Acetylation of Raw Cotton for Oil Spill Cleanup Application - An FTIR and ^{13}C MAS NMR Spectroscopic Investigation

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Abstract

Fourier transform infrared (FTIR) and ^{13}C MAS NMR spectroscopy have been used to investigate the acetylation of raw cotton samples with acetic anhydride without solvents in the presence of different amounts of 4-dimethylaminopyridine (DMAP) catalyst. This is a continuation of our previous investigation of acetylation of commercial cotton in an effort to develop hydrophobic, biodegradable, cellulosic sorbent materials for cleaning up oil spills. The FTIR data have again provided a clear evidence for successful acetylation. The NMR results further confirm the successful acetylation. The extent of acetylation was quantitatively determined using the weight percent gain (WPG) due to acetylation and by calculating the ratio R 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 FTIR technique was found to be highly sensitive and reliable for the determination of the extent of acetylation. The level of acetylation of the raw cotton samples was found to be much higher than that of cotton fabrics and the previously studied commercial cotton. The variation of the R and WPG with reaction time, amount of DMAP catalyst and different samples of raw cotton is discussed.

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1. Introduction

Natural sorbents and a wide variety of natural organic products such as rice straw, corn corb, peat moss, wood, cotton, milkweed floss, kapok, kenaf and wool fibres are presently attracting attention for development as sorbents for oil spill cleanup applications [1-5]. This is due to their relatively high sorption capacity, biodegradability and cost-effectiveness in comparison to the synthetic polymeric fibres that are normally used.

Recently, Sun et al. [6] demonstrated that acetylation of free hydroxyl groups in rice straw with acetic anhydride without solvents provided a suitable and effective method for the preparation of rice straw acetates that have a more hydrophobic characteristic and high oil sorption capacity. The acetylation was performed at different reaction times and temperatures in the presence or absence of catalysts. Among the catalysts used, 4-dimethylaminopyridine (DMAP) was found to be the most effective. Fourier transform infrared (FTIR) and solid state carbon-13 nuclear magnetic resonance (^{13}C NMR) spectroscopy were used to investigate the acetylation reaction. Frisoni et al. [7] have also recently investigated the heterogeneous acetylation kinetics and biodegradation behaviour of natural cellulose fibres from flax (*Linum usitassimum*) for applications as polymer composite reinforcements. Natural vegetable products like acetylated rice straws have the added advantage of low cost. Hence, the acetylation of biodegradable lignocellulosic materials such as cotton, sugar cane, paper, wood etc. may prove economical, technically feasible and environmentally acceptable for applications in oil spill cleanup operations. Thus, we have, more recently, used FTIR and ^{13}C NMR spectroscopy to conduct a preliminary investigation of the acetylation of commercial cotton in the presence of DMAP catalyst [8]. The FTIR results provided clear evidence for successful acetylation though the NMR results indicate that the level of acetylation was low. Since the cotton samples used were commercial samples purchased from the market, it was suggested that the acetylation reaction could have been hindered by some kind of chemical treatment to which the cotton samples might have been subjected. In this work, we have therefore conducted further investigation of the acetylation reaction on raw cotton fibres instead of the

commercial samples. Some cotton fabric samples were also used. FTIR and ^{13}C NMR were again used to follow the acetylation reaction. Our previous investigation [8] also indicated that de-acetylation, the reverse of the equilibrium acetylation reaction, occurred when the acetylation reaction was prolonged beyond 3 hours. This behaviour is investigated further in the present work. We have also investigated the effect of amount of catalyst and the ml acetic anhydride (the acetylating reagent)/g cotton ratio on the acetylation reaction.

2. Experimental

2.1 Materials and reagents

The raw cotton fibres used in this work were obtained from Wee-Waa, NSW (Agricsolutions Australia samples) and Goodanwindi at the border of NSW and Queensland, Australia (Bayer CropScience Laboratory samples). Some cotton fabrics were also employed. Acetic anhydride and DMAP were purchased from Asia Pacific Specialty Chemicals Ltd. and Aldrich Chemicals, respectively, and were used without further purification.

2.2 Acetylation reaction

A mixture of about 6-7 g of oven-dried raw cotton and an acetic anhydride/DMAP catalyst blend was heated at 140 °C under reflux in a 500 ml round-bottom flask at atmospheric pressure. The reaction was conducted for 1 - 10 hours. The amounts of catalyst used were 2, 3.5, 5, 8 and 10 % of the amount of cotton by weight while the volume of acetic anhydride was varied between 25 and 50 ml/g cotton (i.e. the solid-to-liquid ratio was between 1g/25 ml and 1g/50 ml). The solid DMAP catalyst dissolved very readily in acetic anhydride at the concentration 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 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 using GRAMS/32 (Galactic Industries Corporation, Salam, NH, USA), Microsoft EXCEL 2000 spreadsheet and PeakFit™ software packages. ^{13}C solid state NMR spectra of the cotton samples were recorded at the University of Queensland Centre for Magnetic Resonance, Brisbane, Australia on a Bruker MSL-300 NMR spectrometer operating at a magnetic field strength of 7.2 T.

