amine is an anionic one and that propagation proceeds via two reactions: (1) acylation and (2) the reaction between epoxide and carbonyl derivatives [20, 23, 25, 27, 29, 30, 33-35]. There is still no definite validation regarding the question whether the initiator remains chemically bound during the whole course of the reaction. Some authors describe a release of the initiator [28, 29] but there is disagreement on this point [36, 37]. The fact that the competing epoxy-homopolymerization is effectively suppressed has been independently reported in literature [20, 24, 25].

### 2.2 Experimental

#### 2.2.1 Materials

A commercial multifunctional aminoglycidyl-resin, Araldite®MY721 (Vantico, Switzerland) mainly based on N,N,N',N'-tetraglycidyl-4,4'-diamino-diphenylmethane (TGDDM) was used as epoxy monomer for all investigations. Araldite®MY721 is most commonly synthesized by a reaction that involves several sequences as shown in Figure 10. In this sequence the
stepwise reaction of 4,4'-diaminodiphenylmethane (DDM) with a slight excess of epichlorohydrin yields chlorohydrin which is subsequently dehydrochlorinated with sodium hydroxide to form epoxy groups [38, 39].

\[
\begin{align*}
\text{NH}_2 \text{CH}2\text{NH}_2 + 4 \text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} & \rightarrow \left[ \text{ClCH}_2\text{CH}_2\text{CH}_2\text{N} \right]_2 \left[ \text{N} \text{CH}2\text{CH}_2\text{CH}_2\text{N} \right]_2 \\
& \quad + 4 \text{NaOH}
\end{align*}
\]

Figure 10: Idealized reaction scheme for the synthesis of N,N,N',N'-tetraglycidyl-3,3'-4,4'-diamino-diphenylmethane (TGDDM)

An anhydride hardener mixture consisting of maleic anhydride (MA) and hexahydrophthalic anhydride (HHPA), both supplied by Fluka, was used to cure the TGDDM resin. MA is a white crystalline solid with a theoretical molecular weight of 98.16 g/mole and a melting point of 53°C. HHPA is a waxy solid having a theoretical molecular weight of 154.17 g/mole and melting point of about 35°C. The chemical structures of the used materials are shown in Table 2. The mixing ratio, unless other stated, was 100/48/32 (TGDDM/MA/HHPA) by weight, reflecting a molar anhydride to epoxy ratio, \( r \), of 0.8.

<table>
<thead>
<tr>
<th>Chemical name /Tradename</th>
<th>Chemical structure</th>
<th>Molecular weight [g/mole]</th>
<th>Weight fraction [%]</th>
<th>Molar fraction [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N,N,N',N'-Tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM); Araldite® MY721</td>
<td><img src="image1" alt="Chemical Structure" /></td>
<td>468</td>
<td>55.55</td>
<td>55.09</td>
</tr>
<tr>
<td>Maleic anhydride (MA)</td>
<td><img src="image2" alt="Chemical Structure" /></td>
<td>98.16</td>
<td>26.67</td>
<td>31.53</td>
</tr>
<tr>
<td>Hexahydrophthalic anhydride (HHPA)</td>
<td><img src="image3" alt="Chemical Structure" /></td>
<td>154.17</td>
<td>17.78</td>
<td>13.38</td>
</tr>
</tbody>
</table>

*) Determined by potentiometric titration according to DIN 16945 standard
2.2.2 Sample preparation

The epoxy monomer was preheated to 65°C to reduce the viscosity of the MY721-resin, before the premixed hardener-mixture was added and dissolved with an Ultraturrax™ high shear mixer at 13,500 rpm for 5 minutes to obtain a homogeneous mixture. To prevent a temperature rise and any further reactions during mixing, all samples were cooled during the mixing process in ice water. Afterwards, the mixture was degassed for 3 minutes at pressures below 100 mbar and stored in liquid nitrogen in order to prevent further curing.

2.2.3 Wide angle x-ray diffraction (WAXD)

X-ray diffraction graphs were recorded at room temperature using a Siemens D-5000 instrument, operated at 50 KV and 50 mA with a Ni-filtered Cu-Kα radiation source. The scanning speed and step size were 0.05°/s and 0.05°. Intensities were quantified with a Braun position sensitive counter. The samples were placed on a background-free amorphous glass plate and analyzed as produced.

2.2.4 Differential scanning calorimetry (DSC)

The epoxy mixture (10±2 mg) was filled in sealed aluminum pans with a pin-hole in the lid and stored in liquid nitrogen to prevent further curing. All measurements were carried out on a Perkin-Elmer differential scanning calorimeter, Model DSC-7. The continuous heating scans were performed at heating rates (\(\phi\)) of 2.5, 5, 7.5, 10, 15 and 20°C/min, respectively, in a temperature range from –60°C to 300°C. Isothermal scans were accomplished at 100, 110, 120, 140 and 160°C. The reaction was considered complete when the rate curve leveled off to a baseline. The total area under the exothermal curve, based on the extrapolated baseline at the end of the reaction, was used to calculate the isothermal heat of cure at a given temperature. The experimental data were analyzed for the kinetic models using a least squares curves fitting routine based on the Marquardt-Levenberg algorithm. In each case the fitted data were verified for the presence of a global minimum, so that the values of the kinetic rate parameters obtained from the fit were “best values”.

2.2.5 Gas chromatography (GC)
A two column micro gas chromatograph (MTI M200H) equipped with a 8 m Poraplot Q and a 10 m molecular sieve (5 Å) column was used to separate the trapped gaseous products during isothermal cure at 65°C. Helium with a flow rate of 10 ml/min was used as a carrier gas. Continuous data acquisition was carried out every 3 minutes until the samples reached the point of gelation.

2.2.6 Temperature modulated differential scanning calorimetry (TMDSC)

Temperature modulated DSC (TMDSC) is a novel thermal analysis technique, which clearly separates thermal transitions that have reversing and non-reversing components with respect to a small amplitude temperature oscillation [40, 41]. This is accomplished by imposing a sinusoidal temperature modulation on top of a constant underlying heating rate or constant temperature. When the temperature is oscillated around a constant underlying heating rate or temperature, the response of the sample consists of an oscillating heat flow, which has both reversing and non-reversing components. A discrete Fourier transformation is then used to deconvolute the signal into a conventional DSC curve and to separate the reversing and non-reversing components. Additionally, the separation of the heat flow into its components facilitates determination of heat capacity from a single MDSC experiment as opposed to multiple conventional DSC experiments.

TA Instruments DSC 2910 Differential Scanning Calorimeter with the MDSC capability was used to study the epoxy systems. In all experiments the cooling accessory was used to facilitate accurate temperature control and to achieve sub-ambient temperatures at –60°C. A temperature ramp at a constant heating rate of 1°C/min and an underlying modulation with a 0.2°C amplitude, and a period of 60 seconds under nitrogen purge at 40 ml/min was used in all experiments.

2.2.7 Chemorheological analysis

A dynamic rheometer (Bohlin CVO75) was used to determine the rheological characteristics of the studied epoxy formulations. Complex viscosity, \( \eta' \), storage modulus, \( G' \) and loss modulus \( G'' \) were obtained by oscillatory shear measurements. All measurements were carried out in a plate–plate configuration (diameter=40 mm; gap=0.3 mm) at temperatures of 30, 40, 50, 60, 70, 80, 90, 100 and 110°C, respectively. Isothermal dynamic tests were performed to determine the time to gelation, as the time where the storage (\( G' \)) and loss (\( G'' \)) moduli cross over (\( \tan \delta = 1 \)), at a constant frequency, \( \omega \). All tests were made at a frequency of 1 Hz and a strain of 3%. The temperature reached the set point 1min after sample insertion. The steady state temperature was kept within 0.5°C of the set point.
2.2.8 Fourier-Transform Raman Spectroscopy (FT-Raman)

All spectroscopic experiments were carried out on a Perkin-Elmer System 2000 NIR FT-Raman spectrometer, powered by a diode pumped Nd-YAG laser (λ=1064 nm) as an excitation source and a room temperature InGaAs photoelectric detector. The backscattered radiation was collected at 180° to the excitation. Typical spectra were recorded in a range of 200 to 3800 cm\(^{-1}\) at a laser power of 320 mW. Every 4 minutes a spectrum was collected consisting of 32 co-added scans with spectral resolution of 8 cm\(^{-1}\). The premixed epoxy mixture (4±0.2 g) was filled in a NMR sample tube and placed in the preheated heating block under isothermal conditions at 55, 65, 75, 100, and 120°C, respectively. The steady state temperature was controlled with an accuracy of ±0.2°C. Spectra were recorded from the moment the tube was introduced in the heating block. To reach the ultimate conversion some samples were also post-cured at 150°C for 1 hour.

2.3 Results & discussion

2.3.1 Phase behaviour of the binary MA-HHPA mixture

The phase behaviour of the various MA-HHPA mixtures was analyzed using continuous heating DSC analysis and X-ray diffraction (XRD) techniques at room temperature as shown in Figure 11. The DSC scans in Figure 11(a) show two phenomena. First, the continuous decrease in the melting temperature of the HHPA-rich phase with increasing HHPA content. Second, the presence of a constant melting temperature at round 7°C, indicating that the phase diagram (see Figure 12) of both anhydrides has a eutectic point between a molar MA fraction of 0.2 and 0.4. The XRD data in Figure 11(b) also reveal a depression in the melting point of the eutectic temperature below room temperature. Consequently, only a broad amorphous peak centered at around 2θ=17° was observed between the molar maleic anhydride fractions of 0.2 to 0.5 in the MA/HHPA system.
Figure 11: (a) Continuous heating DSC-thermograms ($\varphi=10^\circ$C/min) of the system maleic anhydride and hexahydrophthalic anhydride (MA/HHPA) as a function of the MA fraction, indicative of eutectic phase behaviour. (b) XRD-data of the system maleic anhydride and hexahydrophthalic anhydride (MA/HHPA) as a function of the MA fraction measured at room temperature.

The behaviour of the experimentally determined melting point as a function of the MA-content in the binary MA/HHPA phase diagram is shown in Figure 12. The continuous lines in this plot represent the decrease of the melting point for the ideal situation, and were calculated using the Flory-Huggins equation (2.1), assuming zero interaction energy, and using the theoretical melting points (MA=55.2°C, HHPA=31.8°C) and melting enthalpies from the pure anhydrides (MA=14038 J/mol and HHPA=15456 J/mol):

$$\frac{1}{T_m^\varphi} - \frac{1}{T_m} = \frac{R}{\Delta H} \ln \varphi$$  \hspace{1cm} (2.1)

The excellent agreement between the experimental and predicted phase behaviour in Figure 12, confirms the ideal mixing assumption (zero interaction energy), which was used for the theoretical prediction.
2.3.2 Curing reaction studied by differential scanning calorimetry (DSC)

Thermal curing kinetics of epoxy systems has been the subject of many studies in the past [1, 42-51]. The most common way to study curing is to use differential scanning calorimetry (DSC). DSC is a powerful technique that provides information about the exothermicity of the epoxy ring opening reaction. Assuming that there are no other enthalpic events contributing to the heat flow than the chemical curing reaction, the absolute recorded value of heat flow, \( \frac{|dH|}{dt} \), is proportional to the reaction rate or rate of conversion, \( \frac{d\alpha}{dt} \): \[
\frac{|dH|}{dt} = \frac{d\alpha}{dt}
\] (2.2)

Considering the validity of this basic assumption, the DSC technique can be used to study the curing kinetics of the investigated thermosets.

2.3.2.1 Non isothermal DSC

The overall cure behaviour of the MY721 in combination with only pure MA or HHPA and the mixture of both hardeners was followed by DSC with a continuous heating rate of \( \varphi = 10^\circ \text{C}/\text{min} \). The obtained results are shown in Figure 13. It was observed that all systems react in an exothermic manner. The combination of both hardeners results in a single exothermal event and no overlapping exothermic doublet peak was detected in the kinetic DSC-scan, which confirms the existence of a quasi-eutectic hardener mixture. Furthermore,
if only MA is used as hardener, the exothermic peak temperature ($T_m \approx 160^\circ \text{C}$) is lower than when HHPA ($T_m \approx 220^\circ \text{C}$) alone is used as hardener showing that MA reacts faster with MY721.

Besides, directly after adding maleic anhydride to the epoxy resin a visible change in color from light yellow to a deep red-brown was observed. It is proposed that the observed discoloration can be related to the interaction between MA and the tertiary amine structure of the used TGDDM-molecule (see Table 2). This tertiary amine-activated color change in maleic anhydride containing polymers has been described for the first time by Martz et al. [52]. The authors reported that all anhydrides, which contain a carbon-carbon unsaturation in direct conjunction with the anhydride ring, e.g. maleic anhydride, give in combination with tertiary amines dark colored solutions. Later McCormick and Chang [53] proposed that the color change mechanism was based on the formation of zwitterions intermediates; while Panarin and Sevetlova [54] hypothesized that maleic anhydride interacts with the tertiary amine to give charge transfer complexes.

![Figure 13: Continuous DSC heating thermogram ($\varphi=10{^\circ \text{C/min}}$) of pure anhydride (MA and HHPA) and co-anhydride (MA/HHPA) MY721-resin system. The stoichiometric anhydride/epoxy ratio is r=0.8 for all systems.](image)

The influence of different heating rates on the curing behaviour of the MY721/MA/HHPA-system is illustrated in Figure 14. To compare the different runs, the measured heat flow, $dH/dt$ [W], was normalized by the sample weight, $m$ [g], and the heating rate, $\varphi$ [°C/s]. The resulting unit is the specific heat, [J/g°C]. The exothermal peak area in a plot of the specific heat as a function of temperature represents the reaction enthalpy of curing. In addition, the broad exothermal reaction above 250°C, reflects the onset of thermal degradation reactions, which is in accordance with earlier results from Morgan et al. [5] for TGDDM-based epoxy...
systems. The increased heating rate shifted the onset-, peak- and offset- temperatures of the curing reaction to higher temperatures. Also, it reduced the peak height, the peak area and therefore the exothermic reaction enthalpy ($\Delta H_{\text{tot}}$), see table in Figure 14. This kind of dependency is in accordance with other studies on epoxy-systems [55-58], but the decrease in $\Delta H_{\text{tot}}$ with increased heating rate was less than 20%, which is much less than the change of $\sim$40% observed for the MY721/MA/HHPA-system here.

![Figure 14: Dynamic DSC scans at different heating rates ($\varphi$=2.5, 10 and 20°C/min) of the unreacted MY721/MA/HHPA-system(r=0.8), directly after mixing.](image)

Consequently, the large difference in the total reaction enthalpy ($\Delta H_{\text{tot}}$) values is attributed to the specific behaviour of MA in the investigated system. This can been seen in Figure 15 which shows the behaviour of $\Delta H_{\text{tot}}$ as a function of heating rate for the MY721/HHPA-, MY721/MA- and MY721/MA/HHPA-system with a fixed anhydride to epoxy ratio of r=0.8. For the MY721/HHPA-system an increase in $\Delta H_{\text{tot}}$ of about 15% with increased heating rates ranging from 2 to 20°C/min can be observed. On the other hand the MY721/MA-system shows a significant decrease in $\Delta H_{\text{tot}}$ by about 134% when varying the heating rate in the same range. This significant increase in the total reaction enthalpy at decreased heating rates may be attributed to the higher temperatures attained in these samples, due to the decomposition of maleic anhydride. In addition, maleic anhydride may homopolymerize [59] in the presence of nitrogen bases, i.e. the TGDDM structure, so providing a contribution to the total heat flow that is not directly linked to the curing reaction.
Evidence on a significant amount of volatiles that were already lost at relatively low curing temperatures at 65°C was given by *in-situ* gas chromatography (GC), see Figure 16. During cure mainly water (H$_2$O) and carbon dioxide (CO$_2$) were released, which can be attributed to the spontaneous decarboxylation of maleic anhydride, since no H$_2$O and only very small traces of CO$_2$ were detectable by the same GC-method when using only HHPA as pure curing agent (Figure 16). This observation is in agreement with previous studies [59-61], although the exact mechanism remains unclear. Davie *et al.* [61] postulated that the decomposition of liquid maleic anhydride is activated by the presence nitrogen bases (here the tertiary amine structure of TGDDM structure, see Table 2).

The significant shift in the baseline of the thermograms in Figure 14 at the higher heating rates may reflect the artifacts due to the side reactions described above. As will be noted later, the significant differences between dynamic DSC methods and isothermal techniques can arise from high temperature reaction pathways not encountered during the normal isothermal cure process.
The single heating method as proposed by Barrett [42], based on the following general expression used in the analysis of dynamic DSC data, where the rate of conversion \( \frac{d\alpha}{dt} \) and the rate constant \( k \) lead to the following expression:

\[
\frac{d\alpha}{dt} = kf(\alpha) \quad (2.3)
\]

At a given time during the DSC scan \( t \) and temperature \( T \), \( f(\alpha) \) is a function of the fractional conversion \( \alpha \) and is assumed for a reaction of \( n \)-th order to be as follows:

\[
f(\alpha) = (1 - \alpha)^n \quad (2.4)
\]

The apparent rate constant \( k \) is assumed to have an Arrhenius dependence on temperature, as given in eqn (2.5):

\[
k = A \exp\left(-\frac{E_a}{RT}\right) \quad (2.5)
\]

where \( A \) is the frequency factor, \( E_a \) the apparent activation energy, \( R \) the universal gas constant and \( T \) the absolute temperature.

The combination of eqns (2.3) and (2.4) and transformation into the logarithmic form leads to the following expression:

\[
\ln\left(\frac{\frac{d\alpha}{dt}}{(1 - \alpha)^n}\right) = \ln(A) - \frac{E_a}{RT} \quad (2.6)
\]

If the reaction order \( n \) is known Barrett [42] proposed a plot of the left-hand side of eqn (2.6) against the inverse temperature, \( 1/T \). The appropriate value for the apparent activation energy can then be obtained by the linear regression.
To calculate the reaction order \( (n) \), eqn (2.7) can be rearranged and the derivative taken with respect to \( \ln(1-\alpha) \), yielding to the Freeman-Carroll relation in term of fractional conversion [45]:

\[
\frac{d\ln(\alpha/dt)}{d\ln(1-\alpha)} = -\frac{E_a}{R} \left[ \frac{d(1/T)}{d\ln(1-\alpha)} \right] + n
\]

(2.7)

By use of the Freeman-Carroll relationship (eqn (2.7)) the reaction order \( (n) \) and the activation energy \( (E_a) \) was calculated. The kinetic parameters obtained for the Freeman-Carroll method by linear regression for different constant heating rates are listed in Table 3. The average values for the activation energy \( (E_a) \) and the reaction order \( (n) \) are \( E_a=113.2\pm13.3 \) kJ/mole and \( n=2.0\pm0.2 \), respectively.

With the calculated reaction order of \( n=2.0 \), the Barrett relation (eqn (2.6)) was plotted as shown in Figure 17. The linear regression yielded the activation energies \( (E_a) \) and the frequency factors \( (\ln A) \), which are tabulated in Table 3 as well. The average of the overall activation energy and the frequency factor is \( E_a=112.6\pm5.3 \) kJ/mole and \( \ln A=27.4\pm1.6 \), respectively.

![Figure 17: Typical Barrett plot (eqn (2.6)) of the MY721/MA/HHPA-system with an anhydride to epoxy ratio of \( r=0.8 \). Experimental data were obtained from a continuous heating scan \( (\varphi=10^\circ C/min) \).](image-url)
Table 3: Reaction order, $n$, and activation energy, $E_a$, calculated using the Freeman-Carroll relation eqn (2.3). The average value of the reaction order, $n=2.0$, was used to calculate the activation energy and the frequency factor using the Barrett relation eqn (2.6).

<table>
<thead>
<tr>
<th>Heating rate, $\phi$ [°C/min]</th>
<th>Freeman-Carroll Relation</th>
<th>Barrett Relation with $n=2.0$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reaction order, $n$</td>
<td>Activation energy, $E_a$ [kJ/mole]</td>
</tr>
<tr>
<td>20</td>
<td>2.3</td>
<td>135.1</td>
</tr>
<tr>
<td>15</td>
<td>1.9</td>
<td>100.9</td>
</tr>
<tr>
<td>10</td>
<td>1.9</td>
<td>114.4</td>
</tr>
<tr>
<td>5</td>
<td>1.8</td>
<td>111.0</td>
</tr>
<tr>
<td>2.5</td>
<td>2.0</td>
<td>104.5</td>
</tr>
</tbody>
</table>

The calculated values for the activation energies obtained by the Barrett- and the Freeman-Carroll relations are consistent. This is not too surprising, since the Freeman-Carroll relation (eqn (2.7)) is only the derivative with respect to $\ln(1-\alpha)$ of the Barrett eqn (2.6). The relatively high values of the obtained overall activation energies have been noted before [50, 51, 57]. The discrepancy can be probably attributed to the fact that a single pair of Arrhenius parameters may not adequately describe the temperature dependence of the epoxy cure rate. Furthermore, the two single-heating models are predicated on the assumption that simple $n$-th order kinetic is able to describe the entire cure reaction of the investigated epoxy-anhydride system. It is known that many systems show autocatalysis (described by eqn below) and so the value of the above methods for analyzing a single-temperature-scanned DSC curve is rather limited.

Other phenomenological multiple-heating methods, as originally proposed by Kissinger [44], and by Ozawa [46], have shown that these methods are also effective for both $n$-th order reaction and autocatalysis. Both models are fairly similar and based on the assumption that the reaction rate at a constant extent of conversion is only a function of temperature ($iso$-conversion approach) and therefore eqn. (2.8) applies:

$$\left[ \frac{d \ln(d\alpha/dt)}{dT^{-1}} \right] = \frac{E_a}{R} \frac{E_a}{R}$$

(2.8)

The Kissinger method describes the relation, that for a crosslinking reaction, the extent of conversion at the peak temperature, $T_m$, is constant and independent of the heating rate ($\phi$), thus eqn (2.9) yields:

$$\frac{d\left[\ln\left(\frac{T}{T_m}\right)\right]}{d\left(\frac{T}{T_m}\right)} = -\frac{E_a}{R}$$

(2.9)

In contrast Ozawa's approach yields a simple relation between the activation energy ($E_a$), heating rate ($\phi$), and $iso$-conversion temperature:
Since both methods are independent of the reaction order, \( n \), the calculated activation energies from iso-conversional models are able to provide the activation energy over the entire course of reaction as shown in Figure 18.

![Graph showing activation energy as a function of fractional conversion](image)

**Figure 18:** Activation energy \( (E_a) \) as a function of fractional conversion \( (\alpha) \) as calculated by the Ozawa method eqn (2.10) for the MY721/MA/HHPA-system \( (r=0.8) \).

However, both theories reduce the complexity of a multi-step curing reaction to a single reaction path by ignoring the reaction order, \( n \), thus the calculated activation energies \( E_a=63.5 \text{ kJ/mole (Kissinger)} \) and \( E_a=67.3 \text{ kJ/mole (Ozawa)} \), respectively can only be considered as approximate values. Therefore, although the Ozawa and Kissinger methods yield almost identical values, they are at variance with the values obtained by the Barrett and Freeman-Carroll relations. Such deviation has been previously reported by Rogers and Smith [51], in the calculation of the activation energy for the decomposition of hexahydro-1,3,5-trinitro-s-triazine where a divergence of up to 46% between the methods was observed.

### 2.3.2.2 Isothermal DSC

Isothermal DSC experiments have been used in several studies to determine various kinetic parameters [1, 50, 55, 62-71]. To describe the curing kinetics of thermosetting materials two general kinetic models, the \( n \)-th order and autocatalysis, can be applied. The curing kinetics of a reaction with an autocatalytic and a noncatalytic contribution was for the first time analytically described by Kamal and Sourour [65, 70]. Later this approach was modified by
Kenny et al. [66, 67, 72, 73], who developed and proposed the generalized mathematical relation by considering the maximum possible conversion, $\alpha_{\text{max}}$, as shown in eqn (2.11):

$$\frac{d\alpha}{dt} = k(T) f(\alpha) = \left( k_1 + k_2 \alpha^n \right) \cdot \left( \alpha_{\text{max}} - \alpha \right)^n$$  \hspace{1cm} (2.11)

where $m$ and $n$ are the empirical power-law exponents, whose sum represents the overall reaction order. In eqn (2.11) $k_1$ indicates the reaction rate, which is independent of the reaction advancement and is therefore related to noncatalytic rate constant as opposed to $k_2$, which is the autocatalytic rate constant. Furthermore, the specific reaction rates, $k_1$ and $k_2$, are assumed to have an Arrhenius temperature dependence as shown in (2.12):

$$k_i = A_i \exp \left( -\frac{E_{ai}}{RT} \right)$$  \hspace{1cm} (2.12)

where $E_{ai}$ and $A_i$ denotes the activation energy and the frequency factor of the part reactions, respectively, $R$ the gas constant, and $T$ the absolute temperature.

By a linear regression of $\ln k_i$ versus $1/T$ the activation energies and frequency factors of the noncatalytic and autocatalytic reactions can be calculated separately, and used to classify the polymerization process. The modified Kamal approach is considered to be generally valid and has been employed for a wide range of thermosetting systems [74].

In Figure 19 the conversion of the isothermal curing reactions at temperatures of 100, 110, 120, and 140°C respectively is shown as a function of the curing time. At constant curing temperatures below 100°C the reaction rate is very slow and a meaningful analysis of the heat flow signal was not possible. The conversion, $\alpha$, was calculated according to eqn (2.13) and normalized to the total reaction enthalpy ($\Delta H_{\text{tot}}$) obtained from extrapolated dynamic scans with $\varphi=0^\circ\text{C/min}$ (see dynamic DSC-scans). After each isothermal run, the sample was quenched to room temperature and afterwards reheated at 10°C/min to 250°C in order to determine the residual heat of reaction, $\Delta H_R$.

$$\alpha = \frac{\Delta H_{\text{tot}} - \Delta H_R}{\Delta H_{\text{tot}}} = \frac{\Delta H}{\Delta H_{\text{tot}}}$$  \hspace{1cm} (2.13)

The absolute value of $\alpha$ is sensitive to the magnitude of $\Delta H_{\text{tot}}$, which as seen in Figure 15 is not constant for the investigated system, but dependent on temperature scan rate ($\varphi$). This dependence on $\varphi$ is unusual, because the cure reaction is interfered by other exothermal events. Thus the uncertainty in $\alpha$ is potentially larger than normally expected [1, 56]. To minimize this general DSC limitation the extrapolation of total reaction enthalpy to $\varphi=0^\circ\text{C/min}$ was performed by only using heating rates of 10, 15, and 20°C/min (see Figure 15 dotted line). At these relatively high heating rates the interference with the simultaneously occurring decarboxylation of maleic anhydride was greatly minimized and the obtained $\Delta H_{\text{tot}}$ value of 301 J/g was used for further calculations. This obtained $\Delta H_{\text{tot}}$ value is in the same
order of magnitude than other reported values for anhydride cured epoxy-systems, ranging from \( \Delta H_{\text{tot}} = 306 \text{ J/g} \) [75] to \( \Delta H_{\text{tot}} = 389 \text{ J/g} \) [55].

![Figure 19: Isothermal conversion, \( \alpha \), as a function of time at curing temperatures of 100, 110, 120, and 140°C, normalized with the total reaction enthalpy of \( \Delta H_{\text{tot}} = 301 \text{ J/g} \) as obtained from the extrapolated dynamic DSC scan to \( \varphi = 0^\circ\text{C/min.} \)](image)

From the initial slope of the curves in Figure 19 it can be seen that the reaction is progressing faster at higher temperatures, which is even more obvious in Figure 20 where the rate of conversion, \( d\alpha/dt \), is shown as a function of conversion, \( \alpha \). The curves in Figure 20 show a maximum in conversion rate, which is a typical indication for autocatalytic reactions or reactions including an autocatalytic step [76].

![Figure 20: Rate of conversion, \( d\alpha/dt \), as a function of conversion, \( \alpha \), at curing temperatures. The solid line represents the experiment and the dotted line the model relation described by (2.11) with parameters obtained by least squares curve fit. The (♦) symbol indicates the maximum rate of conversion. All curves are normalized with the total reaction enthalpy of \( \Delta H_{\text{tot}} = 301 \text{ J/g} \) obtained from extrapolated dynamic DSC scans to \( \varphi = 0^\circ\text{C/min.} \)](image)
The appropriate kinetic parameters were determined using the modified Kamal relation eqn (2.11) by best curve fitting. A good agreement of the analytical model (dotted line) with the experimental data (solid line) was observed (Figure 20). A constant extent of reaction at the maximum rate of conversion was observed between 0.29<\alpha<0.35. Moreover, it can be seen that at early stages of cure, before gelation and vitrification occur, the reaction takes place in the liquid phase and is controlled by chemical kinetics. The kinetic described by the modified Kamal relation (eqn. (2.11)) coincides with the experimental data. As the reaction progresses a deviation from the symmetric reaction rate curves appears, at conversions above 0.6 to 0.7. This observation can be related to the change of the reaction mechanism from a kinetic to a diffusion-controlled reaction due to the hindered mobility of reactive groups [77].

An interpretation of the maximum in the curve on the chemical level is that the increase in the reaction rate up to the maximum reaction rate is governed by the accelerating effect of typical catalysts, e.g. tertiary amines, and is mainly described by the apparent reaction order for the autocatalytic part (m in eqn (2.11)). Due to the absence of externally added catalysts it is believed that the TGDDM-monomer might provide the tertiary amine sites on its own structure (Table 2), which act as an internal catalyst for the anhydride ring. The decreasing slope of the curve beyond the maximum is dominated by the consumption of the reactive species of the mixture and is predominately influenced by the reaction order for the non-catalytic reaction (n in eqn (2.11)).

The obtained values for the reaction orders and the reaction rates of the phenomenological Kamal equation, m, n, k_1 and k_2, are plotted in Figure 21 with respect to the curing temperature. The reaction order, n, increases linearly with the curing temperature whereas, m, remains almost on a constant level. A similar dependency has been observed by Mezzenga et al. [69] for an epoxy/amine system (DGEBA/isophorone diamine), whereas other studies state that the overall reaction order (m+n) remains at a constant level of 2 [78], depending on the epoxy/amine systems. The calculated arithmetic mean over the investigated curing temperature range was n=1.04 and m=0.4.

As seen from Figure 21(b), k_1 values are small compared with those obtained for k_2 indicating that the latter reaction rate is the rate determining part reaction. The reaction rate for the autocatalytic reaction, k_2, increases with temperature, whereas the reaction rate corresponding to the noncatalytic reaction, k_1, remains almost unaffected by temperature.
Figure 21: Dependence on curing temperature of (a) reaction exponents $n$ and $m$ and (b) reaction rates $k_1$ and $k_2$ in the modified Kamal eqn (2.11) as obtained by best fitting of experimental data. All curves are normalized with the total reaction enthalpy of $\Delta H_{\text{tot}} = 301 \text{ J/g}$ obtained from extrapolated dynamic DSC scans to $\varphi = 0^\circ \text{C/min}$.

The activation energy related to the cure reaction, obtained from eqn (2.12), is $E_1 = 0.04 \text{ kJ/mole}$ and $E_2 = 51.2 \text{ kJ/mole}$ and the corresponding logarithm of the frequency factor is $\ln A_1 = -7.7$ and $\ln A_2 = 14.3$, respectively. Herein, the subscripts ‘1’ and ‘2’ denote the noncatalytic and the autocatalytic part reaction, respectively. The calculated activation energy agrees reasonably well with other reported values for isothermal anhydride/epoxy curing reactions that vary between 58 to 87 kJ/mol [20, 55, 56, 79, 80].

Even more obvious is the negligible contribution of the noncatalytic part during the complete curing reaction in Figure 22. Here the catalytic and noncatalytic contributions from the modified Kamal equation are separated and plotted in comparison to experimental results.
The observation that the overall reaction is dominated by the autocatalytic contribution is consistent with studies by Montserrat et al. [81, 82]. They used a similar model to describe the curing reaction of DGEBA and methyl-tetrahydrophthalic anhydride in combination with a tertiary amine catalyst and also found that the noncatalytic contribution was negligible.

Figure 22: Conversion rate, $d\alpha/dt$, as a function of conversion, $\alpha$. Comparison of the autocatalytic (dotted line) and non-catalytic (dashed line) model contributions according to eqn (2.11) to the experimental results (solid line) measured for the MY721/MA/HHPA-system ($r=0.8$) at 120°C

The nature of the pseudo-autocatalytic rate curve appearance is not fully understood. Kamal and Chanda [68], and Ghaemy and Riahy [62] reported earlier an autocatalytic rate cure profile for an anhydride/epoxy curing reaction. However, the uncatalyzed anhydride/epoxy curing reaction as proposed by Fischer [25] and schematically shown in Figure 6, cannot be strictly assigned to an autocatalytic reaction scheme. Thus, the formation of a pseudo-autocatalysis conversion rate profile can only explained by the significant difference in the appropriate reaction rate constants, $k_2 >> k_1$ [83] from the involved reaction steps as shown in reaction (V) to reaction (VI) Figure 6. Hence the reaction does not follow simple $n$-th order kinetic profile straight from the beginning of the reaction.

Moreover, it can be stated that the kinetic parameters obtained from isothermal experiments are inconsistent with the values obtained from the dynamic scans. Riccardi et al. [50] observed similar differences between the isothermal and dynamic DSC measurements for a diglycidyl ether/ethylenediamine-system. They explained the serious disagreement between the kinetic parameters obtained from dynamic and the isothermal DSC measurements with a change in the curing mechanism with varying curing temperature. At low temperatures, the dynamic experiment is comparable with the conditions of isothermal DSC measurements, where the autocatalytic reaction is dominant. This is also consistent with the fit of our data to
the modified Kamal equation (Figure 21). At higher isothermal curing temperatures, comparable to the dynamic DSC conditions, the noncatalytic part of the reaction becomes more significant so that apparent $n$-th order kinetics is obtained. The kinetic models used for dynamic DSC analysis do not separate the different kind of reaction mechanism and just deal with general constants and reactions. The parameters obtained from dynamic-DSC models have consequently no mechanistic meaning.

### 2.3.2.3 Temperature modulated differential scanning calorimetry (TMDSC)

As discussed in the sections before, conventional DSC does not clearly distinguish the reaction rates of the two different used anhydrides in the co-anhydride mixture. Consequently, an unambiguous identification of the network structure is limited, because the signal obtained from conventional DSC was too low to separate possible sub-transitions from the baseline. For this reason temperature modulated differential scanning calorimetry (TMDSC) experiments were performed to study the thermal cure reaction (Figure 23(a)) and the final network-structure (Figure 23(b)) of the MY721/MA/HHPA-system. Typical Fourier deconvoluted TMDSC thermograms for a constant heating ramp at 1°C/min with underlying oscillation amplitude of 0.2°C for a period of 60 seconds, are shown in Figure 23.
For the uncured MY721/MA/HHPA-system the non-reversing heat flow component (Figure 23(a)) clearly indicates that MA and HHPA obey different reaction rates during the crosslinking reaction. Conventional DSC-experiments of the pure anhydride/epoxy mixtures (cf. Figure 13) have confirmed that the low reaction peak temperature (T~85°C) can be attributed to the MY721/MA reaction, and the high reaction peak temperature (T~130°C) to the MY721/HHPA reaction, respectively.

