RECYCLING OF VALUELESS PAPER DUST TO A LOW GRADE CELLULOSE ACETATE: EFFECT OF PRETREATMENTS ON ACETYLATION

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The feasibility of the production of cellulose acetate (CA) from recycled paper dust from carton boxes was examined. Two pre-treatments were carried out on the carton box's paper dust (CPD) to improve the pulp properties for better effect of synthesis. The results showed that the acid and oxygen-alkaline pretreatments were capable of increasing the alpha-cellulose content from 80.5 percent to 87.3 percent and 85.3 percent, respectively. Both pre-treatments also decreased the hemicellulose and ash contents by more than 50 percent. The degree of substitution (DS) of the resultant CA from pre-treated paper dust was improved from 1.94 to 2.13-2.16. The CA that was synthesized from the recycled paper dust showed comparable DS and had a similar trend of Fourier Transform Infrared (FTIR) spectra. Both pretreated pulps also showed an increment in the degree of crystallinity and had maximum degradation effect of temperature when compared to CPD CA. However, all the cellulose acetates produced showed a lower DS and thermal stability compared to commercial cellulose acetate (C CA). The degree of crystallinity of all the cellulose acetate was decreased in comparison to the original material.

INTRODUCTION

Cellulose acetate (CA) is one of the most commercially important cellulose derivatives. It has been used in several applications such as textiles, cigarette industries, and in the production of membranes for separation processes such as dialysis, reverse osmosis, gas separation, and hemodialysis (Cao et al. 2007; Cerqueira et al. 2007).

In general, CA is normally prepared by using dissolving pulp or so-called chemical cellulose with high alpha cellulose content (normally more than 95 percent) (He et al. 2008; Matsumura and Saka 1992). Currently, the main raw materials (dissolving pulps) for CA come from cotton linters and wood pulp, with the latter being the most important. The acid sulphite and prehydrolysed-sulphate (kraft) processes are the two foremost processes for the manufacturing of wood-derived dissolving pulp, since they are capable of hydrolyzing most of the hemicellulose. During the production of dissolving pulp, besides lignin, hemicellulose should also be eliminated in order to increase the efficiency of conversion during the synthesis of cellulose derivatives (Hinck et al. 1985).

Dissolving pulps are normally bleached to achieve high brightness and remove the impurities from the pulp; thus a series of bleaching stages are necessary. After

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undergoing both the pulping and bleaching processes, and even an extensive purification treatment, the yield of dissolving pulp retained is as low as 29 percent. Since the production of dissolving pulp requires higher production cost but lower pulp yield, as compared to paper grade pulp, the worldwide production of dissolving pulp occupies only a small part (approximately 1.6 percent) of the world pulp production, according to the FAO Pulp, Paper and Paperboard Capacity Survey (2002-2007). This indicates that the raw material for CA is fairly expensive to obtain (Barkalow et al. 1989; Cao et al. 2007; Yang et al. 2008).

For above reasons, attempts to find alternative sources of raw material for CA have been carried out. Acetylation on mechanical pulp (whole wood) has been carried out by Barkalow et al. (1989) by using both solution and fibrous methods. The resultant CA was then isolated by differential solubility. Since whole wood was used in their study, the CA obtained was only 84 percent, and the remains were acetylated lignin and hemicellulose. Liu et al. (2007) synthesized CA with a high degree of substitution (DS) up to 2.5 from ramie fibre that has high crystallization and orientation by pretreating them with water and glacial acetic acid before acetylation with acetic anhydride.

To maximize the value of resources, there is a trend of using recycled fibre, such as from old newspaper, for CA production (Rodrigues Filho et al. 2008). Nevertheless, similar to the acetylation of the mechanical pulp (Barkalow et al. 1989), synthesis of CA from newsprint recycled fibre also required several stages of pretreatment before the acetylation. This is because the raw materials for newsprint are bleached mechanical or chemi-mechanical pulps that containing high lignin content. Even with pretreatments, newsprint fibres required a lengthy acetylating time, as long as 24 hours, to achieve the DS up to 2.79. On the other hand, for the newsprint fibres without pretreatment, the DS of the resultant CA was only 1.98 after an extended 48 hours of acetylating.