3. Results and Discussion

3.1 FTIR Investigation

3.1.1 FTIR spectra

As illustrated in Fig 1 for Bayer CropScience (BCS) samples, the FTIR spectra of all the raw cotton and cotton fabric samples again show evidence of acetylation with three ester bands appearing and/or enhanced at 1740-1745 (carbonyl C=O stretching of ester), 1369 [C-H in -O(C=O)-CH_3] and 1234 cm^{-1} (C-O stretching of acetyl group. The lowering of intensities of OH stretching band at 3337 cm^{-1} and OH in-plane bending bands at 1337, 1310 and 1200 cm^{-1} in the spectra of the acetylated cotton samples also provides 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 unreated acetic anhydride [6]. 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 [6]. The Bayer CropScience (BCS) and Agricsolutions raw cotton samples were found to exhibit much more pronounced acetylation peaks in the FTIR spectra than the commercial cotton and cotton fabric samples as illustrated in Fig. 2.

This indicates that the raw cotton samples were more successfully acetylated than the commercial cotton and cotton fabrics. As already mentioned, the commercial cotton and cotton fabrics might have been subjected to some chemical treatment that is capable of hindering the acetylation reaction.

3.1.2 Extent of Acetylation

In order to confirm the higher level of acetylation of the raw cotton samples, the extent of acetylation for all the samples was quantitatively determined by calculating the ratio R between the intensity of the acetyl C=O stretching 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}. The extent of acetylation was also estimated by the weight per percent gain (WPG). The values of R and WPG are then compared. Fig. 3 further confirms the much higher level of acetylation of the two different samples of raw cotton compared with cotton fabrics and commercial cotton beyond 1 h reaction with or without DMAP catalyst. Fig. 3 also shows that the extent of acetylation for all samples is generally much lower in the absence of DMAP catalyst.

The variation of R with reaction time for both the raw cotton and cotton fabrics follows the same pattern with R reaching a maximum at 3 h and then increasing again beyond 4 h (Figs. 3 and 4). After 3 h, the level of acetylation decreased probably due to de-acetylation mechanism as proposed in our previous article on acetylation of commercial cotton [8]. Thus, it is possible that the extent of acetylation far exceeded de-acetylation of the cotton samples beyond 4 h reaction.

Figs. 4 and 5 demonstrate that the variations of both WPG and R with reaction time and amount of DMAP catalyst follow the same pattern. This shows that the FTIR data are very sensitive to the determination of the extent of acetylation reaction, thus indicating the reliability of the FTIR technique for the determination.

Within the range of catalyst amounts studied, both WPG and R reach a maximum in the presence of 5% catalyst when the reaction was carried out for 3 h (Fig. 5). This behaviour may again be attributed to a combination of acetylation and de-acetylation mechanisms. It appears that the problem of de-acetylation may also be overcome by increasing the amount of catalyst beyond 8% (Fig. 5). This is further illustrated by the observation in Fig. 3 that the level of acetylation increased more sharply in the

presence of 10% catalyst as the reaction is raised from 2 to 4 h than in the presence of 5% catalyst for both BCS and Agricsolutions raw cotton samples. However, the amount of catalyst would have to be increased to a reasonable level in order not to jeopardize the cost effectiveness of the acetylation procedure.

In addition to the effect of acetylation and de-acetylation mechanisms, the complications in the variations of the level of acetylation with reaction time and amount of catalyst may also be due to the complex nature of a substrate like cotton. Apart from cellulose which is the major component of cotton fibres (more than 95%), other constituents in cotton include lignin and hemicelluloses such as xylose or mannose. Phenolic, benzylic or alcoholic (primary and secondary) hydroxyl groups are present in the lignin region while only the alcoholic hydroxyl groups are found in the carbohydrate. Phenolic hydroxyl groups are attached to aromatic ring containing various substituents [9]. The different types of hydroxyl groups will therefore undergo different reactivity with acetic anhydride. For example, in their study of the acetyl distribution in acetylated whole wood and reactivity of isolated wood cell wall components to acetic anhydride, Rowell et al. [10] observed the order of reactivity to be lignin > hemicelluloses >> holocellulose (the remaining product after removal of lignin from wood). Cellulose was observed not to react with acetic anhydride in the absence of a catalyst. It has also been previously reported by various workers [9, 11] that the initial step in the mechanism for the reaction of acetic anhydride with a hydroxyl group involves a nucleophilic attack on the acyl carbon centre of the acetic anhydride molecule by a lone pair of the alcoholic (or phenolic) hydroxyl group followed by subsequent loss of acetic acid to generate the ester. The rate of diffusion of acetic anhydride into the cell wall can also limit the rate of reaction for whole cotton. It is possible too that the use of DMAP catalyst increases the rate of reaction by enhancing the electrophilic character of the acyl carbon centre through formation of a substituted pyridinium salt intermediate that has a positively charged pyridinium nitrogen adjacent to the acyl carbon centre [9].