After cooling the sample back to room temperature the same sample was subjected to a second TMDSC-run under comparable conditions. The total heat flow and its reversing and non-reversing components are shown in (Figure 23(b)). The glass transition temperatures could not be accurately determined from the total heat flow curve, since reversing (glass transition) and non-reversing (enthalpic relaxation) events significantly overlap. However, upon deconvolution of the signal into the appropriate reversing heat flow and non-reversing heat flow, two $T_g$’s ($T_{g1}$=105°C and $T_{g2}$=220°C) can be determined from the reversing heat flow component. This observation provides reliable indication that the studied MY721/MA/HHPA-system consists of a heterogeneous network structure. Due to the different used anhydrides (co-anhydride) it is proposed that at least two independent sub-networks consisting of MY721/MA and MY721/HHPA are present in the final structure.
2.3.2.4 Relationship between glass transition temperature and conversion

The variation of the glass transition temperature ($T_g$) with the extent of reaction ($\alpha$) of the MY721/MA/HHPA-system was determined, in order to establish a full analytical expression of the reaction kinetics when it becomes diffusion controlled on vitrification. It has been demonstrated [84, 85] that a unique relationship between $T_g$ and $\alpha$ is valid when the curing reaction involves the formation of predominately one type of chemical linkages or when competing reactions yielding different structures have similar activation energies or occur sequentially. Considering these fundamental assumptions DiBenedetto [86], and Nielsen [87], proposed a theoretical model based on the lattice energy and the segmental mobility of the involved species to predict the glass transition temperature as function of conversion as given in eqn (2.14):

$$\frac{T_g - T_{g0}}{T_{g0}} = \frac{(E_x / E_m - F_x / F_m) \alpha_{gel}}{1 - (1 - F_x / F_m) \alpha_{gel}}$$  \hspace{1cm} (2.14)

Where $T_{g0}$ is the glass transition temperature of the unreacted system ($\alpha=0$), $F_x/F_m$ is corresponding to the ratio of segmental mobility. The subscripts 'm' and 'x' denote the unreacted and crosslinked states, respectively. The ratio of the energies associated with an element in the lattice space for the crosslinked and un-crosslinked resins ($E_x/E_m$) can be approximated [86] by eqn (2.15):

$$\frac{E_x}{E_m} = \frac{d_m (M_0)_x}{d_x (M_0)_m} \left( \frac{\delta_x}{\delta_m} \right)^2$$  \hspace{1cm} (2.15)

Where $d$ represents the density, $M_0$ is the molecular weight of the constituent repeating unit, and $\delta$ is the solubility parameter. Later Enns and Gillham [88] demonstrated that a sufficient agreement between a curve fit and numerous experimental data could be obtained when both $F_x/F_m$ and $E_x/E_m$ parameter were determined as adjustable values. From eqn (2.14) the ratio of both parameters is then given by eqn (2.16):

$$\frac{E_x}{E_m} / \frac{F_x}{F_m} = \frac{T_{g-}}{T_{g0}}$$  \hspace{1cm} (2.16)

Where $T_{g-}$ is defined as the maximum glass transition temperature, obtained at the ultimate conversion ($\alpha_{max}$).

Introducing eqn (2.14) in eqn (2.16), and substituting the ratio of sequential mobility, $F_x/F_m$ by the constant $\lambda$, results in eqn (2.17), which is referred as the modified DiBenedetto equation:

$$\frac{T_g - T_{g0}}{T_{g-} - T_{g0}} = \frac{\lambda \alpha}{1 - (1 - \lambda) \alpha}$$  \hspace{1cm} (2.17)

Where $\lambda$ must be considered as an adjustable parameter with a value between 0 and 1. $T_g$ values of the MY721/MA/HHPA-system cured isothermally for various periods of times and a comparison of the experimentally data of the MY721/MA/HHPA-system with eqn (2.14) using $\lambda=0.193$ obtained from nonlinear least square fit are given in Figure 24. The non-
linearity of the $T_g$ behaviour as a function of conversion is in agreement with earlier work on thermosetting materials [89, 90]. Moreover, the general non-linear shape of the resulting curve shows that the relative increase of the glass transition temperature is greater at higher extents of conversion. This fact is consistent with the steep increase in the crosslink density beyond the gel point.

Figure 24: Glass transition temperature ($T_g$) as a function of the degree of conversion ($\alpha$), for the MY721/MA/HHPA-system ($r=0.8$) as determined by dynamic DSC ($\varphi=10^\circ$C/min) on partially isothermal cure samples. The solid line represents the best fit of data to the modified DiBenedetto eqn (2.17).

Consequently, if one can assume the validity of the relationship between the glass transition temperature and the conversion the studied MY721/MA/HHPA-system can be expressed as:

$$T_g = \frac{45.626\alpha}{1 - 0.807\alpha} - 20$$  \hspace{1cm} \text{(2.18)}

or

$$\alpha = \frac{T_g + 20}{61.78 + T_g 0.807}$$  \hspace{1cm} \text{(2.19)}

### 2.3.3 Curing reaction studied by chemo-rheology

The successful processing of thermosetting materials requires accurate knowledge and precise control of the viscosity development during the crosslinking reaction. Especially the changes in viscosity during the fluid to solid transformation, at a certain degree of conversion, determine many aspects of the processing, e.g. equipment, temperature window and deformation regime of processing.

As expected, the initial complex shear viscosity ($\eta'$), directly after mixing and before cure, was reduced from the initial 130 mPas to 35 mPas with increasing cure temperature from
40°C to 100°C. The obtained data agree reasonably well with an Arrhenius temperature-dependent viscosity as depicted in Figure 25 and \( \eta_0^* \) can be described as:

\[
\eta_0^*(T) = 4.18 \times 10^{-6} \exp\left(\frac{3.21 \times 10^3}{RT}\right) \text{ [Pas]}
\]  

(2.20)

Figure 25: Arrhenius plot of the initial complex shear viscosity \( (\eta_0^*) \) as a function of temperature for the MY721/MA/HHPA-system (r=0.8).

The prediction of the onset of the gelation phenomenon by dynamic rheometry has been the subject of many studies in the past. For the investigated epoxy systems, the crossover point between the storage \( (G') \) and the loss \( (G'') \) moduli \( (\tan \delta = 1) \), as originally introduced by Tung and Dynes [91] and widely established as a reliable method [92-97], has been used here as a criterion to determine the gel-point. In this work the effect of the frequency was not investigated, because satisfactory information on the thermal cure behaviour of the system was obtained by comparing the results with respect to the control system at a fixed frequency value. An example of an isothermal cure of the MY721/MA/HHPA-system at a curing temperature of 40°C is shown in Figure 26.
Figure 26: Dynamic rheological spectra of storage modulus ($G'$), loss modulus ($G''$), and loss factor ($\tan\delta$) during isothermal cure of the MY721/MA/HHPA-system ($r=0.8$) at 75°C to determine the time of gelation at $G'=G''$.

A better view over the overall cure process can be seen in the plot of the complex shear viscosity ($\eta^*$), the storage modulus ($G'$), and the loss modulus ($G''$) as a function of reaction time and isothermal cure temperatures for the MY721/MA/HHPA-system as illustrated in Figure 27. As the reaction starts the storage modulus ($G'$) rapidly increases whereas the loss factor ($\tan\delta$) shows a reverse trend near the gel point. Consequently, the time to gelation decreased significantly with increasing temperature, due to an increasing reaction rate of the epoxy system.

In order to determine the extent of conversion at the point of gelation ($\alpha_{gel}$) isothermal FT-Raman experiments (cf. chapter 2.2.8) were combined with the rheological experiments. Figure 28 shows the complex viscosity versus conversion data for the MY721/MA/HHPA-system during an isothermal cure at 75°C. The extent of conversion at the point of gelation, as marked by an arrow, was obtained at $\alpha_{gel}$$\sim$0.68. Assuming that the epoxy group and the cyclic anhydride are both bi-functional [34, 35, 98] and that the conversion of the functionalities is a random reaction, general mean field theories [99-101] allow the prediction of the theoretical extent of conversion at the gel point between the tetra-functional epoxide (TGDDM) with an mono-anhydride, resulting in a value that approaches $\alpha_{gel}$$\sim$0.43. The experimentally determined conversion level at gelation is significantly higher than the theoretical prediction (or theoretical gel times are significantly lower). However, higher experimental values have been previously reported in the literature [88] emphasizing the limitations of the underlying assumptions of the theoretical model and the complexity in the reaction chemistry in anhydride-cured systems compared to amines-cured resins.
Figure 27: Dynamic rheological spectra versus time during isothermal cure from 30°C to 120°C of the MY721/MA/HHPA-system (r=0.8). (a) Dynamic shear viscosity ($\eta^*$) the dots indicate the time to gelation ($t_{gel}$); (b) dynamic storage modulus ($G'$); and (c) dynamic loss modulus ($G''$)
The apparent activation energy ($E_a$) for the crosslinking reaction can be calculated from the knowledge of the gel time at different temperatures. An increase in conversion in the region where the crosslinking is kinetically controlled can be expressed by a constitutive equation as:

$$\frac{\alpha}{d\alpha} = A_{(\text{theo})} f(\alpha) \exp \left( -\frac{E_a}{RT} \right)$$

(2.21)

Integrating eqn (2.21) at constant temperature and taking natural logarithms leads to eqn (2.22):

$$\ln \left( \frac{1}{t_{gel}} \right) = \ln \int_0^{tgel} \frac{d\alpha}{f(\alpha)} + \ln A_{(\text{theo})} - \frac{E_a}{RT}$$

(2.22)

where $E_a$ is the crosslinking activation energy, $t_{gel}$ is the time to gelation, $R$ is the universal gas constant, and $T$ is the cure temperature. Since the time to gelation represents a specific extent, and the gel-time is inversely related to the rate of reaction, the gel-time-temperature profile follows an Arrhenius relationship, where the cure is represented by eqn (2.23):

$$\ln \left( \frac{1}{t_{gel}} \right) = \ln A_{(\text{theo})} - \frac{E_a}{RT}$$

(2.23)

There is a linear relationship between $\ln(1/t_{gel})$ and the inverse of temperature for an isothermal curing reaction. From the slope of this relationship the apparent activation energy, $E_a$, of the reaction can be calculated. Figure 29 shows $\ln(1/t_{gel})$, obtained from the point where $\tan \delta=1$, as a function of the reciprocal temperature, giving: $\ln A_{(\text{theo})}=11.5$ and $E_a=58.7\pm 1.9$ kJ/mole.
Figure 29: Arrhenius plot of $\ln(1/t_{gel})$ as a function of inverse temperature ($1/T$) for the MY721/MA/HHPA-system (r=0.8) for determination of the activation energy for gelation ($E_a$).

The value for the overall activation energy obtained by rheological measurements agrees reasonably well with that from studies of the chemical reactions measured by isothermal-DSC as discussed under section 2.3.2. The small differences between absolute values might be caused by different thermal temperature gradients, related to the different sample sizes and the different instrumental configurations.

### 2.3.4 Curing reaction studied by FT-Raman spectroscopy

The objective of this section was to study the low temperature curing behaviour of the same epoxy/co-anhydride mixture by means of vibrational FT-Raman spectroscopy under isothermal conditions. As a complementary technique to mid infrared spectroscopy, FT-Raman is able to provide fundamental vibrational information. Based on the different selection rules of these two spectroscopic techniques, polar bonds tend to yield strong IR and weak Raman bands, whereas non-polar groups give rise to strong Raman and weak IR bands. FT-Raman also allows one to monitor the curing reaction over the complete conversion range, although the material undergoes several state transitions during curing, i.e. gelation and vitrification. These transitions have only a limited influence on the vibrational spectrum. The quantitative aspects of FT-Raman spectroscopy permit quasi real time in situ studies of the crosslinking reaction and the direct calculation of the concentration profiles of various reactive species. Further advantages compared to mid-IR are the lack of interferences from water vapor and glass, which is very convenient because glass sample containers can be used for the experiments.
Conversion of the functional groups is followed by means of real-time FT-Raman spectroscopy and the results are validated against empirical relationships describing the conversion versus time as a function of cure temperature. Kinetic analysis from the conversion of the functional groups is used to obtain the empirical rate curves. Moreover, it is attempted to propose a reaction mechanism for the uncommon cure behaviour of the uncatalyzed MY721/MA/HHPA-system.

### 2.3.4.1 Functional group analysis

The spectra of the unreacted MY721 epoxy monomer as well as the two carboxylic acid anhydrides can be seen in Figure 30. Detailed peak assignments of the main absorption bands are listed in Table 4.

Table 4: Raman spectral peak assignments of (a) carboxylic acid anhydrides and (b) epoxy resin [102-107]

<table>
<thead>
<tr>
<th>Peak Assignment</th>
<th>Wavenumber</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν(CH2)</td>
<td>3072 cm⁻¹</td>
<td>C-H groups of the epoxy ring</td>
</tr>
<tr>
<td>νs(CH2)</td>
<td>3008 cm⁻¹</td>
<td>C-H groups of the epoxy ring</td>
</tr>
<tr>
<td>ν of epoxide ring</td>
<td>1260 cm⁻¹</td>
<td>breathing of the epoxide ring</td>
</tr>
<tr>
<td>νas of epoxide ring</td>
<td>902 cm⁻¹</td>
<td>C-H groups of the epoxy ring</td>
</tr>
<tr>
<td>νs of epoxide ring</td>
<td>866 cm⁻¹</td>
<td>C-H groups of the epoxy ring</td>
</tr>
</tbody>
</table>

The band assignments were made using standard spectroscopy literature [102-105] and by considering results of previous Raman studies [106, 107]. In the spectrum of MY721 five bands attributable to the epoxy ring are easily observed. These are located at 3072 cm⁻¹ [νas (CH2)] and 3008 cm⁻¹ [νs(CH2)] due to C-H groups of the epoxy ring and at 1260 cm⁻¹ [breathing of the epoxide ring], 902 cm⁻¹ [νas of epoxide ring], and 866 cm⁻¹ [νs of epoxide ring] due to vibrations of the entire epoxy ring. In the spectra of the crystalline anhydrides the bands of major interest are those due to the vibrations of cyclic anhydride groups, such
as the intense symmetric and antisymmetric stretch of the carbonyls at 1840 and 1780 cm\(^{-1}\), respectively. This is because the anhydride group is the reactive center and the bands would be expected to decrease during curing with the epoxy. Real-time FT-Raman spectroscopy was performed to monitor the curing process. It was assumed and later confirmed by the experiments that the aromatic hydrocarbon groups, corresponding to the characteristic vibration at 1615 cm\(^{-1}\) [aromatic quadrant stretch], are not involved in the curing reaction and hence the peak area does not change over the entire curing period. Therefore, the invariant peak at 1615 cm\(^{-1}\) was used for all spectra as an internal normalization standard [106, 107].

From the recorded spectra, the fractional consumption of functional groups, \(\alpha\), can be calculated by eqn (2.24):

\[
\alpha(t) = 1 - \left( \frac{I(t)}{I_{1615}^0} / \frac{I_{1615}^0}{I_{1615}^0} \right) 
\]

where \(I_0\) and \(I_t\) are the relative intensities (peak height) of reactive species at time zero, and after a certain time interval, \(t\), of the cure cycle. Due to the epoxy excess \((r<1)\), the concentration curves of epoxy and anhydride groups can be directly compared only if we consider the absolute conversion. In terms of spectroscopic parameters, the absolute conversion is given by \(C_0\alpha(t)\), where \(C_0\) refers to the initial concentration of the reactive species.

Curing data obtained after different reaction times and reaction temperatures are shown for the MY721/MA/HHPA-system with a molar anhydride to epoxy ratio, \(r=0.8\), at 65°C in Figure 31 and Figure 32. Interferences from thermal emission bands or fluorescence, as reported by Walton and Williams [107], were not obtained. Subsequently, the spectral changes were monitored quantitatively and detailed results are discussed in the following sections.
Figure 30: FT-Raman spectra of unreacted anhydride hardeners (a) hexahydrophthalic anhydride; (b) maleic anhydride and (c) epoxy resin Araldite® MY721

Figure 31: FT-Raman spectra of MY721/MA/HHPA at various extents of cure at 65°C and after 1 hour post-curing at 120°C
Figure 32: Difference of FT-Raman spectra obtained by spectrum “after 1 hour at 100°C” minus spectrum “uncured” directly after mixing of the MY721/MA/HHPA-system. Changes in peaks marked with a symbol are discussed in the text.

Anhydride:

The peaks from the mixture at 3111, 1850, 1780, 1060, 868, and 636 cm\(^{-1}\), respectively, can be assigned to the two anhydrides used in the co-anhydride mixture. Peaks corresponding to the individual MA and HHPA components are not reliable due to peak overlap. Hence, although a clear band due to MA is seen at 3111 cm\(^{-1}\), in the presence of the epoxy, the respective functional groups consumption of the two anhydrides, hexahydrophthalic anhydride and maleic anhydride, cannot be further differentiated by FT-Raman spectroscopy. However, it can be expected that both anhydrides compete for the reaction with the epoxy groups as shown in Figure 6, even when the two anhydrides show similar reactivity as reported in [108] for the same system.

All anhydride functional group peak intensities decrease progressively throughout the entire cure. The total conversion of the functional anhydride groups can be gained using the typical in-phase (symmetric) and out-of-phase (anti-symmetric) carbonyl stretching vibrations at 1850 and 1780 cm\(^{-1}\) \([\nu_s(C=O)\text{ and }\nu_{as}(C=O)]\), and 1060 cm\(^{-1}\) \([\nu_{as}(C-O-C)]\), respectively. In this study the reaction of anhydrides was followed by means of the 1850 cm\(^{-1}\) \([\nu_s(C=O)\text{ of the anhydride ring}]\) as proposed in the past [24] and the results are illustrated in Figure 33(a) and (b). To convert peak areas for the evolution of anhydride concentration, \([Anh]\), as shown in Figure 33(b), the initial anhydride concentration of 3.89 mol/kg was considered. It can be seen that the anhydride peaks have not fully extinguished at lower curing temperatures and
Epoxy-anhydride crosslinking reaction

hence the anhydride concentration curve stabilized on a quasi-stationary plateau after a certain time period. This observation can be explained by the fact that the anhydride consumption is limited due to a physical liquid-to-solid transformation of the material. From this point, the reaction becomes diffusion controlled and a significant decrease of the reaction rate is observed; see Figure 33(b). To reach a complete conversion of the reactive groups isothermal curing temperature above 75°C or extended post curing steps are necessary.

Figure 33: (a) FT-Raman spectra of the anhydride peak [1850cm⁻¹] at (1) 0, (2) 30, (3) 60, (4) 120 min of cure at 75°C; (b) Plot of anhydride group concentration versus cure time at (1) 55°C, (2) 65°C, (3) 75°C, (4) 100°C; (c) FT-Raman spectra as a three-dimensional plot of the intensity versus time for polymerization temperature of 65°C

In particular the maleic anhydride ring opening reaction and the related changing substitution pattern can be followed by the disappearance of the characteristic C=C vibrations from maleic anhydride 1590 cm⁻¹ [ν(C=C)] as shown in Figure 34(a) and Figure 34(b). The simultaneously resulting formation of the appropriate acid group can be clearly
seen by the broad growing intensity situated at 1640 cm$^{-1}$ [$\nu$(C=COOH)] as shown in Figure 34(a) and Figure 34(c). This observation provides ample evidence that the unsaturation of maleic anhydride is not reactive at low temperatures.

Figure 34: (a) FT-Raman spectra at (1) 0, (2) 30, (3) 60, (4) 120 min of cure at 75°C. (b) plot of MA [$\nu$C=C; 1590 cm$^{-1}$] fractional group consumption and (c) new formed acid [$\nu$(C=COOH); 1640 cm$^{-1}$] peak versus cure time at as a function of isothermal curing temperature (1) 55°C, (2) 65°C, (3) 75°C.

Epoxide:
A typical decrease of peak intensities corresponding to the epoxy group consumption at 3072, 3008 and 1260 cm$^{-1}$ can be observed during the entire curing reaction. The epoxide ring breathing vibration at 1260 cm$^{-1}$ is well-resolved and essentially Lorentzian shape, as seen in Figure 35(a) and (c). Hence this peak was utilized to monitor the epoxy conversion as proposed previously [106, 109]. To enable peak height measurements a baseline correction was performed and an initial epoxide concentration of 4,72 mol/kg was considered to create the epoxide group concentration profile. A plot of the epoxide group concentration, $[EP]$, over time for different temperatures is given in Figure 35(b). A sigmoidal curve is obtained for all curing temperatures. It can be seen that at curing temperatures
below 100°C the crosslinking reaction is quenched by a liquid to solid transition before it can reach the 100% conversion. This behaviour is consistent with the observed anhydride consumption behaviour. At an isothermal curing temperature of 55°C almost 68% of epoxy groups were converted, while during a curing at 75°C, 76% of epoxide groups were converted. However, it can be expected that the polyesterification reaction will continue also into the glassy state, but at a significantly decreased reaction rate.

Figure 35: (a) FT-Raman spectra of the epoxy peak [1260 cm\(^{-1}\)] at (1) 0, (2) 30, (3) 60, (4) 120 min of cure at 75°C; (b) plot of epoxy group concentration versus cure time at (1) 55°C, (2) 65°C, (3) 75°C, (4) 100°C; (c) FT-Raman spectra as a three-dimensional plot of the intensity versus time for polymerization temperature of 65°C

Ester group:
The relative increase of bands due to ester group formation upon cure can be observed at 2963 cm\(^{-1}\) \(\nu_{\text{as}}(\text{CH}_2)\) adjacent to the ester group, and 1730 cm\(^{-1}\) \(\nu(\text{C}=\text{O})\) aromatic ester. The latter total aromatic ester peak contains both monoester and diester contributions and was used to determine the extent of curing reaction according to eqn (2.25) as:
where $\beta$ is the extent of the esterification reaction, $I_t$, the Raman intensity at time, $t$, and $I_0$ corresponds to the intensity at $t=0$, and $I_\infty$ is the intensity at time of curing completion, $t=\infty$. It was assumed that the ultimate conversion ($t=\infty$) of reactive groups was reached after a post-curing step at 150°C for 1 hour, which defines 100% cure.

The total formation of aromatic ester groups ($\beta$) during the curing reaction at different temperatures is given in Figure 36(b). An extended delay before start of the ester formation as reported by Stevens [83, 110] was not observed. Besides, it can be seen that ester formation approaches a limiting value at long curing times, which is in agreement with the anhydride and epoxy consumption behaviour.

Figure 36: (a) FT-Raman spectra of aromatic ester peak [1732 cm$^{-1}$] at (1) 0, (2) 30, (3) 60, (4) 120 min of cure at 75°C; (b) Plot of extent of ester group reaction ($\beta$) as a function of cure time at (1) 55°C, (2) 65°C, (3) 75°C, (4) 100°C; (c) FT-Raman spectra as a three-dimensional plot of the intensity versus time for polymerization temperature of 65°C
Side reactions:
The disappearance of the characteristic C=C vibrations from maleic anhydride at 3111 cm\(^{-1}\) \([\nu (=C-H)]\), 1590 cm\(^{-1}\) \([\nu (C=C)]\), and 636 cm\(^{-1}\) \([\gamma (=CH-H)]\) is clearly visible in Figure 32. Detail of the region from 1670 cm\(^{-1}\) to 1570 cm\(^{-1}\) is shown in Fig. 9(a) and the decrease in the C=C band intensity of MA at 1590 cm\(^{-1}\) and an increase in a broad band that first appears as a shoulder around 1640 cm\(^{-1}\) are shown in Fig. 9(b) and 9(c) respectively. This could suggest that the unsaturation of maleic anhydride is being consumed at low temperatures. If so, then it could provide ample evidence for the reaction of maleic anhydride by anionic initiated homopolymerization through charge-transfer reactive intermediates zwitterions as reported by Zweifel et al. [111] and Ricca et al. [59] and shown in Figure 37 (reaction XVI to VXIII). Maleic anhydride is difficult to homopolymerize by a conventional free radical or anionic initiator, but it can be easily initiated by nitrogen bases to yield poly(maleic anhydride). The monomer is an excellent organic electron acceptor and hence it forms zwitterions with a suitable base. In the investigated system the zwitterions are spontaneously formed in the presence of nitrogen bases (TGDDM monomer) at room temperature and appear to be the true initiator for poly(maleic anhydride) as shown in Figure 37. Additional indication for the zwitterions formation is given by the immediate color change of the mixture, from light yellow to dark red, as soon as maleic anhydride was added. This amine activated color change of maleic anhydride has been observed earlier for maleic functional copolymers [53, 112] and was related to the formation of zwitterion intermediates.

This image is not available online. Please consult the hardcopy thesis available from the QUT Library.

Figure 37: Polymerization mechanisms of maleic anhydride in the presence of tertiary amine as proposed by Zweifel et al. [111].
However, a more detailed analysis of this spectral region suggests that the changes may be linked to the primary esterification reaction and result from changes to conjugation following ring opening of MA. The evidence for this may be seen from an analysis of the extended spectral region shown in Figure 38.

![Figure 38: Expanded region of FT-Raman spectrum during the cure of MY721 with MA/HHPA at 75°C showing isosbestic point at 1760 cm\(^{-1}\).](image)

This is evidenced by the isosbestic point in the spectrum at 1760 cm\(^{-1}\) that supports the smooth conversion of anhydride (1780 cm\(^{-1}\)) to ester (1734 cm\(^{-1}\)) that parallels the changes in the MA band at 1590 cm\(^{-1}\) and the growth of the broad band near 1640 cm\(^{-1}\). This is shown in Figure 39 in which the intensities of the four bands are plotted during cure. They appear to all follow the same kinetic relationship so that the change in the band at 1590 cm\(^{-1}\) is most probably a result of the ring opening reaction of the MA producing a change in the conjugation of the C=C rather than its actual consumption. The broadening of the band at around 1640 cm\(^{-1}\) most probably reflects the range of environments that the C=C encounters after ring opening as cure takes place.
The absence of a broad band at 1080 cm⁻¹ \( [\nu(C-O)] \) shows that no ether groups were formed, even at curing temperatures up to 150°C, supporting the statement that polyetherification, as illustrated in Figure 5 (reaction IV), is effectively suppressed. This is in accordance with earlier results obtained by Tanaka and Kakiuchi [20], Fischer [25], and Luston et al. [30]. Additionally, we were unable to observe changes of the peak position and intensity at 1615 cm⁻¹ [aromatic quadrant stretch] of FT-Raman spectra that supports the hypothesis that a “back-biting” cyclization of chlorohydrin impurities in MY721 at higher curing temperatures as reported by St. John et al. [106, 111] does not occur.

2.3.4.2 Rate curves and kinetics analysis

Empirical rate curves were generated for the different reaction species by applying a weighted smoothing function using a minimum number of iterations to obtain a curve. This procedure ensured that the instantaneous reaction rates obtained from the concentration profiles were not affected by single data point scattering.

To study this epoxy/anhydride reaction the empirical rate curves were calculated by taking the first derivative of the epoxy concentration versus time data (Figure 33) as shown in Figure 40(a). The obtained rate curves have a pronounced maximum which, in the reaction scheme, may represent the development of the steady state concentration of the reactive intermediates. This behaviour is more pronounced at lower isothermal curing temperatures. Assuming a non-catalyzed mechanism this induction period is reflecting the generation of intermediate COOH and OH-groups. While, considering a catalyzed reaction mechanism the
presence of an induction period can be attributed to a rather slow initiation step when polymerizing at low temperatures.

An alternative explanation for the maximum in the rate curve, Figure 40(a), is that it indicates the reaction is autocatalytic in nature. Autocatalysis is observed when the tertiary amine structure of the TGDDM-monomer acts as catalyst in epoxy/anhydride curing reaction. A further possible source of any autocatalytic contribution could be reaction products between MA and the aminoglycidyl monomer, as discussed before, and schematically shown in Figure 37. These reaction products, especially the proposed formation of carboxylate anions, could act as an additional initiator in the curing reaction.

Despite, the catalyzed reaction mechanism has obviously an autocatalytic nature; isothermal kinetic runs have been analyzed with an excellent agreement by first-order kinetics, particularly under isothermal curing conditions [66]. To account for this observation, Riccardi and co-workers [118] developed and experimentally validated a mechanistic model that predicts a chainwise polymerization proceeding by an anionic mechanism (epoxy/anhydride/tertiary amine) an induction period followed by first-order kinetics when using low isothermal cure conditions. Therefore, it was considered here that it is not necessary to invoke autocatalysis in order to explain the observed concentration profiles obtained from spectral data.

The measured data for the consumption of the epoxy groups are shown in a linearized first-order kinetic plot in Figure 40(b). It can be seen that the reaction obeys first order behaviour \( [(1-\alpha)^1] \). For an extent of conversion of around 70%, a significant drop in the experimental reaction rate is observed due to diffusional restrictions indicating the change of the reaction mechanism from kinetic to diffusional control. Therefore, the apparent first-order rate constants were calculated as a function of temperature from the initial slopes and are listed in Table 5.

Assuming the Arrhenius dependency of temperature on the rate constant, as depicted in Figure 40(c), an activation energy of 71.01kJ/mol and a frequency factor of 19.85 min\(^{-1}\) was calculated, respectively. This obtained activation energy is in excellent agreement with other studies where the activation energy for base catalyzed anhydride/epoxy curing reactions is reported in the range of 70-75 kJ/mole [66, 118].
Figure 40: (a) Empirical epoxide reaction rate \(-d[EP]/dt\) as a function of curing time; (b) first order kinetic regression plot of epoxide reaction, for 55°C (◇), 65°C (△), 75°C (+) as measured by FT-Raman; (c) Arrhenius plot of the apparent first order epoxy reaction rate constant, \(k_2\).
Table 5: First order rate constants and time of deviation from first order kinetic ($t_{dev}$) as a function of curing temperature for the MY721/MA/HHPA-system ($r=0.8$) as determined by FT-Raman spectroscopy.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Anhydride ($k_1$) [sec$^{-1}$]</th>
<th>Epoxide ($k_2$) [sec$^{-1}$]</th>
<th>$t_{deviation}$ [sec]</th>
</tr>
</thead>
<tbody>
<tr>
<td>55°C</td>
<td>3.5e-5</td>
<td>2.9e-5</td>
<td>27360</td>
</tr>
<tr>
<td>65°C</td>
<td>5.7e-5</td>
<td>4.5e-5</td>
<td>15120</td>
</tr>
<tr>
<td>75°C</td>
<td>26.1e-5</td>
<td>19e-5</td>
<td>5880</td>
</tr>
<tr>
<td>100°C</td>
<td>3.5e-3</td>
<td>2.7e-3</td>
<td>1260</td>
</tr>
</tbody>
</table>

2.3.4.3 Cure mechanisms

The overall curing pattern clearly indicates that the network mainly consists of ester linkages build by polyesterification. The observed reaction rates for the studied curing temperatures are significantly higher than values reported for the non-catalyzed curing reaction [15]. This observation provides an indication that the thermal cure of the investigated TGDDM/MA/HHPA-system is probably catalyzed by the tertiary amine structure of the TGDDM-monomer used. Hence, the curing reaction favors an anionic alternating chain-polymerization as shown in Figure 6. However, the experimentally obtained FT-Raman data cannot unambiguously used to clearly differentiate between a non-catalyzed and a catalyzed mechanism, because the expected new vibrational bands are overlap with conjugated species from the MA (cf. section 2.3.4.1). By plotting the empirical data in an epoxy-anhydride conversion-conversion diagram, it is possible to establish the stoichiometry of the reaction and to detect possible changes of the mechanism with conversion. A plot of this type is shown in Figure 41 for the investigated system cured at 65°C. It can be seen that all data points can be exactly accommodated on a single master curve. In particular, over the complete isothermal low temperature curing, the data fit to an iso-conversion line with a slope equal to one. This indicates a mechanism whereby, in the presence of sufficient concentration of hardener, a single epoxy group reacts with one anhydride group in an alternating co-polyesterification. However, from the data presented here it is not possible to distinguish between the two anhydrides, hence it is not known if both anhydrides were consumed at an equal rate. Moreover, the good fit to the iso-conversion line indicates that the dominance of polyesterification excludes the potential polyetherification side reaction, e.g. homopolymerization, in the investigated temperature range. However, the curing proceeds not only by the polyesterification reaction between anhydride and epoxy. Especially at higher curing temperatures a significant amount of TGDDM (tertiary amine) initiated homopolymerization of maleic anhydride has been identified.
2.3.5 Time-Temperature-Transformation (TTT)

The solidification behaviour during cure defines the processing window and additionally determines the properties of the final material. Curing of epoxies is usually characterized by different independent phenomena.

In order to visualize the sequences of different occurring events for different curing temperatures, generalized time-temperature-transformation (TTT) graphs, representing the specific times to gelation and vitrification as a function of cure temperature have been developed [10, 88, 113, 114]. The TTT-cure diagrams enable the description of complex processes that occur during the cure of a thermoset under isothermal cure conditions [88] and have been established for a wide variety of different thermoset materials.

In these diagrams $T_g$ characterizes the glass transition temperature of the initial mixture containing the unreacted precursor monomers. Below $T_g$ the crosslinking reactions are frozen-in and the reaction rates are extremely slow. At temperatures above $T_g$ the crosslinking reaction results in the formation of small aggregates. With the progressing curing reaction these species grow and become interconnected until the point of gelation is reached. At gelation, the liquid to rubber transition corresponds to a non-reversible incipient formation of a network with an infinite weight-average molecular weight. The gelation step is of great technological interest because after it no material flow is possible [91, 115]. In general gelation occurs at a fixed extent of conversion ($\alpha_g$), as long as the reaction mechanism does not change with temperature [88, 99].
The glass transition temperature, $T_g$, of the system rises simultaneously with the advancement in reaction. The moment when the $T_g$ becomes equal to the curing temperature is called vitrification. Vitrification involves a gradual, thermo-reversible process describing the transformation from a liquid or rubbery state to a glassy state [88, 116, 117]. Therefore, the detection of vitrification processes varies with the analysis technique employed. After vitrification the reaction rate is slowed considerably and the reaction becomes diffusion controlled. The temperature at which gelation and vitrification occur simultaneously is called $\text{gel}T_g$. Above $\text{gel}T_g$ the gelation occurs before vitrification, whereas no gelation occurs below $\text{gel}T_g$. The further critical temperature, $T_{g\infty}$, corresponds to the ultimate glass transition temperature of the fully cured network.

The times to gelation ($t_{\text{gel}}$) can be obtained by setting $\alpha=\alpha_{\text{gel}}$. Integrating the eqn (2.11) between $\alpha=0$ and $\alpha_0$, and taking the natural logarithms yields:

$$\ln \left( \int_0^{\alpha_0} \frac{d\alpha}{f(\alpha)} \right) = \ln k(T) + \ln(t_{\alpha_0})$$  \hspace{1cm} (2.26)

Assuming further the Arrhenius form of $k$ the left-hand side of eqn (2.26) being temperature independent:

$$\ln(t_{\alpha_0}) = C + \frac{E_a}{RT}$$  \hspace{1cm} (2.27)

From experimental data, linear regression when plotting $\ln(t_{\alpha_0})$ versus $1/T$ provides the constant, $C$, and thus it is possible to trace the iso-conversion lines in the kinetically controlled regime, as shown in Figure 39. Moreover, the connection between $T_g$ and conversion is given by eqn (2.17), and consequently it is possible to convert all the iso-conversion curves to iso-$T_g$ curves. Vitrification curves can then be theoretically predicted using the intersection of the iso-$T_g$ curve and $T_g=T_{\text{cure}}$, which is the fundamental criterion for the point of vitrification. The calculated S-shape of the vitrification curve is influenced by the function of the kinetics as well as the physical parameters $T_{g0}$, $\text{gel}T_g$, $T_{g\infty}$, and the relationship between the glass transition temperature and the conversion ($\alpha$) at $T_g$. Wisanrakkit and Gillham [85] have confirmed the S-shape of the vitrification line by direct experiments. The TTT-diagram for the MY721/MA/HHPA-system $(r=0.8)$ using the physical constants from Table 6 is shown Figure 42. It can be seen that the theoretical curves agree fairly well with the experimental data. The obtained deviations depend on the determination and the high sensitivity of the involved parameters. For example, a variation of only 1% in the apparent activation energy leads to a $\sim$20% deviation of the calculated time to gelation at a curing temperature of 100°C.
It was observed that the time to deviation obtained from the first order kinetic analysis of FT-Raman measurement (see Table 5) agrees very well with the time to gelation data obtained from rheological experiment as shown in Figure 42.