Recycled paper dust, which is generated in the processes of a carton box converting mill, indeed has a low recycle value, as its fibre length is relatively short for recycling in paper mill. To recycle and add value to the material, synthesizing it to CA is a possibility. For the production of linerboard or corrugated mediums, high-yield kraft or chemi-mechanical pulps are used. Hence, in comparison to mechanical pulps and secondary pulps from old newspapers, paper dust contains a lower lignin content. Therefore, it requires less pretreatment prior to acetylation.

In view of environmental and economic considerations, only simple pretreatments would be approached in this study to improve the paper dust properties for better acetylation. The resultant CA that is prepared from the paper dust of the carton box would be characterized based on the degree of substitution (DS), Fourier Transform Infrared (FTIR) spectra, degree of crystallinity, and thermal stability.

EXPERIMENTAL

Materials

Massive Paper Product Sdn Bhd, Kedah, Malaysia, provided the paper dust from packaging carton box production. The paper dust was collected using a cyclone dust

collector. For comparison purposes, commercial softwood dissolving pulp obtained from Western Pulp Inc. Canada was also used as a reference sample for the production of CA.

Methods

Pretreatment

Acid and oxygen-alkaline pretreatments were carried out on carton box dust. For the former, paper dust was treated at pH 2 (adjusted by using diluted sulfuric acid) in 10 percent consistency and heated at 80°C for 1 hr. For the later, paper dust was treated with 4 percent NaOH, and 1 percent $MgSO_4.7H_20$ in 10 percent consistency, heated at 100°C with the oxygen gas pressure of 70 psi for 30 min.

Determination of chemical properties

The pulp samples were analyzed for the kappa number using Micro Kappa number based on TAPPI standard (TAPPI Useful Method UM-246). The ash in the pulp was determined using TAPPI method T211. The contents of alpha-, beta-, and gamma-cellulose were determined according to JIS P 8101. The starch in the paper was determined based on TAPPI method T419.

Synthesis of cellulose acetate

Synthesis of cellulose acetate (CA) was conducted following the method obtained from Tanghe et al. (1963), with minor modification.

Activation of cellulose

About 5 g of cellulose sample was activated in distilled water for 10 minutes. The sample was then filtered using a G3 glass crucible and subsequently dipped in 100 mL of glacial acetic acid for 10 minutes. The sample was shaken occasionally and filtered again through the G3 glass crucible. The steps of dipping sample in acetic acid and filtering through the G3 glass were repeated with 100 mL fresh glacial acetic acid.

For the pretreated paper dust, no activation of cellulose in water was done prior the acetylation, as the condition in pretreatment was enough to swell the cellulose for further acetylation.

Acetylation

90 mL glacial acetic acid and 0.5 mL concentrated sulfuric acids were mixed in a 250 mL Erlenmeyer flask. After that the flask was closed with a stopper, a 25°C cellulose sample was added to the flask and shaken thoroughly for 1 min. After that, 25 mL of acetic anhydride was added, and the flask was shaken again thoroughly for 1 min.

Time for dissolving the specimen was fixed at 60 min. After that, 12.5 mL of acetic acid-water mixture (CH_3COOH: water = 7:3 in volume) was added to the cellulose solution, and the mixture was continuously and thoroughly stirred at 25°C for 30 min.

Precipitation

Approximately 1.2-1.4 L of distilled water was prepared in a 2 L glass beaker with consistent stirring. Acetylated cellulose was then poured into the beaker slowly. The precipitated cellulose acetate (CA) was then squeezed manually using a cloth bag. The

ester was dispersed into a beaker with distilled water and stirred slowly for a few minutes. This procedure was repeated a few times.

After washing, the sample was dispersed into distilled water again with the addition of a few drops of phenolphthalein as an indicator. Subsequently, sodium carbonate was added slowly until the mixture became a pinkish color. Finally, the mixture was filtered followed by a final wash of the sample with distilled water to remove any excess salt, and then it was dried in an oven at 60°C.

Determination of acetyl content and degree of substitution

The determination of acetyl content was conducted based on the ASTM method (D871-96). The acetyl contents obtained were then used to calculate the degree of substitution as follows (Samios et al. 1997):

$$DS= (3.86 \text{ x \% acetyl}) / (102.4 - \text{\% acetyl}) \tag{1}$$

Fourier Transforms Infrared Spectroscopy (FTIR)

Fourier Transform Infrared (FTIR) was carried out to determine the IR spectra of the cellulose acetate (CA) samples by using Nicolet Avatar 260 FTIR spectrometer. The test specimens (CA ground powder) were prepared by the KBr-disk method, where the test specimens were mixed with KBr in the proportion of 2/100 (w/w).

