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Raman Spectroscopic Investigation of Acetylation of Raw Cotton

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Abstract

Raman spectroscopy has been used to investigate the acetylation of raw cotton using acetic anhydride/4-dimethylaminopyridine (DMAP) catalyst blend without solvent. The Raman data further confirm successful acetylation as shown by FTIR technique that was demonstrated previously to be highly sensitive for determining the level of acetylation. However, the Raman peaks are much weaker than the FTIR bands. Nevertheless, the variations of the extent of acetylation estimated from both Raman and FTIR spectra with weight percent gain due to acetylation (WPG) were observed to follow the same pattern. The degrees of acetylation calculated from Raman data were also found to increase linearly with that calculated from the more sensitive FTIR technique. The Raman technique is therefore suitable for further development as an analytical tool for determining the level of acetylation of natural cellulose fibres. Raman data have also shown that the crystallinity of cotton is reduced by the acetylation reaction.

Keywords: Acetylation, Cotton, Cellulose, Raman spectroscopy, Fourier transform infrared (FTIR) spectroscopy.

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1. Introduction

Recently, it was shown by Frisoni et al. (*1*) that natural cellulose fibres chemically modified by acetylation can find interesting applications as reinforcing agents in biodegradable polymer composites. This is because cellulose fibres are inexpensive, biodegradable and possess high mechanical properties. However, these fibres are highly hygroscopic and therefore absorb a large amount of moisture. The acetylation of the fibres was therefore used to improve the fibre-polymer matrix compatibility and the mechanical properties of the resulting composites. The acetylation reaction was used to reduce the very high polarity of the fibres. Thus, the acetylated fibres become more hydrophobic and consequently more compatible with most synthetic polymers. A review of the processing of thermoplastics reinforced with wood fillers that are subjected to various chemical modifications including acetylation was published recently (*2*)

Cotton contains mainly cellulose of high molecular weight ranging from 2.5 x 10^5 to 1 x 10^6 or more. The cellulose structure consists of long chains of α-D-glucose units joined by β-1,4-glycosidic links. The anhydroglucopyranose units that are in a chair conformation together with β-1,4-glycosidic links make cellulose to have a rigid structure unlike starch amylose that has α-glycosidic links between the 1,4-anhydroglucose units. Apart from cellulose, the major component of cotton (more than 95%), other constituents in cotton include lignin and hemicelluloses such as xylose or mannose.

We have previously used FTIR spectroscopy to investigate the acetylation of raw and commercial cotton (*3*). The level of acetylation was determined as the ratio between the intensity of the acetyl C=O stretching band at 1740-1745 cm^{-1} and the intensity of C-O stretching vibration of the cellulose backbone at about 1020-1040 cm^{-1}. The results of the FTIR investigation of raw cotton acetylation (*3*) indicate that the technique is highly sensitive and reliable for the determination of the level of acetylation. Raman spectroscopy has also been used to determine the structure cellulose in cotton (*4, 5*) and the level of acetylation in modified starches (*6, 7*). In particular, Raman spectroscopic technique has been found to allow faster determination of the degree of acetylation and is non-destructive and less susceptible to interference from residual impurities than the currently used traditional wet chemistry methods (*6, 7*). Raman spectroscopy has also been found to be a linear technique in which the intensity of the Raman peak is directly proportional to the amount of substance in the sample (*8, 9*). Raman scattering also has the advantage of being essentially unaffected by water because water is a weak Raman scatterer whereas water must be carefully removed for IR spectroscopic studies due to strong IR absorption by water. Raman scattering, being a low probability phenomenon, also makes it possible to study even very thick samples whereas IR scattering is readily absorbed by most materials such that only very thin polymeric samples can be investigated. In this paper, we report the use of Raman and infrared spectroscopic techniques for the investigation of the acetylation of raw cotton samples.

2. Materials and Methods

2.1 Materials and reagents

The raw cotton fibres used in this work were obtained from Wee-Waa, NSW (Sample AS) and Goodanwindi at the border of NSW and Queensland, Australia (BCS samples). Acetic anhydride and 4-dimethylaminopyridine (DMAP) were purchased from Asia Pacific Specialty Chemicals Ltd. and Aldrich Chemicals, respectively, and were used without further purification.

2.2 Acetylation of cotton

A mixture of 6-7 g of oven-dried raw cotton and an acetic anhydride/DMAP catalyst blend was heated at 140 ºC under reflux in a 500 ml round-bottom flask as atmospheric pressure. The reaction was conducted for 3-10 h. The amount of DMAP catalyst used was 5 or 10% of the amount of cotton by weight while the volume of acetic anhydride used was 50 ml g^{-1} cotton (i.e. the solid-to-liquid ratio was 1g:50 ml). The solid DMAP catalyst dissolved very readily in acetic anhydride at the concentrations studied. At the end of each acetylation reaction, the hot reagent was decanted off and the acetylated cotton product was thoroughly washed with ethanol and acetone to remove the unreacted acetic anhydride and the acetic acid product. The acetylated products were then dried in an oven at about 60-80 °C overnight and subsequently stored in a desiccator at room temperature. The weight percent gain

(WPG) due to acetylation was then calculated on the basis of oven-dried unreacted raw cotton fibres.

2.3 FTIR and Raman spectroscopic characterisation

The FTIR spectra were recorded on Nicolet Nexus 870 FTIR spectrophotometer equipped with a deuterated triglycine sulfate (DTGS) detector and a Diamond Attenuated Total Reflectance (ATR) Smart Accessory. 64 scans were collected for each measurement over the spectral range of 4000 - 525 cm^{-1} with a resolution of 4 cm^{-1}. All the FTIR spectra were recorded with a Omnic E.S.P. software on a PC computer connected to the spectrophotometer and then saved for further manipulation and processing.