It is shown in Fig. 6 that R, the extent of acetylation reaches a maximum at 35 ml acetic anhydride/g cotton. Frisoni et al. [7] recently reported that a linear relationship was observed between R and the degree of substitution (DS) for acetylated cellulose fibres with $R \leq 0.40$. This linear relationship was found to be $DS = 0.7\ R$. The plot of

DS calculated using this linear relationship against the volume of acetic anhydride/g cotton is included in Fig. 6.

The extent of acetylation, R, of the Agricsolutions raw cotton samples was found to be slightly higher than that of the BCS samples especially in the presence of higher amounts of DMAP catalyst (Figs. 3 and 7). However, in the absence of the catalyst, the BCS sample was acetylated to a greater extent. The observed differences which are found to be within 5 - 16 % are significant considering the fact the values of R was reproducible to within 0.6% when the acetylation reaction was repeated twice (Fig. 6). These differences in the extent of acetylation of both samples may be attributed to a combination of variations in the particle sizes of the cotton fibres and in the composition of their main constituents (lignin, hemicelluloses or holocellulose) as mentioned earlier.

3.2 Solid state MAS ^{13}C NMR spectra

The successful acetylation of raw cotton samples was further confirmed by MAS ^{13}C NMR spectra shown in Figure 8. This is evident since spectra 2 and 3 of Agricsolutions raw cotton samples acetylated for 4 h in the presence of 5 and 10% DMAP, respectively shows the presence of methyl band of acetyl group (OCH_3) at about 20.7 ppm as observed previously for commercial cotton [8]. This band is more pronounced in the spectra 2 ad 3 shown in Fig 8 than in the spectrum of the acetylated commercial cotton reported recently [8]. In addition, the carboxylic group band at about 171 ppm was also observed. It should be recalled that this 171 ppm band was not detectable in our previous report [8] on commercial cotton due to the very low intensity of the 21 ppm OCH_3 band observed. It therefore follows that the level of acetylation obtained in this work for raw cotton fibres is much higher than that of commercial cotton as revealed by the FTIR data presented in the previous section. The intensities of the 21 and 171 ppm peaks are, nevertheless, still low indicating a relatively small amount of acetylation. This is in agreement with the WPG values that were calculated to be less than 6% for the various acetylated BCS raw cotton samples (Figs. 4 & 5).

Fig. 8 also shows that the spectra of both the untreated raw and acetylated raw cotton samples are very similar in the carbohydrate region as observed recently for

commercial cotton [8]. It is shown in Fig. 8 that the same peaks observed in our earlier report on commercial cotton are obtained in this region. However, Fig. 8 shows two extra peaks, one at 72 ppm and the other appearing as a shoulder band at 65 ppm. The 72 ppm peak is attributed to C-2, C-3 and C-5 of 4-linked polysaccharides while the 65 ppm shoulder band is assigned to C-6 of crystal-interior cellulose [12]. The 89 ppm band assigned to C-4 of crystal-interior cellulose is also much more pronounced in the spectra of Fig. 8 than what was obtained earlier for commercial cotton. Thus, the commercial cotton used previously is more amorphous than the raw cotton used in the present investigation. The small 97.9 ppm band (C-1 of xylan) observed previously for commercial cotton is also missing in Fig. 8, indicating a much lower amount of xylan in the raw cotton samples. The complete resonance assignments of the peaks are shown in Table 1.

Fig. 8 also shows that there is no significant difference in the lignin pattern in the spectra of the acetylated cotton and the spectrum of the untreated sample. This is in contrast to the significant weakening of the same pattern reported in our previous paper [8] in the spectrum of acetylated commercial cotton or the unusual strengthening reported by Sun et al. [6] in the spectrum of acetylated rice straw compared with the respective spectra of the unmodified materials. An observation similar to that of Sun et al. has also been previously reported by Boonstra et al. in their investigation of the chemical modification of Norway spruce and Scotch pine. In their study, they stated that the increased spacing due to the bulking action of the chemical and the slight carbohydrate cleavage by the treatment could create a more open structure of the network, thus leading to a more noticeable NMR signals pattern of lignin compared to the spectrum of the unmodified wood. There is therefore need to further investigate this effect and particularly to resolve the lack of agreement between the previous reported studies and the present investigation of raw cotton acetylation.

Conclusion

In conclusion, it is evident that the raw cotton samples used in this work were successfully acetylated by reaction with acetic anhydride in the presence of DMAP catalyst as indicated by both FTIR and NMR data. The level of acetylation for the two different samples of raw cotton (BCS and Agricsolutions) was observed to be much

higher than that of commercial cotton and cotton fabrics beyond 1 h with or without DMAP catalyst. The extent of acetylation for all samples is generally much lower in the absence of DMAP catalyst. The variation of WPG and R, the extent of acetylation, with reaction time and amount of catalyst was found to follow the same pattern, indicating the reliability and sensitivity of the of the FTIR technique for the determination of the level of acetylation reaction. Below 4 h reaction time and using less than 8% DMAP, the extent of acetylation goes up and down reaching a maximum at 3 h and 5% DMAP. This is attributed to a combination of acetylation and de-acetylation mechanisms and the complexity of the cotton substrate. It appears that the problem of de-acetylation may be overcome by carrying out the reaction for relatively long period of time using catalyst amounts higher than 8%.

