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Polymer nanocomposites based on P3OT, TPU and SWNT: preparation and characterization.

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Abstract—Single walled carbon nanotubes (SWNTs) were incorporated in polymer nanocomposites based on poly(3-octylthiophene) (P3OT), thermoplastic polyurethane (TPU) or a blend of them. Thermogravimetry demonstrated the success of the purification procedure employed in the chemical treatment of SWNTs prior to composite preparation. Stable dispersions of SWNTs in chloroform were obtained by non-covalent interactions with the dissolved polymers. Composites exhibited glass transitions, melting temperatures and heat of fusion which changed in relation to pure polymers. This behavior is discussed as associated to interactions between nanotubes and polymers. The conductivity at room temperature of the blend (TPU-P3OT) with SWNT is higher than the P3OT/SWNT composite.

Keywords—Carbon nanotubes, polymer composites, thermal characterization, conductivity

I. INTRODUCTION

The most successful approaches to take advantage of the remarkable properties of single-walled carbon nanotubes have involved chemical modification of the tubes [1]. These strategies significantly alter the SWNT properties with the risk of partial destruction of the tubes. The polymer wrapping of SWNTs with typical non-conducting polymers [2] or conjugated polymers [3] has been explored as an attractive supramolecular approach to render SWNTs soluble. This method opens the possibility of being able to organize NTs into ordered networks. In this study we describe the preparation of stable dispersions of SWNT in P3OT, TPU and a blend of TPU-P3OT. The concentration of SWNT in the polymer matrices was of 1 wt%.

Thermal conductivity of carbon nanotubes has been reported to exceed 3000 W/mK [4,5]; this value is much higher than, for instance, for carbon fibres (<600 W/mK). The thermal expansion coefficient of SWNT bundles was determined by X-ray diffraction studies [6]. Three values were obtained for the temperature 300K to 950K:

- . $(-0.15 \pm 0.20) \times 10^{-5} \text{ K}^{-1}$ for the tube diameter;
- . $(0.75 \pm 0.25) \times 10^{-5} \text{ K}^{-1}$ for the triangular lattice; and
- . $(4.2 \pm 1.4) \times 10^{-5} \text{ K}^{-1}$ for the intertube gap.

Heat capacity (Cp) of SWNTs has been measured from 300 down to 2 K [7]. The Cp data for ropes were found to agree with an isolated tube model down to 5 K. At 300K the Cp value is approximately 0.652 J/(g K).

The consequences of the unique thermal properties of SWNTs on polymer composites are being explored more in recent years [8]. In this work we investigate the thermal properties of binary and ternary polymer/SWNT systems characterized by Differential Scanning Calorimetry (DSC).

Moreover, conductivity measurements were performed for the composites by using Impedance spectroscopy. Neutral P3OT is an insulator and shows conductivity as low as $1 \times 10^{-10} \text{ S/cm}$ [9]. Kymakis *et al.* [10] reported conductivity measurements of P3OT/SWNT for 1 to 35 wt% SWNT. They observed percolation for SWNT content higher than 12 wt%. TPU/MWNT conductivity was investigated by Koerner *et al.* [11]. These authors reported a conductivity of 1 S/cm for a composite with 10 wt% of MWNT.

II. EXPERIMENTAL

A. Materials

SWNTs as-prepared from Carboxex were purified following a procedure adapted from C.A Furtado *et al.* [12]. Briefly the steps of purification are: selective oxidation at 395°C, followed by reflux in HCl (3 mol L⁻¹) and rigorous washing. The purified yield of SWNT was 6 wt% of the as-prepared sample. P3OT synthesis was conducted according to the procedure given by M. R. Andersson *et al.* [13], using FeCl₃ suspension in chloroform. The yield of regular polymer was 80%. Thermoplastic polyurethane Irogram from Huntsman, containing 58 wt% of diol [11], was used as received. SWNT and polymers were separately dispersed and dissolved in chloroform, then mixed to prepare 1 wt% nanotube composite films. Sonication was used to improve dispersion and dissolution. A TPU-P3OT blend with 10 wt% of P3OT and SWNT at the same concentration of 1 wt% was also prepared. Coatings of nanocomposites were obtained with

spin casting, drop and conventional casting in order to prepare samples for characterization by different techniques.