X-ray diffraction

X-ray diffraction was carried out to determine the crystallinity index and the crystallite sizes of paper dust. X-ray diffraction of specimens was recorded at room temperature from 5°C to 50°C at a scanning speed of $0.02°/s$ with Siemens-D5000 powder diffractometer using Ni-filtered Cu Kα radiation of wavelength 0.1542 nm. The operating voltage and current was 40 kV and 30 mA (He et al. 2008), respectively.

The crystallinity index of cellulose, I_c was calculated from the following formula (Regiani et al. 1999),

$$I_c = 1 - \frac{I_{min}}{I_{max}} \tag{2}$$

where, I_c is the crystallinity index, I_{min} is the intensity minimum between $2\theta=18°$ and $19°$, and I_{max} is the intensity of the crystalline peak at the maximum between $2\theta=22°$C and $23°$C.

The crystallite sizes were determined by using the diffraction pattern obtained from the 002 (hkl) lattice planes of the cellulose specimen. The Scherer equation with the method based on the width of the diffraction patterns obtained in the X-ray reflected crystalline region was used to calculate the average size of crystallite (He et al. 2008),

$$D_{(hkl)} = \frac{k\lambda}{B_{(hkl)} \cos\theta} \tag{3}$$

where (hkl) indicates the lattice plane, $D_{(hkl)}$ is the size of the crystallite, k is the Scherrer constant (0.84), λ is the X-ray wavelength (0.154nm), $B_{(hkl)}$ is the FWHM (full width half

maximum) of the measured hkl reflection, and 2θ is the corresponding Bragg angle (reflection angle).

Thermogravimetry analysis (TG)

Thermogravimetric analysis (TG) was carried out to evaluate the initial degradation and the maximum degradation temperature of the resultant cellulose acetate. The analysis was carried out with a Pyris 1 themogravimetic analyzer at a heating rate of 10°C min^{-1} under purging gas of nitrogen with a gas flow of 30 mL/min.

RESULTS AND DISCUSSION

Chemical Properties of Materials

As shown in Table 1, the paper dust of the packaging carton box (CPD) had a much higher kappa number (43.8-47.6) and gamma-cellulose content (expressed to hemicellulose content, 13.7 percent) but lower alpha-cellulose (α-cellulose) content (80.5 percent) in comparison to the commercial dissolving pulp (DP). Since CPD possessed fairly high percentage of lignin, hemicellulose, and ash contents, it is not so suitable for synthesizing cellulose derivatives. This is because acetylation of pulps containing hemicellulose of more than 5 percent will cause the formation of hemicellulose acetates such as xylan acetate and glucomannan acetate, consequently resulting in industrial problems such as poor filterability, turbidity, and false viscosity (Matsumura and Saka 1992; Ueda et al. 1988). In addition, the presence of lignin also reduces the accessibility of hydroxyl content of cellulose.

Results in Table 1 show that both acid and oxygen-alkaline pretreatments successfully increased the α-cellulose content of CPD to 87.3% and 85.3%, as well as decreased the hemicellulose content (γ-cellulose content) from 13.7% to 5.6% and 9.8%, respectively. However, the β-cellulose content of acid pretreated carton box dust (ACPD) was adversely increased from 5.9% of the original CPD to 7.2%. In contrast, the oxygen-alkaline pretreatment gave a positive effect by decreasing the β-cellulose content to 5.0%.

Table 1. Chemical Compositions of Dissolving Pulp, Tissue Paper Dust, and Carton Box Paper Dust

	Kappa no	Alpha cellulose (%)	Beta cellulose (%)	Gamma cellulose (%)	Ash content (%)	Starch content (%)
Dissolving Pulp (DP)	n/a	94.4 ± 0.2	4.6 ± 0.1	1.0 ± 0.2	0.3 ± 0.1	NIL
Carton box paper dust (CPD)	43.8-47.6	80.5 ± 0.5	5.9 ± 1.6	13.7 ± 2.0	9.4 ± 0.1	6.0 ± 0.2
Acid pretreatment carton box paper dust (ACPD)	48.1-49.7	87.3 ± 0.2	7.2 ± 0.8	5.6 ± 1.3	4.1 ± 0.1	0.8 ± 0.0
Oxygen-alkaline pretreatment carton box paper dust (OCPD)	38.5-39.3	85.3 ± 0.1	5.0 ± 0.4	9.8 ± 0.4	4.2 ± 0.1	0.2 ± 0.0