Raman spectra were collected using an Olympus BHSM microscope equipped with 10x and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system which also includes a monochromator, a filter system and a charge-coupled device (CCD) detector. Raman spectra were excited by a Spectra-Physics Model 127 He-Ne laser operating at 633 nm with a resolution of 2 cm^{-1}. The spectra were recorded in the spectral range of 100-4000 cm^{-1}. Repeated acquisition using the highest magnification was accumulated to improve the signal-to-noise ratio. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer.

Further manipulation and processing of the FTIR and Raman spectroscopic spectra were done using GRAMS/32 (Galactic Industries Corporation, Salam, NH, USA), Microsoft EXCEL 2000 spreadsheet and PeakFit™ software packages.

3. Results and Discussion

3.1 FTIR spectra

As illustrated in Fig. 1, the IR bands at 1740-1745 (carbonyl C=O stretching of ester), 1368 [C-H in -O(C=O)-CH_3] and 1234 cm^{-1} (C-O stretching of acetyl group) provide evidence of acetylation. The lowering of the intensities of OH stretching band at 3337 cm^{-1} and OH in-plane bending mode at 1337, 1312 and 1203 cm^{-1} in the acetylated cotton spectra also provide further evidence of successful acetylation. No absorption was observed in the region 1840-1760 cm^{-1} in the spectra of all the acetylated cotton samples indicating that the acetylated products are free of unreacted acetic anhydride (*10*). The absence of a peak at 1700 cm^{-1} for a carboxylic group in the all the spectra of the acetylated samples also indicates that the acetylated products are free of the acetic acid by-product (*10*).

3.2 Raman Spectra

The Raman spectra of untreated and acetylated cotton samples in the range 180-3600 cm^{-1} are shown in Figs 2-5. All the major Raman bands observed in the spectra are listed in Table 1. The bands observed in the spectra reflect the presence of cellulose as the major chemical component of cotton. Vibrational band assignments shown in Table 1 have been provided according to the comprehensive molecular assignments for cotton proposed recently (*4, 11*). Some of the strongest bands associated with the untreated cotton include the peaks observed at 2895, 1477, 1378, 1334, 1153, 1121, 1094, 517, 457, 434 and 378 cm^{-1}. The strong band at 2895 is due to symmetric and asymmetric stretching vibrations of CH_2. The bands at 1477, 1378 and 1334 cm^{-1} are associated with CH_2 deformation vibrations. The 1334 cm^{-1} can also be due to OH deformation vibrations. The bands observed at 1153, 1121 and 1094 cm^{-1} are the stretching vibrations of the β-1,4-glycosidic ring linkages between the D-glucose units in cellulose. The 1153 cm^{-1} band is ascribed to C-C ring asymmetric stretching vibrations while the 1121 and 1094 cm^{-1} bands are due to C-O-C glycosidic link symmetric and asymmetric stretching modes, respectively. The bands at 457 and 434 are ascribed to C-C-O ring deformation modes while 517 and 378 peaks are due to C-O-C glycosidic link deformation and C-C-C ring deformation vibrations, respectively.

The most intense Raman peak that further confirms successful acetylation was observed at about 1735 cm^{-1} (Figs. 2, 3 and 5). This peak is ascribed to C=O stretching vibration of ester. Other weaker peaks that show evidence of acetylation are 1460 (CH_3 symmetric deformation), 835 (H_3C-C stretching) and 655 cm^{-1} (O-C=O in-plane deformation). However, all the Raman peaks including the 1735 cm^{-1} band that show evidence of acetylation are much weaker than the IR acetylation bands.

3.3 Extent of acetylation

The degree of acetylation was estimated from the infrared spectra by calculating the ratio R_1 between the intensity of the acetyl C=O stretching band of ester at 1740-1745

cm^{-1} and the intensity of C-O stretching vibration of the cellulose backbone at about 1020-1040 cm^{-1}, i.e. $R_1 = I_{1740}/I_{1020}$. The extent of acetylation was estimated too from the Raman spectra by calculating the ratios R_2 and R_3. R_2 and R_3 are the ratios between the intensity of the 1735 cm^{-1} peak and the intensity of COC β-glycosidic link asymmetric and symmetric stretching bands at about 1094 and 1121cm^{-1}, respectively, i.e. $R_2 = I_{1735}/I_{1094}$ and $R_3 = I_{1735}/I_{1121}$. The weight percent gain (WPG) due to acetylation was also used to determine the degree of acetylation. The WPG was found to be less that 5% for all the samples. The rather low intensities of the Raman acetylation peaks may therefore be due partly to the relatively small amount of acetylation.

Figs 6 and 7 demonstrate that the variation of R_1 (obtained from FTIR spectra) as well as R_2 and R_3 (from Raman data) with WPG follow the same pattern. The data plotted in Figs 6 and 7 are those for the untreated cotton and 3 cotton samples acetylated using 5% DMAP for 3, 4 and 10 hours. As mentioned earlier, we have previously demonstrated (*3*) that the FTIR technique is highly sensitive and reliable for the determination of the level of acetylation. Thus, it follows that the Raman data might also be sensitive enough for the measurement of the level of acetylation in spite of the weaker signal-to-noise ratio of the Raman acetylation peaks. Figs 6 and 7 also show that R_1, R_2 and R_3 show an initial increase with increase in WPG from 0 to 2.6, then a decrease on increasing the WPG to 3.3 followed by another increase beyond WPG of 3.3. This pattern for the variation of R_1, R_2 and R_3 with WPG may be attributed to a combination of acetylation and de-acetylation mechanisms occurring during the course of the reaction as proposed in our earlier investigations (*3, 12*). Acetylation of cellulose is an equilibrium reaction just like any other esterification reaction such that de-acetylation reaction can occur under appropriate reaction conditions (*13*). The increase in the R values with increase in WPG is due to acetylation while the decrease in these values with increase in WPG is attributed to de-acetylation mechanism. The WPG values of 0, 2.6, 3.3 and 4.9 correspond to the untreated cotton and the cotton samples acetylated for 3, 4 and 10 h, respectively. Thus, it is possible that the extent of acetylation far exceeded de-acetylation of the cotton samples beyond the 4 h reaction with a WPG of 3.3.