Table 6: Physical constants and other parameters used for TTT-diagram calculations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_g of the uncured resin [°C]</td>
<td>T_g0</td>
<td>-21</td>
<td>Non-isothermal DSC</td>
</tr>
<tr>
<td>T_g of the fully cured resin [°C]</td>
<td>T_g∞</td>
<td>216</td>
<td>Non-isothermal DSC</td>
</tr>
<tr>
<td>Ratio of segmental mobility</td>
<td>λ</td>
<td>0.193</td>
<td>DSC</td>
</tr>
<tr>
<td>(crosslinked/monomer)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extent of conversion at gelation</td>
<td>α_{gel}</td>
<td>0.68</td>
<td>Rheology/Raman spectroscopy</td>
</tr>
<tr>
<td>Kinetic activation energy [kJ/mole]</td>
<td>E_a</td>
<td>70.1</td>
<td>Raman spectroscopy</td>
</tr>
<tr>
<td>Kinetic Arrhenius factor [sec^{-1}]</td>
<td>A</td>
<td>2.2 *10^6</td>
<td>Isothermal DSC</td>
</tr>
</tbody>
</table>

Figure 42: Time-temperature-transformation (TTT) diagram for the MY721/MA/HHPA-system (r=0.8). Dotted lines represent iso-conversion contours. Solid lines represent the behaviour of the time to gelation (t_{gel}) and the time to vitrification (t_{vit}). The (■) symbols represent the time to gelation (t_{gel}) experimentally determined by dynamic rheology; and the (△) symbols denote the time to deviation (t_{dev}) from n-th order kinetics experimentally obtained by FT-Raman analysis.

Figure 43 shows the extent of conversion at vitrification. It is a fit of eqn (2.17) to the extent of conversion at vitrification as a function of the isothermal curing temperature. Below the curve the investigated MY721/MA/HHPA-system is liquid or gelled rubber, whereas above the curve the material is in the state of an ungelled or gelled glass. The graphical determination of g_{gel}T_g yields 53°C.
2.4 Concluding remarks

Kinetics analysis of the thermal cure process of the MY721/MA/HHPA-system has been studied by means of calorimetry, rheometry, and FT-Raman spectroscopy under isothermal and non-isothermal conditions.

It was found that the results obtained from dynamic and isothermal DSC analysis yielded a serious disagreement between these two methods. In particular the application of single heating methods, e.g. the Barrett and the Carroll-Freeman relation, revealed generally higher values for the calculated kinetic parameters than those calculated from non-isothermal measurements. The relevance of the reaction order ($n$) in an autocatalytic environment at normal processing temperatures as well as the apparent activation energy ($E_a$) seems to be highly questionable. A more detailed mechanistic analysis prior to computation of the reaction order ($n$) is necessary if dynamic methods should be employed. More meaningful kinetic parameters were obtained by multiple-heating methods (Kissinger and Ozawa). However, these model-free methods are independent of the reaction order and hence not accurate for more complex reactions ($n \neq 1$).

Kinetic parameters obtained from isothermal methods (DSC, rheometry and Raman spectroscopy) are consistent in the studied curing temperature range. However, the quality of the DSC-kinetic analysis is greatly influenced by the total reaction enthalpy ($\Delta H_{tot}$). For the presently investigated system the total reaction heat is significantly superimposed by competitive exothermal events, e.g. decarboxylation reaction of MA, which outlines the principal limitations of the underlying DSC assumptions.
Isothermal FT-Raman spectroscopy was identified as the most powerful method to study the curing kinetics. Quantitative analysis of in situ FT-Raman spectra showed that the total anhydride and epoxy consumption, as well as the ester formation follows pseudo-first order kinetics up to the point where the reaction becomes diffusion controlled (α ~70%) in accordance to the proposed mechanistic reaction scheme. The obtained kinetic parameters for different methods and models are summarized in Table 7.

The observed deviations between isothermal and non-isothermal kinetic calculations can be related to mainly two facts. Firstly, the fit of non-isothermal data to hypothetical and mechanistically free models results in a highly uncertain set of single Arrhenius parameters that cannot bemeaningfully compared to isothermal data. Secondly, the isothermal and non-isothermal experiments are conducted at different temperature ranges. Since measurement conditions in all applied isothermal methods are more similar to the processing environment in many technical applications, these methods should be favored for detailed process optimizations.

Table 7: Calculated kinetic parameters for the MY721/MA/HHPA-system (r=0.8) cure under isothermal and non-isothermal cure conditions

<table>
<thead>
<tr>
<th>Analytical method</th>
<th>Model</th>
<th>Activation energy ((E_a)) [kJ/mole]</th>
<th>Frequency factor ((lnA)) [sec(^{-1})]</th>
<th>Reaction order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynamic DSC</td>
<td>Freeman-Carrol</td>
<td>113.2</td>
<td>n.a.</td>
<td>(n=2.0)</td>
</tr>
<tr>
<td>Dynamic DSC</td>
<td>Barrett</td>
<td>112.6</td>
<td>27.4</td>
<td>(n=2.0)(^1)</td>
</tr>
<tr>
<td>Dynamic DSC</td>
<td>Kissinger</td>
<td>63.5</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Dynamic DSC</td>
<td>Ozawa</td>
<td>67.3</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Isothermal DSC</td>
<td>Autocatalysis</td>
<td>(E_1=51.2)</td>
<td>14.2</td>
<td>(m=0.40)(^2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(E_2=0.04)</td>
<td>-7.7</td>
<td>(n=1.04)(^2)</td>
</tr>
<tr>
<td>Isothermal Rheometry</td>
<td>Isoconversion</td>
<td>58.7</td>
<td>11.5</td>
<td>n.a.</td>
</tr>
<tr>
<td>Isothermal FT-Raman</td>
<td>(n)-th order kinetic</td>
<td>70.0</td>
<td>15.8</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

\(^{1}\) Reaction order value obtained from the Freeman-Carroll relation
\(^{2}\) Arithmetic mean of reaction orders \((m\) and \(n\)) obtained at curing temperatures of 100, 110, 120 and 140°C

In addition, FT-Raman spectroscopy was used to monitor the anhydride/epoxy curing reaction in order to investigate the curing mechanism. Therefore, real-time quantitative concentrations of epoxy, anhydride and ester groups were measured during the cure of MY721/MA/HHPA-system at temperatures between 55°C to 100°C. Conversion data of the functional groups were determined and used to evaluate the reaction mechanisms. It was shown that the investigated anhydride-cured epoxy system reacts mainly by consecutive-step polyesterification. FT-Raman and gas chromatography support the hypothesis that the tertiary amine structure of the investigated amino-glycidyl resin is able to initiate homopolymerization of maleic anhydride, which is followed by decarboxylation and the
Chapter 2

The release of water and carbon dioxide. The formation of these reaction products could contribute to an autocatalytic curing reaction but the kinetic analysis does not indicate autocatalysis is significant under the conditions of low-temperature cure.

The use of temperature modulated DSC (TMDSC) technique enables differentiation of the MY721/MA and MY721/HHPA reaction rates by monitoring the non-reversing heat flow signal. Additionally, TMDSC experiments provide evidence of a heterogeneous sub-network structure for the co-anhydride cured epoxy network.

A generalized time-temperature-transformation-diagram was developed in order to predict the complex material transformations (e.g. gelation and vitrification) occurring during the entire isothermal cure process.

2.5 References

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Chapter 3

3 Deformation and fracture behaviour

One common feature of epoxy thermosets is their inherent brittleness which is a direct consequence of the highly crosslinked network structure. Upon deformation these dense networks exhibit only minor elastic deformation and low elongation at break. Thus, this intrinsically brittle behaviour often limits the use of epoxy materials in numerous industrial applications. For this reason, the knowledge of the deformation and the connected fracture behaviour is one of the most important to enable design of structural parts out of thermosets materials.

At the beginning of this chapter a general introduction to the linear fracture mechanics is given, followed by an extensive review of the different toughening approaches and related toughening mechanisms. The deformation behaviour of the co-anhydride cured TGDDM-formulation under tensile and compressive load was studied, and the influence of test temperature and strain rates on the basic yield and deformation behaviour was evaluated. Microscopy analysis was used to investigate the microstructure in order to identify the deformation mechanisms.

The fracture behaviour of the highly crosslinked epoxy was examined and toughening attempts with inorganic hard particles were carried out. The effects of external test parameters such as temperature and strain rate, as well as the influence of compositional variations like filler fraction, filler size and filler surface-treatment have been studied. Moreover, the potential of using reactive, polydisperse and highly branched polymers (hyperbranched polymer; HBP) as novel tougheners as well as the HBP application in hybrid-compositions (silica+HBP) has been extensively examined. In order to obtain a fundamental understanding of the involved micro-deformation and fracture mechanisms this study focused primarily on the structure-property relationship, which is a result of the curing kinetics, thermo-mechanical properties, and morphology of epoxy-silica and epoxy-HBP blends.

3.1 Introduction to fracture toughness

The term fracture toughness, in a broader sense, is a measure of a material's resistance to failure. Fracture toughness is usually measured as either the stress or the energy required for failure of a specimen under a specific load condition. Therefore, toughness can be
defined more specifically as (1) the area under the tensile stress-strain curve, (2) the Izod/Charpy impact strength, (3) the critical stress intensity factor ($K_c$) under plane strain conditions, or (4) the critical strain energy release rate ($G_c$) under plane strain conditions. Although the definition of toughness varies from application to application, it is nowadays in generally agreed that, either $K_c$ or $G_c$ –values should be considered for the “worst case scenario”.

3.2 Linear elastic fracture mechanics (LEFM)

Linear elastic fracture mechanics describes the behaviour of sharp cracks in linear, perfectly elastic materials. From the comprehensive literature on this subject only a few works deal with the deformation and fracture of polymers [1-4]. The foundation of the linear fracture mechanics was originally laid by Griffith [5], who recognized for the first time in 1920, that the strength of crystalline or glassy solids was much lower than those based on theoretical considerations. Theoretical strengths can be calculated from the force-displacement curves of interatomic bonds, since the strength of a solid is limited ultimatively by the strength of its atomic bonds [6]. Typical values are of the order of $E/10$, where the $E$ is the Young’s modulus. For neat epoxy resins with typical values of Young’s modulus in order of 3 GPa the calculated theoretical failure strength is in the range of 300 MPa. In general, however, experimental evidence clearly indicated that the failure strength is orders of magnitude below the theoretical value [7]. This clearly indicates that the distribution of local stresses between individual bonds, even in an apparently homogeneous material under uniform stress conditions, is not uniform. Griffith explained this effect by the presence of small defects and/or flaws in the material, which lead to a significant stress enhancement on a microscopic scale. The material is assumed to obey Hooke’s law so that the stress is directly proportional to the infinitesimal strains. For any loaded body, therefore, a linear load-deflection relationship will result. Nowadays, the linear fracture mechanics is based on two independent fracture conditions, the energy analysis ($G$-approach) and the localized stress field analysis ($K$-approach). A more detailed explanation of these two methods will be given in the following sections.

3.2.1 Strain energy release rate criterion ($G$-Approach)

Griffith’s explanation of the deviation between the theoretical calculated strength and the experimentally observed values was based on the presence of micro cracks in the material. Moreover, Griffith considered that the elastically stored energy is not distributed
uniformly throughout the sample but is locally concentrated near the flaw. He used an
energy balance approach and calculated the energy released by introducing an elliptical
Crack of a length (l=2a) and width (b) into the plate under a constant applied stress (see
Figure 44), and related this to the energy required to create two new fracture surfaces.

\[ P \]

\[ a \]

\[ b \]

\[ x \]

\[ y \]

Figure 44: Generalized loading of a cracked body which exhibits bulk linear elastic
behaviour

Thus the total energy of the cracked plate (\( U_{\text{tot}} \)) can be written as eqn (3.28):

\[ U_{\text{tot}} = U_0 + U_\gamma + U_a - P \]  

(3.28)

where

- \( U_0 \) = elastic energy of the loaded uncracked plate (a constant)
- \( U_\gamma \) = change in the elastic energy due to the formation of two crack surfaces
  (elastic surface energy)
- \( U_a \) = the additional change in the elastic energy in the plate due to the
  presence of the crack
- \( P \) = work performed by external forces

If it is assumed that the material behaves in a perfectly linear elastic manner, the
Corresponding change in the elastic energy due to the formation of the two crack surfaces,
\( U_\gamma \), is simply equal to the product of elastic surface energy of the material, \( \gamma \), and the new
surface area of the crack:

\[ U_\gamma = 2(2a\gamma) = 4a\gamma \]  

(3.29)

To determine the change in the elastic energy in the plate due to the presence of the crack
\( (U_a) \), Griffith's calculation requires integration over the stress field around the crack using
the mathematical solution as proposed by Inglis [8] yielding to eqn (3.30):

\[ U_a = \frac{\pi \sigma^2 a^2}{E} \]  

(3.30)

where \( E \) represents the Young's modulus of the material comprising the plate, and \( \sigma \)
denotes the macroscopic stress.

Assuming a “fixed grip” condition (\( P=0 \)) and the change in elastic energy \( (U_a) \) is negative,
the total energy of the cracked plate is:
\[ U_{\text{tot}} = U_0 + U_\gamma + U_a = U_0 - \frac{\pi \sigma^2 a^2}{E} + 4a \gamma \quad (3.31) \]

Consequently, the equilibrium condition for crack extension is obtained by taking the derivative with respect to crack length \( (dU/da) \) and setting this sum equal to zero:

\[ d \left( -\frac{\pi \sigma^2 a^2}{E} + 4a \gamma \right) \over da = 0 \quad (3.32) \]

Eqn (3.32) states that when the elastic strain energy released due to a potential increment of crack growth \( (da) \) outweighs the demand for surface energy for the same crack growth, then the crack grows in an unstable manner, causing fracture. The results of this equilibrium condition can be written as:

\[ \frac{2\pi \sigma^2 a}{E} \geq 4\gamma \quad (3.33) \]

This equation can be rearranged to the general fracture criterion, as given by eqn (3.34):

\[ \sigma_f = \sqrt{\frac{2E\gamma}{\pi a}} \quad (3.34) \]

where \( \sigma_f \) is the fracture stress.

Eqn (3.34) is the common form in which the Griffith criterion is expressed, but it is only strictly applicable for thin plate and when plane stress conditions prevail. For a thick plate and under plane strain conditions it becomes eqn (3.35):

\[ \sigma_f = \sqrt{\frac{2E\gamma}{\pi(1-\nu^2)a}} \quad (3.35) \]

where \( \nu \) is the Poisson's ratio.

The specific values for the fracture surface energy \( (\gamma) \) can be calculated using the Griffith eqn (3.35). However, for epoxy resins these values are calculated to be between 50 and 200 Jm\(^{-1}\) [9], which are much higher than the theoretical surface energy of epoxy resins, which are thought to be of the order of 1 Jm\(^{-1}\). This discrepancy is due to Griffith's underlying assumption of only pure elastic behaviour of the material and the absence of any plastic deformation.

Irwin [10] has developed a theory for fracture of slightly ductile materials, which undergo a small amount of plastic deformation in a plastic zone in front of the crack tip. The energy absorbed during plastic deformation is much higher than the surface energy and this is reflected in the measured values of \( \gamma \) for most materials, which are much larger than the theoretical ones. For this reason the strain energy release rate, \( G \), instead of the \( 2\gamma \) has been introduced and this represents the total work of fracture and not only the true surface energy. The Griffith eqns (3.34) and (3.35) for plane strain and plane stress conditions,
respectively, can be modified to eqns (3.36) and (3.37). Fracture occurs when $G$ reaches the critical value $G_c$:

\[
\sigma_f = \frac{G_c E}{\pi a} \tag{3.36}
\]

\[
\sigma_f = \frac{G_c E}{\pi(1-\nu^2)a} \tag{3.37}
\]

### 3.2.2 Stress intensity factor (K-Approach)

An alternative approach was proposed by Irwin [11], that considers the stress field near an idealized crack of $2a$ length, as shown in Figure 45.

![Figure 45: The stress field near an idealized crack of length 2a](image)

A more accurate stress analysis has been proposed by Westergaard [12]. In his model the stresses at any point, with the distance ($r$) from the crack tip and an angle ($\theta$) to the crack propagation direction, are given by:
\[ \sigma_{xx} = \frac{K_1}{(2\pi)^{1/2}} \cos \left( \frac{\theta}{2} \right) \left[ 1 - \sin \left( \frac{\theta}{2} \right) \sin \left( \frac{3\theta}{2} \right) \right] \]  

(3.38)

\[ \sigma_{yy} = \frac{K_1}{(2\pi)^{1/2}} \cos \left( \frac{\theta}{2} \right) \left[ 1 + \sin \left( \frac{\theta}{2} \right) \sin \left( \frac{3\theta}{2} \right) \right] \]  

(3.39)

\[ \sigma_{zz} = \sqrt{\sigma_{xx} + \sigma_{yy}} \] for plane strain conditions

(3.40)

\[ \sigma_{zz} = 0 \] for plane stress conditions

(3.41)

\[ \sigma_{xy} = \frac{K_1}{(2\pi)^{1/2}} \cos \left( \frac{\theta}{2} \right) \sin \left( \frac{\theta}{2} \right) \cos \left( \frac{3\theta}{2} \right) \]  

(3.42)

\[ \sigma_{yz} = \sigma_{zx} = 0 \]  

(3.43)

The value of Irwin’s approach is that the stress field around crack is identical for all types of loading situations normal to the crack. If the magnitude of the stresses (i.e., their intensity) is constant for a given load and geometry, than \( K_i \) is called the stress intensity factor. The subscript \( J \) denotes to the loading mode of the crack.

For an infinite sheet with a central crack of length \( 2a \), it was shown by Irwin that when \( \sigma \) reaches the fracture stress \( \sigma_f \), \( K_i \) has a critical value that is termed the critical stress intensity factor \( K_{ic} \) as given by:

\[ K_{ic} = \sigma_f \sqrt{\pi a} \]  

(3.44)

Consequently, a mathematical link with the previously proposed Griffith criterion is given by a transformation of eqn (3.44) to eqn (3.45), which is identical in form to eqn (3.34).

\[ \sigma_f = \sqrt{\frac{K_{ic}^2}{\pi a}} \]  

(3.45)

### 3.2.3 Fracture toughness test modes

For the determination of the material properties \( K_{ic} \) and \( G_{ic} \) three experimental methods (Figure 46) of controlled crack propagation are predominantly used:

- Mode \( I \), crack opening for tensile mode
- Mode \( II \), sliding or in-plane shear mode
- Mode \( III \), tearing or anti-plane shear mode

More details on these methods, their evaluation, and possible influence of sample geometry on the resulting material values are given in [13-16]. A general case of cracking
may include superposition of all three modes. Nonetheless, mode 1 is the most critical mode, hence it is the only one that will receive detailed consideration in this work.

Figure 46: Experimentally used modes of controlled crack propagation: (left) the crack opening or tensile mode I, (middle) the sliding or in-plane shear mode II, and (right) the tearing or anti–plane shear mode III

3.3 Toughening of epoxy thermosets

Common ways to toughen brittle epoxies, which typically have $G_{ic}$-values less than 200 J/m$^2$, include (1) chemical modifications of a given rigid epoxy backbone to a more flexible backbone structure, (2) increase the molecular weight of the epoxy monomer, (3) lowering of the crosslinking density of the cured resin by mixtures of high monomer molecular epoxy weight or low functional curing agents, and (4) incorporation of dispersed toughener phase(s) in the cured epoxy matrix.

Toughening via dispersed phase(s) morphology has proved to be the most effective without a significant reduction of crosslink density ($T_g$) as occurs with the first three methods. Taking this into account, fracture toughness of brittle epoxies can be most effectively improved by using at least one of three following major methods, which all based on the addition of second phase particles. The differences between them are the types of particles employed; hence these modified-epoxies have different designations. When the particles used are soft rubber, the material is called rubber-modified epoxy. When the particles consist of hard inorganic particles, the material is known as particulate-filled epoxy. When the particles are composed of rigid thermoplastic resin the modified material is termed thermoplastic modified epoxy. In the following sections of this work the different modifications are reviewed with respect to their toughening mechanisms and applications.

3.3.1 Epoxy toughening with soft particles (rubber toughening)

The technology of rubber-modified epoxies is at least thirty years old and has been extensively studied in traditional diglycidyl ether of bisphenol-A (DGEBA) and diglycidyl
ether of bisphenol-F (DGEBF) resins. The work of McGarry et al. [17-19] is among the first to show that significant improvements in toughness are obtainable by adding certain liquid rubbers to epoxy formulations. Since their exploratory work, a tremendous amount of research on the nature of toughening mechanisms has been carried out [20-47]. This resulted in a wide range of different toughened epoxy materials. The type of rubber to be added to toughen the resin is mainly determined by two factors [6]: (1) the compatibility requirement: the rubber must be totally miscible in the resin prior to cure, but separates as a second phase during the cure of the resin. (2) The chemical requirement: the rubber should react with the epoxy group in order to form chemical linkages between the modifier and the matrix.

Different types of acrylonitrile-based copolymers generally fulfill both requirements and therefore they are widely established as toughening modifiers. The effects of the rubber concentration, acrylonitrile content, molecular weight, solubility parameter, and end-group functionality on the fracture toughness of epoxy/rubber blends have been extensively studied. Carboxyl-terminated butadiene-acrylonitrile (CTBN) rubber is the most widely investigated toughening modifier currently used [24, 25, 39, 45, 48, 49]. To a lesser extent amino terminated butadiene-acrylonitrile (ATBN) [35, 50-54], epoxy-terminated butadiene-acrylonitrile (ETBN) [50, 55-57] and hydroxyl-terminated butadiene-acrylonitrile (HTBN) [58-61] have also been considered to toughen epoxies.

Even if the huge amount of available information is in some cases contradictory, for the relationship between the micro-structural parameters and mechanical properties it can be generally stated that:

- Phase separated morphologies outperform homogeneous structures in terms of improvement of fracture toughness.
- The toughness of phase separated rubber modified DGEBA-thermosets increases with volume fraction of the dispersed rubbery phase. An optimum of the mechanical properties is obtained by a phase-separated morphology with a rubber content between 10 to 20 parts per hundred resin (phr).
- The toughening is primarily attributed to the size and distribution of the precipitated rubber. Large rubber particles (>5 µm) show only a moderate increase in fracture toughness by a particle bridging/crack deflection mechanism. In contrast smaller particles (1-3 µm) provide a significant increase in toughness through cavitation-induced shear banding.
- However, the main deficiency in the use of the above reported oligomers is the high level of unsaturation in their structure, which provides sites for degradation reactions in oxidative environments [62]. Consequently, thermosetting materials toughened with elastomeric particles are predominately used in low temperature applications [63]. To
overcome this intrinsic limitation, other elastomeric modifiers have been investigated as well. For example, Banthia et al. [29] have used acrylic elastomer oligomers as dispersed phase to improve fracture toughness. Wang and co-worker [64] obtained similar results with epoxy functionalized poly(n-butylacrylate) (ETPnBA) and carboxyl functionalized poly(n-butylacrylate) (CTPnBA) as novel modifier. Fluorocarbon elastomers [65-68] have also been the focus of several research activities.

The incorporation of different rubbers to an inherently brittle resin generally modifies its characteristics. For example, it significantly increases the fracture toughness and related toughness improvements depend upon various parameters, such as particle size and volume fraction, strain rate, temperature and other environmental factors. The major postulated toughening mechanisms are schematically illustrated in Figure 47. Consequently, because of such a gain in toughness for relatively loosely cross-linked thermosets (e.g. low glass transition temperature), rubber toughened epoxies are being successfully used in various engineering applications.

![Figure 47: Schematic representation of several toughening mechanisms proposed by Pearson [69] for rubber-modified epoxies: 1) rubber tearing; 2) particle bridging; 3) crack path deflection, 4) particle cavitation; 5) cavitational induced shear bending; 6) micro-cracking](image)

On the other hand the rubber toughening approach causes the disadvantages of a reduction in stiffness, lowers $T_g$, plasticizes the matrix (if the rubber is not fully separated from the solution in the resin), reduces yield strength and increases the linear thermal expansion coefficient, and hence adversely affects the resin performance in hot/wet conditions in comparison to the unmodified system. These limitations are often unacceptable for many structural and long-term applications. A further limitation is the fact that the rubber toughening method becomes progressively less effective as the crosslinking density of the matrix increases (multifunctional epoxy systems), as summarized in Figure 48.
The effect of the matrix crosslink density on toughness has been extensively analyzed [44, 72, 73]. Rubber toughening of thermosetting resins depend primarily upon micro-deformation in the resin matrix, which is usually accompanied by cavitation within the rubber particles, and consequent stress whitening of the yield zone. As the resin matrix is crosslinked more densely, its capability to plastically deform by shear yielding is reduced [74]. In view of this inherent problem in causing yielding in high glass transition temperature resins, it appears that successful toughening can be achieved only by introducing energy absorption processes that do not depend upon matrix ductility. Following the need to increase the toughness by maintaining a high glass transition temperature, hard particles and/or high performance ductile thermoplastics can be used instead of rubber to modify dense epoxy resins. These two toughening concepts will be further reviewed and discussed in the following sections.

![Critical stress intensity factor (K\textsubscript{IC}) as a function of carboxyl-terminated butadiene-acrylonitrile co-polymers (CTBN) fraction for different highly crosslinked epoxy-systems](image)

**Figure 48**: Critical stress intensity factor (K\textsubscript{IC}) as a function of carboxyl-terminated butadiene-acrylonitrile co-polymers (CTBN) fraction for different highly crosslinked epoxy-systems (◆) ref. [41], (■) ref. [70], (○) ref. [70], ref. (▲) [70], (☆) ref. [71]. All values were measured at room temperature.

### 3.3.2 Epoxy toughening with hard inorganic particles

The technology of reinforcing epoxies with inorganic hard particles is at least as old as the rubber modification approach. Mechanisms proposed for particle-filled epoxies include (1) an increase in fracture surface due to the irregular path of the crack, (2) plastic deformation of the matrix around the particles; and (3) the crack pinning and debonding and/or micro-cracking mechanism. These mechanisms are schematically illustrated in Figure 49. As described above, toughening through the use of inorganic particles has some rather complicated aspects and it is improbable that a simple mechanism can
explain the complex fracture behaviour. Despite this reservation, today the crack pinning (crack bowing) mechanism is considered as the most relevant toughening mechanism for inorganic particle toughening.

Figure 49: Schematic toughening mechanisms for glass-filled epoxies: (1) crack pinning, (2) particle bridging, (3) crack path deflection, (4) debonding, (5) crack branching and (6) micro-cracking [69].

3.3.2.1 Crack pinning mechanism of hard particles

Lange has proposed the development of the crack pinning mechanism for a two-phase brittle material in 1968 [75, 76]. He explained the toughening effect of rigid particles in brittle matrices with the “line tension concept” that has been originally developed for dislocation motion in ceramic materials. The obstacles (rigid filler particle) create an obstruction for the propagation of the primary linear crack front, and cause an increase in toughness by increasing the crack length compared with the unfilled system (compare $L(u)$ and $L(f)$ in Figure 50).

Figure 50: Crack-pinning mechanism as proposed by Lange [77]. (a) side view, (b) top view. $L(u)$ is the line length of the crack front in an unfilled resin. In a filled resin the line is bowed and thus $L(f)$ is longer than $L(u)$. 

This image is not available online. Please consult the hardcopy thesis available from the QUT Library.
A simple mathematical description based on this line tension concept and related to the increase in fracture energy, $G_0$, due to pinning, was derived:

$$G_0 = G_{lc} \text{(matrix)} + 2T_L / D_s$$  \hspace{1cm} (3.46)

Where $T_L$ is the line energy per unit length, and $D_s$ is the interparticle distance. This eqn (3.46) presumes that the crack front breaks away from the pinning positions when it attains a radius of $D_s/2$. In addition, the interparticle distance can be obtained from eqn (3.47), [78]:

$$D_s = \frac{2d(1-V_f)}{3V_f}$$  \hspace{1cm} (3.47)

where, $d$ is the average particle diameter and $V_f$ is the volume fraction of rigid filler.

For a penny-shaped crack, Lange [79] showed that the line energy $T_L$ predicts an inversely proportional relationship between the increase in fracture energy, the filler size, and the filler volume fraction. Nonetheless, Lange’s equation has been found to be inadequate to describe the crack pinning mechanism in practice [75, 76, 78] except for the case of a glass filled alumina [79]. In particular, the initial slopes of plots of $G_f$ against $D_s^{-1}$ are often a function of volume fraction [80] and thus the value of $T_L$ is not invariant with the particle size as suggested in (3.46). Consequently, more satisfactory theoretical models have been proposed.

Evans [81], refined the original concept developed by Lange and calculated the increase in strain energy necessary to bow out the crack between the particles by a detailed calculation of $T_L$. Evans assumed the existence of semi-elliptical crack fronts between particles, and demonstrated that the line energy contribution to the fracture energy depends on both the particle size and spacing as given by eqn (3.48):

$$\frac{K_c}{K_0} = \left( \frac{\pi}{2 + d_p / D_s} \right)^{0.5} \left[ \tan \left( \frac{\pi}{2 + d_p / D_s} \right) \right]^{0.5}$$  \hspace{1cm} (3.48)

Where $K_c$ and $K_0$ is the critical stress intensity factor of the modified and the unmodified epoxy, respectively, $D_s$ is the surface-to-surface obstacle spacing, and $d_p$ is the particle diameter. Evans also calculated the ratio of $G_{ic}$ of the composite to that of the resin or the ratio of the tensile strength of the composite to that of the resin, assuming that the flaw size is constant. Evans model predicts a non-linear increase in fracture toughness with increasing filler fraction and the prediction appears to give a better fit to the data of Lange and Radford [78]. Although, in most analyses performed by Evans, particles were considered as impenetrable obstacles, he mentioned the importance of the impenetrability of particles. He proposed the use of an impenetrability factor ($\varepsilon_0$), but did not study the effects of impenetrability, which was instead performed later by Green et al. [82, 83].
Green and co-workers extended the work of Evans and observed a bowed secondary crack front using ultrasonic fractography. They have examined, both experimentally and theoretically, the effects of particle shape, particle fraction, fracture toughness of particles, particle thermal expansion and particle/matrix adhesion on fracture in model composites of nickel spheres in a brittle glass matrix. At lower filler contents, the theoretical values are in very good agreement, however, at higher volume fractions there is a deviation from the theoretical prediction [84]. This probably arises because the crack front bows out in an elliptical rather than in a semi-circular manner [83, 85].

Even if the discussed crack pinning theories still exhibit some uncertainties, such as the different geometries of crack front bowing have never actually been experimentally confirmed, the different models can be satisfactorily used to explain the fracture toughness changes with varying volume fraction and size of inorganic particles.

### 3.3.3 Epoxy toughening with thermoplastics

Since the initial work in the eighties, toughening with engineering thermoplastics has received much attention in the last decade. Many studies using a variety of different thermoplastic grades have been published [69, 86-91].

In order to avoid deterioration of the stiffness, the strength and the glass transition temperature of the cured resins an engineering thermoplastic has to be blended. In particular polyethersulphone (PES) and polyetherimide (PEI) have been widely used to produce blends consisting of ductile and tough thermoplastic particles dispersed in highly crosslinked epoxy formulations. PES and PEI have high glass transition temperatures (210 to 225°C), possess an excellent chemical resistance and are stable at temperatures <200°C. Because of the high molecular weight of PES and PEI, the amount which can be dissolved in epoxy resins is rather limited for industrial processes. Hence both thermoplastic modifiers have to be mixed together with an appropriate solvent and the solvent has to evaporate before adding the curing agent to the mixture.

Raghava [91] has examined the enhancement in fracture toughness of PES modified TGDDM-epoxies cured in the presence of aromatic anhydrides. Especially, he studied the influence of morphology on toughness and observed a two-phase structure and a bimodal particle size distribution by dynamic mechanical analysis and microscopy. However, the obtained increase in fracture toughness was only negligible. As an explanation for this observation the poor interfacial adhesion between the separated PES-particles and the epoxy matrix was outlined. To overcome this limitation Raghava [89] has blended a low molecular weight polyethersulphone containing hydroxyl end groups (H-PES) with a TGDDM/DDS matrix, expecting that the reactive end groups of H-PES can participate in
the chemical reactions during curing of the epoxy and achieve in this way a high level of interfacial adhesion. The increase in toughness that has been achieved with these two-phase epoxy-polyethersulphone systems, however, was only marginal. For a 15 phr H-PES modified network the critical stress intensity factor \((K_{IC})\) determined at room temperature increased only by about 0.1 MPam\(^{0.5}\). The obtained results were attributed to the fact that the highly crosslinked TGDDM-matrix remains brittle, even after inclusion of low concentration of H-PES, and thus formation of shear bands, the primary energy dissipation mechanism, is not possible.

Bucknall and Partridge [90] have confirmed the results reported from Raghava by using a commercial PES (Victrex 100P) to toughen various blends of tetrafunctional (TGDDM) and trifunctional (TGpAP) epoxy resins cured with diaminodiphenyl-sulphone (DDS) and dicyandiamide (DICY). They also reported that the PES-toughened TGDDM-resin cured with both type of hardeners did not show phase separation. In contrast, phase separation was observed in the case of trifunctional TGpAP epoxy resin. For all studied PES-modified systems the toughness increase remains a secondary effect.

Based on the available literature it can be concluded that the blends of epoxy resins with polyethersulphone (PES) up to a critical concentration of 15 wt.% show only modest improvements in the fracture toughness properties [86, 91-95] compared with the unmodified systems as summarized in Figure 51. However, if the PES concentration increases above 15 to 20 phr an increase in fracture toughness can be obtained.

Figure 51: Critical stress intensity factor \((K_{IC})\) as a function of polyethersulphone (PES) weight fraction for various highly crosslinked epoxy-systems (■) ref. [94, 95], (△) ref. [92], (▼) ref. [92], (◇) ref. [94, 95]. All values were measured at room temperature.
Early toughening studies from Diamont and Moulton [70] showed that thermoplastic loading of 10 wt% polyetherimide (PEI) can be used as an effective modifier in a TGDDM-resin, provided that phase separation combined with good interfacial adhesion is obtained. They observed that a mixture of TGDDM/DDS and PEI built a two-phase structure and, hence, the fracture toughness was significantly improved ($\Delta K_{IC}=0.24 \text{ MPam}^{0.5}$) compared with the reference system.

Hourston, Lane and McBeath [96] reported that a rapid increase in fracture toughness occurs for a TGDDM/DDS-system blended with PEI when the morphology changed from particulate to co-continuous. Their results demonstrated that a significant increase in $K_{IC}$ by almost 100% was obtained with a 15 phr addition of PEI.

Chen et al. nitrated a PEI thermoplastic to study the effects of interfacial adhesion of a TGpAP/DDS system by comparing the toughness of nitrated and un-nitrated PEI at various concentrations. They observed that, for cured and post-cured samples, $K_{IC}$ decreased for the nitrated compared with the unmodified PEI. Scanning electron microscopy also revealed that nitrated PEI was substantially more compatible with the TGpAP/DDS-system resulting in totally miscible blends. Consequently the obtained improvements in fracture toughness remain of secondary influence.