B. Techniques

Scanning electron microscopy (SEM) was performed with a FEI Quanta 200 ESEM. A drop of SWNT-chloroform dispersion was dried on a aluminium stub. Thermogravimetry was carried out in TGA Q500 TA Instruments apparatus using 5°C/min heating rate in air atmosphere. DSC was performed in a Q100 TA Instruments equipment at 10°C/min in nitrogen atmosphere. Impedance spectroscopy was used to measure conductivity of composite films placed between two stainless steel electrodes. The impedance data was obtained with a EGG Princeton applied Research PAR273A potentiostat and Signal Recovery Lock in 5210.

III. RESULTS

A. Carbon nanotube purification and preparation of dispersions

Figure 1 shows TG results which indicate that the as-prepared SWNTs contain 41 wt% metallic species. The decomposition of the carbonaceous materials starts at 348°C for this raw sample. The purification procedure allowed the preparation of SWNT 88% pure, which decomposes from 574°C. The impurities remaining are 5 wt% of amorphous carbon and 7 wt% of metal oxides. With stronger conditions such as nitric acid digestion it is possible to further eliminate metal particles [12, 14]. However, these aggressive conditions are reported to damage the nanotube walls, which can be reversed by thermal annealing at high temperature in vacuum [14]. The addition of SWNT in this work seeks to take advantage of the intrinsic functionalization that occurs during selective oxidation and digestion with HCl, to suspend the nanotubes in solution by interaction with polymers. Therefore, no further vacuum annealing was required for our purposes. The choice of purification procedure was driven by these constraints.

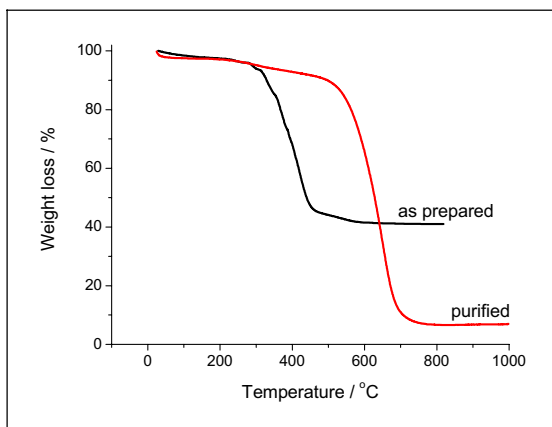


Figure 1. TG curves for SWNT as prepared and purified

The as-prepared material from Carboxlex contains typically bundles of ~100-400 SWNTs, ~1-5 μm long and with nanotube diameter of ~1.4 nm [12]. For a typical SWNT

rope the cohesive energy is reported to be as high as 2.9 keV [2]. Therefore, it is very difficult to actually isolate SWNT species. Figure 2 shows that the SWNT purified in this work exhibited extensive, yet incomplete, debundling, which is an important result to allow the effective interaction with polymers. The approximate diameter of purified bundles is in the range 30-60 nm. Further improvement of this debundling process is in progress.

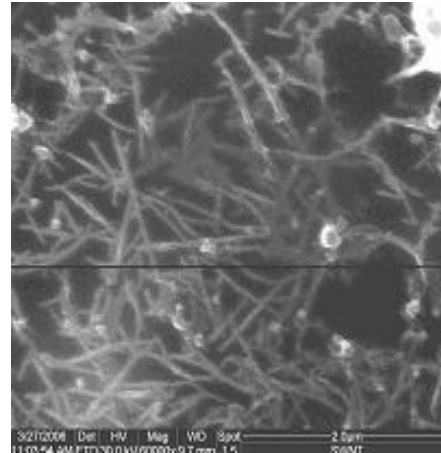


Figure 2. SEM image of SWNT debundled rope coating from chloroform solution.

Figure 3 shows the dispersion of SWNT in polymer solutions of P3OT, TPU and a mixture of them. The dispersions are stable for more than 2 weeks.

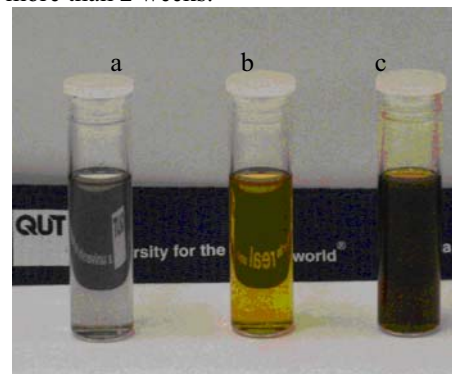


Figure 3. Stable solutions/dispersions of a) TPU/SWNT, b) TPU/P3OT/SWNT with 10 wt% of P3OT and c) P3OT/SWNT.