It is also demonstrated in Fig 8 that both R_2 and R_3 increase linearly with R_1. The equations $R_2 = 4.6146R_1-0.0108$ ($r^2 = 0.9772$) and $R_3 = 6.2025+0.0006$ ($r^2 = 0.9921$) are obtained from the linear graphs. This indicates that the Raman data correlate well with the data obtained from the more sensitive FTIR technique. This linear correlation observed between the degrees of acetylation measured by Raman spectroscopy and that obtained from the more sensitive FTIR data implies that the former technique is suitable for further development for application as analytical tool for the measurement of the degree of chemical modification of acetylated cotton.

3.3 Effect of acetylation on crystallinity of cotton cellulose

About 65-80% of cotton fibre is crystalline (*14, 15*). The physical and chemical properties of cotton cellulose are therefore influenced by its highly crystalline nature (*16*). Previous spectroscopic studies have also indicated that the bands at 1160, 1122 and 1096 cm^{-1} (observed in this work at 1153, 1121 and 1094 cm^{-1}, respectively) reflect the crystalline fraction of cotton-cellulose and could therefore be used to monitor changes in crystallinity (*4, 17, 18, 19*). Thus, the ratio $R_4 = I_{1094}/I_{1121}$ has been used to estimate the crystallinity of the untreated and acetylated cotton. The plot of the extent of acetylation R_2 and R_3 against R_4 is shown in Fig 9. It is demonstrated in Fig. 9 that R_4 decreases gradually with increase in the degree of acetylation. This indicates that the chemical modification of cotton by the acetylation reaction reduces the crystallinity of the cotton.

In conclusion, Raman together with FTIR spectroscopy has been used to investigate the acetylation of raw cotton samples. Such acetylated cotton samples can find potential applications as reinforcing agents in biodegradable polymer composites due to their hydrophobicity, cost-effectiveness, biodegradability and high mechanical properties. Both techniques indicate successful acetylation though the Raman technique is much less sensitive than FTIR spectroscopy.

In spite of the low signal-to-noise ratio of the Raman acetylation peaks due partly to the low level of acetylation as measured by the weight percent gain, the extent of acetylation estimated from both Raman and FTIR data was found to follow the same pattern with increase in WPG. The degrees of acetylation calculated from the Raman data were also found to follow a linear relationship with that calculated from the more sensitive FTIR technique. Thus, the Raman technique is suitable for further development for application as an analytical tool for the measurement of the degree of chemical modification of natural cellulose fibres. It has also been demonstrated that the crystallinity of cotton is reduced by chemically modifying it with acetylation reaction.

Acknowledgements

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Literature Cited

(1) Frisoni, G.; Baiardo, M.; Scandola, M.; Lednická, D.; Cnockaert, M. C.; Mergaert, J.; Swings, J. Natural cellulose fibers: Heterogeneous acetylation kinetics and biodegradation behaviour. *Biomacromolecules* **2001**, *2*, 476-482.

(2) Bledzki, A. K.; S.Reihmane; Gassan, J. Thermoplastics reinforced with wood fillers: A literature review. *Polym.-Plastics Technol. Eng.* **1998**, *37*, 451-468.

(3) Adebajo, M. O.; Frost, R. L. Acetylation of raw cotton for oil spill cleanup application:an FTIR and 13C MAS NMR spectroscopic investigation. *Spectrochim. Acta, Part A* **2004**, *60*, 2315-2321.

(4) Edwards, H. G. M.; Farwell, D. W.; Williams, A. C. FT-Raman spectrum of cotton: a polymeric bimolecular analysis. *Spectrochim. Acta, Part A* **1994**, *50*, 807-811.

(5) Liu, Y.; Kokot, S.; Sambi, T. J. Vibrational spectroscopic investigation of Australian cotton cellulose fibres - Part 1. A Fourier transform Raman study. *Analyst* **1998**, *123*, 633-636.

(6) Phillips, D. L.; Pan, D.-H.; Liu, H.-J.; Corke, H. Raman spectroscopic determination of the percent of acetylation in modified wheat starch. *Anal. Lett.* **1998**, *30*, 2105-2114.

(7) Phillips, D. L.; Liu, H.-J.; Pan, D.-H.; Corke, H. General application of Raman Spectroscopy for the determination of level of acetylation in modified starches. *Cereal Chem.* **1999**, *76*, 439-443.

(8) Hendra, P. J.; Jones, C. H.; Warnes, G. M. *Fourier Transform Raman Spectroscopy, Instrumentation and Chemical Applications*; Ellis Harwood: Chichester, England, 1991.

(9) Long, D. A. *Raman Spectroscopy*; McGraw-Hill: London, 1977.

(10) Sun, X.-F.; Sun, R.; Sun, J.-X. Acetylation of rice straw with or without catalysts and its characterization as a natural sorbent in oil spill cleanup. *J.Agric. Food Chem.* **2002**, *50*, 6428-6433.

(11) Edwards, H. G. M.; Ellis, E.; Farwell, D. W.; Janaway, R. C. Preliminary study of the application of Fourier Transform Raman spectroscopy to the analysis of degraded archaeological linen textiles. *J. Raman Spectrosc* **1996**, *27*, 663-669.