Studies on polyetherimide (PEI) modifications of high performance epoxies have reached similar conclusions than PES modified multifunctional epoxy systems. However, significantly higher improvements in toughness were obtained in the case of epoxy/PEI blends. An overview of results from different studies on highly crosslinked epoxy/PEI blends is given in Figure 52. From comparison of Figure 51 and Figure 52 it can be clearly seen that PEI modifications exhibited a superior improvement in toughness over PES.

![Figure 52: Critical stress intensity factor ($K_{IC}$) as a function of polyetherimide (PEI) weight fraction for various highly crosslinked epoxy-systems (ref. [96]) ref. [94, 95], (Ref. [70], (ref. [94, 95], (ref. [97], (Ref. [98], (ref. All values were measured at room temperature.](image-url)
More recently, Boogh and co-workers [99] demonstrated a novel thermoplastic toughening procedure. They used a low viscosity polyester based hyperbranched polymer (HBP) with reactive epoxy-endgroups as toughening modifier for bisphenol F resin (DGEBF) cured with isophorondiamine. By tailoring the epoxy functionality of the hyperbranched modifier, a chemical induced phase separation (CIPS) was demonstrated resulting in a two-phase morphology of the cured system. Remarkably, they did not report a significant decrease in stiffness and glass transition temperature, which they attribute to an almost perfect phase separation. An outstanding performance of the multifunctional epoxidized hyperbranched polymers yielded an increased fracture toughness of around 140%.

In contradiction, Wu et al. [100] showed only a moderate increase in fracture toughness for a HBP modified two-phase epoxy system. They added a commercial hydroxyl-functionalized hyperbranched polymer to a diglycidyl ether of bisphenol-A (DGEBA) matrix cured with diaminodiphenylsulfone (DDS) and reported an increase in $K_{IC}$ of 60%. They additionally reported, that an increased molecular weight of the HBP (higher generations) enhanced the effectiveness of the modifier by decreasing the reduction of the glass transition temperature of the phase-separated composite. The poor interfacial adhesion between the HBP particles and the matrix, due to the absence of chemical reactions between the matrix and the HBP-shell, probably explained the differences between these two studies. However, by a cross-comparison to linear polyesters as impact modifiers, they stated that the linear counterparts performed essentially as well as the hyperbranched polymer modifiers at identical molecular weights.

Further studies on thermo-mechanical properties and morphology on third generation, hydroxyl-functionalized hyperbranched polymers in an epoxy resin have been performed by Ratna and Simon [101]. Depending on the epoxy monomer used, they observed either a phase separated morphology for liquid DGEBA, or a homogeneous structure in the presence of a trifunctional aminoglycidyl (TGPAP) resin. For both matrices the addition of hyperbranched polymers accelerates the epoxy-amine curing reaction due to the catalytic effect of the HBP hydroxy end groups. A significant improvement in impact strength was observed at higher concentrations (>10 wt.%) for both examined epoxy formulations. The enhancement of toughness was mainly attributed to elastification of the matrix, having a drawback of lowering the network density and finally reducing the mechanical properties.

Despite the large number of experimental studies, the number of theoretical models that are able to predict improvements in toughness in thermoplastics-modified epoxies in a quantitative way is rather limited. The main mechanisms are illustrated in Figure 53. Enhancement in toughness is often explained in terms of crack pinning [79, 81, 83] or particle bridging [38, 102] in a manner very similar to that explained for hard particle filled epoxy. However, in contrast to hard particles, thermoplastic inclusions are able to yield
and this yielding can provide an additional source of toughness. Even though no model has been developed so far for predicting the phenomenon, shear-yielding events seems to be mostly involved in thermoplastic epoxy toughening.

Figure 53: Mechanisms for toughening of thermoplastic-modified epoxies; (1) crack pinning, (2) particle bridging, (3) crack path deflection, (4) particle yielding, (5) particle yielding induced shear banding and (6) micro-cracking [69].

3.4 Experimental

3.4.1 Materials

For details on the used epoxy monomer and hardeners as well as the system composition the reader it is referred to section 2.2.1.

3.4.1.1 Hyperbranched polymers (HBP) modifier

The hyperbranched polymers used in the present study are commercially available under the trade name Boltorn® (Perstorp, Sweden). The HBP’s molecules used are synthesized from a tetrafunctional ethoxylated pentaerythritol core (C₉H₁₂O₄), with an average of five ethoxy units per pentaerythritol [103], and multiple 2,2-diethylol propionic acid (C₅H₁₀O₄) chain extenders or repeating units. An idealized reaction scheme for the acid catalyzed condensation reaction is shown in Figure 54 and a more comprehensive description of the synthesis can be found elsewhere [104-107]. The HBP’s are primarily produced by a divergent synthesis, but to some extent, also through a convergent reaction [108]. The growth is controlled by stoichiometric ratios of core to chain extenders under carefully selected processing conditions to avoid side reactions. The resulting polydisperse and highly branched polymer has a main core shell function and a minor fraction consisting of COOH-functional branches. A degree of branching is typically about 45% [105].
The unmodified shell consists mainly of hydroxyl functional groups but the end-groups are generally accessible for further functionalization as described in literature [110]. In this study three unmodified hydroxyl functional products (Boltorn®H-20, H-30, and H-40) and two epoxy functionalized third-generation HBP products (Boltorn®E1 and E2) were utilized as toughening additives. For the epoxy functionalization of the hydroxyl terminated precursor product (H-30), a partial epoxidation step was carried out. In all cases, a minimum of an average of 5%, of the theoretical 32 functional groups in the HBP shell was remaining hydroxyl groups. The other 95% of the end groups were reacted with 10-undecenonic-acid by an esterification reaction. Afterwards the oxirane ring was formed by epoxidation of the conjugation by use of hydrogen peroxide. Further details of the procedure are described in [111, 112]. A typical property profile of the used aliphatic hyperbranched polyesters is given in Table 8.
3.4.1.2 Inorganic filler

All investigations on particulate filled systems were carried out with a commercial non-surface treated white crystalline silica flour of type Millsil-W10 (Quarzwerke, Germany). The specific physical properties and corresponding scanning electron micrographs are given in Table 9 and Figure 55. To study the influence of the filler size, different filler fractions were separated in a sieving tower. The particle size distribution of the silica fillers were measured by a non-contact liquid sedimentation method using a Horiba CAPA-700 particle size analyzer. Data were obtained from the change in particle concentrations on the basis of light transmission. For the experimental particle size distribution measurements, the silica fillers were thoroughly mixed in ethylene glycol (carrier medium) and sodium hexametaphosphate (dispersion agent) in an ultrasonic bath for 45 minutes. The concentrations of silica and sodium hexametaphosphate were 0.01 and 0.1 wt% respectively. Particle size distribution curves were obtained as average curve from at least five independent measurements.
Table 9: Specific properties of the silica filler Millsil-W10 used [115]

This table is not available online. Please consult the hardcopy thesis available from the QUT Library.

3.4.2 Sample preparation

The viscosity of the commercial MY721-epoxy monomer was reduced by pre-heating to 65°C, before the premixed hardener-mixture was added and dissolved with a high shear mixer at 13,500 rpm for 10 minutes to obtain a homogeneous mixture. Afterwards the mixture was degassed for about 5 minutes at pressures below 100 mbar in order to remove trapped air. For blend compositions containing silica filler and/or hyperbranched polymer components, the appropriate weight fractions of the components were added slowly and mixed under vacuum for an additional 15 minutes.

The final mixture was poured into steel moulds (4 mm thick plates and tensile dumbbells) that had been preheated at 60°C. Curing was carried out at 60°C for 4 hours in an air-circulating oven. Then the specimens were demoulded and post-curing was continued at 200°C for 3 hours. After the post-curing period, the oven was switched off and the samples were allowed to cool back to room temperature slowly in order to minimize internal stresses.

To study the effects of different filler surface treatments, the silica filler W10 was pre-treated with γ-glycidoxy-propyl-trimethoxy-silane (Silquest A187, Witco) to promote adhesion and a commercial siloxane based mold release agent (Aquathan®, Block-
Chemie) to reduce the adhesion to the epoxy resin. The molecular structure of the used silane adhesion promoter is shown in Figure 56.

The filler particles were treated using the procedure based on that suggested by Trachte and DiBendetto [116]. 200 g of filler were immersed either in a 5% solution of the Silquest A187-silane in n-heptane or directly in Aquathan®. The suspensions were stirred for 8 hours at 40°C and then filtered, rinsing with n-heptane. The treated filler was then dried at 80°C under vacuum for at least 16 hours.

\[
\begin{align*}
\text{H}_2\text{C} & \text{CH} - \text{CH}_2 - \text{O} \left[ \text{CH}_2 \right]_3 \text{Si} \left[ \text{O} \right. \\
& \left. \text{CH}_3 \right]_3
\end{align*}
\]

Figure 56: Silquest A-187 adhesion promoter used

### 3.4.3 Double torsion test (DT)

The double torsion test (DT) for the evaluation of fracture properties, such as the critical stress intensity factor and the critical energy release rate, has been increasingly used for testing brittle materials, including polymers and metals [117-123].

The basic geometry of the double torsion specimen is illustrated in Figure 57. It consists of a plate in which a machined V-groove runs a length of the test piece and is centered at \( w/2 \). The V-groove provides a route for crack propagation through the centre of the sample. Each of these beams is loaded in torsion, usually by a four-point loading at the ends, causing the crack to propagate down the centre of the specimen leading to mode-I fracture. The plate is normally notched, or side grooved, on one side to help constrain the propagating crack to the centre of the specimen. In this study sharp cracks were introduced by applying controlled force to a very sharp razor blade, which induced a sharp natural crack ahead of the razor cut.

![Figure 57: Schematic representation of the Double-Torsion (DT) test configuration.](image-url)
The crack does not propagate directly across the thickness of the sample, but extends further along the tensile side of the plate to form a curved crack front as shown in Figure 58.

![Figure 58: Typical curved front crack profile for the Double Torsion test specimen.](image)

The critical stress intensity factor \( K_{IC} \) and the critical strain energy release rate \( G_{IC} \) of the materials were experimentally determined using the double torsion (DT) geometry (cf. Figure 57) on a Z100-Zwick universal testing machine. The specimens were loaded in compression, with various rates of crosshead displacements ranging from 0.01 to 10 mm/min at several temperatures between \(-40\) and \(200^\circ\text{C}\). For all performed experiments the test specimens were isothermal conditioned for one hour at the appropriate test temperature and \( K_{IC} \) was calculated for plane strain conditions according to eqn (3.49) as proposed in [124]:

\[
K_{IC} = F_{\text{max}} W_m \left[ \frac{(1 + \nu) \cdot 3}{1000 \cdot w \cdot t^3 \cdot a} \right]^{0.5} \tag{3.49}
\]

where \( F_{\text{max}} \) denotes the fracture load; \( W_m \) is the moment arm (13 mm); \( w \) is the specimen width (\( \sim 34 \) mm); \( t \) is the specimen thickness (\( \sim 4 \) mm); \( a \) represents the specimen thickness in the plane of the crack (\( \sim 3 \) mm).

In addition, \( G_{IC} \) was calculated from the stress intensity values using the relationship from Matios and Small [125] as given in eqn (3.50):

\[
G_{IC} = \frac{K_{IC}^2}{E(1 - \nu)} \tag{3.50}
\]

where \( \nu \) is the Poisson’s ratio (taken as 0.4 for unfilled resins and 0.3 for filled resins), and \( E \) is the Young’s modulus (determined from tensile tests).

In all figures the given results were based on the arithmetic mean of at least 5 measured values and the error bar indicates the standard deviation. The 4 mm plate thickness of the DT-specimens was chosen to be well within the requirements of ASTM E399-83 [16] for plane-strain conditions.

Depending upon composition of the material and the external test conditions, such as test temperature, strain rate etc. two principal modes of crack propagation can be distinguished by the profile of the related DT-load/displacement trace:
3.4.4 Tensile test

The tensile strength ($\sigma_{rm}$) and the Young's modulus ($E$) of the unfilled and filled samples were determined in a tensile test according to standard DIN-EN-ISO 527-1 [126] on a mechanical Zwick universal testing machine type Z100. It was equipped with a temperature chamber capable of temperatures ranging from –40 to 200°C. For all performed experiments the test specimens (dumbbell type-A) were isothermally conditioned for one hour at the appropriate test temperature. Tensile tests were performed at strain rates varying between 0,1 to 50 mm/min. In all figures the given value is the arithmetic mean and the error bar represents the standard deviation of at least 5 measured samples.

3.4.5 Compression test

Compression tests were carried out on a mechanical Zwick universal testing machine type Z100 according to the standard DIN-EN-ISO 604 [127]. For all performed experiments the cylindrical test specimens (Ø=20 mm, height=40 mm) were isothermally conditioned for one hour at the appropriate test temperature. Compression tests were performed at strain rates of 0,1 and 10 mm/min and temperatures at 50, 100, 150 and 200°C. A lathe was used to ensure a perpendicular cut and the specimens were lubricated with silicone grease before they were compressed between parallel plates. In all figures the given value is the
arithmetic mean and the error bar represents the standard deviation of at least 5 measured samples.

### 3.4.6 Dynamic mechanical analysis (DMA)

The dynamic mechanical analysis was performed using a Perkin-Elmer DMA-7e analyzer equipped with a three point bending assembly (15 mm span length). Bending-bars of 18 x 4 x 2 mm$^3$ were cast into a steel mould and cured at room temperature. The DMA was operated in the temperature-scanning mode with a constant displacement amplitude and frequency. The frequency was fixed at $f=1$ Hz using a strain amplitude of $\pm 10$ µm. The temperature ramp covered a range from 30 to 280°C with a continuous heating rate of 3°C/min under helium atmosphere.

### 3.4.7 Microscopy

Microscopic characterization of the inorganic particle size and distribution, as well as the fracture surface of a large number of specimens was examined using scanning electron microscopy (SEM). All SEM-experiments were carried out on a CAMSCAN microscope. Fractured samples were mounted on an aluminum sample holder using a conductive paint. The specimens were sputtered with a thin Au-Pd layer (~20 nm) to reduce surface charging. SEM-micrographs were obtained under conventional secondary electron imaging conditions and an accelerating voltage of 20 kV. Optical microscopy (OM) was mainly used to examine sub-surface damage in compressed samples. Therefore, thin-microtomes with a thickness from 20 to 100 µm were prepared using a polishing and sectioning technique as proposed by Smith [77]. Afterwards, all samples were examined in transmitted mode using a Zeiss-Axiolab microscope in polarized or cross-polarized light. In some cases a quarter wave plate was used to visualize the contrast of the birefringent regions.
3.5 Results & discussion

3.5.1 Effects of strain rate and temperature on the tensile deformation

The changes of the tensile strength ($\sigma_{rm}$) as a function of temperature and strain rate for the unfilled and silica-filled MY721/MA/HHPA-system are shown in Figure 60. It can be seen that the tensile strength for both systems tends to increase with increasing strain rate and decreasing test temperature, providing evidence that the results for different temperatures could be superimposed with the applied strain rates. Furthermore, it can be seen that the silica filled system exhibits slightly higher absolute tensile strength values.

Figure 60: Tensile strength ($\sigma_{rm}$) as a function of strain rate and temperature for (a) unfilled MY721/MA/HHPA-system; (b) 60% w/w silica filled MY721/MA/HHPA-system.
The influence of the test temperature and loading rate on the initiation and development of the fracture process under tension load was studied more in detail for the neat MY721/MA/HHPA-system. A sub-critical and smooth zone, as shown on the fracture surface of the tensile bars in Figure 61 and 62, increases with higher temperatures and lower strain rates. These observed effects agree well with earlier observations by Cantwell et al. [128].

Figure 61: Optical micrographs of the fracture plane as a function test temperature for the neat MY721/MA/HHPA-system tested with a constant strain rate of 0.1 mm/min under tension load; (a) 23°C, (b) 100°C, (c) 150°C, (d) 200°C.

Figure 62: Optical micrographs of the fracture plane as a function of strain rate for the neat MY721/MA/HHPA-system tested at 150°C under tension load; (a) 50 mm/min, (b) 10 mm/min, (c) 1 mm/min, (d) 0.1 mm/min

A more detailed examination of the fracture surface highlighted three distinct zones or regions as shown schematically in Figure 63. The irreversible damage initiates under normal circumstances at some internal defects or from regions corresponding to an area of increased stress concentration, i.e. the edge of the specimen. After the crack initiation at an internal defect, the crack followed slow crack propagation in the sub-critical zone,
before it accelerates into the smooth zone and finally reaches the highest crack propagation velocity in the rough zone [6].

![Figure 63: Typical fracture surface of silica filled epoxy tensile bar.](image)

Analysis of the microstructure by means of optical microscopy techniques revealed that none of the tested specimen yielded in tension and all samples fractured in brittle manner. The absence of any yielding can be theoretically explained by the fact that the specific fracture stress is lower than the intrinsic material's yield stress under the investigated temperature/strain rate conditions. Furthermore, Griffith’s defect theory [5] assumes that many more defects are active under loading in tension than in compression mode, which explains that yielding is generally much more difficult to observe in tension mode.

### 3.5.2 Effect of the filler fraction on the tensile deformation

Inorganic fillers are commonly used to modify various properties of epoxy polymers, or simply as extender filler for lowering the price/volume ratio of the material. In any case, it is essential to know the dependence of the material composition on the various properties. In particular the tensile strength ($\sigma_{rm}$), Young’s modulus ($E$), and yield stress ($\sigma_y$) are of primary importance for technical applications.

Figure 64(a) shows the tensile strength ($\sigma_{rm}$) as a function of the silica-filler fraction. It can be seen that the MY721/MA/HHPA-system does not exhibit any significant dependency of the ultimate tensile strength on the filler content between 0 to 50 vol.%, which is consistent with previously performed work on different epoxy systems [129]. Therefore, it can be assumed that the critical debonding strength or strain of the investigated system remains almost constant and independent of the filler content.

Additionally, the obtained $\sigma_{rm}$-data fit reasonably well within the upper boundary of a simple mathematical prediction as proposed by Nicolais and Nicodemo [130], which is given by eqns (3.51) and (3.52) and also depicted in Figure 64(a).

For the upper boundary condition:
\[ \sigma_m = \sigma_p \]  \hspace{1cm} (3.51)

For the lower boundary condition:

\[ \sigma_m = \sigma_p \left( 1 - 1.21 V_f^{2/3} \right) \]  \hspace{1cm} (3.52)

where \( \sigma_p \) is tensile strength of the polymer matrix, and \( V_f \) denotes the volume fraction of inorganic filler.

In agreement with several other studies [131-133], the Young’s modulus, as obtained from the initial slope of the tensile stress-strain curves, gradually increases with increasing inorganic particle content as shown in Figure 64(b). Many different theoretical predictions have been proposed to determine the elastic modulus of particulate filled composites in the past. One of the most widely accepted model is the theoretical approach proposed by Ishai and Cohen [134]. Ishai and Cohen’s equations originally derived from a two-phase model of a cubic matrix containing spherical inclusions and assuming either a uniform stress eqn (3.53) or a uniform strain eqn (3.54) condition (i.e. comparable to a series and parallel model in fiber composite theories).

\[ \phi_f = \frac{E_c}{E_m} = \frac{1 + (m-1)V_f^{2/3}}{1 + (m-1)(V_f^{2/3} - V_f)} \]  \hspace{1cm} (3.53)

\[ \phi_f = 1 + \frac{V_f}{m/(m-1) - V_f^{1/3}} \]  \hspace{1cm} (3.54)

where

\[ m = E_f/E_m \]

\( E_f \) = Young’s modulus of the filler

\( E_m \) = Young’s modulus of the matrix

\( E_c \) = Young’s modulus of the composite

\( V_f \) = Volume fraction of the filler

In Figure 64(b), the theoretical predictions from eqns (3.53) and (3.54) are compared to the experimentally obtained values from the tensile test. A fairly good agreement between the theoretical predictions assuming uniform strain conditions in the material and the experimental data can be seen.
Figure 64: Influence of the silica volume fraction in the MY721/MA/HHPA-system on (a) tensile strength ($\sigma_{\text{rm}}$) and (b) Young’s modulus ($E$). All tensile measurements were performed at 23°C with a constant strain rate of 1 mm/min.

### 3.5.3 Effect of strain rate and temperature on the compressive deformation

The behaviour of the ultimate compression strength as a function of temperature and strain rate for the unfilled and silica filled MY721/MA/HHPA-system is shown in Figure 65.
Figure 65: Compression strength ($\sigma_{m}$) as a function of temperature and strain rate for (a) unfilled and (b) 60% w/w silica-filled MY721/MA/HHPA-system.

In contrast to experiments performed under tension load, where only brittle fracture was observed, the load displacement curves in compression mode conditions were non-linear. This indicates that a substantial plasticization process occurred in the investigated temperature range between 23°C to 200°C. The curves for both the unfilled and the silica filled-system exhibited a peak stress (yield stress, $\sigma_y$) and a post yield-softening phenomenon before fracture occurred in a brittle manner (cf. small stress-strain curves in Figure 65). Moreover, both investigated systems show a decrease of the elastic Young’s modulus and the maximum compression strength with increasing temperature. This is a consequence of an increased molecular mobility on the scale of molecular chains and local groups at elevated temperatures; hence, the resistance to deformation becomes
Deformation and fracture behaviour

weaker. In particular, for the neat resin system the elongation at break is significantly increasing with increased temperature. On the other hand, the elongation at break remains nearly unaltered in the studied temperature range for the silica filled system.

Based on optical microscopy investigations under polarized light, it was possible to identify the primary inelastic micro-deformation mechanisms. It was primarily established that shear processes, which are increasing with increased temperatures, are responsible for relatively large strains in the glassy epoxy polymers. As expected the strain softening behaviour promoted the localized shear yielding in the form of shear bands preferably at stress inhomogeneities, e.g. the silica obstacles. These shear processes include both diffuse shear yielding and localized shear band formations, and occur without loss of intermolecular cohesion in the polymer, so that they finally produce only little, if any change in volume. In agreement with other studies, cavitation processes, e.g. crazing, have not been observed [6, 135-137]. It is hypothesized that the large number of crosslinking points and the high entanglement density can effectively restrain crazing in the studied MY721/MA/HHPA-system.

The observed bulk shear bands produce the classic shear offset at the edges of the unfilled specimen. A typical shear band formation of the neat MY721/MA/HHPA compression specimen is shown in Figure 66. It is obvious that the coarse band is approximately at an angle of 45° to the applied stress. Conducting similar tests with the filled epoxy was more difficult due to the non-transparent nature of the system. However, some evidence was found from the thin sectioning and microscopic analysis to propose that shear yielding is also the primary deformation mechanism in the filled resin.

![Figure 66: Transmission optical micrograph of a thin-section (25 µm) of a neat MY721/MA/HHPA specimen compressed at 200°C (a) non-polarized, transmitted light, (b) same specimen viewed between two crossed polarizers. The compression direction is horizontal as indicated by the arrows.](image)

For the filled system the first visual indication of irreversible damage occurs at the yield point ($\sigma_y$) where the stress-strain curve shows a maximum. Beyond this characteristic stress point, the highly filled material begins to stress-whiten reflecting the initiation of an irreversible damage processes. The stress-whitening phenomenon occurs in a diffuse
band that runs diagonally across the specimen, i.e. along the direction of maximum shear stress angle of 45°. At higher strains (~3%) the band becomes visually denser (whiter) and wider. It was observed that all compression specimens were severely whitened, independent of the test temperature and the rate of deformation. Typical examples of stress whitened and fractured compression specimens are shown in Figure 67. In particular the sample in Figure 67(a), where a specimen was loaded to 65% of the ultimate load at 150°C, two intersecting stress-whitened bands extending at approximately 45° can be clearly seen. The macroscopic stress-whitening effect is mainly provoked by the presence of new surfaces or voids, which scatter light within the solid. Considerations on the microscopic scale reveal that primarily particle-matrix debonding with minor contributions due to particle fracture and inelastic matrix deformation occurred in the particulate filled systems.

Figure 67: Silica-filled (60% w/w) MY721/MA/HHPA samples of uniaxially compressed specimen at 150°C. The different deformation stages are; (a) 65% ultimate load deformed specimen showing stress-whitening before failure; (b-d) specimen deformed to failure showing fracture at the dead-zone deformation-zone interface

3.5.4 Characterization of the fracture toughness behaviour

3.5.4.1 Effect of the test temperature

Glassy polymers such as epoxies are generally considered to be inherently brittle materials when tested at temperatures well below their glass transition temperature. In this section a series of fracture toughness tests at different temperatures were undertaken in order to determine the effect of the test temperature on the fracture toughness behaviour of the MY721/MA/HHPA-system. In the examined temperature range between
-40°C to 200°C all samples failed predominantly in an unstable crack propagation manner as shown by the corresponding DT-load/displacement curves in Figure 68. However, it can be seen that with decreasing test temperature the tendency to a mixed crack propagation appears, see Figure 68.

Moreover, variations of the test temperature significantly affect the characteristic fracture toughness values $K_{Ic}$ and $G_{Ic}$ as shown in Figure 69. Both, the neat and the silica filled formulation, exhibited an almost identical $K_{Ic}$- and $G_{Ic}$-temperature behaviour, i.e. with increasing temperature the material becomes more brittle resulting in a reduction of the $K_{Ic}$ and $G_{Ic}$-values. In particular, between 60 and 100°C a substantial decrease in the fracture toughness, $K_{Ic}$ was observed.

Figure 69: Variations of (a) critical stress intensity factor ($K_{Ic}$), and (b) critical strain energy release rate ($G_{Ic}$) as a function of test temperature. The silica fraction of the filled MY721/MA/HHPA-system (r=0.8) was fixed to 60% w/w. All DT-tests were performed at a strain rate of 0.1 mm/min.
This observation is very remarkable because a continuous increase in the fracture toughness up to the ultimate glass transition temperature was generally expected and previously reported for different TGDDM-based epoxy formulations [71]. Moreover, the Ludwig-Davidenkov-Orowan (LDO) theory predicts an increase in the fracture toughness properties with increasing test temperature [138, 139], because the yielding stress decreases with increasing temperature and hence micro-deformation processes will be favored and consequently can occur before fracture. This finally leads to an increase of fracture toughness with increasing temperature. However, for the studied MY721/MA/HHPA system the opposite behaviour, that means with increasing yield stress the material becomes tougher, was observed (Figure 70). As explanation for the observed behaviour, it is postulated that at elevated temperature the fundamental principles of the linear elastic fracture mechanics (LEFM) are not any longer valid, because the LEFM can only be applied at temperatures clearly below the glass transition temperature where plain strain condition can be applied. As soon as the test temperature increases above the glass transition temperature of the material the viscoelastic material properties become more dominant and thus a sharp decrease of the fracture toughness, i.e. $K_{IC}$, appears. Moreover a broadening of the Tg region may occur due to an inhomogeneous network structure.

![Figure 70: Critical stress intensity factor ($K_{IC}$) as function of compressive yield stress ($\sigma_y$) for the silica-filled (60% w/w) MY721/MA/HHPA (r=0.8).](image)

Additionally performed experiments on a same set of samples verified that the observed reduction of the $K_{IC}$-values (~50%) between room temperature and 200°C is a reversible process. This fact provides evidence that irreversible material changes, e.g. post-curing processes at higher temperature, can be unambiguously excluded. Therefore, the experimentally observed embrittlement with increasing temperature can be most probably explained by the presence of an inhomogeneous multiphase-network consisting of an independent MY721/MA and a MY721/HHPA sub-network. Moreover, it is proposed that
most probably the MY721/HPPA sub-network shows an underlying primary relaxation, i.e. a glass transition temperature, between 60 to 100°C.

To obtain more evidence for the hypothesis of an inhomogeneous network structure further fracture tests have been performed. The MY721-resin was cured with only pure MA (48 phr) and pure HHPA (32 phr), reflecting the equivalent hardener weight fraction as used in the co-anhydride mixture. As shown in Figure 71(a), the $K_{\text{IC}}$ of the MA-cured system is clearly independent of temperature as long as the material is in its glassy state. This results in an almost constant $K_{\text{IC}}$-value until the test temperature finally reached the glass transition at around 180°C. On the other hand, the MY721/HHPA-system (Figure 71(b)) exhibited a continuous increase of the fracture toughness with increasing temperature until the glass transition temperature at 64°C. At temperatures above this transition area a sharp decrease of experimental $K_{\text{IC}}$-data was induced by a change of the material from the glassy state to a highly viscoelastic material.

Assuming that both used anhydrides reacted independently from each other, a simple mixing rule that considered the molar co-anhydride proportions of the MA/HHPA mixture can be applied as shown in Figure 71(c). It can be seen that the experimental $K_{\text{IC}}$-data showed a fairly good agreement with the trend predicted by this simple mixing rule. These observations provide some additional indications that confirm the existence of a multi-phase network structure.

Figure 71: Variation of the critical stress intensity factor ($K_{\text{IC}}$) as a function of temperature for (a) MY721/MA (100/48) (b) MY721/HHPA (100/32) and (c) MY721/MA/HHPA (100/48/32). The dotted line represents the trend as predicted by a mixing rule considering the molar ratio of MA/HHPA=(0.7/0.3). All DT-tests were performed at a constant strain rate of 0.1 mm/min.
3.5.4.2 Effect of the strain rate
Since polymeric materials are generally viscoelastic by nature, the effects induced by increasing test temperature are often analogous to those produced by decreasing the strain rate. To determine the effect of strain variations on the fracture behaviour of the neat and silica filled MY721/MA/HHPA-system Double Torsion (DT) fracture tests have been performed at room temperature.

The obtained DT-load/displacement curves exhibited a “saw-tooth” appearance for both studied systems up to a strain rate of less than 10 mm/min. This also called “slip-stick” crack mode is the unambiguous indication of unstable crack propagation and allows the determination of the critical stress intensity factor for crack initiation \( (K_{ic}) \) and crack arrest \( (K_{ica}) \) [140-144]. Increasing the strain rate to 10 mm/min results in a different DT-load/displacement curve appearance, which corresponds to a change of the intrinsic crack propagation mode. The crack propagation under higher strain rate conditions occurs almost at a constant load until the final fracture of the sample. This type of continuous crack growth is generally described as stable, brittle crack mode and is favored by higher displacement rates [136, 145-147].

In Figure 72 the effects of a variable strain rate on the critical stress intensity factor is shown. It can be seen that an almost 10% increase in fracture toughness was obtained over a range of approximately three decades of strain rates. These results are in good agreement with the previously discussed mechanical tensile and compression behaviour that exhibited similar behaviour \( (cf. \text{chapter 3.5.1and 3.5.3}) \). The determined \( K_{ic} \)-values slightly decreased with increasing strain rate. On the other hand the corresponding \( K_{ica} \) values remain on an almost constant level and thus strain rate independent.

The first qualitative explanation for the obtained “slip-stick” crack propagation has been given by Phillips and co-workers [146, 147]. They explained the observed “slip-stick” phenomenon in terms of crack tip blunting during re-loading after crack arrest due to the ability of the material to deform plastically in the vicinity of the crack tip. At a certain increased load a new sharp crack initiates and extends rapidly until the load corresponds to the stress intensity value for crack arrest. Later on scanning electron microscopy studies [148] and also in-situ video recording of scanning electron microscope experiments [149] have confirmed this theory.
Figure 72: Variation of the critical stress intensity factor for crack initiation ($K_{ic}$) and crack arrest ($K_{ica}$) as a function of the strain rate. The silica content of the filled MY721/MA/HHPA-system was fixed to 60% w/w. All DT-tests were performed at room temperature.

3.5.4.3 Effect of the inorganic filler fraction

Unmodified epoxy resins in the uncured state have relatively high viscosities when compared with other thermosets, i.e. polyesters. Thus, for most technical systems the maximum volume fraction of fillers, which can be added to the resin, is limited to 50% w/w without impeding the flow characteristics of the composite. Moreover, it becomes increasingly difficult to degas the mixture to obtain a void free system. On the other hand at volume fractions below 30% w/w sedimentation effects could occur resulting in an inhomogeneous filler distribution in the material. In order to produce homogeneous castings, the mixture containing a filler content less than 30% w/w were cast just prior to gelation as described elsewhere [150]. Afterwards a DT-fracture test was performed and the fracture toughness properties were determined. From the corresponding DT-load/displacement curves (cf. Figure 73) it can be seen that all examined samples exhibited continuous crack propagation independent of the applied silica volume fraction. Furthermore, a constant increase of the critical load, associate to the maximum force before the crack started to propagate, was obtained by increasing filler fraction.
Figure 73: DT-load/displacement curves of the MY721/MA/HHPA-system as a function of silica weight fraction (a) unfilled, (b) 10%, (c) 20%, (d) 40%, (e) 50%, (f) 60%. All DT-tests were performed at room temperature with a strain rate of 0.1 mm/min.

The specific fracture toughness, expressed here as the critical stress intensity factor ($K_{ic}$) and the critical energy release rate ($G_{ic}$), of the silica filled epoxies are significantly affected, see Figure 74. It can be seen that the $K_{ic}$-values of the investigated system increase gradually with increasing filler fraction. This behaviour is in agreement with previous studies [78, 80, 85, 129, 145, 151, 152]. However, most of this research work concentrated on the effects of volume fraction upon the fracture energy in term of $G_{ic}$ [78, 80, 152, 153]. This has led to a more complex analysis, since the filler content has a strong influence on the Young’s modulus ($E$) of the composite as already discussed in section 3.5.2.

In this study the critical strain energy release rate ($G_{ic}$) was computed from eqn (3.50) by using the $K_{ic}$ (Figure 74(a)) and the appropriate modulus data (Figure 64(a)) as determined before. The calculated dependency of $G_{ic}$ as a function of the filler fraction is illustrated in Figure 74(b). One can see that the general trend of the obtained $G_{ic}$-behaviour is different to the $K_{ic}$-evolution. The initial $G_{ic}$-value of fracture energy shows a maximum at a filler weight fraction of $\sim 0.4$. This observed peak behaviour has been a focus of a number of discussions in the past. Some explained the observed behaviour with a change in failure mechanism [153]. However, another reasonable explanation for the difference curve trend between the $K_{ic}$ and the $G_{ic}$ response can be given by considering their final mutual relationship as given by eqn (3.50). For particulate filled materials, the elastic modulus ($E$)
generally increases more rapidly than $K_{IC}$ with a comparable volume fraction of inorganic particles [145]. Consequently, $G_{IC}$ has the common ability to decrease even while $K_{IC}$ increases.

![Graph](image1)

**Figure 74:** (a) Critical stress intensity factor ($K_{IC}$) and (b) critical strain energy release rate ($G_{IC}$) as a function of silica weight fraction for the MY721/MA/HHPA-system. All DT-tests were performed at room temperature with a constant strain rate of 0.1mm/min.

The fracture surfaces of ruptured samples were examined using SEM-technique, see Figure 75. From the micrographs of the neat resin system (Figure 75(a)) one can clearly see the smooth fracture surface with cracks in different planes. This unambiguously indicates the brittle fracture nature of the unmodified epoxy network, which accounts for its poor toughness ($K_{IC} \approx 0.6 \text{ MPa m}^{0.5}$) and limited deformation ability. For low silica volume fractions it can be seen that the particles are widely spaced, while with increased filler fraction the interparticle distance decreased and the connectivity significantly increased. Various theories concerned with the mechanisms involved in the particulate toughening have been reviewed in the introduction section. It is proposed that crack pinning (cf. 3.3.2.1) is the dominant mechanism for the obtained increase of fracture toughness, even when none of the filled samples exhibited a typical tail structure behind each particle, as expected for the crack pinning mechanism. However, the absence of these tails does not necessarily mean that no crack pinning has occurred, because the irregular filler shape and the relatively high filler content may produce considerable overlap of the secondary cracks. The simple fact that the surface roughness increases with increasing filler content indicates already an extension of the crack path.
Figure 75: Scanning electron micrographs of the fracture surface topology as a function of the silica weight fraction; (a) unfilled, (b) 10%, (c) 20%, (d) 40%, (e) 50%, (f) 60%.