It is therefore very clear that raw cotton fibres are potential candidates suitable for further development via acetylation into hydrophobic sorbent materials for subsequent application in cleaning up oil spills.

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Figure Captions

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

Figure 2. FTIR spectra of acetylated (1) BCS raw cotton, (2) commercial cotton fibres and (3) cotton fabric samples prepared in the presence of 5% DMAP at 140 °C for 3 h.

Figure 3. Plot of extent of acetylation against reaction time for various cotton samples prepared at 140 °C.

Figure 4. Plot of WPG and R against reaction time for acetylation of BCS raw cotton in the presence of 5% DMAP catalyst at 140 °C.

Figure 5. Plot of WPG and R against amount of DMAP catalyst for acetylation of BCS raw cotton for 3 h at 140 °C.

Figure 6. Plot of WPG and DS against volume of acetic anhydride/g cotton for acetylation of BCS raw cotton for 4 h at 140 °C in the presence of 5% DMAP catalyst.

Figure 7. Plot of WPG and R against amount of DMAP catalyst for acetylation of raw cotton samples for 4 h at 140 °C.

Figure 8. ^{13}C MAS NMR spectra of untreated Agricsolutions raw cotton (spectrum 1) and the acetylated samples prepared at 140 °C for 4 h in the presence of 5% (spectrum 2) and 10% (spectrum 3) DMAP catalyst.

Table 1. Assignments for ^{13}NMR signal shifts of Agricsolutions raw cotton [6, 12]

Chemical shift (ppm)	Assignment
171	Carboxylic group of acetyl
104.5	C-1 of cellulose
88.6	C-4 of crystal-interior cellulose
83.4	C-4 of amorphous cellulose
72, 74.7	C-2, C-3 and C-5 of 4-linked polysaccharides
65	C-6 of crystal-interior cellulose
62	C-6 of crystal-surface cellulose and C-5 of xylan
20.7	Methyl band of acetyl group