The removal of hemicellulose was the major factor that contributed to the increase of α-cellulose content after the pretreatments. Nevertheless, the acid pretreatment exhibited greater effectiveness than oxygen-alkaline pretreatment. The higher reduction of hemicellulose content of ACPD (64.8%) than oxygen-alkaline pretreated carton box paper dust (OCPD) (28.5%) was mainly owing to the fact that hemicellulose is more easily hydrolyzed under an acidic conditions rather than an alkaline conditions. Both pretreatments decreased the starch content of CPD effectively. The starch content of CPD was decreased from 10.4% to only 0.8% and 0.2% after acid and oxygen-alkaline pretreatments, respectively.

On the other hand, the kappa number of OCPD was decreased by about 15%, whereas that of ACPD slightly increased. The increase of the kappa number was mainly due to the decrease of hemicellulose content (or generally, the carbohydrate content) of the material, and thus indirectly increased the lignin content.

X-ray Diffraction

The x-ray spectra for all the raw material, as demonstrated in Fig. 1, showed diffraction at the 002 lattice plane, which is the peak between 22° and 23° at 2-theta degree. The intensity of the peak indicates the degree of crystallinity. The highest intensity of a peak means that the pulp has the highest degree of crystallinity, and vice-versa. From Fig. 1, it can be observed that the arrangements for the tested specimens accordingly to the degree of crystallinity were: DP > OCPD > ACPD > CPD.
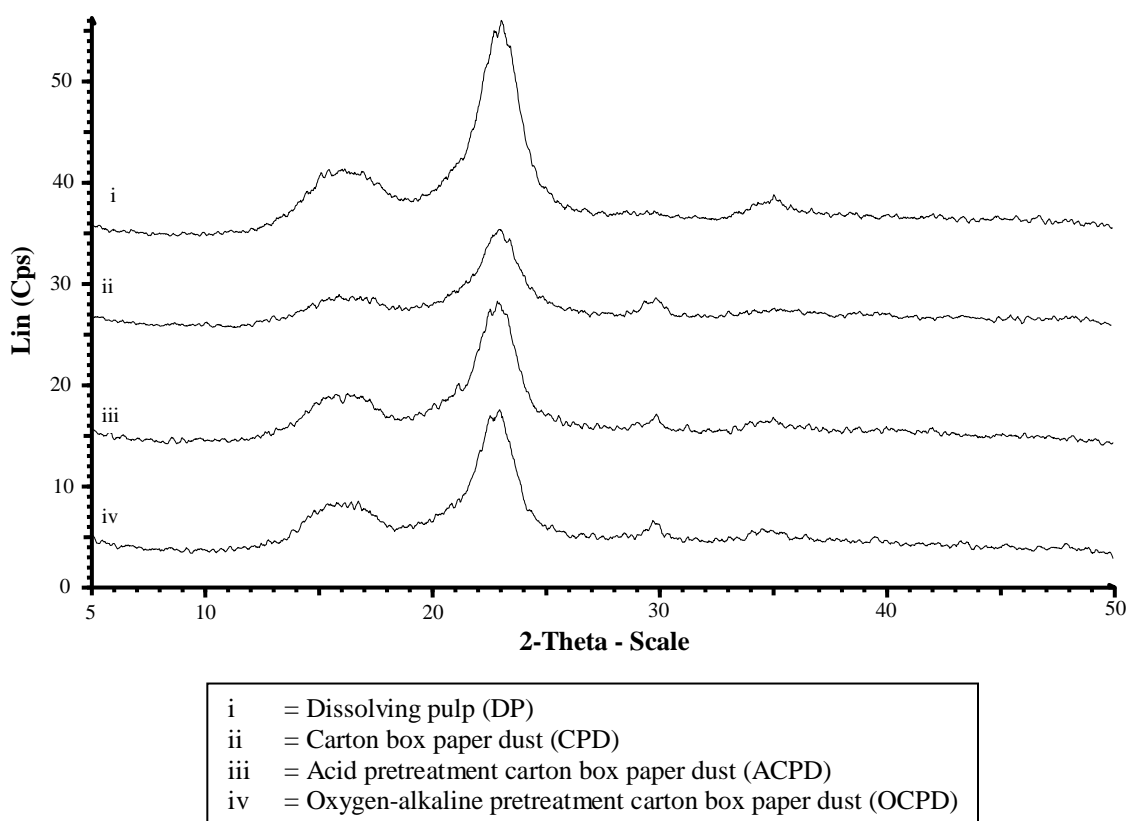

i	= Dissolving pulp (DP)
ii	= Carton box paper dust (CPD)
iii	= Acid pretreatment carton box paper dust (ACPD)
iv	= Oxygen-alkaline pretreatment carton box paper dust (OCPD)