A comparison of the theoretical models and the experimental values is given in Figure 76, where the reduced critical stress intensity factor ($K_c/K_{ic0}$) is plotted against the ratio between the average particle size ($d_p$) and the interparticle distance ($D_s$) as calculated according to eqn (3.47). The different lines represent theoretically calculated data as predicted by Green’s [83] and Evans’ [81] theories.

It can be seen that the agreement between Evans’ theory and the experimental data is fairly good. The fact that the microscopic investigation of the fracture surfaces showed a considerable breakdown of the particle/matrix interface underline the observation that the crack bowing mechanism might be more difficult to occur. On the other hand this observation gives a reasonable explanation for the fact that the measured data are generally lower than the predicted values.
Figure 76: Variation of \((K_{IC}/K_{IC0})\) as a function of \((d_p/D_s)\) for different silica-filler fractions. The full lines represent the theoretical predictions of Green [83] and Evans [81] for interacting and non-interacting elliptical cracks. Symbols denote the experimentally obtained values of the DT-test.

### 3.5.4.4 Effect of the inorganic filler size

To study the influence of the silica filler size on the deformation and fracture behaviour of filled epoxies, silica filler grades with five different particle size distributions were used. Typical particle size distributions and the corresponding SEM-micrographs of the classified fillers are shown in Figure 77.

Unfortunately, a generally accepted prediction of the stiffness and toughness properties as a function of the particle size is not available hitherto, because most of the developed theories explain the variations of the mechanical behaviour of polymeric composites without considering the particle size and their size-distribution. However, from Figure 78(a) it can be clearly seen that there is an increase of the tensile Young’s modulus with increasing the average particle size. The elastic modulus of the investigated MY721/MA/HHPA-composites increased by \(-35\%\) with increasing the average particle size from 2 to 160 µm. The distinctly affected stiffness of the samples with a relatively small average particle size, i.e. 2 µm, can be most probably to the poor wetting behaviour of smaller particles, due to the fact that the greater surface area considerably increases the final mixture viscosity.
Figure 77: Particle size distribution and the corresponding SEM-micrographs of different used silica filler grades with an average particle size of (a) 2 µm, (b) 7 µm, (c) 38 µm, (d) 160 µm
Unlike the particle volume fraction, the varying average particle size does not significantly affect the fracture toughness behaviour above a threshold value of about 10 µm, see Figure 78(b) and (c). Similar to the range of particle sizes investigated by Spandoukis and Young [145], the experiments performed on the silica filled MY721/MA/HHPA-systems showed that varying the particle size between 7 and 160 µm did not appreciably change the fracture toughness behaviour, and hence the experimental $K_{ic}$ and $G_{ic}$-data remain almost on a constant level. Moreover, all tested samples showed stable crack propagation independent of the particle sizes. However, it is clear that there is a lower and upper boundary in particle size where the mechanical composite-properties will be adversely affected due to the higher probability of a flaw being present within the particle or the matrix.

Figure 78: (a) Tensile Young’s modulus ($E$), (b) critical stress intensity factor ($K_{ic}$), (c) critical energy release rate ($G_{ic}$) as a function of average silica particle size. For all samples a fixed silica filler fraction of 60% w/w and a constant strain rate of 0.1 mm/min was used.
3.5.4.5 Effect of the filler/matrix adhesion

In order to investigate the effects of the resin-filler adhesion on the composite mechanical properties different filler pre-treatments were studied. The silica particles were treated with a mould release agent Aquathan® (Block-Chemie, Germany), which should effectively reduce the filler-resin adhesion. Furthermore, a commercial silane-coupling agent γ-glycidoxy-propyltriethoxysilane, Silquest-A187 (Witco, Switzerland) was applied to enhance the interface adhesion between the matrix and filler. Despite the differences in particle adhesion, as shown by the appearance of the fracture surfaces, it was observed that the different silica pre-treatments had only a minor effect on the tensile modulus of the composite as shown in Figure 79(a). Similarly, one can also observe that the filler-matrix adhesion does not significantly change the fracture toughness properties of the composites (Figure 79(b-c)). The \( K_{ic} \) and \( G_{ic} \)-values of the two different pre-treated fillers varied only within the normal scatter range. Recorded DT-load/ displacement curves revealed, that in case of poorly bonded silica-particles unstable crack propagation was obtained, whereas stable propagation was reached for well-bonded silica particles. This observations are consistent with previously performed studies by Spandoukis and Young [145, 151], who used glass beads treated with a mould release agent and a silane coupling agent and observed that the surface treatment had only a little effect on the composite modulus and fracture behaviour. It follows that very good interfacial bonding is not absolutely necessary to reach high fracture toughness properties.

The filler surface treatment, however, has a significant influence on the maximum mechanical strength of the studied samples. Well-bonded filler provides composites with notably higher tensile strength values (\( \sigma_m = 84.2 \pm 6.9 \) MPa) compared to poorly bonded particles (\( \sigma_m = 28.9 \pm 8.7 \) MPa). This observation may be explained by the fact that weakly bonded particles act as sources of “inherent” flaws and hence induce micro-crack initiation.
Figure 79: (a) Tensile Young’s modulus ($E$), (b) critical stress intensity factor ($K_{IC}$) and (c) critical energy release rate ($G_{IC}$) as function of different silica filler treatment. All measurements were performed at room temperature with constant silica filler content of 60% w/w.

### 3.5.5 Hyperbranched polymer toughening

Hyperbranched polymers (HBPs) are characterized by dendritically branched structures and in contrast to traditional rubber modifiers (e.g. CTBN) or thermoplastic modifier (e.g. PES, PEI) by a large number of functional end groups. The high density of the terminal groups on the HBP-modifier further offers the ability for tailoring their compatibility either through conversion of the accessible end groups to chemically suitable moieties or through in-situ reaction to form covalently bound networks. Apart from the higher functionality, HBPs differ generally from common rubber and thermoplastic-modifiers in their rheological property profile. The densely branched polymer backbone of the HBP contributes with less entanglement and a more globular structure, and hence to an essentially lower viscosity and Newtonian behaviour when comparing HBPs of a given molecular weight with conventionally branched or linear polymers of the same molecular weight. This specific property profile demonstrates the unique potential of HBPs as effective low viscosity tougheners for densely crosslinked thermosets [99-101].

In this section the dependency of the final morphology and the related thermo-mechanical properties of blends between the MY721/MA/HHPA-system and different functionalized HBPs were examined. The aim of this investigation is to characterize and understand the physical properties of these epoxy-HBP blends. In particular the miscibility, stiffness, glass transition temperature and fracture toughness properties of cured epoxy-HBP blends have been studied more in detail.

#### 3.5.5.1 Effects of the hyperbranched polymer end-groups

The effects of the shell chemistry of three commercially available HBP grades (referred collectively as Boltorn®H-type) on the solubility and morphology of blends with the
MY721/MA/HHPA-system were studied. The used H-types are all hydroxyl functionalized but differ in molecular weight and number of hydroxyl end groups, see Table 8. The compatibility of the 10% w/w HBP modified epoxy systems was studied by gradually heating the mixtures (\(\varphi = 1^\circ\text{C/min}\)) from room temperature to determine the solution temperature (\(T_s\)=cloud point temperature) by using optical microscopy. It was observed that the solubility of the modifier in the MY721/MA/HHPA-matrix decreased with increasing number of terminal hydroxyl groups of the HBP, and hence the measured critical solution temperature (\(T_s\)) showed an analogous behaviour as illustrated in Figure 80.

![Critical solution temperature (\(T_s\)) as a function of terminal hydroxyl groups for a 10% w/w modified MY721/MA/HHP-system. \(T_s\)-data were experimentally determined by optical microscopy with a heating rate of 1°C/min.](image)

It is assumed that the polar OH-end groups form strong hydrogen bonds that tend to contribute to the relatively high solution temperatures (\(T>150^\circ\text{C}\)) of the modified epoxy-systems. However, pre-curing of the utilized epoxy system cannot be performed at temperatures above 85°C, due to the required control of the exothermal energy release in order to avoid a thermal runaway during cure. Therefore, it was not possible to start with an initial homogeneous blend mixture prior to cure. Consequently, a polar solvent (acetone) was used to pre-dissolve the OH-terminated HBPs before adding the modifier to the epoxy/anhydride-system. After pre-dissolving the HBP-modifier and mixing thoroughly all components, the solvent was removed again in vacuum (2 hours at 45°C), followed by curing for 4 hours at 65°C and post-curing for 2 hours at 160°C. The obtained morphology of a 10% w/w Boltron®H-40 modified MY721/MA/HHPA-system is shown in the corresponding SEM-micrographs in Figure 81. It can be seen that the spherical H-40 rich domains are randomly dispersed within the cured epoxy matrix. However, a significant coarsening of the primary HBP-particles occurred during the curing reaction at elevated temperature. Consequently, a precise control of the finally obtained morphology when
applying a solvent methodology is rather limited. For this reason and the fact of very inhomogeneous obtained samples further mechanical analyses were abandoned.

Figure 81: SEM-micrographs of a cryo-fractured plane of MY721/MA/HHA systems modified with 10% w/w Boltron®H-40 pre-dissolved in acetone. Acetone was removed in vacuum for 2 hrs at 45°C. The sample was cured for 3 hours at 65°C and post-cured for 3 hours at 160°C.

The solubility of the HBPs within the epoxy matrix, however, can be greatly improved by a chemical derivatisation of a partial fraction of the polar OH end-groups. Thus not only the number of end groups but also the chemical nature of these end groups is expected to play an important role in the solubility of the HBP modifier. Decreasing the epoxy equivalent weight (EEW), that is increasing the number of epoxy groups on the HBP shell at a fixed total molecular weight, was anticipated to increase the initial miscibility of the HBP in the epoxy resin.

For instance the practical end group capping of an average 30 of the theoretical 32-hydroxyl groups to less polar epoxy groups (e.g. HBP-E2; EEW 402 g/eq.) resulted in an improved miscibility between the resin and the hyperbranched polymer modifier. This modification is seen as an obvious reduction of the related critical solution temperature ($T_s$) from about 160°C to a temperature below 25°C. Thus finally processing and curing of blends consisting of the MY721/MA/HHPA matrix and end-group tailored HBPs is feasible without any additional solvent at cure temperatures below 85°C.

3.5.5.2 Hyperbranched polymer modifier with a high epoxy functionality

In the previous section it was shown that partial end capping of the high amount of hydroxyl end-groups of the HBP led to a significant reduction of the critical solution temperature in the studied epoxy system. This finally enables the processing of the end-group tailored HBP-modifiers without the additional use of a solvent. In this section the effects of such a tailored HBP (HBP-E2) composition on the morphology of the MY721/MA/HHPA-system and the related thermo-mechanical and fracture properties were studied in more detail. Therefore, the hyperbranched molecule HBP-E2 (3rd generation, cf. Table 8), where theoretically thirty primary epoxy groups are grafted onto the shell, has
been blended with the epoxy-system in weight ratios between 0 to 100%. The HBP-E2, with the relatively low epoxy equivalent weight (EEW) of 402 g/eq. induces total miscibility of blends up to 80% w/w modifier fraction at room temperature. Furthermore, the samples remain absolutely miscible over the entire curing and post-curing process and no micro phase separation was detected by SEM examinations.

The curing kinetics of the reactive HBP-E2/MA/HHPA system, as determined from isothermal DSC measurements, was observed to be very similar to that of the neat MY721/MA/HHPA-system. Consequently, it is proposed that phase separation process is effectively suppressed by that fact that during the initial state of cure the HBP-molecule is already linked to the network.

The effect of the HBP-E2 concentration on the thermo-mechanical properties as determined by DMA is shown in Figure 82(a) and (b). The normalized DMA-thermograms clearly indicate that the reactive HBP-E2 modifier acts as a chain extender as manifested by the continuous drop of the Young’s modulus (E) with increasing modifier fraction (see Figure 82(d)). This behaviour is in accordance to the continuous decrease of the glass transition temperature with increasing HBP-E2 concentration as determined from tanδ-peak values of the same DMA-scans as shown in Figure 82(c). However, the experimentally determined glass transition temperatures decreased only moderately from about 220°C for the neat system to 203°C for a 20% w/w HBP-E2 modified system. The Fox-equation [154], which is widely used to predict the ultimate glass transition temperature (Tg∞) of statistical co-polymers, estimates the Tg∞ of the HBP-E2/epoxy compositions only in an approximate way. All experimentally measured Tg∞-data showed significantly higher glass transition temperature than the predicted values. Thus, it is proposed that the HBP-E2 might be partially separated in sub-micron domains that do not necessarily lead to a pronounced decrease of the thermo-mechanical properties, e.g. the glass transition temperature. Moreover, strong interactions between the individual components, such as hydrogen bonding interactions [155, 156] may additionally contribute to a reduced influence on the thermo-mechanical behaviour. Nonetheless, a confirmation of this hypothesis by means of microscopic investigations was not possible, because the phase contrast between potential sub-micron domains and the epoxy matrix was not sufficient to be resolved by scanning and transmission electron microscopy. In addition, OsO₄ and RuO₄-staining of fractured surfaces in order to enhance the phase contrast were not successful.

Since no direct assessment of the stiffness of the continuous and dispersed phase is possible in this case, an approximation using an upper and lower boundary condition was applied. The lower boundary was estimated by considering the tensile Young’s modulus (E) to be a linear function of composition. For the upper boundary it was assumed that the
blend formed a continuous phase where the stiffness is equal to that of the ultimately crosslinked MY721/MA/HHPA-matrix. However, experimental studies revealed, that for the fully cured HBP-E2 modifier with a $T_g$ below room temperature, a more complex behaviour was obtained (Figure 82(d)). Herein a slight but almost linear decrease of the $E$-value was obtained until the $T_g$ of the blend composition approached room temperature. Moreover, it can be see that up to 80% w/w HBP-E2 fraction the epoxy matrix preferably dominates the elastic tensile properties of the blends. Decreasing further the $T_g$ ($T_g<RT$), the Young’s modulus rapidly decreased to the value of the crosslinked HBP-E2/MA/HHPA value of 570 MPa. Hence the prediction of $E$ at temperatures below room temperature leads to a linear extrapolation towards the lower matrix boundary.

![Graphs showing normalized storage modulus, mechanical loss factor, glass transition temperature, and tensile Young's modulus](image)

Figure 82: (a) Normalized storage modulus ($G'/G'_{RT}$); (b) mechanical loss factor ($\tan \delta$); (c) glass transition temperature ($T_g$) as obtained from DMA measurements; (d) tensile Young’s modulus as a function of the HBP-E2 weight fraction.

The toughening effects between the “fully” miscible HBP-E2 and MY721/MA/HHPA resin system were determined by DT-fracture tests at room temperature. It can be seen from the corresponding DT-load/displacement curves in Figure 83 that the crack propagation mode changed from initially stable towards unstable behaviour with increasing fraction of the HBP-E2 modifier.
The fracture toughness corresponding to the critical stress intensity factor ($K_{IC}$) and the critical energy release rate ($G_{IC}$) increased almost linearly with the HBP-E2 modifier fraction, as shown in Figure 84. For a blend with a 20% w/w fraction of HBP-E2 the averaged critical stress intensity factor increased from initial 0.58 MPam$^{0.5}$ for the neat resin system to 0.88 MPam$^{0.5}$ for the modified resin blend. Considering further the only moderate decrease in the Young's modulus in this composition area (cf. Figure 82(d)), the critical strain energy release rate ($G_{IC}$) yields to a ~3.5-fold increase from initial 82 J/m$^2$ for the neat resin to 290 J/m$^2$ for the 20% w/w HBP-E2 modified system.

The obtained fracture toughness results clearly demonstrate that the use of a tailored HBP-modifier ($K_{IC}$~0.9 MPam$^{0.5}$) represents a good alternative to traditional rubber modification with CTBN ($K_{IC}$~0.7 MPam$^{0.5}$, cf. Figure 48). However, compared to particulate filled systems ($K_{IC}$~1.6 MPam$^{0.5}$, cf. Figure 74) as investigated in
section 3.5.4.3 the toughness improvement remains low. Therefore, a combination of the two different toughening modifiers (HBP and silica filler) may result in synergistic toughening effects. This so-called hybrid-concept is known from previous studies on hard particle/rubber-modified epoxies [7, 46, 157-159]. Moreover, the hybrid approach balances the intrinsic drawbacks of rubber- or thermoplastic-toughening arising from pronounced variations of the thermo-mechanical property profile.

Experimental fracture toughness data of the hybrid-composites using a fixed silica fraction (60% w/w) and a varying HBP-E2 content are given in Figure 85. It can be seen that for the investigated system no synergistic toughening effects between the silica-filler and the HBP-E2 modifier were observed. All obtained $K_{ic}$-values of the hybrid-composites were on a stabilized level at $-1.6$ MPam$^{0.5}$ and independent of the HBP-E2 fraction between 0 to 10% w/w of the epoxy mixture (resin and hardener). Consequently, the final toughness properties are predominately governed by the inorganic filler fraction and the implemented crack pinning mechanism. The small increase in the critical strain energy release rate ($G_{ic}$) is likely caused by the moderate decrease of the corresponding elastic modulus ($E$). Consequently, the obtained changes cannot be really considered as an enhancement of the fracture toughness properties due to synergistic HBP and silica toughening effects.

It is proposed that most probably the added HBP modifier interfere with the polar silica filler surface. Thus, a diffusion of the HBP to the filler surface will additionally explain the only marginal influence on the fracture toughness properties, because as discussed already in section 3.5.4.5, modifications of the filler/matrix adhesion have no significant effect on the final fracture toughness.

Figure 85: (a) Critical stress intensity factor ($K_{ic}$), and (b) critical strain energy release rate ($G_{ic}$) of a hybrid-composite (MY721/MA/HHPA+silica+HBP-E2) as a function of HBP-E2 weight fraction. The silica filler content was fixed to 60% w/w. All DT-fracture tests were performed with a constant strain rate of 0.1 mm/min at room temperature.
3.5.5.3 Hyperbranched polymer modifier with a low epoxy functionality

In section 3.5.5.1 it was shown that blends of epoxy and HBPs with a high number of hydroxyl end groups resulted in compositions with a critical solution temperature above 150°C. On the other hand in the previous section it was verified that a conversion of the terminal hydroxyl groups into more non-polar epoxy groups lead to fully homogeneous epoxy-HBP blends without macroscopic phase separation (particles >0.5 μm) over the entire cure and post-cure process. Therefore, the procedure of modifying the final morphology by tailoring the modifier shell nature was shown to be sensibly larger in the case of HBPs than with other traditional toughening modifiers.

To promote a more favourable two-phase morphology by means of a thermodynamically controlled phase separation the use of a HBP modifier with only partially end capped hydroxyl groups has been studied more in detail. Therefore, a third-generation epoxidized HBP-E1 (Boltorn®E1) has been blended with the MY721/MA/HHPA-system in different compositions. The shell of the HBP-E1 contains in average 21 hydroxyl groups and 11 secondary aliphatic epoxy groups yielding to an epoxy equivalent weight of 402 g/eq. (see Table 8). The concentration of the added HBP-E1 has been varied between 0 to 95% w/w fractions.

After mixing all investigated systems the visual mixture appearance changed spontaneously from transparent to turbid. This observation provides evidence that there is presumably no marked nucleation barrier for phase separation. The obtained morphologies depend on the initial HBP-concentration. Some corresponding optical micrographs of the blends recorded directly after mixing at room temperature are given in Figure 86. It can be seen that up to a HBP-E1 weight fraction of 40% w/w the epoxy matrix builds the continuous phase and the HBP-E1 phase separates as spherical particles. Increasing further the HBP-E1 fraction above ~40% w/w the finally obtained morphology gradually shifted towards co-continuous morphology consisting of the epoxy and the HBP-E1 phases. At HBP-E1 weight fractions higher than 80% w/w a phase-inverted morphology is obtained wherein the HBP is the continuous phase and the epoxy is the dispersed phase.
A simplified temperature-composition phase diagram of the epoxy/HBP-E1 system was constructed from the related cloud point temperatures using a hot-stage in combination with optical microscopy. As shown in Figure 87 the obtained phase diagram for the blended systems exhibited an enhanced miscibility with increasing temperature. The experimentally obtained temperature maximum of liquid–liquid ($L-L$) phase-separation line between the homogeneous and two-phase appearance was determined at 82°C for a 5% w/w modifier fraction. Increasing further the HBP-E1 modifier content line resulted in a gradually shifted of the $L-L$ transition towards lower temperatures again. For a 30% w/w HBP-E1 modifier fraction the $L-L$ transition temperature was observed at 48°C. This obtained reversible phase transition behaviour is corresponding to an upper critical solution temperature behaviour (UCST) [160].

Figure 86: Optical micrographs of the obtained thin films morphology for HBP-E1-MY721/MA/HHPA-blends as a function of HBP-E1 weight fraction for (a) 0%, (b) 10%, (c) 20%, (d) 40%, (e) 80% and (f) 95%. All examinations were performed directly after mixing at room temperature.
Figure 87: Left: Experimental phase diagram of the MY721/MA/HHPA-system (r=0.8) as a function of HBP-E1-modifier weight fraction. The (▽) symbols denote to experimental cloud point temperatures determined by optical microscopy with a heating rate of 1°C/min. Right: Optical transmission micrograph (magnification 500x) of the uncured MY721/MA/HHPA-system (r=0.8) modified with 10% w/w HBP-E1 modifier (a) at 85°C, and (b) at 65°C

The general application of the Flory-Huggins lattice theory allows reconstructing phase diagrams to express the L-L phase separation behaviour. Assuming the validity of the ordinary Flory-Huggins equation [161] and dividing this mathematical relation by the overall volume, the free energy of mixing per unit volume, $\Delta G_v$, can be expressed as:

$$\Delta G_v = RT \left( \frac{\Phi_1}{V_1} \ln \Phi_1 + \frac{\Phi_2}{V_2} \ln \Phi_2 + \Phi_1 \Phi_2 \chi_{12} \right)$$

where $T$ is the absolute temperature, $R$ is the ideal gas constant, $\Phi_1$ and $\Phi_2$ are the volume fractions of the components 1 and 2 (resin and modifier), $V_1$ and $V_2$ is the molar volume of the two components, and $\chi_{12}$ is the interaction parameter expressing the interactions between the two species present. According to eqn (3.55) the free energy of mixing is a function of temperature, the interaction parameter, and the volume fraction. The occurrence of phase separation and the related appearance of the phase diagram depend strongly on the interaction parameter ($\chi_{12}$), which is a material specific parameter. Moreover, the interaction parameter is not a constant value, but depends on temperature, the composition, and even the pressure. Assuming the simplification that the interaction parameter is predominantly affected by temperature, the temperature dependence can be described, as originally proposed by Huggins [162], by:

$$\chi_{12} = a + \frac{b}{T}$$

From eqn (3.56) two types of phase diagrams can be derived. If the value of $\chi_{12}$ is positive and the increases linearly with 1/T, the resulting phase diagram will exhibits an upper
critical solution temperature (UCST) behaviour. If $\chi_{12}$ is negative and the decreases linearly with $1/T$ the system displays a lower critical solution temperature (LCST) behaviour [163]. Besides, if curing of reactive compounds is carried out, the molecular weight gradually increases from the initial monomers towards an infinite molecular weight. Though this is a simplified picture of the more complex reaction scheme, it can be used for a qualitative description of the reaction induced phase separation process that is alternatively known as chemically induced phase separation (CIPS). In terms of the temperature-composition phase diagram, the increase of the molecular weight can be pictured as a shift of the $L-L$ phase transition line to higher temperatures, assuming that the system generally exhibits a UCST behaviour. This general behaviour is schematically shown in Figure 88. At the start of polymerization at temperature, $T$, the system with composition, $C$, is initially homogeneous. As the polymerization proceeds, the modifier becomes less miscible and the system is thrust into the two-phase region, eventually leading to phase separation into a modifier-rich and modifier lean phase. Depending on the initial modifier concentration, the modifier rich phase will become the dispersed or the continuous phase (phase inverted) [50, 164].

![Figure 88: A schematic representation of the evolution of the liquid-liquid (L-L) phase transition line for upper critical solution temperature (UCST) phase behaviour upon polymerization ($t_1 < t_2 < t_3$). The point $C$ represents the starting temperature and concentration.](image)

Consequently, the CIPS during cure of the epoxy resin enables a more precise control of the phase separation mechanism and hence the resulting morphology and related structure-property relationship. Some examples of reactive systems that exhibit an UCST phase behaviour are found for most rubber–modified epoxy systems [17, 18, 21, 23, 30] as
well as in PPE/epoxy-systems [165, 166]. Herein the CIPS-methodology has been widely used for blending numerous thermosets with a number of high molecular compounds in the past [50, 52, 167-169], because the obtained two-phase nature of the material greatly improves crack and impact resistance of the inherently brittle epoxy matrix. An example of the LCST behaviour for reactive systems is the polyethersulphone/epoxy system [170-172]. Since the given examples all involve crosslinking reactions, the evolution of the phase behaviour as depicted in Figure 88, only meaningfully describes the situation in the pre-gel state.

Curing experiments that have been performed slightly above the liquid-liquid phase transition line at 85°C (cf. Figure 87) started with an initially one-phase mixture. However, none of the examined samples showed a micro-phase separation and remained totally homogeneous upon completion of the curing reaction as investigated by scanning electron microscopy.

The absence of the chemically induced phase separation (CIPS) can be explained in two different ways. Firstly, the cloud point conversion ($\alpha_{cp}$) of the system is higher then the conversion at the point of gelation ($\alpha_{cp}>\alpha_{gel}$). Thus, the fast network formation of the matrix links the reactive hyperbranched molecules already in the initial stages of cure, and hence phase separation is limited by the diffusional restrictions which take place upon gelation of the epoxy matrix.

The second explanation can be given by thermodynamic consideration of the blend-composition. Separating eqn (3.55) into the two specific contributions of the interaction enthalpy of mixing ($\Delta H_v$), and the entropy of mixing ($\Delta S_v$), yields:

$$\Delta H_v = RT \Phi_1 \Phi_2 \chi_{12}$$

$$\Delta S_v = -RT \left( \frac{\Phi_1}{V_1} \ln \Phi_1 + \frac{\Phi_2}{V_2} \ln \Phi_2 \right)$$

(3.57)

(3.58)

So far a chemically induced phase separation of HBPs have only been successfully demonstrated for amine-cured epoxy compositions that exhibit a distinct polarity change upon cure [99, 173-176]. Due to significant changes of the molecular structure of the reactive components, caused by the ring opening reaction of the epoxy group and the subsequent formation of new hydroxyl groups, a 3.9 fold increase in polarity of an amine-epoxy system has been reported by Boogh et al. [99]. As a result, the related enthalpy change ($\Delta H_v$) can be considered as the major contribution for changes of the Gibb’s free energy of mixing.

The entropic contribution ($\Delta S_v$), which is generally related to the configurational orders of the blend, generally increases with size of the molecules. However, for polymer-polymer systems the entropic contribution (cf. eqn (3.58)) is reported to be relatively small [177].
Consequently, the major thermodynamic driving potential for a chemically induced phase separation processes in epoxy resins can be related to the pronounced enthalpy changes and their significant influence on the Gibb’s free energy of mixing. On the other hand the esterification reaction during the epoxy/anhydride polymerization does not generally result in a pronounced polarity change of the systems upon cure. Hence, the related energetic enthalpy changes can only be stated as secondary effects. The simultaneously occurring configurationally entropic changes ($\Delta S_v$) are not sufficient to enter the thermodynamically meta-stable region in order to precipitate the hyperbranched molecules from the epoxy matrix. As a consequence, if a change in polarity is the primary trigger for a chemically induced phase separation process, this phenomenon may not apply to the blends studied here.

Samples of a 10% w/w HBP-E1 modified epoxy were isothermally pre-cured below the $L-L$ phase separation line at 65°C and afterwards post-cured at 160°C. The initial two-phase structure retained over the entire cure process yielding a continuous epoxy matrix and spherically dispersed HBP-inclusions as co-continuous phase. Nevertheless, cryogenic-fRACTured samples showed a distinct distribution gradient of the randomly dispersed HBP-inclusions over the entire sample height, as shown in Figure 89. It can be seen that the dispersed particle size increases with sample height due to substantial particle coalescence of the primary HBP-E1 domains. Consequently, a tacky surface layer consisting of merely crosslinked HBPs was detectable on all blended samples. Moreover, the thickness of the surface layer steadily increased with the HBP-E1 concentration on the studied systems.

The observed structural coarsening mechanism is probably favored by phase instabilities that can be attributed to discrepancies between the specific densities of the cured HBP-E1 ($\rho=1.08 \text{ g/cm}^3$) and the crosslinked epoxy resin ($\rho=1.27 \text{ g/cm}^3$). Additionally, the long time to gelation ($t_{gel}$) and the relatively high values of the diffusion coefficient (low system viscosities) may contribute further to the particle coalescence and thus to the macroscopically inhomogeneous morphology. Besides, it is also possible that a critical interfacial energy balance between the modifier and the epoxy mixture further supports the observed segregation effects as shown in Figure 89.
3.6 Concluding remarks

In this chapter the fundamental understanding of the deformation and fracture behaviour of highly crosslinked epoxy-systems has been reviewed and experimentally studied. It has been shown that the investigated neat and silica-filled MY721/MA/HHPA-system deforms predominantly by shear yielding processes that are sensitive to the presence of inhomogeneities. Moreover, specific test conditions such as compressive load, high temperature, and low strain rate additionally amplify the initiation of shear banding processes. Under compressive load the particulate filled epoxy system exhibited extensive stress-whitening damage that generally starts above the yield stress. Particle-matrix debonding has been identified as a primary mechanism for this irreversible deformation phenomenon.

The crack propagation and fracture of the neat and silica filled MY721/MA/HHPA-system have been examined using the Double-Torsion (DT) test method. In particular the effects of the strain rate, temperature, volume fraction, particle size and filler surface-treatment were assessed and discussed. It has been shown that with increased strain rates, the studied systems failed preferentially in an unstable crack propagation manner. At
increased test temperatures the critical stress intensity factor \((K_{IC})\) and the critical strain energy release rate \((G_{IC})\) significantly decreased. It is proposed that the observed behaviour provides evidence of an existing sub-network structure. The two independent MY721/MA and MY721/HHPA networks are strongly related to the co-anhydride mixture used, and the different curing rates of the individual anhydrides.

For the particulate filled system it was observed that an increase of the silica filler fraction leads to a continuous increase of the critical stress intensity factor \((K_{IC})\) and the corresponding critical energy release rate \((G_{IC})\). Micro-structural investigation and theoretical models have provided evidence that the toughening behaviour can be predominately related to the crack pinning mechanism. A fairly good agreement between the experimental data and a theoretical prediction, as previously proposed by Evans et al., has been obtained. It was demonstrated that different pre-treatment of the filler surface and thus the filler-matrix adhesion has only a minor influence on the final fracture toughness. Although there might be some exceptions, some general trends describing the influence of filler particles on the short-term deformation and fracture behaviour of epoxy thermosets are summarized in Table 10.

Table 10: Parameters determining the modulus, fracture toughness and mechanical strength of particulate filled thermosets

<table>
<thead>
<tr>
<th>Property</th>
<th>Effects on Modulus</th>
<th>Fracture toughness</th>
<th>Mechanical strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increased filler fraction</td>
<td>+</td>
<td>+</td>
<td>0</td>
</tr>
<tr>
<td>Increased particle size</td>
<td>0, - 1)</td>
<td>0, - 1)</td>
<td>0, - 1)</td>
</tr>
<tr>
<td>Improved filler/matrix adhesion</td>
<td>0</td>
<td>0</td>
<td>+</td>
</tr>
<tr>
<td>Increased strain rate</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

+: increase; 0: constant; -: decrease; 1) above a particle size threshold level of 2 to10 µm

The effects of modifying the epoxy matrix with different hyperbranched polymer (HBP) additives have been studied in order to assess and demonstrate their toughening efficiency as potential low viscosity modifiers. It was confirmed that the final blend morphology and the corresponding structure-properties strongly depend on the HBP shell chemistry. An increased number of polar hydroxyl end groups leads to a decreased compatibility between the modifier and the epoxy matrix. Moreover, tailoring the end-groups functionality by conversion of the accessible hydroxyl-groups to more non-polar epoxy-groups, e.g. HBP-E2 (EEW 402 g/eq.), leads to an enhanced solubility of the HBP and hence provides totally miscible compounds at every concentration. Indication that the HBP-E2 acts as internal chain extender was obtained from thermo-mechanical analysis. However, the related ultimate glass transition temperature of the blends is not strongly
affected. Therefore, it is proposed that the HBP-E2 possibly arrange in sub-domains that consequently induce only minor changes in the related network structure and the corresponding property profile. A homogeneous blend with 20% w/w HBP-E2 modifier leads to about 50% increase in the $K_{IC}$-values. Consequently, specifically tailored HBPs can be considered as good alternatives to traditionally used rubber-modifiers, e.g. carboxyl-terminated butadiene-acrylonitrile rubber (CTBN). However, synergistic effects between the silica filler and HBP-modifier of envisaged hybrid formulations have not been observed.

Epoxy/HBP blends with only partially epoxidized HBP-modifier (HBP-E1; EEW 902 g/eq.) revealed an upper critical solution temperature (UCST) phase behaviour. However, samples that have been cured slightly above the determined liquid-liquid phase separation temperature ($T=85^\circ C$) line remain homogeneous upon the entire cure and no chemically induced phase separation (CIPS) was observed. It is proposed that the absence of a CIPS could be mainly attributed to only minor polarity changes of anhydride cured epoxy formulations upon cure. Consequently, the resulting enthalpy changes in the investigated system, and the direct influence on the Gibb’s free energy of mixing limits the thermodynamically induced phase separation process.

3.7 References

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Chapter 4

4 Thermo-oxidative degradation behaviour

4.1 Introduction to thermo-oxidative degradation

Polymer degradation generally involves changes in the chemical structure of the materials and can include oxidation, chain-scission or crosslinking (post-curing). Several authors have intensively reviewed these processes in the past [1-3]. Struik [4] firstly separated polymer degradation processes into two different categories based on chemical and physical mechanisms that will be reviewed in the next sections. Before giving more details about these two fundamental aspects of degradation, it should be pointed out that a strong inter-relationship exists between these two modes. For example, since it is difficult to obtain a chemically pure polymeric composite, it is not easy to separate thermal and thermo-chemical degradation. Indeed, impurities present in the material might react with the polymeric matrix.

Although the above-described phenomena are important for practical reasons, the focus in the current work will be on the chemical and the thermo-oxidative degradation, which are the main technical interests.

4.1.1 Physical ageing of epoxy-networks

In contrast to the chemical degradation, which is caused by mutual reactions with various chemicals (e.g. acids, bases, solvents and reactive gases i.e. oxygen), the phenomenon of physical ageing involves changes in the physical network structure, e.g. embrittlement, increase in tensile modulus, decrease in loss modulus, increase in shrinkage and densification of the polymer matrix, when continuously exposed to elevated temperatures for prolonged periods. Many conventional methods have been applied to measure physical ageing in epoxy resins, which include volumetric [5, 6], free volume [7] and enthalpy techniques [5, 8, 9]. Besides, the phenomenon has been studied by changes in deformation properties such as viscoelasticity [5, 10-14], yielding [8, 9, 11, 15] and fracture behaviour [5, 11, 15]. In general physical ageing is associated with the slow approach to equilibrium of a system quenched to below its glass transition temperature [4, 16-18]. The quenching process freezes into the system disorder (entropy), which reflects the thermal history of the sample. It has been postulated [4] that physical ageing can be provoked by molecular
segmental rearrangement causing a decrease in free volume, densification of the structure and the tendency of the material to rearrange towards the thermodynamic equilibrium state.