(12) Adebajo, M. O.; Frost, R. L. Infrared and 13C MAS nuclear magnetic resonance spectroscopic study of acetylation of cotton. *Spectrochim. Acta, Part A,* **2004**, *60*, 449-453.

(13) Klemm, D.; Philipp, B.; Heinze, T.; Heinze, U.; Wagenknecht, W. *Comprehensive Cellulose Chemistry - Functionalization of Cellulose*; Wiley-VCH: Weinheim, 1998.

(14) Gohl, E. P. *Textile Science*, 2nd ed.; Longman Cheshire: Melbourne, 1983.

(15) Ghosh, S. In *Making Light Work: Advances in Near Infrared Spectroscopy*; I. Murray and I. A. Cowe, Eds.; Ian Michael Pubs: UK, 1992.

(16) Cook, J. G. *Handbook of Textile Fibres: Natural Fibres*; Merrow: Durham, UK, 1984.

(17) *Instrumental Analysis of Cotton Cellulose and Modified Cotton Cellulose*; O'Connor, R., Ed.; Marcel Dekker: New York, 1972.

(18) Blackwell, J.; Vasko, P. D.; Koenig, J. L. Infrared and Raman spectra of the cellulose from the cell wall of *Valonia ventricosa*. *J. Appl. Phys.* **1970**, *40*, 4375-4379.

(19) Wiley, J. H.; Atalla, R. H. Band assignments in the Raman spectra of celluloses. *Carbohydr Res.* **1987**, *160*, 113-129.

Table 1. Assignments for vibrational Raman bands for acetylated raw cotton (*4, 11*)

Wavenumbers (cm^{-1})	Assignment
3339 w	ν(OH) free
3289 w, br	ν(OH), COH, hydrogen-bonded
2966 mw, sh	ν(CH_2)
2962 mw, sh	ν(CH_2)
2928 m, sh	ν(CH_2)
2895 s	ν(CH_2) symmetric and asymmetric
2869 m, sh	ν(CH_2)
2738 w	ν(CH) methine
2718 w	ν(CH) methine
1735 w	ν(C=O) carbonyl stretching of ester (evidence of acetylation)
1477 m, br	δ(CH_2) scissors
1468 mw, sh	δ(CH_2); δ(COH), primary alcohol
1462 mw, sh	δ(COH) 1° and 2° alcohol groups
1460 vw, sh	δ(CH_3) symmetric deformation (evidence of acetylation)
1409 w	δ(CH_2)
1378 ms	δ(CH_2)
1334 m	δ(CH_2) wagging; δ(OH)
1293 m	δ(CH_2) twisting
1278 vw	δ(CH_2) twisting
1241 vw	δ(COH) out-of-plane
1201 w	δ(COH); δ(CCH)
1153 m	ν(CC) ring breathing, asymmetric stretching
1121 ms	ν(COC) glycosidic link, symmetric; ν(COC) ring breathing
1094 s	ν(COC) glycosidic link, asymmetric stretching
1071 vw	ν(CO)
1057 w	ν(CO) 2° alcohol
1036 w	ν(CO) 1° alcohol
999 mw	ρ(CH_2)
969 mw	ρ(CH_2)
901 m, br	ν(COC) in-plane, symmetric
835 vw	ν(H_3C-C) stretching (evidence of acetylation)
654 vw	δ(O-C=O) in-plane deformation (evidence of acetylation)
607 vw	δ(CCH) twisting
565 w	δ(COC) glycosidic link, in-plane
517 m	δ (COC) glycosidic link
491 w	δ (COC) glycosidic link
457 m	δ (CCO) ring deformation
434 m	δ (CCO) ring deformation
378 ms	δ (CCC) ring deformation
348 mw	δ (CCC) ring deformation
329 w	δ (CCC) ring deformation
304 vw	
253 vw	τ(COH)
171 mw	τ(COH)

Figure Captions

Figure 1. FTIR spectra of (1) untreated BCS raw cotton and (2) BCS raw cotton acetylated at 140 ºC for 3 h in the presence of 5% DMAP catalyst.

Figure 2. Raman spectra in the region 180-3200 cm^{-1} of (1) untreated BCS raw cotton and raw cotton acetylated for (2) 3 h using 5% DMAP (BCS cotton), (3) 4 h using 10% DMAP (AS cotton) and (4) 10h using 5% DMAP (BCS cotton). The level of acetylation decreases in the order 4>3>2.

Figure 3. Raman spectra in the region 180-1780 $cm^{-}1$ of. the same untreated raw cotton (spectrum 1) and acetylated raw cotton samples (spectra 2,3 & 4) as in Figure 2.

Figure 4. Raman spectra in the region 2600-3600 cm^{-1} of the same untreated raw cotton (spectrum 1) and acetylated raw cotton samples (spectra 2,3 & 4) as in Figure 2.