Fig. 1. X-ray spectra of DP, CPD, ACPD and OCPD and TPD

The crystallinity values for the pretreated carton box pulps were shown to be higher, albeit small, in comparison to the CPD. The crystallinity index of ACPD was higher than that of CPD because acid hydrolysis will remove the amorphous substance, including the easily removed hemicelluloses. The amorphous cellulose near the surface of cellulose was also being hydrolyzed during the treatment, thus subsequently increasing the crystallinity.

On the other hand, the higher crystallinity of OCPD than that of CPD and even ACPD was mainly due to both the lignin and hemicellulose, which are the amorphous substances, being eliminated (Table 1) (Fu and Lucia 2003; Roncero et al. 2005). Moreover, the alkaline peeling reaction during the treatment also caused the removal of easily accessible amorphous cellulose, which increased the crystallinity (De Souza et al. 2002). The crystalline index of OCPD has increased to about 4 percent in comparison to CPD, which is similarly observed by Roncero et al. (2005) on the eucalyptus kraft pulp upon oxygen delignification where their crystallinity index has increased by almost 4 percent as well.

Table 2 shows that the average size of crystallites for DP was the smallest (3.91 nm) among all the specimens, whereas CPD had the largest size of crystallites (4.26 nm). After pretreatment, the size of crystallites of CPD had been reduced to 4.04 for acid pretreatment and to 4.12 for oxygen-alkaline pretreatment. There is a reduction in crystalline size after both pretreatments because the thermal stress of both pretreatments partly destroyed the cellulose crystal structure (Liao et al. 2008). Acid hydrolysis probably altered the stabilization of crystalline structures, therefore resulting in the size of crystallites for ACPD being lower than those of OCPD.

Table 2. Crystallinity Index and the Size of Crystallite and of Acetylation Material

Sample Name	Crystallinity index	Size of crystallite (nm)
Dissolving Pulp (DP)	0.77	3.91
Carton box paper dust (CPD)	0.69	4.26
Acid pretreatment carton box paper dust (ACPD)	0.70	4.04
Oxygen-alkaline pretreatment carton box paper dust (OCPD)	0.72	4.12

Acetylation

Even though only simple pretreatments were applied on CPD, a substantial positive effect was observed. As shown in Table 3, without pretreatment, the degree of substitution (DS) of the resultant cellulose acetate (CA) was merely 1.94. By having a pretreatment prior the synthesis, the DS of CA was increased to 2.16 for ACPD and 2.19 for OCPD, respectively. These were comparable to the DS (2.15) of the resultant CA that was prepared from commercial DP.

Table 3. Combined Acetyl Content and Degree of Substitution for Cellulose Acetate from Commercial (C CA), Dissolving Pulp (DP CA), Carton Box Paper Dust (CPD CA), and Cellulose Acetate from Pretreated Carton Box Paper Dust

	Acetyl content (%)	DS
Commercial CA	40.36	2.51
Dissolving Pulp (DP)	36.68	2.15
Carton box paper dust (CPD)	34.27	1.94
Acid pretreatment carton box paper dust (ACPD)	36.70	2.16*
Oxygen-alkaline pretreatment carton box paper dust (OCPD)	37.01	2.19*
* Statistically (T-test) different between the mean of the specimen with CPD at 95.0% confidence level.		

Packaging carton is made from recycled paper. Recycled fibre experiences fibre hornification during the papermaking process when strong intra-fibre hydrogen bonds form during the drying process. This phenomenon causes CPD to have a lower swelling ability. Even though using glacial acetic acid at the ambient temperature had activated CPD, it was not sufficient for destroying the hydrogen bonds, and this effect is believed to have contributed to low DS owing to weak accessibility of the acetate anhydride to the hydroxyl groups.