4.1.2 Thermo-oxidative degradation of epoxy-networks

A great number of scientific publications on thermo-oxidative degradation of epoxy thermosets and degradation effects on mechanical [19-21], viscoelastic [13, 14, 22], and optical properties [23] were published in the past. Nevertheless, postulated degradation mechanisms for anhydride-cured epoxy networks remain rather limited.

Lee [24, 25] has studied degradation of a variety of epoxy resins; both uncured and cured with amine and anhydride hardeners. He showed that in all cases large quantities of phenolic products were formed and proposed several reaction schemes. Cured and uncured resins were not treated as two different systems because the results showed that phenolic products were generated in both cases.

Keenan and Smith [26] used a hot filament technique to study the degradation of crosslinked networks of a diglycidylether of bisphenol-A (DGEBA) and p,p'-diaminodiphenylmethane (DDM). The volatile products were chromatographed utilizing thin layer chromatography. In addition, infrared spectroscopy was carried out and an attempt was made to characterize the residues remaining on the pyrolysis head after degradation. The hypothesized reaction schemes supplemented those as presented by Lee [24, 25].

Leisegang and co-workers [27] studied the thermo-oxidative ageing of stoichiometric mixtures of DGEBA cured with DDM at degradation temperatures below 305°C. The condensable and gaseous decomposition products were collected and the major components were separated as pure compounds and analyzed by chromatography, mass spectroscopy and infrared spectroscopy. They proposed that at relatively low temperatures (220°C to 240°C) a large number of chain scissions of the least stable bonds yield radicals that may recombine, or abstract hydrogen as illustrated in Figure 90 and Figure 91. At higher temperatures (>250°C) the dehydration reaction predominates (see Figure 92), and consequently significantly weakens the network structure for further degradation processes. At temperatures above 280°C, the weakened structure breaks down and small fragments on the network appear as phenolic, benzofuryl and bisphenol-A derivatives.
Levchik and co-workers [28] have investigated the mechanism of thermal decomposition of commercial TGDDM and DGEBA resins cured with Bis(m-aminophenyl) methylphosphine-oxide (BAMPO) or 3,3',5,5'-tetraethyl-4,4'-diaminodiphenylmethane (M-DEA) under nitrogen and vacuum atmospheres. They observed that the decomposition consists of three different stages. The most essential feature in the first step (<320°C) was the elimination of water by dehydration of secondary alcohol groups leading to an unsaturation as shown in Figure 92. This observation is in agreement with studies where a decrease in alcohol concentration was also observed [27, 29-31]. The formed unsaturation weakens the aliphatic C-O and C-N bonds in the β-position and consequently bond scissions lead to amine terminal functions. When the C-N and C-O scissions occur through a molecular or free-radical mechanism with mutual disproportionation various cyclic chain end structures, especially the quinoline-type chain ends (Figure 93) were reported as typical degradation products of TGDDM resins [32].
The second (320-420°C) and the third stage of degradation (>420°C) was mainly attributed to cleavage of remaining C-N and C-O bonds and aromatic substituted carbon bonds, which show relatively low thermal stability in epoxy resins [27]. At the same time, carbonization of the earlier generated conjugated structures may occur as a competition reaction.

Thermal oxidation in an intermediate temperature range (140 to 200°C) of hexahydrophthalic anhydride (HHPA) or methyl-tetrahydrophthalic anhydride (MTHPA) cured epoxy resins have been studied by Le Huy and co-workers [33-35]. They have identified oxidation as a dominating ageing process. Moreover, vibrational spectroscopic measurements revealed the reformation of anhydride structures from presumably monoacid dangling chains by oxidation or hydrolysis as shown in Figure 94 and 95. Moreover, they reported that the unsaturation of MTHPA is bound to the network by radical addition, yielding to a reduction in weight-loss and obvious increase in the glass transition temperature in contrast to HHPA cured epoxy systems.
4.2 Principals of dynamic mechanical analysis (DMA)

Although the Cole-Cole plot is an approved tool to study dielectric relaxation data [36-38] the use of this method to analyse mechanical relaxation phenomena is rather limited [39]. In general a Cole-Cole plot visualizes the linear variation of the storage modulus ($E'$) as a function of the loss modulus ($E''$) with varying temperature or frequency. This type of diagram presents in a simple visual way the individual or collective nature of the microscopic mechanisms controlling the macromolecular relaxation processes. Assuming Maxwell behaviour, the complex modulus ($E^*$) is defined by eqn (4.59).

$$E^* = E' + iE''$$  \hspace{1cm} (4.59)

A solution of this basic differential Maxwell equation reveals that the two frequency dependent components, the in-phase modulus component or storage modulus ($E'$) and the out-of-phase component or the loss modulus ($E''$) can be separated and stated by the so-called dispersion relations as given by eqn (4.60):

$$E' = E_0 \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \hspace{1cm} (4.60)$$

$$E'' = E_0 \frac{\omega \tau}{1 + \omega^2 \tau^2}$$

where $E_0$ is the relaxed modulus referring to the $\alpha$-relaxation, $\omega$ the angular frequency, and $\tau$ the appropriate relaxation time. Considering further the sum of the square moduli, eqn (4.60) can be rearranged to:

$$\left[ E' \right]^2 + \left[ E'' \right]^2 = \omega^2 \tau^2 \left[ E' \right]^2 + \left[ E'' \right]^2 = \left[ 1 + \omega^2 \tau^2 \right] \left[ E' \right]^2 = \left[ 1 + \omega^2 \tau^2 \right] \frac{E_0^2 \omega^2 \tau^2}{\left[ 1 + \omega^2 \tau^2 \right]^2}$$

$$= E_0^2 \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} = E_0^2 E'$$

And, this finally leads to eqn (4.62):
Typically, if the viscoelasticity exhibits only one relaxation time, as in the case of a Maxwell material, the Cole-Cole plot is described by a semi-circular shape, centered on the horizontal $E'$-axis at $E_0/2$ with a radius of $E_0/2$ (see Figure 96). On the other hand, this ideal case does not describe the viscoelastic behaviour of more complex polymer systems where several discrepancies can appear. For instance, when the viscoelasticity is governed by several relaxational events, the Cole-Cole diagram will show a distortion of the semi-circle plot appearance and exhibits more a composite curve with a set of semi-circles connected by transition zones.

\[
\left[ E' - \frac{E_0}{2} \right]^2 + \left[ E'' \right]^2 = \left[ \frac{E_0}{2} \right]^2
\]  
(4.62)

It should be emphasized that the classical Cole-Cole diagram is two-dimensional and hence the temperature is not directly displayed. However, it is implicitly included in the evolution of the moduli. Therefore, it might be useful to see the evolution of the moduli with temperature. This is shown in the Figure 97 where a three-dimensional Cole-Cole diagram giving temperature in $z$-axis and projections of the moduli in the temperature-$E'$ and temperature-$E''$ planes.
Different empirical modifications of eqn (4.62) have been proposed in attempt to represent variations in the complex modulus ($E^*$) [40, 41]. From a thermodynamical analysis of deformation Perez has introduced a theoretical model that describes the linear and non-linear stress-strain behaviour of various amorphous thermoplastics and thermosets [39, 41-44]. Moreover, the model based on a physically consistent theory that allows interpreting the results in terms of structural changes, when two underlying physical assumptions are considered to be valid:

(I) The source of mobility in amorphous condensed polymers is the nanofluctuation of density or quasi-punctual defects (qpd) with a concentration $C_d$. These defects can be characterized by regions with positive fluctuations of packing densities ($d^+ dqp$, or anti-free volume) or negative fluctuations ($d^- dqp$, or free volume) as shown in Figure 98. Both fluctuations are forming more disordered sites with less cohesive energy.

![Figure 98: Representation of the quasi-punctual defects in amorphous polymers according to Perez](image)
Chapter 4

(II) The translational molecular mobility is described in terms of a serial process or a hierarchical correlation leading to the characteristic mean time \((\tau_\alpha)\) for a movement of a molecular unit over a distance comparable to its size. The theory yields:

\[
\tau_\alpha = t_0 \left( \frac{\tau_1}{t_0} \right)^{\frac{1}{\kappa}}
\]

(4.63)

where \(t_0\) is the scaling time parameter and \(\tau_1\) corresponds to the characteristic time of an elemental molecular movement. \(\kappa\) denotes the correlation parameter which is related to the disorder and expresses of how much hierarchically constrained are the correlated molecular entities during the deformation process. The value of \(\kappa\) can vary between zero and one \((0<\kappa<1)\). A value of zero corresponds to a fully constrained situation with an infinite value for \(\tau_\alpha\). In contrast a \(\kappa\)-value of unity reflects a constraint-free situation with \(\tau_\alpha = \tau_1\).

Finally, Perez's model assumes that the response to an applied stress can be described in terms of thermo-mechanical relaxation, growth and coalescence of micro shear-domains, resulting in a elastic and viscous deformation. As a consequence the complex modulus can be expressed as [43]:

\[
E^* = E_0 + \frac{E_\infty - E_0}{1 + (i\omega \tau_\alpha)^{-\kappa} + Q (i\omega \tau_\alpha)^{-\kappa} - \kappa}
\]

(4.64)

where \(E_0\) is the unrelaxed modulus referring to the \(\alpha\)-relaxation (glassy modulus). \(E_\infty\) denotes the relaxed elastic modulus, which corresponds to the value of the modulus at the rubbery plateau. \(Q\) is a material constant that depends on temperature and defect concentration and is close to unity. The \(\kappa^*\) parameter \((0<\kappa^*<1)\) takes into consideration the fact that segmental mobility \((i.e. \kappa)\) of polymers is sensitive by the strain above a threshold, due to the fact that the chains are locally stretched. The maximal value of \(\kappa^*\) is given for molecular glass and decreases with the length of chain segments between chemical crosslink nodes.

Besides, the Perez coefficients \(\kappa\) and \(\kappa^*\) can additionally give valuable insight into the effect of the architecture of the polymer network on molecular motions in the solid state. In physical terms it means when the distance between crosslink points is small, the local percentage extension is large and \(\kappa^*\) becomes more time dependent, which in turn causes \(\kappa\) to become small. On the other hand \(\kappa\) decreases when the number of obstacles (crosslink points) is maximal, \(i.e.\) when these induced a more hierarchical correlation effect.

Consequently, eqn (4.64) describes the complex modulus \((E^*)\) of amorphous polymers in the region of the \(\alpha\)-relaxation by five parameters \((E_0, E_\infty, \kappa, \kappa^*, Q)\). Even though the expression seems to be complicated since it includes five parameters, each parameter can be independently deduced from the characteristic of a Cole-Cole diagram. The parameters \(E_\infty\) ...
and $E_o$ are given by the low and high temperature limits of $E^\prime$, respectively. The Perez parameters $\kappa$ and $\kappa'$ can be determined by the slopes of the $G''/G'$ curve on the low and high temperature side. $Q$ is proportional to the maximum $E''$-value on the Cole-Cole curve and corresponds to the defect concentration $C_d$.

### 4.3 Experimental

#### 4.3.1 Materials

A commercial multifunctional amino-glycidyl-resin, Araldite®MY721 (Vantico, Switzerland) mainly based on N,N,N',N'-tetraglycidyl-4,4'-diamino-diphenylmethane (TGDDM) was used as epoxy monomer for all investigations. The epoxy monomer was cured with either maleic anhydride (MA), hexahydrophthalic anhydride (HHPA), or a hardener mixture consisting of MA and HHPA. In addition, for some long-term experiments, the well-established high performance epoxy system [45-48] consisting of MY721 and 4,4'-diaminodiphenylsulfone (DDS) was selected in order to benchmark the different epoxy/anhydride-systems. All used anhydrides and amine hardeners were supplied by Fluka and used to cure the TGDDDM resin without further purification. The selected mixing ratios of the components are given in Table 11, all reflecting a molar anhydride to epoxy ratio ($r$) of 0.8. For the structure of the used materials the reader is referred to Table 2 in section 2.2.1.

**Table 11: Material compositions**

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>MY721/MA/MA</th>
<th>MY721/MA</th>
<th>MY721/HHPA</th>
<th>MY721/DDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Araldite®MY721</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Maleic anhydride</td>
<td>48</td>
<td>70</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hexahydrophthalic</td>
<td>32</td>
<td>-</td>
<td>110</td>
<td>-</td>
</tr>
<tr>
<td>anhydride</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diamino-diphenylsulfone</td>
<td></td>
<td></td>
<td></td>
<td>44</td>
</tr>
</tbody>
</table>

For details on the epoxy/anhydride sample preparation the reader is referred to section 2.2.2.

The epoxy/amine-system (MY721/DDS), DDS was dissolved in the MY721 resin by thoroughly stirring at 100°C until a homogeneous mixture was obtained. The mixture was then degassed at $p<10$ mbar for 15 minutes before casting into 100°C preheated steel molds. Afterwards curing was carried out in an air-circulating oven for 3 hours at 100°C followed by a post-curing treatment for 8 hours at 160°C and additional 8 hours at 200°C.
4.3.2 Isothermal ageing experiments

Samples for isothermal ageing were prepared from 4 mm thick cast plates. The specimens were aged below the glass transition temperature in air circulating ovens at 150, 170, and 200°C under atmospheric pressure. The steady state temperature was controlled with an accuracy of ±2.0°C. The samples were periodically removed from the oven and allowed to cool down to room temperature in a desiccator prior to analysis.

4.3.3 Dynamic mechanical analysis (DMA)

The dynamic mechanical measurements were performed using a Perkin-Elmer DMA-7e analyser working in three point bending. The selected span length was 15 mm. Rectangular specimens of 18 x 4 x 2 mm³ (length x width x thickness) were cut from cured 4 mm thick plates. All experiments were carried out at a frequency of 1 Hz and a continuous heating rate of \( ϕ=3°C/min \) in a temperature range between 30°C to 300°C under inert helium atmosphere. The glass transition temperature \( (T_g) \) was determined by using the maximum of the loss factor \( (\tanδ) \) as a criterion.

4.3.4 Thermal gravimetric analysis (TGA)

The dynamic thermo-gravimetric measurements were carried out on a Perkin-Elmer TGA 7 thermo-gravimetric analyzer. Non-isothermal experiments were performed at a heating rate of 10°C/min in a temperature range between 30°C to 800°C. In all cases, samples of about 10-12 mg were cut from 4 mm cured plates, and measured either under constant nitrogen or air gas flow of 60 ml/min.

For long-term isothermal thermo-gravimetric studies the samples (70 x 70 x 4 mm³) were dried to a constant weight under vacuum at 70°C before ageing. The gravimetric experiments were performed by simple periodic weight measurements of samples aged at 150, 170 and 200°C for various periods of time. Samples were allowed to cool down to room temperature in a desiccator before weight experiments on an analytical scale with a relative accuracy of 10⁻⁵ g were carried out. After the measurement the samples were returned to their respective ageing environments. Results presented in this work were obtained as the arithmetic mean of at least 3 measured samples. Quantitative reproducibility variations were less than 2% between samples.
4.3.5 Mechanical bending test

The flexural tests were made in a three-point bending configuration according to DIN-EN-ISO 178 [49] on a mechanical Zwick universal testing machine Z100. All experiments were performed on test specimens (80 x 10 x 4 mm³) at room temperature. Bending tests were performed at strain rates 2 mm/min using a bending support length of \( l_0 = 60 \) mm. In all figures the given value represents the arithmetic mean of at least 5 measured samples.

4.3.6 FT-IR micro attenuated total reflection (ATR) spectroscopy

The IR spectra in this study were collected using a Nicolet Nexus-870 FT-IR spectrometer including a Continuum™ IR microscope. The spectrometer was operating with a modulation frequency of 20 kHz and a high sensitivity mercury cadmium telluride photoconductive cell (MCT-detector) at 77K. The ATR lens incorporated a silicon (Si) internal reflection element (IRE). All samples were polished before examination in order to reach a flat contact area. The contact area was circular with an approximate diameter of 100 micron. Reproducible contact between the surface of the epoxy sample and the ATR-crystal was achieved by use of an electronic sensor plate attached to the microscope. Typically, 128 co-added scans were recorded at 4 cm⁻¹ resolutions in a range of 600 to 4000 cm⁻¹. Background spectra were obtained through the ATR element when it was not in contact with the sample. For line maps the stage was moved under computer control with a 20 micron step size.

The control of the penetration depth \( d_p \), the depth at which the electrical field amplitude is reduced to \(-37\%\) (factor \( e^{-1} \) of its initial value), is defined by equation (4.65) as first proposed by Harrick [50].

\[
d_p = \frac{\lambda}{2\pi \left( n_1^2 \sin^2 \Theta - n_{21} \right)^{0.5}}
\]  

(4.65)

where \( \lambda \) is the wavelength of the radiation beam and \( \Theta \) is its incident angle \((-45^\circ)\); \( n_1 \) is the refractive index of the Si-IRE \((n_1 = 3.4)\) and \( n_{21} \) is \( n_2/n_1 \), where \( n_2 \) is the refractive index of the organic matrix. Given a sample refraction index of 1.5, which is appropriate for many polymers [51], then the range of penetration depth that can be achieved is approximately varying between 14.6 micron at 600 cm⁻¹ to 2.2 micron at 4000 cm⁻¹, respectively.
4.4 Results and discussion

4.4.1 Mechanical endurance during thermo-oxidative ageing

4.4.1.1 Dynamic mechanical behaviour of the virgin state

To characterize the viscoelastic properties of the virgin systems, dynamic mechanical analysis (DMA) measurements were performed at 1 Hz. The storage modulus ($E'$) and loss factor ($\tan \delta$) curves for the different systems are given in Figure 99. In each case, a continuous decrease in the storage modulus ($E'$) with increasing temperature between 35 to 200°C was obtained; see Figure 99(a). This behaviour can be explained by thermal expansion that induces higher free volume. At temperatures above 200°C the investigated systems reached their glass to rubber transition region. This transition is assigned to the $\alpha$-relaxation, which is manifested by a sharp decrease of the elastic modulus over nearly two orders of magnitude, before leveling off on the rubber modulus plateau. The $\alpha$-relaxation phenomenon can be attributed to collective chain movements and hence it is associated with the macroscopic glass transition temperature ($T_g$) of the studied networks. A more pronounced indication of the $\alpha$-relaxation mode could be seen in the $\tan \delta$-curve as shown in Figure 99(b). The values of the $\tan \delta$-maxima for the different investigated systems are listed in Table 12. The HHPA cured system revealed the highest $\alpha$-relaxation ($243^\circ$C) followed by the MA-cured ($240^\circ$C) and the MA/HHPA-cured system ($215^\circ$C). However, an unambiguous assignment of $T_g$ in the case of the MY721/MA-system is difficult because the $\tan \delta$ curve exhibits a broad peak appearance and hence no pronounced maximum temperature. The fact that the amplitude of the loss factor is maximal and the width of the $\alpha$-peak (the glassy dispersion) is much sharper for the MY721/HHPA-system may be explained by a higher homogeneity of the MY721/HHPA network. On the other hand, the presence of MA tends to initiate a more heterogeneous network structure, which is reflected in a broad $\alpha$-peak. It is hypothesized that the more inhomogeneous network presumably can be related to the inherent dangling chains (mono-acids, e.g. -CH=CHOOH) in the presence of MA (see section 2.3.4).
Figure 99: Viscoelastic behaviour as a function of temperature for (a) storage modulus \(E'\), and (b) loss factor \(\tan\delta\), as experimentally determined by DMA of virgin samples (→) MY721/MA, (→) MY721/HHPA, (→) MY721/MA/HHPA with a molar anhydride/epoxy ratio, \(r=0.8\).

Table 12: Characteristic DMA values of the different investigated epoxy networks.

<table>
<thead>
<tr>
<th>Systems</th>
<th>(T_g) (°C); (1 Hz)</th>
<th>((\tan\delta)_{\text{max}})</th>
<th>(T_{\text{cure}}/T_g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MY721/HHPA/MA</td>
<td>215</td>
<td>0.21</td>
<td>0.64</td>
</tr>
<tr>
<td>MY721/HHPA</td>
<td>243</td>
<td>0.33</td>
<td>0.81</td>
</tr>
<tr>
<td>MY721/MA</td>
<td>240(^{\dagger})</td>
<td>0.10</td>
<td>0.60</td>
</tr>
</tbody>
</table>

\(^{\dagger}\) Precise determination difficult due to very broad \(\tan\delta\)-peak

Additionally, the co-existence of an additional sub-glass relaxation for MA-cured systems in an intermediate temperature range is noticeable from the behaviour of \(\tan\delta\) (Figure 99 (b)), even when the recorded \(E'\)-curve shows no significant change and remains on the same
order of magnitude over the entire transition range. This intermediate temperature relaxation (50-100°C for MY721/MA-system and 115-150°C for the MY721/MA/HHPA-system), is often recognized as $\omega$-relaxation, and has been the subject of numerous studies in the past [52-54]. Unfortunately, in spite of all these efforts a fully confirmed explanation of the $\omega$-relaxation in terms of molecular mobility remains a controversial matter. While some researchers attributed the secondary $\omega$-relaxation to unreacted molecular segments, chain ends and inhomogeneities in the network [55, 56], other authors assigned the $\omega$-relaxation to motions of the $p$-phenylene groups. In addition, it has been observed that the $\omega$-relaxation is very sensitive to either ‘free’ or ‘bound’ water in the network and thus some considered this intermediate relaxation as rising from micro-structural rearrangement in combination with moisture absorption [53, 57, 58]. Although the explanation of the $\omega$-relaxation is not unambiguous here, we assume that the $\omega$-transition can be mainly assigned to the presence of dangling chain-ends within the maleic anhydride-cured epoxy network-structure.

Classical Cole-Cole plots of all initial systems are shown in Figure 100. As expected, the Cole-Cole plots illustrate different thermo-mechanical behaviour depending on the chemical nature of the hardeners used; hence each epoxy system exhibits a different viscoelastic spectrum. The MY721/HHPA-system displays mainly a high-temperature relaxation, associated with the primary $\alpha$-transition that leads to an almost symmetric Cole-Cole plot appearance. On the other hand the MY721/MA-system shows a more complex curve consisting of partially overlapping $\alpha$ and $\omega$-relaxations. It is surprising that the intermediate $\omega$-dissipation ($\sim$100°C), reveals a higher $E''$-value than the primary $\alpha$-relaxation ($\sim$220°C). In a similar way, the co-anhydride MA/HHPA cured system also displays a non-symmetric Cole-Cole plot. In this case, however, the transition zone between the two different relaxational events was significantly decreased due to a reduced MA content. The Perez parameters of the different systems were graphically determined and the obtained values are summarized in Table 14. Since the theoretical boundary criterion of $1 > \kappa' > \kappa > 0$ (see section 4.2) is fulfilled for all examined systems the molecular model can be applied to explain the experimental results. Despite this, the calculated values are in a good agreement with reported results from similar studies [39, 41].
Figure 100: Cole-Cole plot for virgin epoxy-networks: (a) MY721/HHPA; (b) MY721/MA/HHPA; (c) MY721/MA with a molar anhydride/epoxy ratio, r=0.8

Table 13: Numerical Perez parameters in the glass transition region for the investigated epoxy networks in the virgin state

<table>
<thead>
<tr>
<th>System</th>
<th>$\kappa'$</th>
<th>$\kappa$</th>
<th>$E_0$ (MPa)</th>
<th>$E_\infty$ (MPa)</th>
<th>$E_\infty/E_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MY721/MA$^*$</td>
<td>0.308</td>
<td>0.221</td>
<td>310</td>
<td>2350</td>
<td>7.7</td>
</tr>
<tr>
<td>MY721/HHPA</td>
<td>0.516</td>
<td>0.192</td>
<td>95</td>
<td>1960</td>
<td>21</td>
</tr>
<tr>
<td>MY721/HHPA/MA</td>
<td>0.455</td>
<td>0.066</td>
<td>105</td>
<td>4300</td>
<td>41</td>
</tr>
</tbody>
</table>

$^*$ Interference with the $\omega$-relaxation

4.4.1.2 Effects of thermo-oxidative ageing on the dynamic mechanical behaviour

A comparison of changes in the relaxational spectra during thermo-oxidative ageing can help to understand the micro-mechanisms involved in the ageing process. Therefore, periodical DMA runs were performed over an ageing period of up to 1000 hours at 200°C. Considering the fact that the DMA apparatus is relatively accurate in phase measurements but less precise in determining the absolute components of the complex modulus, the storage- and loss-moduli values were normalized with respect to their value at room temperature. The normalized storage modulus for all investigated systems as a function of ageing temperature and time is shown in Figure 101.

For the pure MA-cured system a continuous increase of the glassy storage modulus and the $\alpha$-relaxation was observed over the entire ageing period, see Figure 101(a). This is a common behaviour of various thermosets during the early ageing period [59]. It can be generally attributed to the “under-cured” state of the industrial materials, which can be only rarely avoided. As a result these materials undergo further post-crosslinking as soon as they are subjected to higher temperatures. However, a common post-curing process over
1000 hours of ageing can only hardly explain the steady shift of the modulus-cure towards higher temperature. Therefore, it is proposed that in addition the conjugation of maleic anhydride tends to react by radical addition at higher temperature, consequently yielding an increased network density of the MA-cured networks.

Figure 101: Normalized storage modulus \( (E/E_0) \) from DMA-measurements as a function of ageing time during thermo-oxidative ageing at 200°C for (a) MY721/MA, (b) MY721/HHPA, and (c) MY721/MA/HHPA with a molar anhydride/epoxy ratio, \( r=0.8 \).

On the other hand the pure HHPA-cured and the co-anhydride-cured network behaved in a completely different way. The analysis of the experimental dynamic mechanical data clearly separated the thermo-oxidative ageing processes into two co-existent stages. In the early period of exposure a post-curing step is predominant (~20 hours for the MY721/HHPA and ~90 hours for the MY721/MA/HHPA-system, respectively), which results in a shift of the sharp modulus drop (\( \alpha \)-relaxation) towards higher temperatures. The obtained increase in the crosslink density coincides with decrease in rigidity in the glassy state \( (T<T_\alpha) \). However, with further increasing ageing time the modulus curve tends to shift again towards lower temperatures. This behaviour is correlated to an increase of the glassy modulus. The observed decrease in the glass transition temperature, caused mainly by irreversible structural network changes can be considered as a decrease in network density. Moreover,
the increase in the glassy modulus with decreasing crosslink density is known as antiplasticization phenomena [59, 60].

The continuous network degradation has a profound influence on the evolution of the glass transition temperature as shown in Figure 102. The MY721/MA-system exhibits an increase of the $T_g$-value over the entire ageing period. This observation provides further evidence that the intrinsic conjugation of MA, tends to react during thermo-oxidative ageing as discussed before. In addition, this behaviour is consistent with a study by Le Huy et al. who reported comparable thermo-oxidative ageing behaviour for epoxy resin cured with unsaturated methyl-tetrahydrophthalic anhydride (MTHPA) [35].

![Figure 102: Behaviour of the glass transition temperature ($T_g$), determined by the maximum of $\tan\delta$, as a function of ageing time at 200°C for the (♦) MY721/MA, (△) MY721/HHPA, (□) MY721/MA/HHPA-system. A molar anhydride to epoxy ratio, r=0.8, was used for all samples.](image)

In both HHPA-containing systems the competition between the post-curing and degradation mechanisms is noticeable by a distinct maximum in the glass transition temperature in Figure 102. The observed behaviour of $T_g$ for the MY721/HHPA- and the MY721/HHPA/MA-system revealed fundamental similarities between the two systems. Both $T_g$’s decreased below the ageing temperature of 200°C after approximately 400 hours and 700 hours for the MY721/HHPA and the MY721/MA/HHPA-system, respectively. The observed behaviour indicates that the presence of HHPA weakens the network structure in terms of thermo-mechanical properties. Consequently, HHPA-cured networks are more susceptible to thermo-oxidative depolymerization processes, e.g. by chain-scission, as proposed by Le Huy and Levchik [29, 35]. The experimental observations tend to support the hypothesis that the MY721/MA/HHPA-system has a multi-phase network structure, which comprises
independent MY721/HHPA and the MY721/MA sub-networks. This conclusion is consistent with experiments performed in section 2.3.2.3 and 3.5.4.1.

The dynamic evolution of the Cole-Cole plot as a function of thermo-oxidative ageing is shown in Figure 103. In particular for the MY721/MA-system (Figure 103(a)) the two Perez coefficients ($\kappa$ and $\kappa'$) only slightly decreased (see Table 14). This corresponds to an almost unchanged network density, which is in agreement with the obtained $T_g$-evolution. Supporting evidence for the disappearance of the intermediate $\omega$-relaxation with ongoing exposure was provided by the Cole-Cole analysis. It can be seen that the influence of the $\omega$-relaxation on the Cole-Cole plot diminishes continuously and the relaxational spectrum for the MY721/MA-system becomes mono-relaxational after about 700 hours.

Figure 103: Dynamic Cole-Cole plot as a function of different ageing times for (a) MY721/MA, (b) MY721/HHPA, (c) MY721/MA/HHPA-system during thermo-oxidative ageing at 200°C. A molar anhydride to epoxy ratio, $r=0.8$, was used for all samples.

For the MY721/HHPA-system (Figure 103(b)) the peak maximum in the Cole-Cole diagram continuously shifted towards higher $E'$-values. This thermal behaviour is consistent with a decrease in the measured $T_g$ and coincides with the fact that after about 700 hours of ageing some of the samples were completely destroyed. Information on the network
architecture on molecular motions can be obtained from the $\kappa$ and $\kappa'$ parameters as shown in Figure 104. In physical terms the observed decrease in the $\kappa'$ parameter in the early period of exposure can be related to a post-curing reaction (increase of crosslink density). The consequently followed monotonous increase in the $\kappa'$-value with increasing ageing time can be correlated with the increased distance between crosslinks points (decrease of crosslink density) due to irreversible network degradation. Moreover, this behaviour is consistent with the behaviour of $\kappa$ as function of ageing time, where $\kappa$ increases when the crosslink density decreases. The fact that for both HHPA-containing samples the parameters $\kappa$ and $\kappa'$ converge to unity with increasing ageing time reflects the sample conversion towards molecular glass ($\kappa'$=1) as proposed by Cavaillé [61].

![Figure 104: Behaviour of the Perez parameter ($\kappa'$) as a function of ageing time at 200°C for (a) MY721/MA, (b) MY721/HHPA, (c) MY721/MA/HHPA. A molar anhydride to epoxy ratio, r=0.8, was used for all samples.](image)

In case of the MY721/MA/HHPA-system the Cole-Cole plot, as shown in Figure 103(c), shows a composite curve of the superimposed mono-hardener systems. The dynamic disappearance of the $\omega$-relaxation with progressing ageing becomes visible in the development of a mono-relaxational Cole-Cole plot, which is consistent with the behaviour of the pure MA cured sample. In comparison to the pure HHPA system, the composite system exhibited a delayed onset of thermal degradation. This effect can be attributed to the partially substituted HHPA content with MA and hence to the higher thermo-oxidative stability of the MA sub-network structure.
Table 14: Numerical Perez parameters in the glass transition region for different investigated networks as a function of thermo-oxidative ageing time at 200°C

<table>
<thead>
<tr>
<th>System</th>
<th>Ageing time [h]</th>
<th>κ’</th>
<th>κ</th>
<th>E₀  (MPa)</th>
<th>E∞  (MPa)</th>
<th>E∞/E₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>MY721/MA</td>
<td>0</td>
<td>0.308</td>
<td>0.221</td>
<td>310</td>
<td>2350</td>
<td>7.7</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>0.264</td>
<td>0.140</td>
<td>90</td>
<td>2050</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>475</td>
<td>0.261</td>
<td>0.213</td>
<td>18</td>
<td>2350</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td>717</td>
<td>0.264</td>
<td>0.208</td>
<td>17.5</td>
<td>1750</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>0.268</td>
<td>0.188</td>
<td>17</td>
<td>2900</td>
<td>171</td>
</tr>
<tr>
<td>MY721/HHPA</td>
<td>0</td>
<td>0.516</td>
<td>0.192</td>
<td>95</td>
<td>1960</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.504</td>
<td>0.172</td>
<td>75</td>
<td>2200</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>186</td>
<td>0.456</td>
<td>0.181</td>
<td>100</td>
<td>3500</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>717</td>
<td>0.840</td>
<td>0.263</td>
<td>40</td>
<td>2800</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>0.971</td>
<td>0.500</td>
<td>3</td>
<td>2750</td>
<td>917</td>
</tr>
<tr>
<td>MY721/HHPA/MA</td>
<td>0</td>
<td>0.455</td>
<td>0.066</td>
<td>105</td>
<td>4300</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.189</td>
<td>0.070</td>
<td>49</td>
<td>2800</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>0.263</td>
<td>0.076</td>
<td>32</td>
<td>3800</td>
<td>119</td>
</tr>
<tr>
<td></td>
<td>186</td>
<td>0.286</td>
<td>0.058</td>
<td>30</td>
<td>4050</td>
<td>135</td>
</tr>
<tr>
<td></td>
<td>475</td>
<td>0.369</td>
<td>0.083</td>
<td>40</td>
<td>3100</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>717</td>
<td>0.381</td>
<td>0.392</td>
<td>20</td>
<td>2300</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>0.471</td>
<td>0.692</td>
<td>9.5</td>
<td>2150</td>
<td>231</td>
</tr>
</tbody>
</table>

*) Interference with the ω-relaxation

4.4.1.3 Effects of thermo-oxidative ageing on the flexural behaviour

As shown in the previous section the thermo-oxidative ageing has a significant effect on the viscoelastic properties of the materials. In order to investigate the correlation between the physico-chemical and the mechanical behaviour the flexural properties as a function of thermo-oxidative degradation were studied. The well-established MY721/DDS-system was used as a reference system in order to benchmark the different epoxy/anhydride systems.

The initial values of the flexural strength and the elastic modulus for the studied systems are listed in Table 15. It can be seen that the flexural strength values of all three anhydride-cured systems are comparable at $\sigma_m=86\pm4$ MPa. In contrast the amine-cured system shows a significantly higher flexural strength.

Table 15: Virgin flexural properties of the investigated epoxy-systems

<table>
<thead>
<tr>
<th>System</th>
<th>Flexural strength [MPa]</th>
<th>Young's modulus [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MY721/MA</td>
<td>86</td>
<td>3.5</td>
</tr>
<tr>
<td>MY721/HHPA</td>
<td>82</td>
<td>3.2</td>
</tr>
<tr>
<td>MY721/MA/HHPA</td>
<td>90</td>
<td>3.4</td>
</tr>
<tr>
<td>MY721/DDS</td>
<td>129</td>
<td>3.71</td>
</tr>
</tbody>
</table>
The dynamic changes of the ultimate flexural strength ($\sigma_{rm}$) as a function of ageing time and temperature are presented in Figure 105. A general trend for all investigated samples was obtained. The ultimate strength of the samples first increases until the ductile-brittle transition is reached. Then the flexural strength passes through a maximum and decreases again into the ‘brittle domain’. It is obvious that the maximum of the flexural strength depends on the nature of the used curing agent and related crosslinking structure. The highest flexural strength was obtained for the MY721/DDS network ($\sigma_{rmax}=150$ MPa), followed by MY721/MA ($\sigma_{rmax}=140$ MPa), MY721/MA/HHPA ($\sigma_{rmax}=115$ MPa), and MY721/HHPA-system ($\sigma_{rmax}=100$ MPa). Moreover, the obtained $\sigma_{rm}$-maxima of the anhydride-cured system are consistent with the $T_g$-maxima as already discussed in section 4.4.1.1. This fact provides evidence that the mechanical changes can be strongly related to the crosslink density variations occurring during thermo-oxidative degradation. If the glass transition temperature increases due to a post-curing effect, the increased crosslink density induces an increase of the yield stress [62]. At a certain point the yield stress becomes too high, consequently the mechanism of brittle fracture becomes competitive, and the sample fractures already in the elastic area at comparatively low deformation resulting in a decrease of the flexural strength.