B. DSC study

Figure 4 shows the DSC curves for P3OT and the composite P3OT/SWNT prepared by casting. The characterization of the synthesized P3OT by GPC shows that the material has a very broad range of molecular weight with Mn (number average molecular weight) of approximately 40,000 D. The DSC for pure P3OT shows an endothermic event at 120°C (Table 1) and a very broad glass transition around -10°C. Monedero *et al.* [15] reported a melting temperature value for a P3OT with Mn (GPC) of 2500 of

158°C and a glass transition value of -9°C. The low melting temperature and broad glass transition observed are associated with the large polydispersity of the synthesized P3OT.

With the addition of 1 wt% of SWNT the endothermic event of P3OT disappears. The glass transition displaces to around 8°C. These results indicate that so far the nanotube addition to P3OT inhibits the crystal formation in the casting film. The shift in the glass transition is an indication of interaction between SWNT and P3OT.

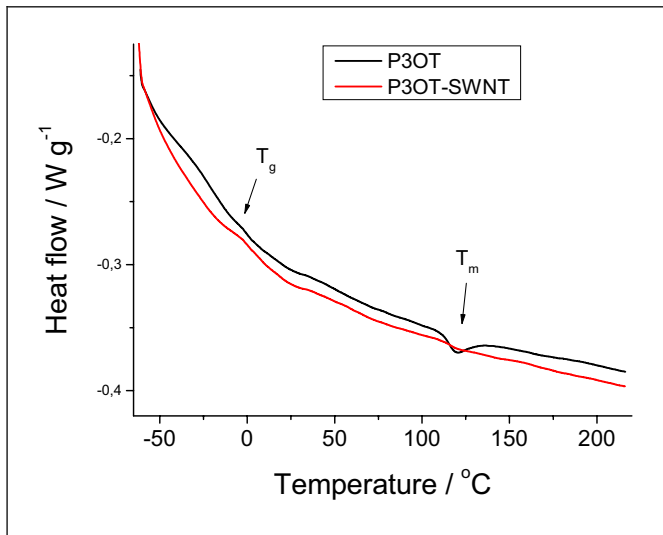


Figure 4. DSC curves for casting P3OT and P3OT/SWNT with 1 wt% of carbon nanotubes.

Koerner *et al.* [11] reported the thermal transitions of TPU- Hunstman as: $T_g = -45^\circ\text{C}$, $T_m(\text{soft segment}) = 48^\circ\text{C}$ and $T_m(\text{hard segment}) = 135^\circ\text{C}$. The results obtained from a casting sample (Figure 5) show differences in the TPU melting temperatures, as can be seen in Table 1, probably associated with the preparation procedure (through solvent). The addition of SWNT does not change the thermal parameters of the TPU as show in Table 1. There is, nevertheless, a change in the feature associated with the soft segment. The introduction of P3OT changes the heat of fusion of the hard segment and the feature of the soft segment melting. These observations indicate a certain degree of interaction between the components of the composite.

TABLE I. DSC RESULTS FOR POLYMERS AND NANOCOMPOSITES

Samples	$T_g/^\circ\text{C}$	$T_m/^\circ\text{C}$		$\Delta H/\text{Jg}^{-1}$
P3OT	~ -10	120		1.1
P3OT/SWNT	~ 8	-		-
Samples	$T_g/^\circ\text{C}$	$T_m^{\text{soft seg}}/^\circ\text{C}$	$T_m^{\text{hard seg}}/^\circ\text{C}$	$\Delta H^{\text{hard seg}}/\text{Jg}^{-1}$
TPU	-40	31	114	4.9
TPU/SWNT	-40	30	113	4.9
TPU/P3OT/SWNT	-41	30	114	2.2

* Heat of fusion for the soft segment of the TPU based materials are not quoted because of lack of accuracy.