During pretreatments, high temperature of $80^{\circ}C$ for acid and $100^{\circ}C$ for oxygen-alkaline pretreatments, respectively, had a better effect on enhancing the fibre swelling ability. Therefore, more water could be pumped into the fibres and more inter- and intra-fibre hydrogen bonds were destroyed. Consequently, the DS of the resultant CAs was increased. In addition, the removal of the starch content during the pretreatments also showed a high possibility in contributing to the increase in DS. Since one of the purposes of adding the starch during the papermaking process is to increase the fibre-fibre bonding, the removal of starch to below than 1 percent would definitely improve the acetic anhydride accessibility to some extent. Between the two pretreatments, oxygen-alkaline treatment had a slightly better effect on DS since part of the lignin could be eliminated, thus providing better access for the acetylating agent. Acetic anhydride has an improved accessibility to the hydroxyl groups of cellulose too.

FTIR of Cellulose Acetate

Figure 2 shows the comparison between the FTIR spectra of the reference materials, the commercial dissolving pulp (DP), its cellulose acetate (DP CA), and also the commercial CA (Fluka, Sigma-Aldrich, USA). It was obvious that a strong intensity band was present at 1755 cm^{-1}, which is assigned to the symmetric stretching carbonyl group (C=O) of the acetyl group (-COCH$_3$) in cellulose acetate (Cerqueira et al. 2007; Rodrigues Filho et al. 2008). A reduction in the intensity of the band at 3453 cm^{-1}, representing the hydroxyl groups (-OH), was also observed. The changes of the spectra confirmed the DP was being acetylated.
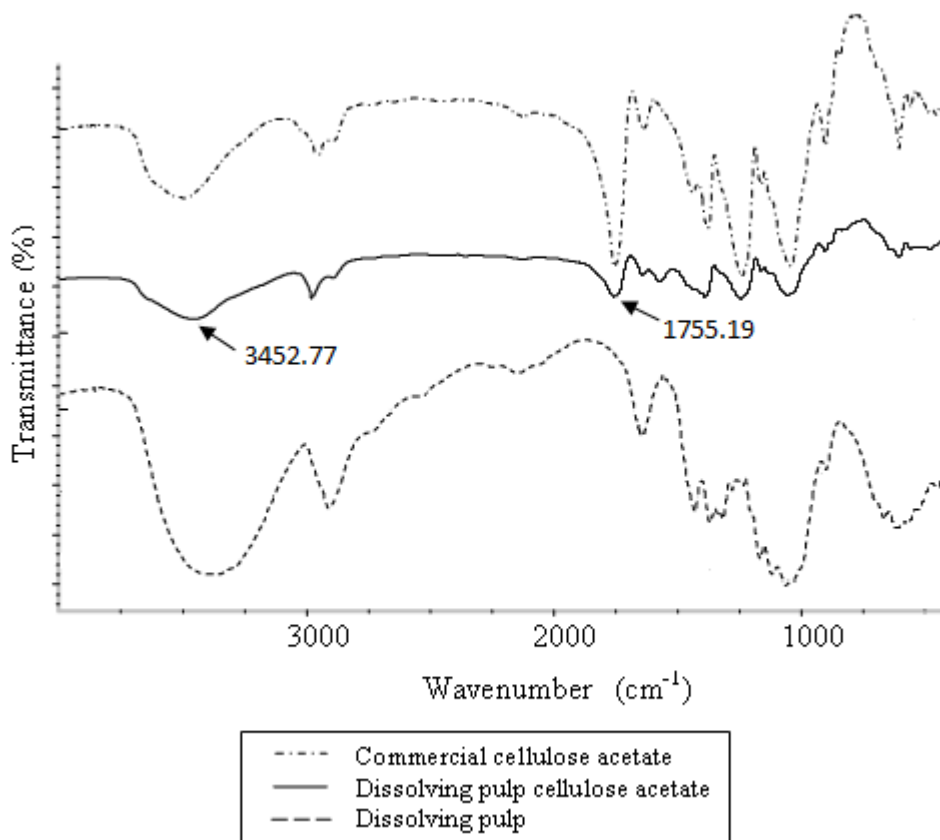
Fig. 2. FTIR comparison of commercial cellulose acetate (CCA) and cellulose acetate produced from dissolving pulp (DP CA), and dissolving pulp

Figure 3 shows the FTIR spectra for carton box paper dust (CPD) compared to the FTIR spectra of CA produced from CPD (CPD CA), ACPD (ACPD CA), and OCPD (OCPD CA). Similar to the reference material, all the CA produced from CPD with and without pretreatment showed the characteristic of being acetylated. It was noticed that the intensity in the band of the hydroxyl group appearing in the raw material paper dust at around 3500 cm^{-1} was decreased in all the CA's FTIR. On the other hand, a strong band of the carbonyl group at around 1760 cm^{-1} was also observed. This clearly indicates that some of the hydroxyl groups (-OH) in the cellulose was replaced by acetyl (-COCH$_3$) groups.