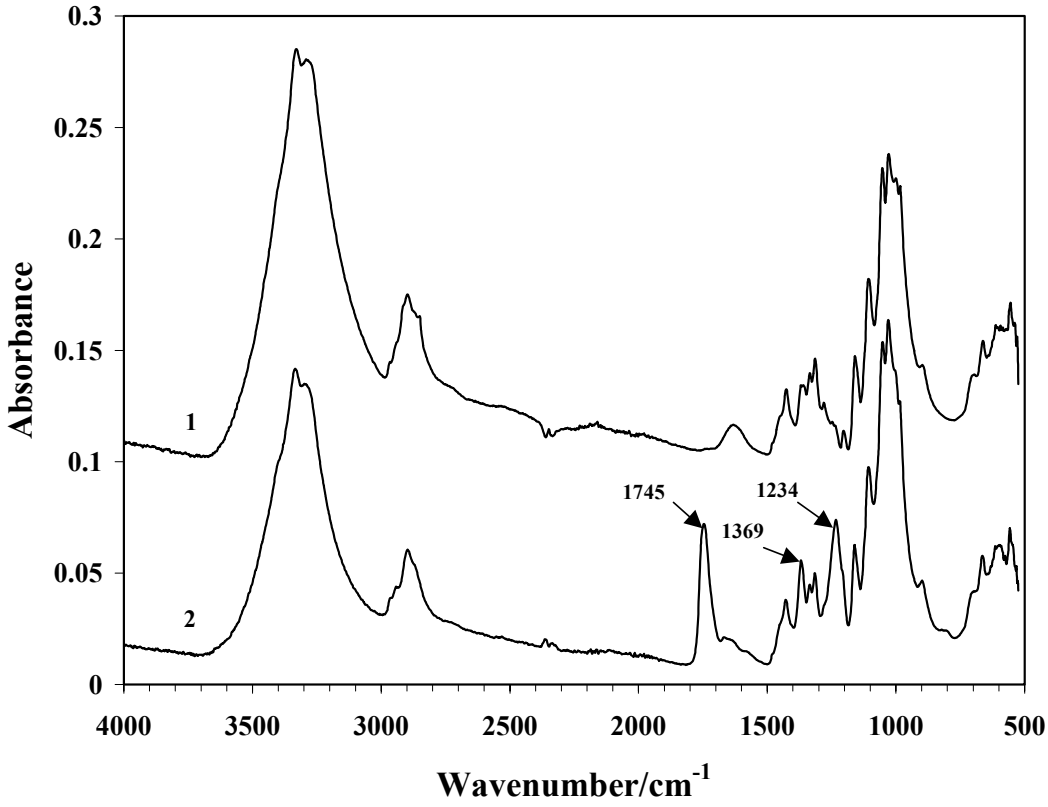
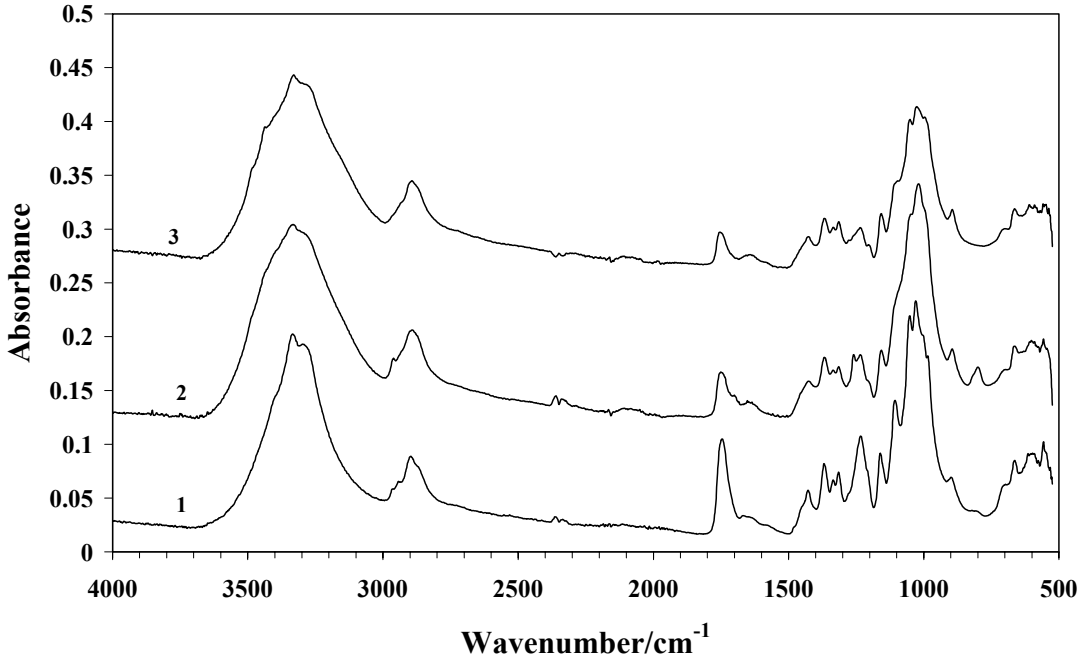


Figure 1. Adebajo and Frost.



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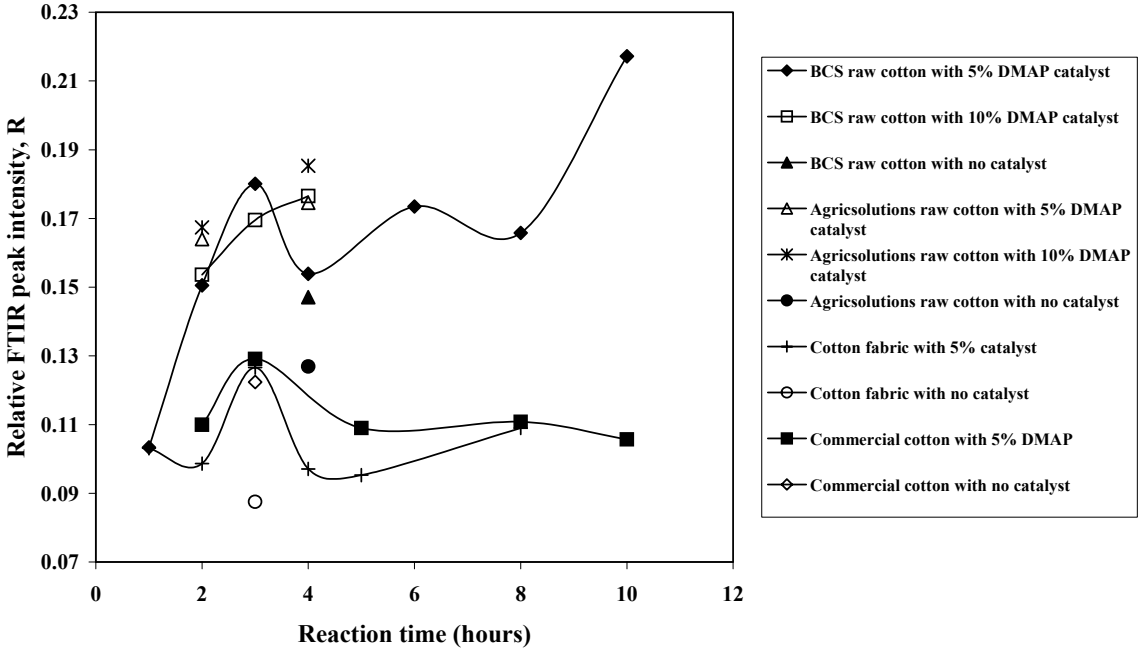


Figure 3. Adebajo & Frost.