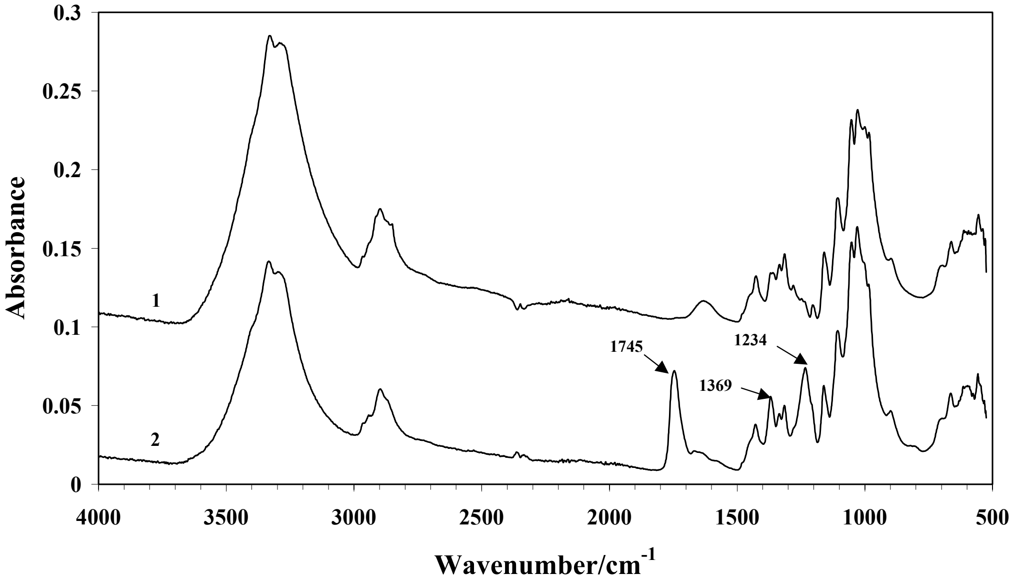
Figure 5. Raman spectra in the region 1650-1850 cm^{-1} of the same untreated raw cotton (spectrum 1) and acetylated raw cotton samples (spectra 3 & 4) as in Figure 2.

Figure 6. Plot of the degrees of acetylation R_1 (from FTIR spectra; $R_1 = I_{1740}/I_{1020}$) and R_2 (from Raman spectra; $R_2 = I_{1735}/I_{1094}$) against WPG for untreated cotton and 3 cotton samples acetylated using 5% DMAP for 3, 4 and 10 hours.

Figure 7. Plot of the degrees of acetylation R_1 (from FTIR spectra; $R_1 = I_{1740}/I_{1020}$) and R_3 (from Raman spectra; $R_3 = I_{1735}/I_{1121}$) against WPG for untreated cotton and the same 3 acetylated cotton samples as in Fig 5.

Figure 8. Plot of the degrees of acetylation R_2 and R_3 obtained from Raman data ($R_2 = I_{1735}/I_{1094}$ and $R_3 = I_{1735}/I_{1121}$) against the extent of acetylation R_1 obtained from the FTIR data.

Figure 9. Plot of the degrees of acetylation R_2 and R_3 obtained from Raman data ($R_2 = I_{1735}/I_{1094}$ and $R_3 = I_{1735}/I_{1121}$) against Raman peak intensity ratio R_4 ($R_4 = I_{1094}/I_{1121}$).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0.15
0.1
0.05
0
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1369
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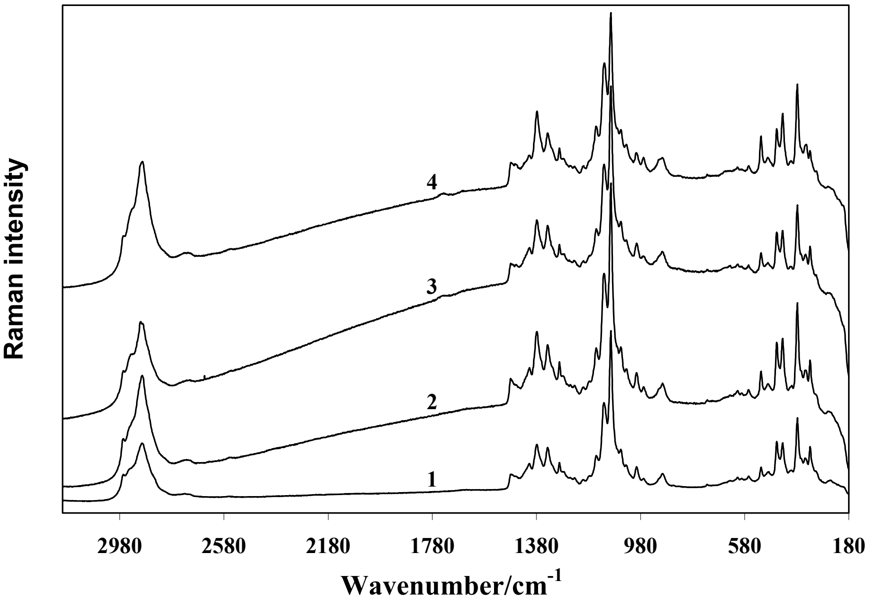
3500
3000
2500
2000
1500
1000
500
Wavenumber/cm^{-1}

Figure 1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1
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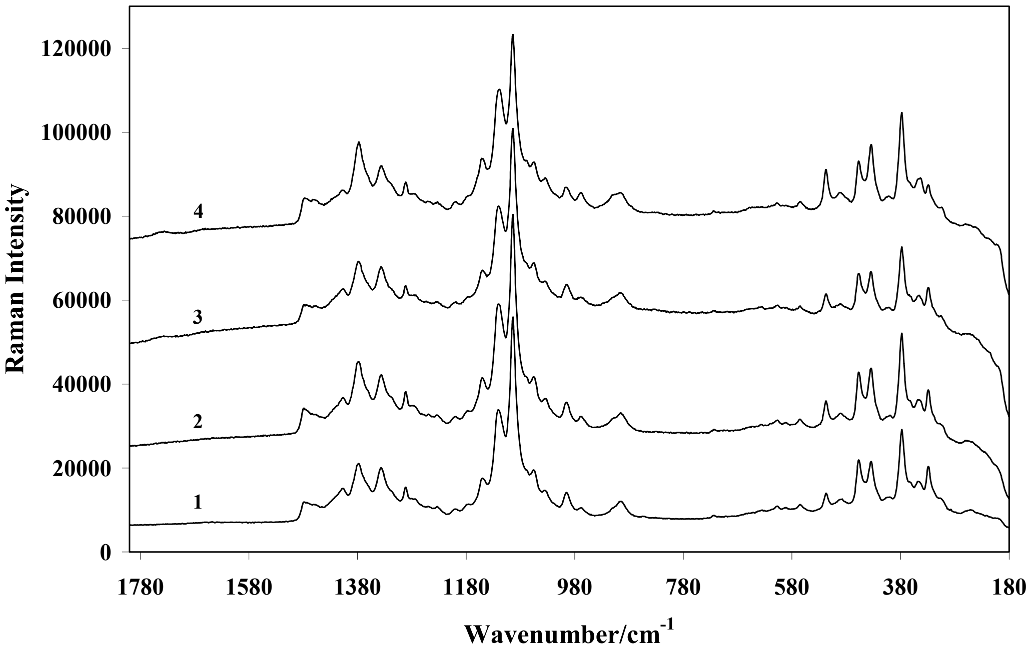
1380
980
580
180
Wavenumber/cm-1