The FTIR spectra of the resultant CA showed a similar trend to commercial CA. However, the FTIR of commercial CA presented a stronger intensity band for the carbonyl group at around 1760cm^{-1}, which coincided with its highest DS in comparison to the others.
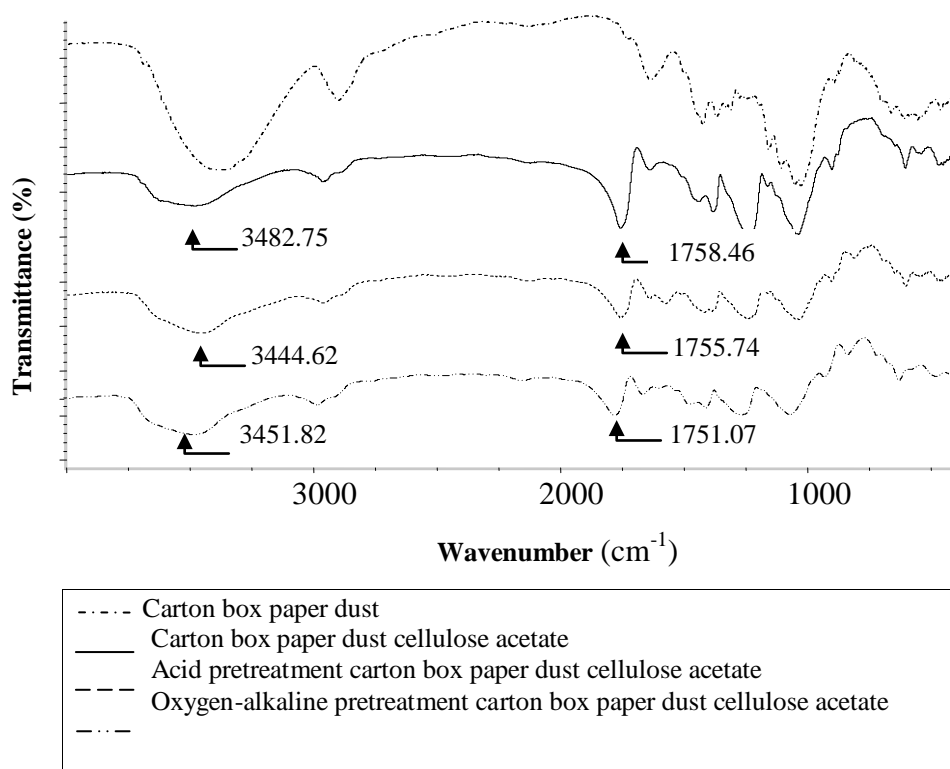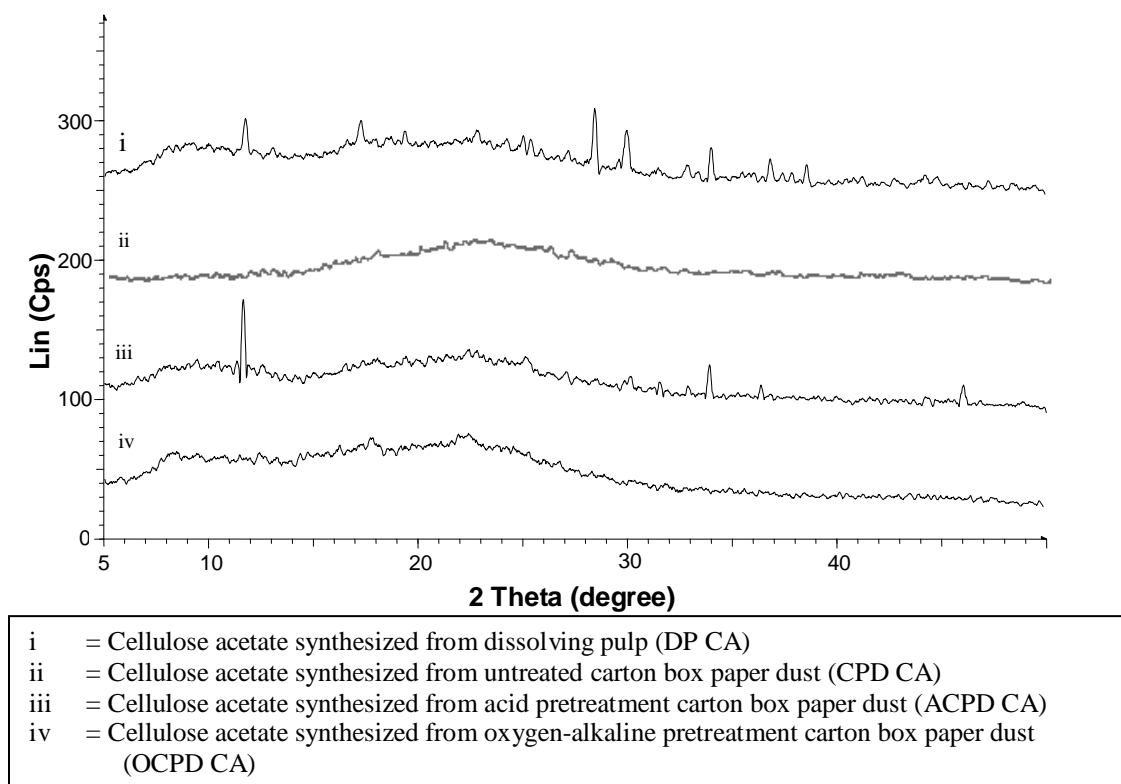
Fig. 3. FTIR comparison of carton box paper dust, cellulose acetate produced from carton box paper dust and pretreated carton paper dust