Figure 105: Flexural strength behaviour as a function of degradation time and temperature in air for (a) MY721/MA, (b) MY721/HHPA, (c) MY721/MA/HHPA, (d) MY721/DDS.
To compare the long-term mechanical behaviour of the studied materials the related 5000 hours temperature index ($TI_{5000}$) was calculated according to DIN-IEC216/T1 [63] wherein as a general end-of-life criterion is defined as a 50% reduction of the initial flexural strength. Moreover, the analysis of $TI_{5000}$ data is based on the assumption that there is a linear relation between the logarithm of time to the end-point and the reciprocal of the thermodynamic ageing temperature (Arrhenius dependency). The thermal endurance graphs for the different epoxy-systems are shown in Figure 106 and the calculated $TI_{5000}$-values are given in Table 16.

Considering the calculated $TI_{5000}$ for a lifetime prediction it can be stated that the thermo-oxidative stability can be ranked as: MY721/MA>MY721/MA/HHPA≥MY721/DDS >MY721/HHPA. Therefore, it can be seen that the stability sequence is related to the hardener nature. However, the fact that different anhydride-cured diglycidylester of bisphenol-A (DGEBA) systems show $TI_{5000}$-values significantly above 220°C [21, 64, 65], gives evidence that the currently studied amino-glycidyl resin structure has more impact on the thermo-oxidative stability than the chemical nature of the used anhydride hardener. Thus, it can be concluded that the presence of relatively unstable C-N bonds from the TGDDM-resin monomer is predominantly involved in the molecular breakdown-process.

Figure 106: Thermal endurance graph for calculation of the 5000 hours temperature index ($TI_{5000}$). The symbols represent (△) MY721/MA, (●) MY721/HHPA, (■) MY721/MA/HHPA, (▽) MY721/DDS. The dotted lines represent the extrapolated $TI_{5000}$-values.
Table 16: 5000 hours temperature index ($T_{I5000}$) of the investigated epoxy-systems. All $T_{I5000}$-values were calculated using a 50% reduction of the initial flexural strength as end-criterion [63, 66].

<table>
<thead>
<tr>
<th>System</th>
<th>$T_{I5000}$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MY721/MA</td>
<td>153</td>
</tr>
<tr>
<td>MY721/HHPA</td>
<td>76</td>
</tr>
<tr>
<td>MY721/MA/HHPA</td>
<td>137</td>
</tr>
<tr>
<td>MY721/DDS</td>
<td>131</td>
</tr>
</tbody>
</table>

4.4.2 Short-term thermo-oxidative stability

The short-term thermal stability in air (thermal-oxidation), and in nitrogen atmosphere was studied by thermo-gravimetric analysis (TGA). The thermograms, as recorded from continuous heating experiments, are shown in Figure 107. It can be seen that the degradation process is accompanied by the release of volatiles above temperatures of 300°C for the systems heated in air (Figure 107(a)-(b)), leading to a decrease in mass. On the other hand for the system heated in nitrogen, a significant weight increase (up to about 10%) was observed. This behaviour can be probably attributed to a buoyancy effect, though 10% increase in mass is very large. Despite, chemical reactions between the nitrogen atmosphere and the cured epoxies cannot generally excluded, even if nitrogen is used in TGA as an inert gas.
Figure 107: TGA-run (ϕ=10°C/min) of MY721-systems (r=0.8) cured with different anhydride hardeners. (a) relative weight-loss; (b) derivative of weight-loss (dm/dt), under (1) air and (2) nitrogen atmosphere.

For a quantitative comparison of different investigated epoxy-networks, values of the following parameters were determined: the degradation onset temperature ($T_i$), the temperature at 50% weight-loss ($T_{50}$) and the temperature of maximum extent of degradation ($T_{max}$). Since the investigated samples exhibited a pronounced double degradation mechanism under air atmosphere, the two individual mass losses $m_1$ and $m_2$, as well as the ultimatively mass loss ($m_\infty$) after $T_{max}$ were analyzed as well. Additionally, the corresponding temperature at the maximum rates of mass loss $T_{m1}$ and $T_{m2}$ for the individual degradation processes were determined from the peaks of the appropriate differential thermo-gravimetric (DTG) curves. The characteristic data obtained from dynamic TGA-experiments in different atmospheres are shown in Table 17 and 18.

**Table 17: Characteristic data obtained from dynamic TGA performed in air**

<table>
<thead>
<tr>
<th>System</th>
<th>$T_i$ [°C]</th>
<th>$T_{50}$ [°C]</th>
<th>$T_{m1}$ [°C]</th>
<th>$T_{m2}$ [°C]</th>
<th>$\frac{dm}{dt}_{\text{max}1}$ [%/min]</th>
<th>$\frac{dm}{dt}_{\text{max}2}$ [%/min]</th>
<th>$m_1$ [%]</th>
<th>$m_2$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MY721/MA</td>
<td>302</td>
<td>491</td>
<td>308</td>
<td>622</td>
<td>6.8</td>
<td>2.0/2.1</td>
<td>69.3</td>
<td>2.6</td>
</tr>
<tr>
<td>MY721/HHPA</td>
<td>341</td>
<td>389</td>
<td>358</td>
<td>564</td>
<td>15.1</td>
<td>2.2</td>
<td>49.0</td>
<td>5.6</td>
</tr>
<tr>
<td>MY721/MA/HHPA</td>
<td>306</td>
<td>472</td>
<td>340</td>
<td>588</td>
<td>5.2</td>
<td>2.3</td>
<td>61.4</td>
<td>5.3</td>
</tr>
</tbody>
</table>

**Table 18: Characteristic data obtained from dynamic TGA performed in nitrogen**

<table>
<thead>
<tr>
<th>System</th>
<th>$T_i$ [°C]</th>
<th>$T_{50}$ [°C]</th>
<th>$T_{\text{max}1}$ [°C]</th>
<th>$\frac{dm}{dt}_{\text{max}}$ [%/min]</th>
<th>$m_1 = m_\infty$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MY721/MA</td>
<td>308</td>
<td>549</td>
<td>341</td>
<td>5.6</td>
<td>46.3</td>
</tr>
<tr>
<td>MY721/HHPA</td>
<td>331</td>
<td>394</td>
<td>359</td>
<td>12.5</td>
<td>32.5</td>
</tr>
<tr>
<td>MY721/MA/HHPA</td>
<td>301</td>
<td>598</td>
<td>342</td>
<td>6.9</td>
<td>47.4</td>
</tr>
</tbody>
</table>
It is obvious that a more complex weight-loss behaviour was observed in air (Figure 107; 1(a)-(b)). Based on the number of peaks in the appropriate DTG-thermograms (Figure 107; 1(b)) the decomposition process can be divided at least into a two-stage mechanism. For maleic anhydride-containing systems a third underlying, but low amplitude stage, located between the two main stages, is visible. This observation indicates that the presence of MA results in a more heterogeneous network structure and different susceptibilities to thermal oxidation. It is proposed that the slightly increased weight-loss of the two MA-cured systems at temperatures below $T_\alpha$ can be mainly attributed to the increased moisture content generated during the curing reaction (cf. Chapter 2).

On the other hand the thermograms in nitrogen atmosphere show that only a one-stage degradation mechanism occurred (Figure 107; 2(a)-(b)). The residual weight at the ‘pseudo-plateau’ as well as the fact that the first degradation stage shows a similar mass-loss profile in both air and nitrogen indicates that presumably thermolysis, i.e. non-oxidative degradation reactions, seems to dominate the degradation process in this temperature region. This observation is in agreement with earlier epoxy ageing studies [67-70]. The fact that in nitrogen atmosphere the high temperature degradation stage is effectively suppressed provides evidence that this decomposition stage can be most probably attributed to reactions between oxygen from the air and epoxy (oxidation). In addition it might be possible that reactions products formed during the first, low temperature degradation step react with oxygen in the second step. Combined TGA and heat flow measurements that have been recently carried out by Lutter-Kayser [71] on the same system, revealed a higher exothermal heat flow for the second stage of degradation. These experimental data confirmed the conclusion that the high temperature decomposition stage can be most probably related to substantial oxidation, since oxidation processes generally increase the sample temperature and the measured heat flow.

The fact that the decomposition temperatures are generally lower (<350°C) than reported values for DGEBA-based epoxy resins [72, 73] emphasizes the reduction of the thermo-oxidative stability due the presence of amino-glycidyl-resin. Considering that the two nitrogen atoms in the TGDDM-adducts are more basic than the DEGBA-counterparts, it is proposed that the related nitrogen interactions are destabilizing the network structure resulting in an adverse effect on the thermo-oxidative stability of TGDDM based networks as also shown for the mechanical endurance in section 4.4.1.3.

The apparent thermo-oxidative stability was assessed by the value of the initial degradation temperature ($T_\alpha$). Using this criterion, amongst the neat resin samples, the most stable was the MY721/HHPA-system. The thermo-oxidative degradation for this system starts at around 340°C. However, compared to the two other investigated systems, the maximum weight-loss rate of about 15%/min after the onset of degradation, reflected a very rapid degradation
reaction. An indication that the presence of MA significantly affects the thermal degradation of the cured epoxy systems is given by the fact that both, the first and the second stage of the thermal degradation mechanism (see Table 17 and Table 18) are affected. While MA decreased the onset temperature of the first degradation stage, it retarded the second thermal degradation step as manifested by the corresponding $T_{m1}$ and $T_{m2}$-values (cf. Table 17).

Numerous publications have described methods for the determination of kinetic parameters by mathematically processing the appropriate TGA-data [74-79]. An extensive study on the degradation kinetics using thermo-gravimetric analysis on the same epoxy systems has been recently performed by Lutter-Kayser [71]. However, due to very complex and simultaneously occurring degradation processes, the applied empirical and semi-empirical methods have not resulted in a satisfactory mathematical description of the overall decomposition process. In this work the estimation of the overall activation energy for the weight-loss was used as quantitative measure. For the studied MY721/MA/HHPA-system an integral method as originally proposed by Flynn-Wall [78] and Ozawa [76, 77] was applied. This method has been widely used for different epoxy networks [13, 79] as it allows for a mathematical description without a prior knowledge of the involved mechanisms of degradation and how those mechanisms change with conversion. The Flynn-Wall relation is given by eqn (4.67):

$$\log(\phi) = \left[ \frac{AE_a}{\alpha R} \right] - 2.315 - \frac{0.457E_a}{RT}$$  \hspace{1cm} (4.66)

where the apparent activation energy ($E_a$) and the corresponding pre-exponential factor ($A$) can be graphically calculated from a plot of logarithm of heating rate ($\phi$) as a function of reciprocal temperature ($1/T$), for a constant extent of thermal degradation ($\alpha$) as defined by eqn (4.68):

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty}$$  \hspace{1cm} (4.67)

where $m, m_0, m_\infty$ are the actual, initial and ultimate weight of the sample, respectively.

This finally leads to the activation energy as a function of the extent of degradation as shown for the MY721/MA/HHPA-system in Figure 108. However, it should be noted that conclusions only drawn from measured values of $E_a$ could lead to erroneous results with regards to thermal stability. The obtained degradation behaviour shows an almost linear increase of the activation energy with increasing extent of degradation. The calculated average activation energies of 174 kJ/mol (0.06$<\alpha<0.3$) is in a good agreement with previously reported values on TGDDM based epoxies, which vary between 124 kJ/mol for a TGDDM/DDS [79] and 191 kJ/mol for a TGDDM/DDS/DDM-system [67], respectively.
Figure 108: Activation energy \( (E_a) \) as a function of the extent of thermo-oxidative degradation as determined by the Flynn-Wall-Ozawa method [78] for the MY721/MA/HHPA-system \((r=0.8)\).

### 4.4.2.1 Effects of the molar anhydride to epoxy ratio

The characteristic property profile of epoxy thermosets is strongly coupled to the resin stoichiometry and related network variations [80]. Therefore, in this section the effects of variations in the stoichiometry on the thermal–oxidative stability will be investigated more in detail. Thermograms obtained from dynamic TGA-measurements of the MY721/MA/HHPA-systems with different anhydride to epoxy ratios are shown in Figure 109. It can be seen that the characteristic weight-loss and rate curves revealed no significant difference in terms of thermo-oxidative stability where identified for the \( r=0.64 \) and \( r=1.0 \) systems, since the onset of degradation \( (T_i) \) started at around 300°C. Only a slightly higher \( T_i \)-value (314°C) was obtained for the \( r=0.64 \) system. Therefore, it can be concluded that thermo-oxidative stability is primarily independent of the molar anhydride to epoxy ratio in the investigated variation range between 0.64 and 1.0.

Figure 109: Non-isothermal thermo-gravimetric analysis of the MY721/MA/HHPA-system in air atmosphere using different molar anhydride/epoxy ratios. (a) relative weight-loss; (b) derivative of weight-loss \((dm/dt)\).
4.4.3 Long-term thermo-oxidative stability

During long term thermal ageing in air, significant color changes appeared in all samples. The initial red color changed successively to green-blue, then brown and finally black. This observation, previously reported by others [20, 81], is indicative of chemical network changes, e.g. increase of conjugation and final carbonization that occurred due to thermo-oxidation processes.

The specific long-term weight-loss behaviour was examined by isothermal ageing experiments that were carried out at 150, 170, and 200°C, respectively, and the weight-loss, \( m(t) \), was calculated using eqn (4.69):

\[
m(t) = \frac{m - m_0}{m_0}
\]

(4.68)

where \( m_0 \) and \( m \) are the initial weight and the weight at time, \( t \), respectively. The weight-loss behaviour of the different anhydride-cured systems are shown in Figure 110. In order to benchmark the different studied epoxy/anhydride-systems the well-investigated MY721/DDS-system [45-48] was selected as high performance epoxy system.

![Graphs showing isothermal weight-loss curves](image)

**Figure 110:** Isothermal weight-loss curves (4 mm thick plates) as a function of ageing time for the unfilled MY721-systems using different hardeners at (a) 150°C, (b) 170°C, and (c) 200°C. The dotted line in graph (d) represents the calculated weight-loss line for the MY721/MA/HHPA system using a molar mixing rule of the two individual anhydrides (MA/HHPA=0.7/0.3) and the experimental data.
As seen from Figure 111 the thermo-oxidative stability depends strongly on the nature of the used hardeners. It should be noted that the time-temperature equivalence principles are also valid, i.e. a short ageing time at higher temperature is comparable with a long ageing time at lower temperature. Thus, for ageing temperatures of 150°C and 170°C, the same stability sequence was obtained; see Figure 110(a) and Figure 110(b). The most stable system was the MY721/HHPA-system ($\Delta m$ about 0.6% at 150°C and 1.2% at 170°C after 1000 hours) followed by the MY721/DDS-system ($\Delta m$ about 0.9% at 150°C and 1.7% at 170°C after 1000 hours). This observation is consistent with the dynamic TGA results, where the highest measured onset temperature ($T_i$) reflects the initial low weight-loss of the MY721/HHPA-system under isothermal long-term ageing conditions. The MY721/MA-system was the least thermo-oxidative stable and a weight-loss ($\Delta m$) of 2% at 150°C and 5% at 170°C after 1000 hours was obtained.

The MY721/MA/HHPA-system exhibited a fairly good thermo-oxidative stability resulting in $\Delta m$ of about 1.8% and 3% after 1000 hours at 150°C and 170°C, respectively. Hence, the co-anhydride cured system can be considered as a “composite” system consisting of two underlying sub-network structures. This finally results in an adaptive weight-loss behaviour of the two individual MY721/MA and MY721/HHPA sub-networks. As a result, a prediction of the overall weight-loss behaviour by applying a simple molar mixing rule (MA/HHPA=0.7/0.3) leads to a fairly good agreement with the experimental data at 150 and 170°C (cf. Figure 110). The overall weight-loss in the early ageing period is mainly attributed to higher thermal susceptibility of the MY721/MA sub-network. In the later ageing period (>500 hours) the experimentally obtained weight-loss is primarily dominated by the rapid degradation behaviour of the MY721/HHPA sub-network.

However, the previously obtained sequence of stability changed when the samples were exposed to an ageing temperature of 200°C. In this case, the thermo-oxidative stability of the MY721/HHPA-system is only superior compared to the amine-cured system (MY721/DDS) up to an ageing time of 500 hours. After 500 hours of thermal exposure, the shape of the corresponding weight-loss curve changed and the weight-loss increased rapidly from this point on (Figure 110(c)). Moreover, it should be noted that all specimens were unanimously destroyed between 500 to 1000 hours at 200°C; see Figure 111. Thus, it can be concluded that a transition of the degradation mechanism for the MY721/HHPA-system is reached after about 500 hours of thermal ageing at 200°C resulting in a rapid decomposition reaction. Consequently, a marked reduction of the network density by intermolecular chain scissions is consistent with a decrease in the corresponding $T_g$-data (cf. Figure 102).
The MY721/MA-system exhibited different isothermal weight-loss behaviour during continuous ageing at 200°C. The lower $T_r$-value from the dynamic TGA-experiments has already provided a first indication for a decreased long-term thermo-oxidative stability. Nevertheless, it is remarkable that the sustainable weight-loss has no direct affect on the network structure as indicated by the analogous glass transition behaviour (cf. Figure 102) under comparable ageing conditions. Therefore, it is proposed that the observed weight-loss is predominantly based on the thermal degradation of dangling network chains (presumably monoacid end groups as identified in section 2.3.4) that are not significantly affecting the final network density. Nevertheless, such chain scissions contribute to the overall weight-loss by the formation of volatile fragments.

The MY721/MA/HHPA-system exhibited the maximal weight-loss during the thermal ageing at 200°C and an almost 25% mass reduction was recorded over the entire ageing period of 1000 hours. Moreover, the validity of weight-loss predictions by using a mixing rule is more questionable, since the calculated values differ significantly and lower absolute weight-loss values were calculated.

### 4.4.3.1 Effects of inorganic fillers

In this section the influence of different disperse inorganic fillers on the long-term weight-loss behaviour was investigated. The weight-loss behaviour of the neat and filled-systems as a function of ageing temperature and time are shown in Figure 112.
It can be clearly seen that substantial differences between filled and neat MY721/MA/HHPA-systems were obtained. As expected, the filled systems exhibited a decreased weight-loss behaviour in comparison to the neat resin. For instance, filling the MY721/MA/HHPA-system with 40 vol.% of alumina (Al₂O₃) reduced the weight-loss by about 1.5% during 1000 hours of thermal ageing at 150°C. However, even if these results seem trivial since the filled systems contain less epoxy per volume unit than the neat systems, it is interesting to study the effects of different fillers on the weight-loss of the resin part of the composites. In this case, it is possible to quantify the efficiency of the filler on the thermo-oxidative stability.

Since the specimens used in this study have different filler-weight fractions, the comparative weight-loss (CWL) as defined by equation (4.70) was used for direct comparison of the different samples:

\[
\text{CWL}(T_a, t_a) = m_a(t) = \frac{m(t)}{1 - V_f}
\]  

(4.69)

where \( V_f \) is the volume fraction of inorganic filler in the material, and \( m(t) \) is the measured weight variation of the composite sample as given by eqn (4.69).
The experimental data for silica (SiO\textsubscript{2}) and alumina (Al\textsubscript{2}O\textsubscript{3}) filled systems at different ageing temperatures are shown in the Figure 113(a)-(c).

![Figure 113: Comparative weight-loss (CWL) of the MY721/MA/HHPA-system \((r=0.8)\) as a function of filler type at (a) 150°C, (b) 170°C and (c) 200°C. A filler fraction of 40 vol.% and a sample thickness of 4 mm were constant for all samples.](image)

It can be seen that the obtained differences can not only be related to the weight-loss of the neat resin but also to the nature of fillers used in the composite systems. For example a weight-loss of 1.78\% for the neat resin was obtained after 1000 hours of exposure at 150°C. Taking into consideration that the volume unit involves 40\% of inert inorganic filler a theoretical weight-loss of about 1.1\% for the filled systems would be expected. However, the experimental data under comparable ageing conditions show only a weight-loss of 0.8\% for the SiO\textsubscript{2} and 0.52\% for the Al\textsubscript{2}O\textsubscript{3} filled composites. It is proposed that this observation can be mainly attributed to the extension of the diffusion length as a consequence of adding impenetrable particles. Hence the diffusion of oxygen into the bulk and the migration of volatile reaction products out of the sample are significantly obstructed, as schematically shown in Figure 114. Further, effects due to filler surface interactions or variations in the particle size distribution cannot be excluded, but stated as minor alterations. Finally, based on the experimental results, it can be concluded that Al\textsubscript{2}O\textsubscript{3} is more efficient in protecting the MY721/MA/HHPA-system against thermo-oxidative degradation than the SiO\textsubscript{2}. 
4.4.3.2 Modeling the isothermal weight-loss behaviour

In order to describe the degradation kinetics and the related lifetime under service conditions, it is necessary to accurately model the weight-loss and thus to estimate the long-term performance of the examined systems. However, to express the degradation process in polymeric materials quantitatively, phenomenological approaches are generally adopted, owing to the complexity of the degradation mechanism. Thus, it is assumed that the rate of weight-loss ($\frac{dm}{dt}$) is generally given by:

$$\frac{dm}{dt} = -kf(m)$$  \hspace{1cm} (4.70)

Where $k$ is an overall kinetic constant that follows an Arrhenius law with respect to temperature, and $f(m)$ is the model equation used to describe the dependence of the degradation rate on weight-loss. A considerable number of different models have been postulated over the last years [13, 73, 82, 83]. Among these, two theoretical models were applied in order to describe the different investigated anhydride/epoxy-systems. The first model is the double-stage mechanism that has been originally proposed by Le Huy [33]. The second one is a Fickian analogy considering diffusional processes.

4.4.3.3 The Double-Stage Mechanism (DSM)

The performed long-term weight-loss experiments allow verifying whether the experimental data can be described by the double-stage mechanism (DSM). The DSM-approach generally assumes two distinct occurring kinetic stages to describe the characteristic shape of the global weight-loss curve (see Figure 115):

(I) a first stage ($m_1$) where the rate of weight-loss ($\frac{dm}{dt}$) is comparatively high but decreases with ageing time, describing a self-retarded step.

(II) a second degradation stage ($m_2$) whereas the whole of the sample degrades with a quasi-constant weight-loss rate ($\frac{dm}{dt}$=constant).
If one denotes \( m \) as the weight-loss (%) of a given epoxy system, the two individual stages (\( m_1 \) and \( m_2 \)) can be described by using the following cumulative relation (4.71):

\[
m = m_1 + m_2
\]  

Assuming that in the first degradation stage the studied epoxy-systems exhibit a limited oxygen permeability, the thermo-oxidative degradation is predominately oxygen-concentration controlled. Under normal conditions, the mass of the degradable species on the polymer are in excess with respect to oxygen, and hence approaching a limiting, residual weight-loss value. Considering a first order homogeneous reaction order model, this effect is quantified by the expression:

\[
mf(t) = B e^{(-k_1 t)} + m_f
\]

where \( k_1 \) is a pseudo-first order rate constant. \( mf \) denotes the residual mass of the reactive species at time \( t \to \infty \). From the initial mass that \( m=m_0 \) at \( t=0 \), it follows that the pre-exponential factor \( B \) is equal to \( m_0-m_f \), i.e. the mass of the reactive species that has been degraded by the end of the process. In terms of relative conversion (\( \alpha \)), since \( \alpha=(1-m/m_0) \), \( \alpha=(1-m_f/m_0) \), and \( m=m_0(1-\alpha) \), equation (4.72) can be rearranged to:

\[
\alpha = \alpha_1 \left(1 - e^{-k_1 t}\right)
\]  

Finally, recalling that \( \alpha=(m_0-m)/m_0 \) the weight-loss conversion equation can be written as eqn (4.74):

\[
m_f (t) = m_0 - m_f \left(1 - e^{-k_1 t}\right)
\]

where \((m_0-m_f)\) is a conversion parameter.
For the second weight-loss stage, $m_2(t)$, the corresponding weight-loss rate shifts towards an almost constant value that can be accurately described by zero-order kinetics such that eqn (4.75) applies:

$$m_2(t) = -k_2 t$$  \hspace{1cm} (4.75)

with $k_2$ being the pseudo-zero order rate constant.

Consequently, the global weight-loss behaviour can be described by a combination of a first- and a zero-order process (eqns (4.74) and (4.75)) as:

$$m(t) = (m_0 - m_1)[1 - \exp(-k_1 t)] - k_2 t$$  \hspace{1cm} (4.76)

A non-linear least square curve regression allows fitting the DMS-model to the experimentally obtained isothermal weight-loss data, and thus the determination of the characteristic kinetic parameters as given in Table 19.

In addition, the specific reaction rates ($r_1$ and $r_2$) of each individual degradation stage can be finally determined by the derivation of the previous part reactions leading to eqn (4.77):

$$r_1 = \left. \frac{dm_1(t)}{dt} \right|_{t \to 0} = \frac{(m_0 - m_1)}{k_1} + k_2 = \frac{(m_0 - m_1)}{k_1} + r_2$$  \hspace{1cm} (4.77)

$$r_2 = \left. \frac{dm_2(t)}{dt} \right|_{t \to \infty} = k_2$$

The finally calculated reaction rates ($r_1$ and $r_2$) are listed in Table 19 as well.
Table 19: Characteristic kinetic parameters of thermo-oxidative degradation of the MY721/MA/HHPA-system (r=0.8) obtained by best fitting to the double-stage mechanism.

<table>
<thead>
<tr>
<th></th>
<th>( m_0-m_f ) (%)</th>
<th>( k_1 ) (h(^{-1}))</th>
<th>( k_2 ) (h(^{-1}))</th>
<th>( r_1 ) (%h(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_a = 150^\circ \text{C} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MY721/HHPA/MA</td>
<td>1.0544</td>
<td>13.8150</td>
<td>0.0008</td>
<td>0.0771</td>
</tr>
<tr>
<td>MY721/HHPA</td>
<td>0.3563</td>
<td>0.9940</td>
<td>0.0003</td>
<td>0.3587</td>
</tr>
<tr>
<td>MY721/MA</td>
<td>1.1287</td>
<td>16.5723</td>
<td>0.0010</td>
<td>0.0691</td>
</tr>
<tr>
<td>MY721/DSS</td>
<td>0.6120</td>
<td>1.1319</td>
<td>0.0004</td>
<td>0.5410</td>
</tr>
<tr>
<td>MY721/HHPA/MA/Al(_2)O(_3) (40 vol.%)</td>
<td>0.0369</td>
<td>1.0052</td>
<td>0.0003</td>
<td>0.0370</td>
</tr>
<tr>
<td>MY721/HHPA/MA/SiO(_2) (40 vol.%)</td>
<td>0.0978</td>
<td>1.0169</td>
<td>0.0004</td>
<td>0.0966</td>
</tr>
<tr>
<td>( T_a = 170^\circ \text{C} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MY721/HHPA/MA</td>
<td>1.3359</td>
<td>15.3717</td>
<td>0.0020</td>
<td>0.0889</td>
</tr>
<tr>
<td>MY721/HHPA</td>
<td>0.4050</td>
<td>1.0490</td>
<td>0.0009</td>
<td>0.3870</td>
</tr>
<tr>
<td>MY721/MA</td>
<td>1.1674</td>
<td>15.1061</td>
<td>0.0004</td>
<td>0.0777</td>
</tr>
<tr>
<td>MY721/DSS</td>
<td>0.8050</td>
<td>1.2945</td>
<td>0.0010</td>
<td>0.6229</td>
</tr>
<tr>
<td>MY721/HHPA/MA/Al(_2)O(_3) (40vol.%)</td>
<td>0.0764</td>
<td>1.0132</td>
<td>0.0009</td>
<td>0.0763</td>
</tr>
<tr>
<td>MY721/HHPA/MA/SiO(_2) (40vol.%)</td>
<td>0.1781</td>
<td>1.0485</td>
<td>0.0010</td>
<td>0.1708</td>
</tr>
<tr>
<td>( T_a = 200^\circ \text{C} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MY721/HHPA/MA</td>
<td>6.0353</td>
<td>91.8784</td>
<td>0.0181</td>
<td>0.0838</td>
</tr>
<tr>
<td>MY721/HHPA</td>
<td>0.3492</td>
<td>1.4227</td>
<td>0.0113</td>
<td>0.2568</td>
</tr>
<tr>
<td>MY721/MA</td>
<td>8.2791</td>
<td>140.1040</td>
<td>0.0101</td>
<td>0.0691</td>
</tr>
<tr>
<td>MY721/DSS</td>
<td>1.3896</td>
<td>19.1890</td>
<td>0.0022</td>
<td>0.0746</td>
</tr>
<tr>
<td>MY721/HHPA/MA/Al(_2)O(_3) (40vol.%</td>
<td>0.4044</td>
<td>1.721</td>
<td>0.0049</td>
<td>0.2399</td>
</tr>
<tr>
<td>MY721/HHPA/MA/SiO(_2) (40vol.%</td>
<td>0.4497</td>
<td>1.6631</td>
<td>0.0056</td>
<td>0.2760</td>
</tr>
</tbody>
</table>

A comparison between the experimental data and the theoretical Double-Stage Mechanism for the MY721/MA/HHPA-system at different ageing temperatures demonstrates the fairly good agreement as shown in Figure 116.
Furthermore, it is assumed that the temperature dependence of the specific reaction rates \( (r_1 \text{ and } r_2) \) obey an Arrhenius relation as given by eqn (4.78):

\[
    r_i = A_i \exp\left[-\frac{E_{ai}}{RT}\right] \quad \text{with} \quad i = (1,2)
\]

Where \( A_i \) is the pre-exponential factor, \( E_{ai} \) is the apparent activation energy of the thermo-oxidative degradation process, \( R \) is the universal gas constant and \( T \) is the absolute temperature. The subscript “i” denotes the two individual degradation stages.

According to the previous mathematical expression, the apparent activation energy \( (E_{ai}) \) is given by the slope of the curve \( \ln(r_i) = f(1/T) \) and the constant \( A_i \) is obtained from the intersection at the origin. An example of such an Arrhenius plot for the second degradation stage of the MY721/MA/HHPA- system is shown in Figure 117. The finally calculated \( E_{ai} \) and the corresponding \( A_i \) for the investigated systems are listed in Table 20.
Table 20: Characteristic kinetic data for thermo-oxidative degradation of different MY721 based epoxy system as experimentally obtained form determined weight-loss data (4 mm thick samples) by applying the Double-Stage Mechanism [33].

This table is not available on line. Please consult the hardcopy thesis available from the QUT Library.

It should be noted that some of the calculated Arrhenius parameters for the first degradation stage (\(E_{a1}\)) in Table 20 must be treated with caution, because the experimental values did not result in an Arrhenius plot with a high correlation coefficient (R<0.9). Nevertheless, the comparison of \(E_a\)-values for the anhydride-cured systems shows that the MY721/MA-network exhibits the lowest apparent activation energy. The MY721/DDS-system revealed the lowest activation energy for the second degradation stage (\(E_{a2}\)) and consequently the lowest overall activation energy (\(E_a\)).

Besides, the data provide evidence that the microstructure of the MY721/MA/HHPA-system is a combination of an independent MY721/MA and MY721/HHPA sub-network. Hence, a simple mixing rule that considers the molar anhydride ratio (MA/HHPA=0.7/0.3) was applied to predict the apparent activation energy (\(E_a\)) of the co-anhydride cured system in a reasonable manner (cf. eqn (4.79)).

\[
E_{a}^{MY721/HHPA/MA} = 57.7 \text{ kJ/mol} \\
0.3 \times E_{a}^{MY721/HHPA} + 0.7 \times E_{a}^{MY721/MA} = \\
0.3 \times \frac{64 \text{ kJ/mol}}{mol} + 0.7 \times \frac{46 \text{ kJ/mol}}{mol} = 56.4 \frac{\text{kJ/mol}}{mol} \equiv E_{a}^{MY721/HHPA/MA}
\]

In addition, the obtained DSM-results allow a correlation to the involved degradation mechanisms. It can be summarized that the first degradation stage can occur in only a minor proportion of the virgin material. Consequently, the fast degradation stage has both a lower activation energy and a lower \(A\)-factor than the slow (second) degradation process. In practical terms, it is proposed that the fast degradation process is associated with a sequential loss of unstable moieties such as structural irregularities (presumably acidic dangling chain ends, cf. section 2.3.4) that are initially present. Since these volatile fragments gradually reduced during thermo-oxidative degradation, the experimentally
observed weight-loss rate decreased as a function of ageing time. Moreover, the higher \((m_0 - m_f)\)-values, see Table 19, for MA-cured systems, give evidence of a higher initial amount of ‘irregular’ structures at the beginning of the degradation process. Consequently, an increased weight-loss rate was observed for MA-cured samples during the initial degradation stage. In addition, the predominant decomposition of dangling chains within the first degradation stage gives a reasonable explanation, while the network density as expressed by the related \(T_g\) remains almost unaffected (cf. Figure 102).

In contrast, the whole of the sample is susceptible to degradation by the second, slow degradation process that is attributed to random chain scissions of more stable backbone structures. Therefore, it has a higher activation energy and a higher pre-exponential factor than the fast process.

A schematic presentation of the proposed network changes is given in Figure 118. Even if the hypothesis has not been experimentally confirmed for the studied epoxy/anhydride networks, it is proposed that a general indication of the two-stage degradation mechanism is valid.

a) 

\[ \text{Figure 118: Schematization of a chain scission processes yielding to volatile fragments occurring (a) during the first degradation stage in dangling chains, and (b) during the second degradation stage in more stable backbone structures.} \]

b) 

4.4.3.4 The Fickian diffusion model

The thermo-oxidative degradation generates volatile degradation products that evaporate according to a diffusion-controlled process that constitute the rate-determining stage. Therefore, the specific isothermal weight-loss behaviour of the investigated glassy epoxy systems has been frequently analyzed by analogy to diffusional processes as originally
introduced by Fick’s second law of diffusion [84]. This theoretical description based on a
differential mass balance, which assumes that the time rate of concentration change is
related to the second derivative of the concentration gradient through the diffusion
coefficient:

\[
\frac{dC_x}{dt} = - \frac{1}{2} \frac{\partial}{\partial x} \left[ -D \frac{\partial C_x}{\partial x} \right] = -D \cdot \frac{\partial^2 C_x}{\partial x^2} \tag{4.80}
\]

where \(D\) is the diffusion coefficient, \(x\) is the space coordinate measured normal the sample
thickness, and \(t\) denotes the time. If the material has a uniform initial diffusant concentration
\((C_0)\) and the surface is kept at a constant concentration \((C_{max})\) the solution of eqn (4.80) is:

\[
\frac{C - C_0}{C_{max} - C_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} (-1)^n \exp \left( -\frac{D(2n + 1)^2 \pi^2 t}{h^2} \right) \cos \left( \frac{(2n + 1)\pi x}{h} \right) \tag{4.81}
\]

The total amount of fragments diffusing out of the polymeric network \((m)\) as a function of
time is given by the integral of eqn (4.81) across the thickness \((h)\):

\[
\frac{m}{m_{max}} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n + 1)^2} \exp \left( -\frac{\pi^2 (2n + 1)^2}{h^2} \right) D t \tag{4.82}
\]

where \(m_{max}\) is the maximum quantity of the diffusing substance at infinite time. A more
simplified form of (4.82) for values of \(m/m_{max}\) lower than 0.6 can be given by:

\[
\frac{m}{m_{max}} = \frac{4}{h^2} \sqrt{Dt} \tag{4.83}
\]

Consequently, if the weight-loss obeys Fickian behaviour, a linear plot of \(m\) against \(t^{0.5}\) in its
initial part can be considered as a validation criterion of Fick’s law. From the slope of the
linear part, the coefficient of diffusion can be calculated. The rearranged weight-loss curves
for the MY721/MA/HHPA-system and the linear regression curves are shown in Figure 119.

\[ \text{a) } \]

\[ \text{b) } \]
Figure 119: Comparison between the experimental weight-loss data (solid line) and the theoretical Fickian model (dotted line) for the MY721/MA/HHPA-system (r=0.8) at an ageing temperature of (a) 150°C, (b) 170°C, and (c) 200°C, respectively.