Figure 2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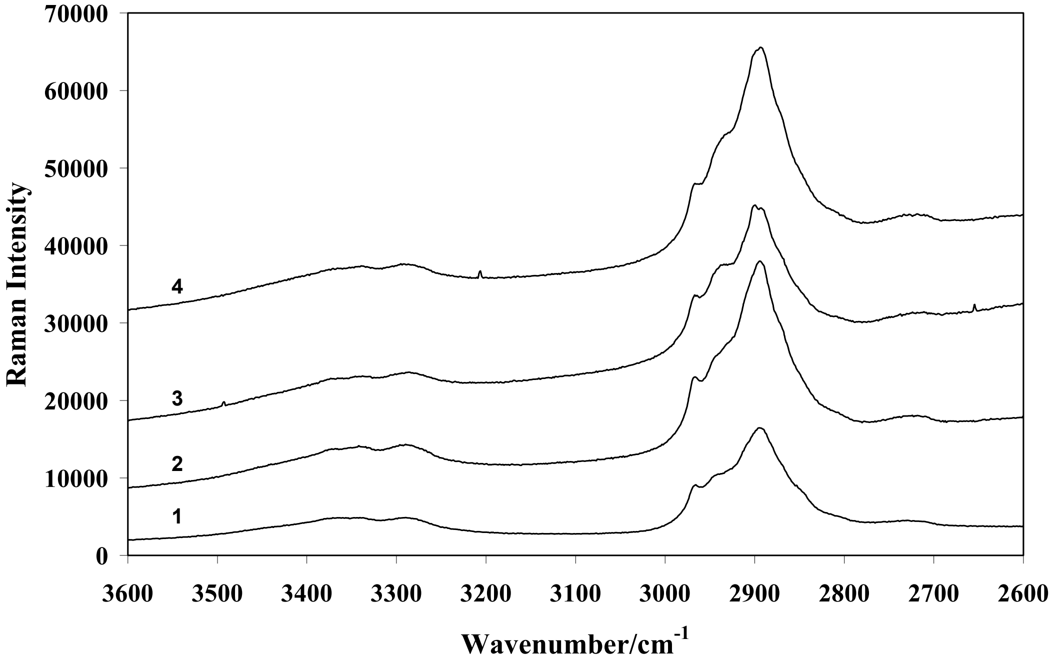
Wavenumber/cm-1

Figure 3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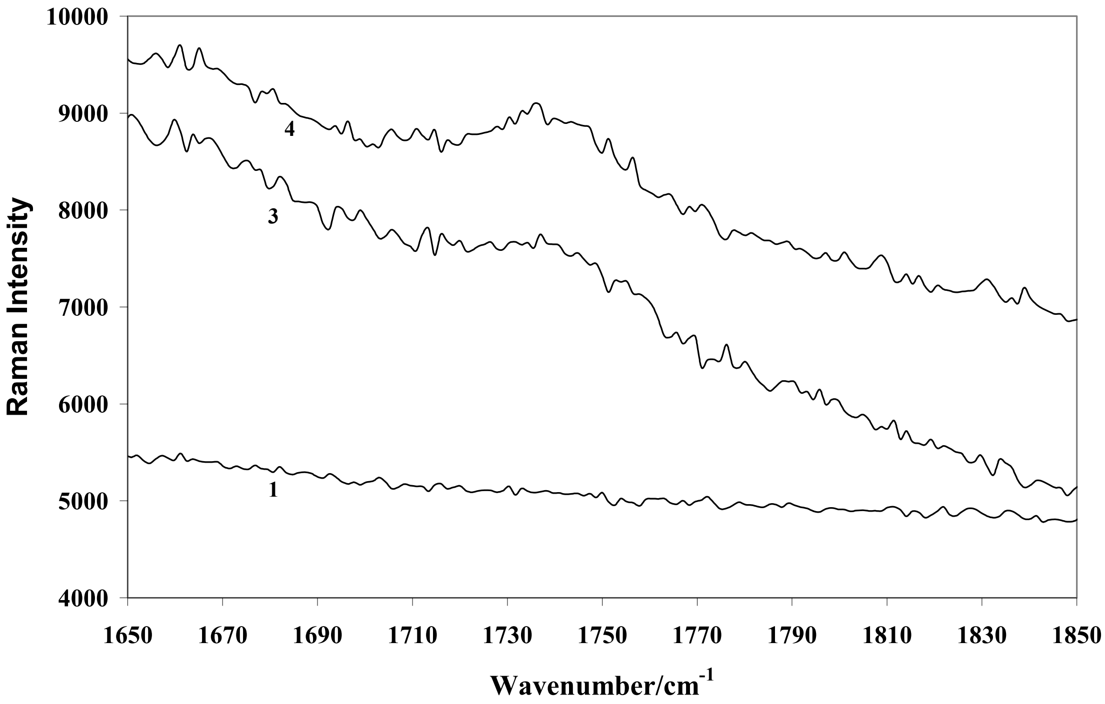
Wavenumber/cm-1