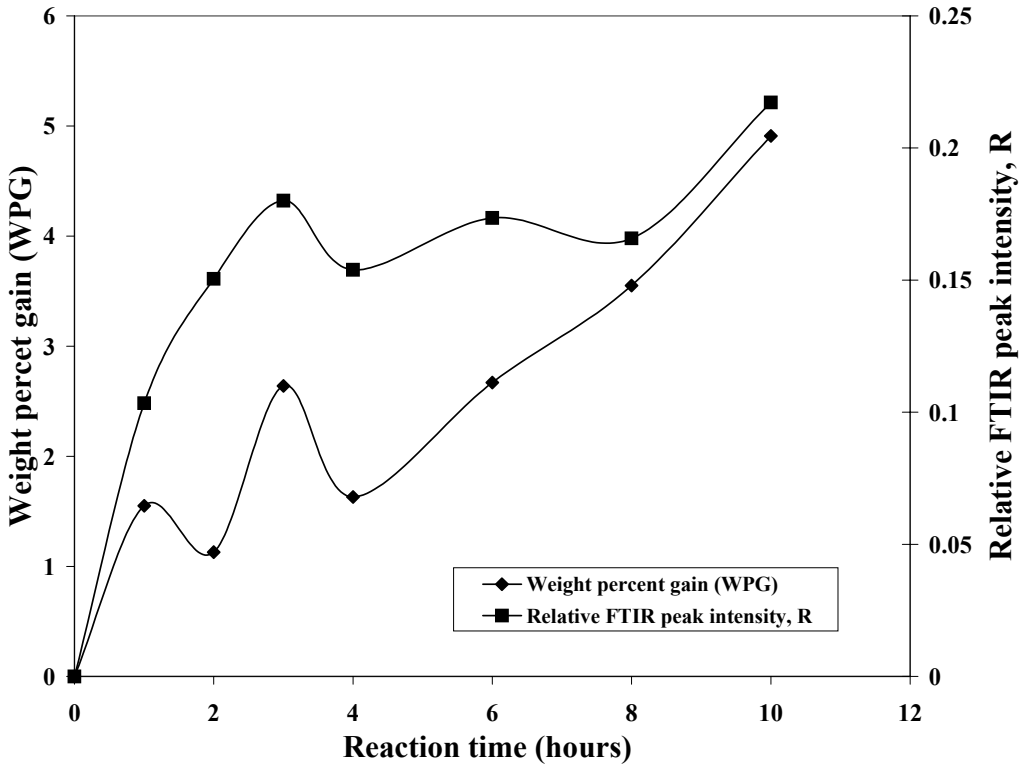
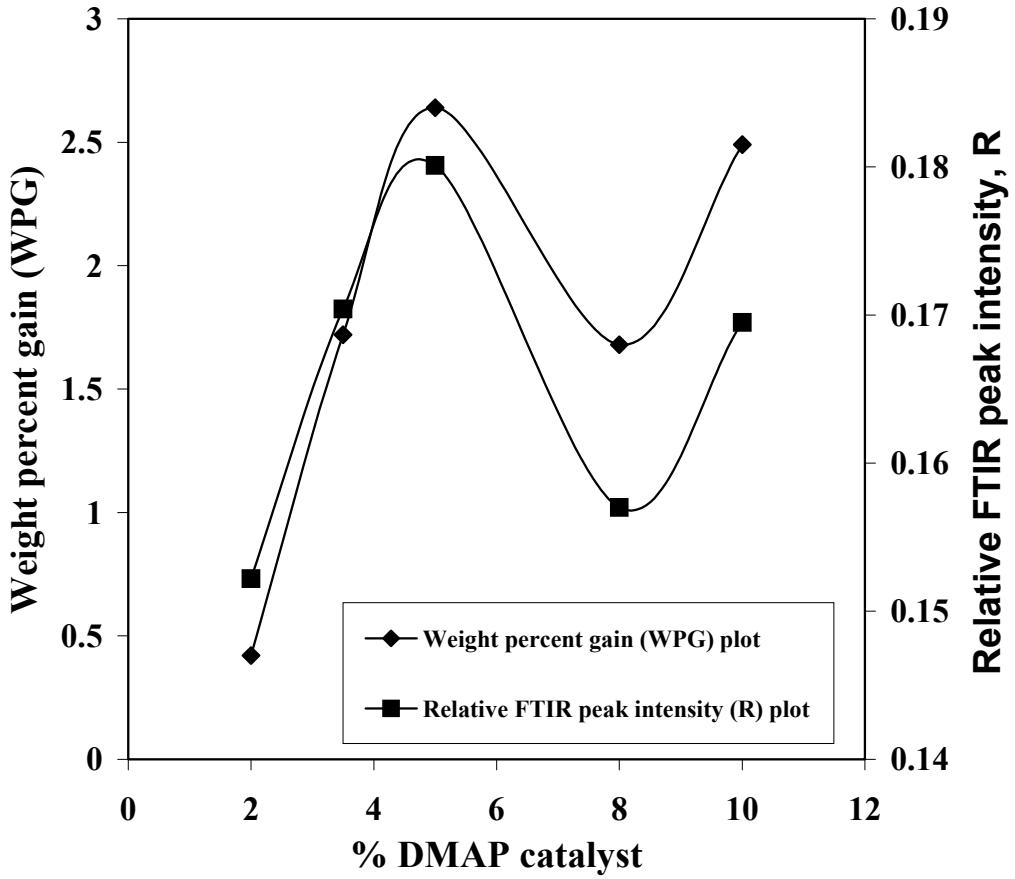