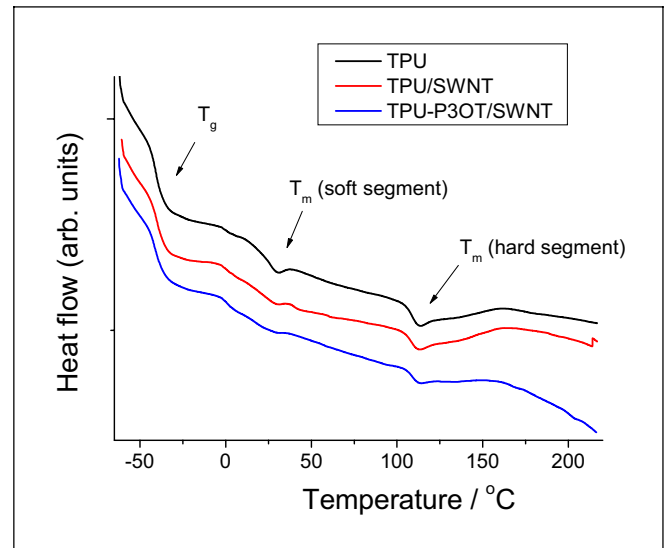


Figure 5. DSC curves for TPU, TPU/SWNT and TPU/P3OT/SWNT with 10 wt% of P3OT.

C. Conductivity Measurements

The films for conductivity measurements were prepared after the solutions were stocked for 1 month. Some black precipitate was observed on the flasks at this point. These precipitates were filtered off the solution before casting. Therefore, the conductivity films are composites with less than 1 wt% of SWNT. During the drying stage black spots were observed on the solutions when they become very concentrated. This led to the conclusion that conventional preparation by casting/dry is not keeping the dispersion of carbon nanotubes in the films as they were in solution. This problem has been discussed recently by Karachevtsev *et al.* [16]. The conductivity measurements performed are, therefore, related to films with less than 1 wt% of SWNT and further aggregation occurred during the drying procedure.

Impedance diagrams in Nyquist plot are shown in Figure 6. TPU and neutral P3OT are insulator polymers. Also, the TPU/SWNT film did not show a resistance lower than $10^8 \Omega$, which is the reasonable limit to measure with the available apparatus. The P3OT/SWNT film measurement exhibited part of a semi-circle in the Nyquist plot and allowed an evaluation of the resistance associated with the electronic transport. The conductivity for the P3OT/SWNT (less than 1 wt% SWNT) film is $2 \times 10^{-10} \text{ S/cm}$. This value is similar to the one obtained by Kymakis *et al* [10].

The composite prepared with the blended TPU-P3OT (10 wt% P3OT) and SWNT showed the best conductivity results (Figure 6). At room temperature a value of $1.4 \times 10^{-9} \text{ S/cm}$ was obtained. At 70°C this value increases to $2.6 \times 10^{-8} \text{ S/cm}$.

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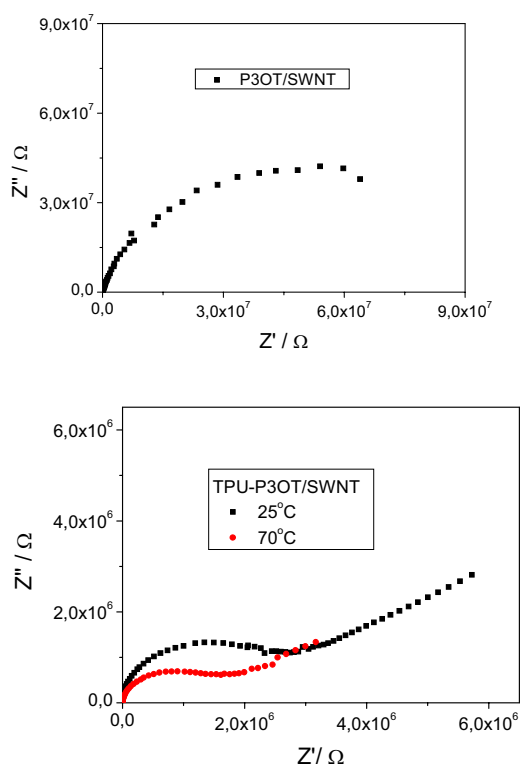


Figure 6. Nyquist plots for P3OT/SWNT and TPU-P3OT/SWNT

IV. CONCLUSION

The purification of SWNT allowed the preparation of stable dispersions of SWNT in P3OT, TPU and TPU/P3OT in chloroform. The DSC behavior of the casted nanocomposite coatings showed indications of interaction between SWNT and polymers producing changes in thermal transitions. TPU interaction with carbon nanotube may be mainly through the functions introduced in the selective oxidation and acid digestion. Functionalities such as C=O or C-O-H would be possible links to TPU through hydrogen interaction. On the other hand, P3OT may interact with the graphene structure of the tubes. Conductivity results show very low values for composites with less than 1 wt% of SWNT. The blend TPU-P3OT with SWNT allowed a slightly better conductivity to be achieved. This may indicate that the blend morphology prevents a high level of SWNT aggregation during the drying stage.