Figure 4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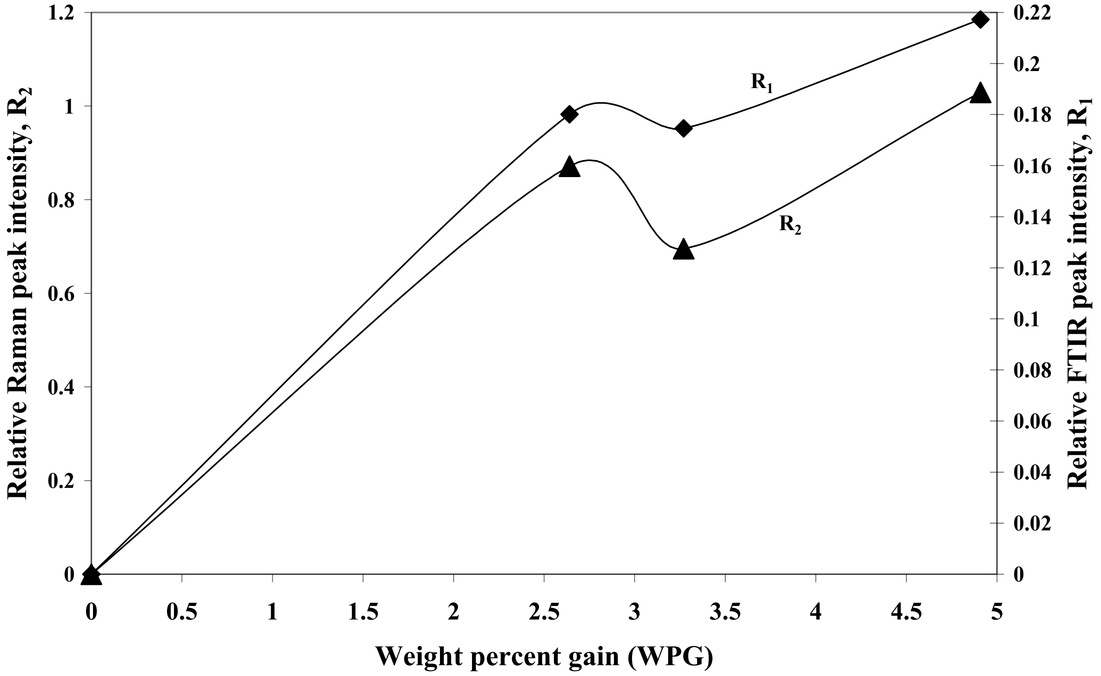
1830
1850
Wavenumber/cm-1
4
3
1

Figure 5


Relative Raman peak intensity, R_2
Relative FTIR peak intensity, R_1
Weight percent gain (WPG)
R_1
R_2
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1
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0.6
0.4
0.2
0
0.22
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
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2
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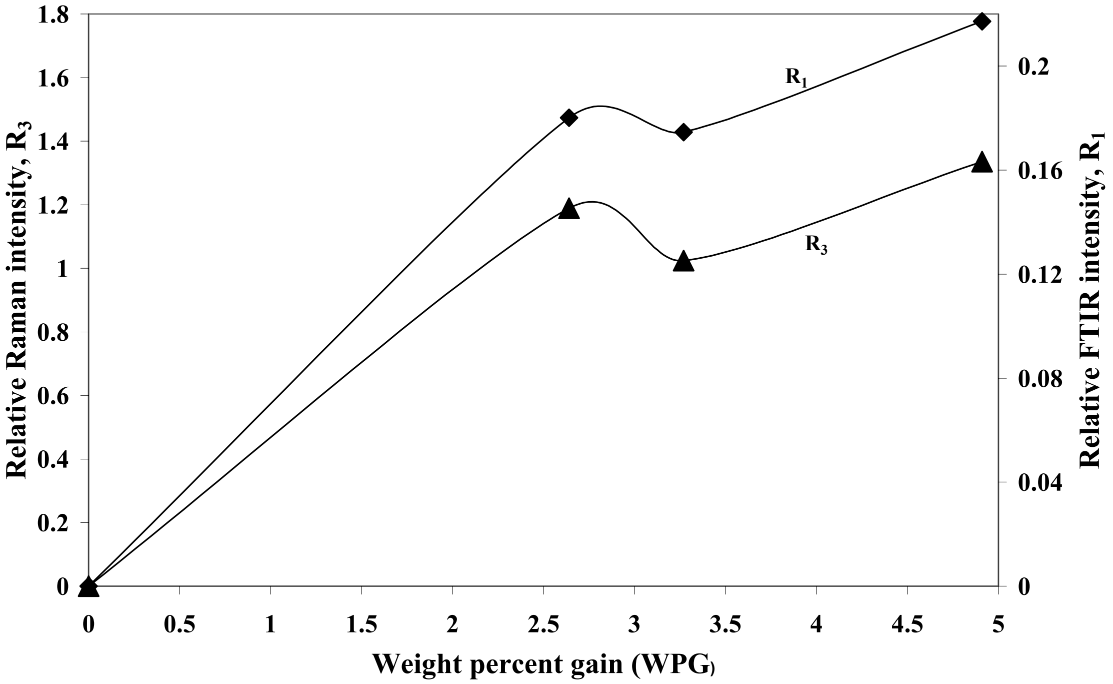
3
3.5
4
4.5
5