Figure 4. Adebajo and Frost.



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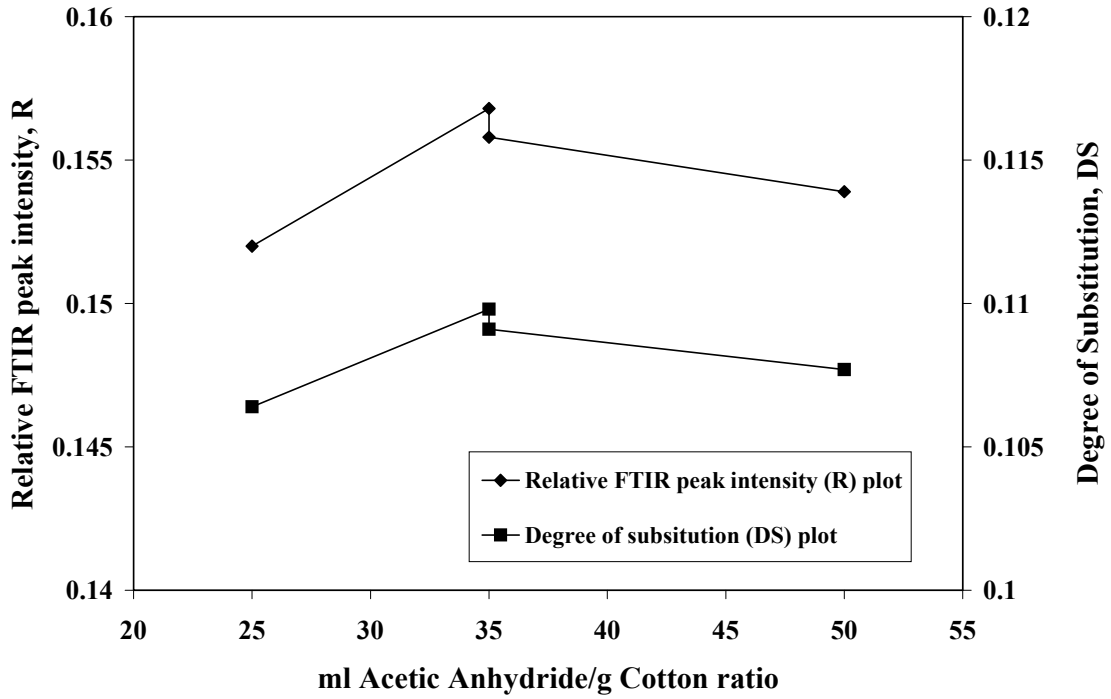

Figure 6. Adebajo & Frost.