From the gravimetric analysis it can be seen that with increasing ageing temperature the weight-loss curves can be more precisely described by the Fickian dependency. Thus, the more accurate agreement with the Fickian diffusion behaviour, even in the initial stage, was obtained for higher ageing temperatures. This observation is consistent with the fact that diffusion processes are generally favoured by elevated temperature. Considering further that the diffusion coefficient \( (D) \) obeys an Arrhenius dependency as given by eqn (4.84):

\[
D = D_0 \cdot \exp \left[ -\frac{E_a}{RT} \right]
\]

and rearranging eqn (4.84) by taking the logarithm leads to eqn (4.85):

\[
\ln(D) = \left( \frac{E_a}{R} \right) \cdot \frac{1}{T} + \ln(D_0)
\]

Thus the global activation energy \( (E_a) \) and the appropriate rate coefficient \( (D_0) \) can be obtained by plotting the \( \ln(D_0) \) versus \( 1/T \) for the three studied ageing temperatures. The obtained kinetic degradation data are summarized in Table 21.

Table 21: Characteristic kinetic data for thermo-oxidative degradation as calculated by the Fickian method [84] for different MY721-systems (r=0.8)

<table>
<thead>
<tr>
<th>Systems</th>
<th>( E_a ) (kJ/mol)</th>
<th>( D_0 ) (%/h(^{1/2}))</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MY721/HHPA/MA</td>
<td>80</td>
<td>4.6*10^8</td>
<td>0.94</td>
</tr>
<tr>
<td>MY721/HHPA</td>
<td>84</td>
<td>4.5*10^8</td>
<td>0.95</td>
</tr>
<tr>
<td>MY721/MA</td>
<td>69</td>
<td>2.1*10^7</td>
<td>0.99</td>
</tr>
<tr>
<td>MY721/DDS</td>
<td>39</td>
<td>2.5*10^3</td>
<td>0.99</td>
</tr>
<tr>
<td>MY721/ HHPA/MA/Al2O3 (70%wt)</td>
<td>92</td>
<td>2.1*10^8</td>
<td>0.99</td>
</tr>
<tr>
<td>MY721/ HHPA/MA/SiO2 (60%wt)</td>
<td>80</td>
<td>1.0*10^8</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Even if the Fickian model used is based on different theoretical assumptions than the Double-Stage Mechanism concept, the calculated kinetic parameters allow the prediction of
the same stability range in terms weight-loss. Thus, a consistent sequence was obtained for the Fickian- and the DSM-model. Nonetheless, the absolute values of the activation energy ($E_a$) slightly differ between the two applied models and generally higher values were obtained for the Fickian model. Moreover, a common behaviour of both models is that the quality of the results increased with increasing temperature, as it can be seen in Figure 116 and Figure 119, respectively. Finally, it can be stated that diffusional processes must be unambiguously included when describing the experimental degradation data.

4.4.4 Thermo-oxidative degradation studied by FT-IR spectroscopy

Numerous analytical techniques, such as gas chromatography [85], mass spectroscopy [86], radiochemical analysis [85, 86], or combinations of these methods have been used to study the degradation mechanisms of polymeric materials. However, a limitation of these techniques arises from the fact that a relatively high degradation temperature is required to produce sufficient amounts of volatile products. Moreover, the degradation products itself may not be stable and react in a second step to more complex structures. Thus, the product analysis may not always be unambiguous to interpret mechanistically and consequently may result in incorrect conclusions. These difficulties can be overcome by FT-IR spectroscopy since this technique examines the behaviour of the polymeric substrate rather than the volatile products formed. The high sensitivity of FT-IR spectroscopy additionally allows an approximate localization and a quantitative determination of chemical species in particular when the chemical degradation reactions are relatively slow [87, 88].

In the present section the thermo-oxidative ageing behaviour of the different anhydride-cured MY721-systems was studied by FT-IR micro ATR-spectroscopy. The interpretation of the recorded spectra and the band assignments are adapted from the information related to the pure components. The used band assignments rely predominately on the comprehensive work of Antoon and Koenig that was based on the characteristic group frequency approach [89, 90]. Further interpretation of the spectra is based on the work of Bellamy [91], Colthup et al. [92], and Pretsch et al. [93], as well as the work presented in Chapter 2 within this thesis.

During the isothermal ageing at 150°C the characteristic spectra significantly changed with increasing ageing time, and hence the spectral features allow an extraction of the relevant molecular information. At higher ageing temperatures the spectra rapidly became featureless and consequently a meaningful interpretation was not possible. The representative time-resolved IR-spectra of the different anhydride/epoxy-systems are shown in Figure 120. The infrared analysis of the crosslinked systems revealed that a variety of molecular changes occurred during thermo-oxidative ageing. Almost all peaks exhibited
intensity changes or peak-shifts when compared to the initial spectra. However, with exception of the fingerprint region, the general changes in relative intensities for all studied systems were similar and independent on the anhydride curing agents that were used. For all investigated samples, an intensity increase of the broad band between 3100 and 3600 cm\(^{-1}\) was clearly visible with progressing ageing. Generally, this broad band is related to \([\nu \text{O-H}]\) or \([\nu \text{N-H}]\) if both are present, however, an assignment to hydroxyl seems in this case more reasonable. Nonetheless, it cannot be further differentiated between hydroxyl due to water that is dissociated and bound in the network or to water as a reaction product. The observed shift of the \([\nu \text{O-H}]\) peak maxima at \(\sim 3500\) cm\(^{-1}\) to a low frequency component centered at \(\sim 3360\) cm\(^{-1}\) indicates the formation of new species absorbing in the lower side of the O-H range. These oxygenated species might be tentatively assigned to hydroperoxide groups and carboxylic acids [91, 94]. However, for quantitative considerations the spectra in this area were disregarded, since all degraded samples provided a significant baseline shift in this region, due to an intense discoloration of the severely degraded material.

An analysis of the data in the area between 800 and 2000 cm\(^{-1}\) revealed that the asymmetric carbonyl stretch of cyclic anhydrides \([\nu_{\text{as}} \text{C}=\text{O}]\) at 1798 cm\(^{-1}\) in the HHPA-cured, and at 1780 cm\(^{-1}\) in the MA/HHPA-cured system, respectively, decreased with increasing exposure time. This observation is related to a further consumption or vaporization of partially unreacted HHPA. On the other hand for purely MA-cured system no vibrational band was observed that confirms the presence of unreacted maleic anhydride.

A peak at \(\sim 1775\) cm\(^{-1}\) (indicated by arrows in Figure 120) gradually increased with ageing. The peak position is in agreement with earlier studies by Le Huy et al. who investigated the thermal degradation behaviour of differently flexibilized anhydride-cured epoxies [33-35]. Le Huy et al. assigned the peak to \([\nu_{\text{as}} \text{C}=\text{O}]\) of reformed anhydride species. However, since the characteristic symmetric carbonyl stretch of cyclic anhydrides at \(\sim 1850\) cm\(^{-1}\), \([\nu_{\text{sym}} \text{C}=\text{O}]\) was not detectable, the 1775 cm\(^{-1}\) band assignment to reformed anhydride species is highly questionable. Even if the peak assignment at 1775 cm\(^{-1}\) is not unambiguous, it is here proposed that this intensity is tentatively assigned to the carbonyl stretch of highly oxygenated species, such as lactones [95].

The distinct carbonyl stretch of the aromatic ester at \(\sim 1730\) cm\(^{-1}\) exhibited a gradual decrease and shifts towards lower frequencies at 1710 cm\(^{-1}\) (indicated by the dotted line in Figure 120). This behaviour is probably related to an extensive oxidation of the ester groups and partial transformation into new aldehyde and ketone species. Moreover, the broadened peak appearance is likely related to the multiplicity of different carbonyl species formed and/or due to the occurrence of molecular interactions, e.g. hydrogen bonding, which generally decreases the frequency of the carbonyl stretching absorption. In addition,
potential C-O and C-N chain scissions yield to an increase of the polar O-H and N-H groups that generally favor hydrogen bonding.

A new absorption band near 1670 cm$^{-1}$, characteristic for enamine groups, increased in intensity during ageing due to the attack of non-stable C-N bonds by oxygen [94, 96-98]. Although polyaromatic carbonaceous compounds that are formed in the TGDDM-resin at high temperature, could also have an IR absorption near 1670 cm$^{-1}$, this potential contribution can be neglected, because of the relatively low ageing temperature and short ageing time used in this study [79]. Additionally, the C=C indication in MA-cured systems at 1640 cm$^{-1}$, which can be assigned to monoacids of partially reacted MA, decreased with progressive ageing.

After longer exposure the bonds between nitrogen and phenyl groups may rupture. The observed decrease in peak intensities at $\sim$1165 cm$^{-1}$ for HHPA-, and at $\sim$1158 cm$^{-1}$ in the case of MA-containing networks, respectively, can be attributed to the cleavage of C-N bonds [99]. Further evidence of C-N cleavage is given by the change of the $\nu \Phi$-$N$ peak at about 1380 cm$^{-1}$ [28, 83, 100].

Indication of a cyclization process to heterocyclic compounds is provided by the changing substitution pattern of the aromatic TGDDM-structure. The intensity shift of the aromatic TGDDM-structure at 1615 cm$^{-1}$ [quadrant, $\Phi$], and 1515 cm$^{-1}$ [semicircle stretching, $\Phi$] (see dotted line in Figure 120) towards lower wavenumbers can be attributed to a cyclization to quinoline-structures [101, 102]. This observation is in agreement with previously performed degradation studies of TGDDM based networks, where a backbiting reaction to 1,2,3,4-tetrahedra-3-hydroxyquiniline structures was postulated [35, 102]. Additional support for this hypothesis is given by the increased intensities above 3000 cm$^{-1}$ that correspond to the formation of the hydroquinoline-compounds. However, this contribution could not be further differentiated from the hydroxyl and amine absorbancies in the same region. With higher exposure times a significant loss of the aromatic character is visible by a decrease of the corresponding intensities.

Evidence for oxidation of the methylene groups linking the two-phenyl groups in the TGDDM-resin (cf. structure in Table 2) is given by the decrease of the characteristic in-plane deformation of the methylene band [$\delta$CH$_2$] at $\sim$1450 cm$^{-1}$ (see Figure 120) [103]. In addition, a progressive decrease of the stretching vibration of the CH$_2$-deformation at 2970 and 2850 cm$^{-1}$ confirmed the degradation of aliphatic CH$_2$-groups.

Additionally, a gradual growth of a new absorption at $\sim$830 cm$^{-1}$ is noted. The hydro-peroxide group is known to exhibit a characteristic peak at $\sim$830 cm$^{-1}$, corresponding to the $\sim$O-O-stretching mode [91, 93]. Hence, the observed peak is associated with a steady increase of the R-O-O-H concentration, which is consistent with the increase of the OH stretching range.
This observation is in agreement with previously performed thermo-oxidative studies where evidence for a free radical formation was postulated [106]. At wavenumbers below 800 cm\(^{-1}\) a meaningful peak analysis was not possible and therefore no discussion about this part of the spectra was performed.
A summary of the characteristic spectral changes and the related interpretations of the investigated anhydride-cured epoxy systems is given in Table 22.

Table 22: Overview of changing FT-IR intensities during thermo-oxidative ageing of anhydride-cured epoxy systems

<table>
<thead>
<tr>
<th>Band [cm(^{-1})]</th>
<th>Assignment</th>
<th>Response on thermo-oxidative degradation</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>3100-3600</td>
<td>[\nu_O-H]</td>
<td>gradual increase and shift lower wavenumbers</td>
<td>formation of new hydroxyl or acid groups</td>
</tr>
<tr>
<td>1798</td>
<td>[\nu_{as}C=O] HHPA</td>
<td>decrease during early exposure in HHPA-cured systems</td>
<td>crosslinking reaction of HHPA</td>
</tr>
<tr>
<td>1775</td>
<td>[\nu_{as}C=O] of lactones</td>
<td>gradual increase</td>
<td>formation of new oxidized lactone structures</td>
</tr>
<tr>
<td>1730</td>
<td>[\nu(C=O) aromatic ester]</td>
<td>gradual decrease and shift to (\sim 1710) cm(^{-1})</td>
<td>reduction of aromatic ester groups</td>
</tr>
<tr>
<td>1670</td>
<td>[\nu_{as}C=O] of amine</td>
<td>gradual increase</td>
<td>formation of new amine groups</td>
</tr>
<tr>
<td>1650</td>
<td>[\nu_{as}C=O] of ketone or aldehyde groups</td>
<td>gradual increase</td>
<td>formation of new aldehyde or ketonic groups</td>
</tr>
<tr>
<td>1640</td>
<td>[\nu_C=C-COOH]</td>
<td>gradual decrease in MA-cured systems</td>
<td>loss of conjugated acids (e.g. monoacids)</td>
</tr>
</tbody>
</table>
4.4.4.1 Thermo-oxidation profiles

As already discussed in the previous sections, thermo-oxidative ageing of polymeric materials often starts by oxidation that is kinetically controlled by oxygen diffusion. When such a kinetic approach exists the whole oxidation process becomes a decreasing function of the initiation rate as a function of temperature. Hence, the depth-distribution of the oxidation products becomes heterogeneous and might be limited to superficial layers [104, 105]. In this case an oxygen-concentration maximum can be observed in the surface zone that decreases continuously over the sample depth. Numerous kinetic models for diffusion-controlled oxidation have been proposed that principally allow predicting the thickness of the oxidized layer (TOL) [34, 106, 107]. However, the main disadvantage of these models is that they mainly consider the oxidation process to be independent on oxygen diffusivity. Moreover, oxidation is a radical chain process and there is yet no consensus on the kinetic scheme [106]. Consequently, many authors have reduced the reaction mechanism to a standard mechanistic scheme for radical chain processes that are initiated by thermolysis or due to hydro-peroxide decomposition [106-108].

In this section the spectroscopic micro-ATR technique was used to determine the spatial oxidation profile of aged samples by line mapping the cross section in selected intervals. Figure 121 shows the measured spectra for the differently cured MY721-systems aged at 170°C. In the obtained spectra the appearance of lactone species, related to the IR-intensity at ~1775 cm⁻¹ [ν C=O] (indicated by the dotted line in Figure 121) was monitored as a function of ageing time. The lactone formation is accompanied by the shift of the aromatic peak at 1615 cm⁻¹ [quadrant, Φ] as indicated by an arrow in Figure 121. It is proposed that the formation of these highly oxidized superficial layers occurred by grafting oxygen to the macromolecular network and some chain breaking reactions with the diffusion of volatile compounds out of the sample. The elimination of the volatile by-products promotes the experimentally observed weight-loss (cf. section 4.4.2.).
Oxidation profiles, for visualizing the depth distribution in which the material degrade, were constructed. The determination of the depth distribution of oxidation products over the sample cross section was experimentally established by taking the deconvoluted peak height at $\sim 1775 \text{ cm}^{-1}$ in ratio to the internal standard at $\sim 1615 \text{ cm}^{-1}$. The latter band was assigned to the quadrant-stretching mode of the aromatic groups and it was not significantly affected by thermo-oxidative degradation in the investigated time frame. Consequently, the reduced local oxygen concentration, $(C/C_s)$, represented by the lactone intensity was calculated according to eqn (4.86):

$$\frac{C}{C_s} = \left( \frac{l_{1775}}{l_{1615}} \right) / \left( \frac{l_{1775}}{l_{1615}} \right)$$

where $l_0$, $l_t$, are the relative intensities of reactive species at time zero, and after a certain time interval, $t$, of the oxidation process. $C$ represents the appropriate lactone concentration as a function of time, and $C_s$ denotes the maximum lactone concentration on the sample surface at infinite time.

The experimentally determined oxidation profiles as a function of ageing time and temperature under atmospheric pressure are given in Figure 122(a)-(c). It can be seen that the oxidation is heterogeneously distributed within the sample thickness and a pseudo-hyperbolic lactone/oxygen concentration was obtained.
After about 400 hours of exposure, which approximately reflects the end of the first degradation stage obtained from the isothermal weight-loss curve (cf. Figure 111), an oxidized layer of about 200-400 µm thickness was formed. However, during the second degradation stage the TOL increased considerably and reached values of ∼1400 µm after 7420 hours of thermo-oxidative exposure. The obtained shape of the TOL-profile changed during exposure indicating that the apparent oxidation rate is a decreasing function of the sample thickness. Additionally, it was apparent that the TOL is a decreasing function of temperature (see Figure 122 (d)). The TOL, and consequently the oxidation susceptibility can be finally ranked in the following order: MY721/HHPA > MY721/MA/HHPA ≥ MY721/MA. The ranking of the oxidation layer thickness, which probably acts as an intrinsic diffusion barrier layer and limits the loss of volatile products, is consistent with the experimentally obtained weight-loss data in the same temperature range. Moreover, the results provide evidence that oxidation is the most important degradation mechanism during thermo-oxidative ageing.

Figure 122: Oxidation profile as determined by the normalized lactone concentration \( \frac{C}{C_0} \) as a function of curing agent and ageing interval at 170°C; (a) MY721/MA, (b) MY721/HHPA, (c) MY721/MA/HHPA; (d) thickness of the oxidized layer (TOL) of 4 mm thick samples as a function of the ageing time and ageing temperature for (▲) MY721/MA, (◆) MY721/HHPA, and (■) MY721/MA/HHPA
4.4.5 Thermo-oxidative degradation mechanism

All investigated anhydride/epoxy samples revealed no significant differences in the thermo-oxidative degradation mechanisms. Even if the thermo-oxidative degradation of the anhydride-cured TGDDM-networks studied here is very complex and involves several competitive mechanisms, the obtained changes are mainly related to the formation of highly oxidized and carbonized network structures involving a large content of aromatic structures. During degradation the networks are below their glass transition temperature and consequently in the highly crosslinked structure the molecular movement of any part of the network relative to another is severely hindered. Despite this, the thermo-mechanical results of the ageing studies revealed that the networks predominantly degrade by the scission of chemical network bonds. Hence, the proposed reactions outlined below illustrate predominantly routes that are basically limited to the consideration of chemical bond scissions and to how such reactions lead to the formation of degradation products that have been identified by FT-IR analysis within this study (cf. section 4.4.4). The exceptional reaction is the dehydration of the network.

In terms of bond dissociation energies, the weakest points in the crosslinked network are the C-N and C-O bonds [26]. However, the relatively high concentration of hydroxyl groups in the cured resin favors localized hydrogen bonding, which consequently promotes initial dehydration. Hence, it is proposed that the thermo-oxidative degradation initiates by the dehydration in agreement with previously reported degradation studies [20, 29, 79, 109, 110]. Moreover, available information emphasize that dehydration precedes, to a large extent, any further degradation of the network [30, 111]. The formation of water from ether oxygen of the network is not reasonable because of the relatively high stability of the aryl-oxygen bond [27]. Consequently, it is more likely that the dehydration of the secondary alcohols, as schematically shown in Figure 123, is primarily involved in this initial degradation reaction [27, 29-31]. The driving force behind these reactions is the large increase in stability of the systems, which follows double bond formation. This is particularly true when the formed double bonds are pseudo-conjugated by a nitrogen atom in conjunction with an aromatic ring [26, 27]. It is postulated that degradation results in the formation of the two unsaturated structures (I) and (II) as depicted in Figure 123. Structure (II) is probably the more favored moiety, because oxygen has a greater negative inductive effect than nitrogen so a hydrogen atom is more easily withdrawn from the CH₂ group adjacent to the oxygen atom. However, increasing IR-absorption in the region at 1650 to 1690 cm⁻¹ suggests that the enamine structure (structure I) is also formed to a certain extent. In addition, the formation of a highly conjugated structure would be consistent with the observed discoloration of the degraded epoxy-samples. Besides, the formed
conjugation induces stiffness into the polymer chains, which can be finally attributed to observed embrittlement and the increase in the glass transition temperature during the early ageing period (cf. section 4.4.1).

Figure 123: Initial dehydration mechanism for thermo-oxidative ageing of the investigated MY721/MA/HHPA-system.

The allylic hydrogen position in structure (I) and (II) weakens the network structure [31] and hence the C-N and C-O bonds are likely to undergo further chain scissions as it accumulates in the first, low temperature decomposition stage.

The enamine structure (I) would favor scissions of the allyl-oxygen bonds followed by cyclization to quinoline type structures (III) as shown in Figure 124. The shift of the intensities at $\sim 1615$ and $\sim 1515$ cm$^{-1}$ indicates the change of the aromatic substitution pattern that can be assigned to cyclization of quinoline-derivatives. The simultaneously generated oxygen radical (IV) would be stabilized by hydrogen abstraction yielding new hydroxylated species (V). This reaction accounts for the experimentally observed increase of the related hydroxyl intensities.

In the enamine (structure II) the allyl-nitrogen chain cleavage occurs preferentially at the position indicated in Figure 125. Evidence for the C-N cleavage was obtained by the decreasing intensity of the corresponding $\nu\Phi$-N peak at 1380 cm$^{-1}$. The obtained radicals are stabilized by hydrogen abstraction yielding primary amines (VI) that could consequently be further converted to secondary amine structures (VII). The experimentally identified C-O and C-N bond scissions mainly caused the instantaneous cleavage of the molecular network structure resulting in a significant decrease of the glass transition temperature, as particularly pronounced for HHPA-cured samples (cf. Figure 102).

In addition, the weak allylic hydrogen in structure (I) and (II) can be easily abstracted by radical species, which are present in trace amounts in the epoxy material (e.g. formed in the high temperature curing or even directly generated by O$_2$ attack). For instance the proposed auto-oxidation sequence leads to hydrogen abstraction of the methylene groups between the aromatic TGDDM-units as shown by structure (VIII) in Figure 124. Finally, stabilized
radicals may be formed as shown by structure (IX). This reaction would finally account for the gradually absorption decrease of the methylene groups $\delta\text{CH}_2$ at 1450 cm$^{-1}$.

Figure 124: Proposed degradation sequences for thermo-oxidative ageing of the investigated anhydride-cured epoxy-system.

Besides, if bond cleavage occurs before dehydration Patterson-Jones [30] postulated that a radical formed by scissions of the C-N undergoes rearrangement followed by elimination to form aldehyde species as shown in Figure 125. In any case the reaction yields to the formation of new aldehyde species (structure X), which was experimentally confirmed by the shift of the related carbonyl intensities to 1650 cm$^{-1}$. 
4.5 Concluding remarks

In this chapter the thermo-oxidative ageing behaviour of different anhydride-cured amino-glycidyl resins was investigated. The effects of long-term ageing on thermo-mechanical properties, thermo-gravimetric behaviour, and architectural network changes were assessed and discussed.

The behaviour of the viscoelastic properties during thermo-oxidative ageing was studied by means of low frequency dynamic mechanical spectroscopy. All TGDDM-based formulations led to highly crosslinked networks ($T_g > 200^\circ C$). However, depending on the type of hardener, a different dynamic mechanical behaviour was observed. It was demonstrated that for maleic anhydride-cured samples the appearance of a secondary $\tilde{\omega}$-relaxation in the intermediate temperature range between 80 to 150$^\circ C$ is associated with network-irregularities (e.g. dangling chain ends). The relaxational behaviour was described as a function of ageing time by means of Cole-Cole plots. The gradual decrease of the $\tilde{\omega}$-relaxation with increasing ageing time can be seen in the formation of a mono-relaxational Cole-Cole plot appearance. It is proposed that this effect can be directly related to the volatilization and loss of primarily dangling chain fragments. Moreover, it explains the fact that the glass transition temperature, and thus the associated network-density, of the purely MA-cured network remains almost unaffected during 1000 hours of ageing. On the other hand hexahydrophthalic anhydride-cured systems revealed a combination of two independent ageing mechanisms. During the early ageing period the viscoelastic behaviour clearly indicates a predominant post-curing process. However, with progressing ageing time, an irreversible degradation mechanism was superimposed leading to a deleterious alteration.
of the thermo-mechanical property profile and the initial network structure. Based on the experimental results it is emphasized that the application of the physical Perez model is meaningful to interpret the viscoelastic property changes in terms of structural network variations.

Thermo-gravimetric analysis of neat and particulate-filled materials revealed a double stage degradation mechanism under air atmosphere. It was demonstrated that the low temperature degradation stage is related to thermolysis and hence independent of the gaseous environment. The second, high temperature degradation stage is primarily attributed to oxidation processes, since it was not detected under nitrogen atmosphere. To determine kinetic parameters experimental long-term weight-loss data at 150, 170, and 200°C were modeled by a double stage mechanism and a diffusion related analogy. The extracted kinetic degradation parameters permit to outline a more generalized two-stage degradation mechanism. The first degradation stage predominantly reflects the degradation of structural irregularities, such as untangled chains or end-groups of dangling chains. Thus, this process has only a secondary influence on the final network density. Even through the accompanied weight-loss (e.g. for maleic anhydride cured systems) was relatively high an almost constant glass transition temperature was observed. The second degradation stage then includes the chemical degradation of the more stable backbone structure, and hence significant network changes. However, differences in the thermal stability ranking were observed at higher ageing temperatures. In particular the MY721/HHPA-network was drastically perturbed when ageing was carried out at 200°C. The obtained weight-loss considerably increased after 450 hours reflecting significant chemical modifications of the network structure, which is consistent with the marked decrease in the related glass transition temperature.

Mechanical endurance tests were performed in order to predict the lifetime under service conditions. It was highlighted by the calculated temperature index that even though MA-cured networks are more susceptible to the first degradation step, the entire thermo-oxidative stability is superior to HHPA and DDS-cured networks. Therefore, the overall thermo-oxidative stability sequence can be ranked as: MY721/MA>MY721/MA/HHPA ≥MY721/DDS>MY721/HHPA. Evidence that the introduction of inorganic disperse silica (SiO₂) and alumina (Al₂O₃) particles improved the thermo-oxidative stability and weight-loss rate, was deduced from the experimental measurements of hybrid systems. It was demonstrated that Al₂O₃-filler outperformed SiO₂-particles.

The obtained initial properties as well as the thermal stability could be estimated, with a fairly good accuracy, by a simple mixing rule and ranked between the two individual anhydride-cured systems. Hence, the experimental results demonstrated that the studied co-
anhydride-cured system involves at least an MY721/MA and MY721/HHPA sub-network as schematic shown in Figure 126.

Figure 126: Proposed network structure for the MY721/MA/HHPA-system. The solid lines represent the MA-segments and the dotted lines the HHPA-segments.

The degradation mechanism and the corresponding oxidation profile were studied by FT-IR micro-ATR spectroscopy. The spectral information provided strong evidence that an initial dehydration-process is mainly followed by aliphatic C-N and C-O chain scissions that triggered more complex degradation processes. Chemical modification of the studied materials induced by thermo-oxidative ageing can be clearly seen by the formation of highly oxidized carbonyl structures (e.g. lactones, ketones and aldehydes) in combination with a cyclization involving the aromatic backbone structure. We have not seen any evidence of an alternative mechanistic degradation pathway to be caused by the presence of different anhydride types or variations in the stoichiometry of the studied networks.

4.6 References

[64] Product data sheet, CY225/HY925, Vantico, Switzerland, 2001
[89] Antoon M.K., PhD-Thesis, Case Western Reserve University, Cleveland (OH), (1980)
Chapter 5

5 General conclusions and perspectives

In this thesis novel co-anhydride cured epoxy formulations have been investigated in order to assess the advantages and limitations of these new thermosetting materials in industrial applications. The main objective of this work was to develop a fundamental understanding of:

- the principal cure mechanism and kinetics
- the general thermo-mechanical deformation and fracture behaviour
- the thermo-oxidative ageing performance and mechanism

1.) Cure mechanism and kinetics

The thermal polymerization as a function of time and temperature was systematically studied by means of differential scanning calorimetry, rheometry and FT-Raman spectroscopy. It was shown that the investigated anhydride-cured epoxy system reacts mainly by polyesterification. Possible side reactions including the homopolymerization of MA were considered. The main identified side reaction was decarboxylation of the anhydrides that may produce some autocatalysis, but this is a minor contribution to the cure kinetics in the investigated temperature range between 55 to 120°C. The applied in-situ methods revealed that isothermal conditions are essential to provide reliable and meaningful results for analysis of the curing reaction. A simple first order reaction scheme for both epoxy and anhydride with carboxylic acid and hydroxyl groups as reactive intermediates described the reaction profile until the polymerization was influenced by chemo-rheological changes due to gelation and vitrification transitions.

The use of a temperature modulated DSC (TMDSC) technique allows the differentiation of the MY721/MA and MY721/HHPA reaction rates that consequently provides evidence for the existence of an independent MY721/MA and MY721/HHPA sub-network in the cured state. Additionally, chemo-rheological studies provided insight in the gelation and a vitrification phenomenon, which finally allows the reconstruction of a principal time-temperature-transformation diagram in order to predict the entire isothermal curing process.
2.) Thermo-mechanical deformation and fracture behaviour

The characteristic deformation and fracture behaviour of neat and silica-filled MY721/MA/HHPA-samples was studied as a function of temperature, stress rate, filler fraction, particle-size and filler-matrix adhesion. Microscopic studies of fractured samples showed that diffuse matrix shear yielding and micro-shear banding are the dominating deformation mechanisms. These processes are amplified by higher temperature and increased stress rates. Moreover, with increasing silica content, the tensile and compression modulus of composites increased whereas the corresponding strength values remain quasi-constant.

The crack propagation and fracture behaviour was examined by applying the concept of linear elastic fracture mechanics. The critical stress intensity factor ($K_{IC}$) and the critical strain energy release rate ($G_{IC}$) significantly decreased at temperatures above 100°C. It was demonstrated that this unconventional behaviour is related to the fact that the MY721/HHPA sub-network was exposed to temperatures above its glass transition temperature.

Attempts to improve the fracture toughness while maintaining the thermo-mechanical property profile has been addressed by using inorganic hard particles, epoxy functionalized hyperbranched polymers (HBPs), and hybrid-composites through a modifier combination. Increasing the inorganic filler fraction resulted in an effective enhancement of the fracture toughness due to the implementation of the “crack-pinning” mechanism. The corresponding $K_{IC}$ value increased from 0.6 MPam$^{0.5}$ for the neat resin to 1.6 MPam$^{0.5}$ for the silica-filled (60 wt.%) system.

The shell chemistry of different HBP-modifiers and the related morphology-property relationship were thoroughly investigated. Tailoring the number of functional shell groups can be effectively used to control the final morphology of the materials. Increasing the number of functional epoxy end-groups increases the solubility of the HBP modifier in the matrix. Thus, it is possible to adapt blends with variable morphologies ranging from phase-separated to totally homogenous. The phase-separated blends revealed a pronounced anisotropic structure in the cured state due to density differences between the modifier and matrix. Consequently, only a moderate improvement in toughness was obtained. On the other hand the homogenous blends showed the best improvement in toughness and the corresponding critical stress intensity factor was increased by about 50% from 0.6 to 0.9 MPam$^{0.5}$. Synergistic effects in hybrid-systems were not observed and the inorganic filler dominated the fracture behaviour. Attempts to establish a chemically induced phase separation process to precisely control the morphology were limited, because of inadequate entropic and enthalpic changes in the investigated anhydride-cured epoxies.
3.) Thermo-oxidative degradation
An important aspect in this thesis was to explore the effects of thermo-oxidative long-term degradation on thermo-mechanical properties, thermo-gravimetric behaviour, and the related architectural network changes.
A new approach for monitoring the ageing process by combining mechanical Cole-Cole plots with the theoretical Perez model has been successfully applied. It was demonstrated that this method provides a meaningful correlation between the relaxational behaviour and the intrinsic network variations. It was shown that the appearance of a secondary $\omega$-relaxation is primarily associated with network-irregularities (e.g. dangling chains) that are related to the presence of maleic anhydride.
Thermo-gravimetric analysis of neat and particulate-filled materials revealed a double stage degradation mechanism under air atmosphere. The low temperature degradation stage predominantly reflects the degradation of structural irregularities, such as untangled chains or end-groups of dangling chains. The followed high temperature degradation stage includes the chemical degradation of the more stable backbone structure.
Thermal endurance of the flexural behaviour showed that entire thermo-oxidative stability of MA-cured networks is superior to HHPA-cured networks. The thermo-oxidative performance of the MY721/MA-system proved to be an economical and environmental alternative to the well-established TGDDM/DDS-system.
The experimental measurements on hybrid-systems showed that the introduction of inorganic particles (e.g. disperse silica (SiO$_2$) or alumina (Al$_2$O$_3$)) improved the thermo-oxidative stability and the weight-loss rate. The addition of alumina-filler outperformed silica-particles.
The degradation mechanism and the corresponding oxidation profile were studied by FT-IR micro-ATR spectroscopy. The spectral information provided strong evidence that the attack of the relatively weak C-N and C-O bonds in TGDDM-based formulations generally limits the use of amino-glycidyl based systems for long-term applications at temperatures above 150°C.
Chapter 6

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Chapter 7

7 Curriculum Vitae (CV)

The author of this thesis was born in Osnabrück, Federal Republic of Germany, on 1st February 1972. After graduation in 1991, he spent one year in military service. In 1993 he started to study Material Science at the University of Applied Science in Osnabrück. Under supervision of Prof. F. Vohwinkel and Dr. F. Greuter he obtained his degree in 1997 on the project "A comparison of Silicone with EPDM for electrical outdoor insulation".

In the same year he joined the Polymer and Process Technologies Group of the Corporate Research Center of Asea Brown Boveri (ABB) in Baden, Switzerland, where he worked as a research scientist on new polymeric outdoor insulation as well as ageing phenomena of polymers.

In 2000, he started working on his doctoral degree in a joint project between the School of Physical and Chemical Sciences, which is part of the Faculty of Science at the Queensland University of Technology in Brisbane, Australia and ABB Corporate Research in Switzerland. The results on the work "Characterization of Novel Co-Anhydride cured Epoxy Resins" are described in this thesis.

In May 2002, he has been promoted to a position of a project leader at ABB Corporate Research. Since the beginning of 2004 he has taken over the lead of the group "Insulation and Polymer Technology". His recent work is mainly focused on the investigation and development of novel polymeric insulation principles and optimization of existing polymer processing technologies in the field of electrical high voltage equipment.

Research Publications


J. Rocks, L.Rintoul, F. Vohwinkel, G. George, The kinetics and mechanism of cure of an amino-glycidyl epoxy resin by a co-anhydride as studied by FT-Raman spectroscopy, submitted to Polymer
Conference presentations


Patents

In the last five years, more than fifteen international patent applications have been filed in the fields of polymeric insulation, polymer processing technologies and electrical equipment