Figure 6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1.2
1
0.8
0.6
0.4
0.2
0
Relative FTIR intensity, R_1
0.2
0.16
0.12
0.08
0.04
0
R_1
R_3
0
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1
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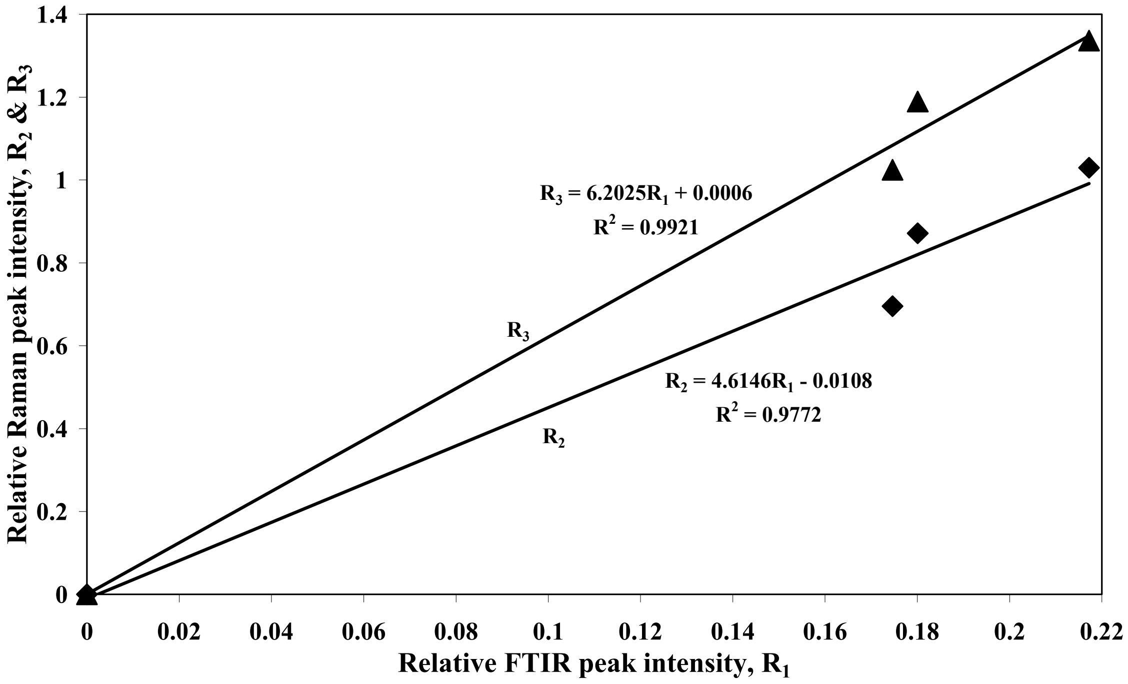
2
2.5
3
3.5
4
4.5
5
Weight percent gain (WPG)

Figure 7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0.12
0.14
0.16
0.18
0.2
0.22
Relative Raman peak intensity, R_2 & R_3
Relative FTIR peak intensity, R_1
$R_3 = 6.2025R_1 + 0.0006$
$R^2 = 0.9921$
R_3
$R_2 = 4.6146R_1 - 0.0108$
$R^2 = 0.9772$
R_2

Figure 8

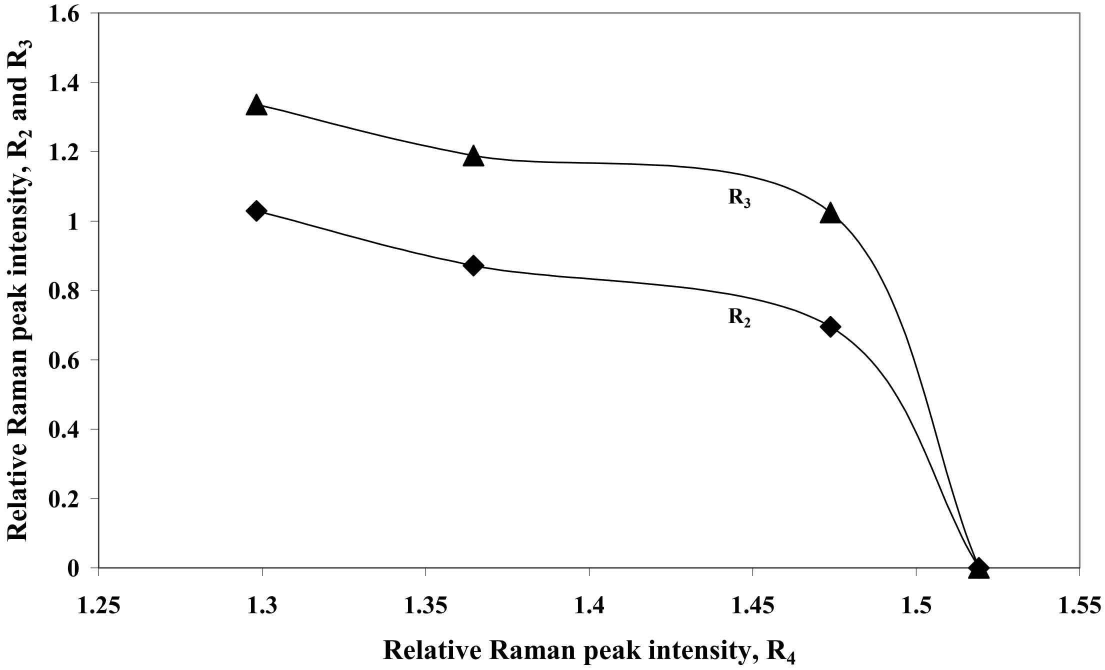
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Relative Raman peak intensity, R_2 and R_3
R_3
R_2
1.25
1.3
1.35
1.4
1.45
1.5
1.55
Relative Raman peak intensity, R_4

Figure 9