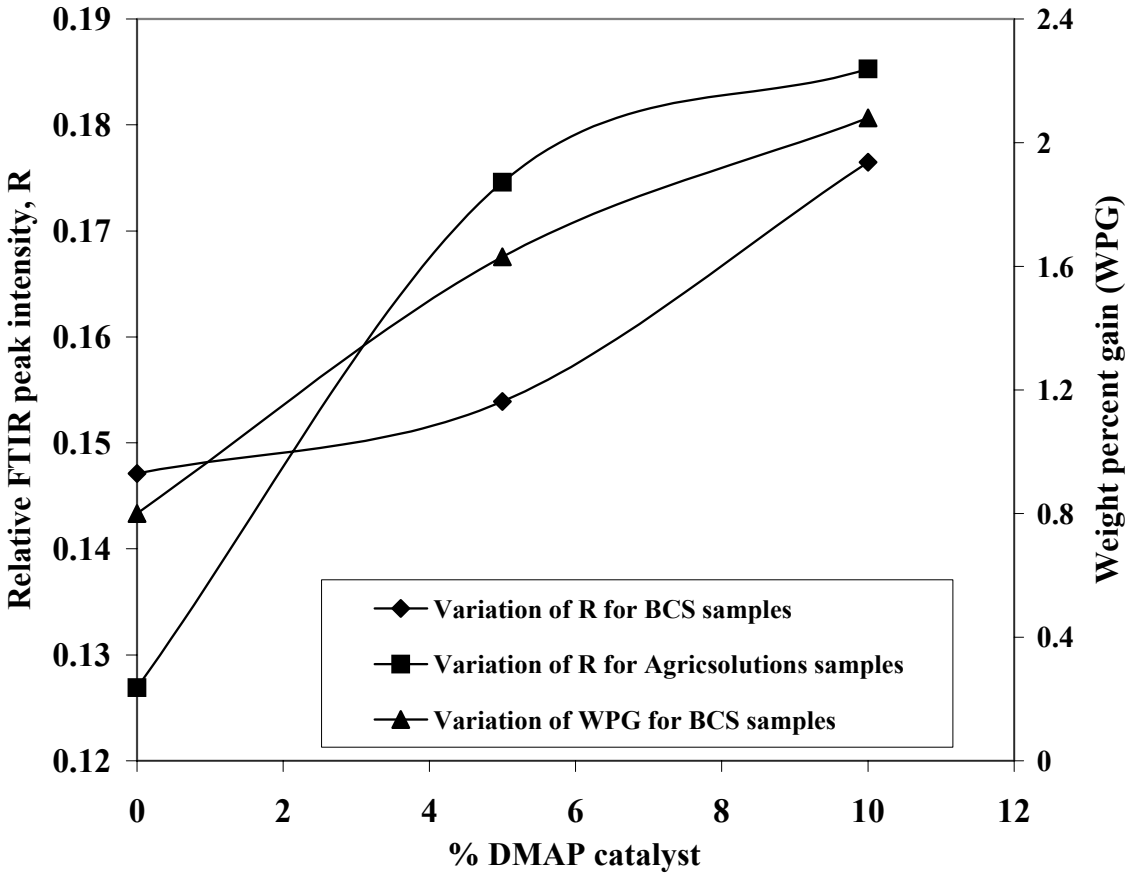

Figure 7. Adebajo & Frost.

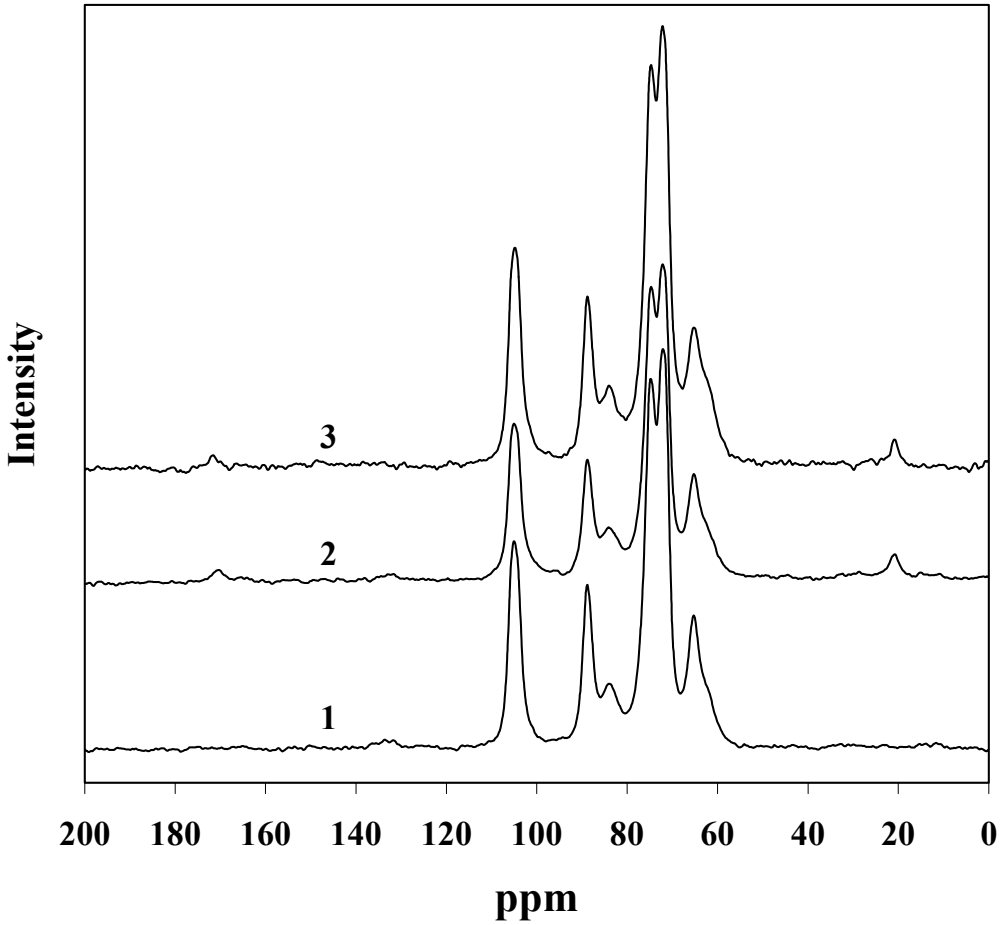

Figure 8. Adebajo & Frost.