X-ray Diffraction

Figure 4 shows the x-ray spectra of the CA produced from DP, untreated, and treated CPD. In comparison to the spectra of raw materials without acetylation, which show an intense diffraction peak (Fig 1), all the spectra of resultant CAs showed no obvious peak. The disappearance of the peak revealed that there was a decrease in crystallinity and a transition of structure from crystalline to amorphous during the acetylation of the raw material to CA (Fan et al. 2010).

The cellulose molecular structure is flat, thin, and long. It contains three active hydroxyl groups in each glucose ring. These hydroxyl groups will form inter- and intramolecular hydrogen bonds and contribute to the formation of crystalline regions (Fan et al. 2010; Fritz and Cant 1986). In this study, the acetylation is a heterogeneous reaction in which the reagent reacts with the amorphous region of the cellulose initially. The cellulose acetate passes into solution when as the reaction product is formed. The crystalline region in the interior will react subsequently after the acetylated amorphous region at the fibre surface becomes dissolved in the acetic acid medium, which results in the original structure of the crystalline region breaking down (Fan et al. 2010; Liu et al. 2007). After the acetylation reaction, the acetate groups have replaced the hydroxyl groups. These acetate groups are positioned randomly, and it is difficult for the molecules to become packed again in regular order (Fritz and Cant 1986). Thus, the crystallinity is decreased.

i = Cellulose acetate synthesized from dissolving pulp (DP CA)
ii = Cellulose acetate synthesized from untreated carton box paper dust (CPD CA)
iii = Cellulose acetate synthesized from acid pretreatment carton box paper dust (ACPD CA)
iv = Cellulose acetate synthesized from oxygen-alkaline pretreatment carton box paper dust
        (OCPD CA)

Fig. 4. X-ray spectra of cellulose acetate cellulose acetate synthesized from dissolving pulp, carton box paper dust, and pretreated carton paper dust

Thermo-gravimetric Analysis (TG)

Figure 5 shows that C CA started to degrade at 352.39°C, and the most apparent weight loss during the thermal degradation was at 376.53°C. DP CA showed a lower initial degradation temperature of 223.2°C and maximum degradation temperature of 337.74°C in comparison to the C CA. In addition, the derivative thermo-gravimetric graph (DTG) (Fig. 6) of DP CA showed a shoulder at around 200°C to 300°C. The thermal properties for cellulose acetate or cellulose triacetate varied due to different preparation methods used (Zugenmaier 2004); thus DP CA, which was prepared in the laboratory without undergoing a same preparation condition, was dissimilar relative to the thermal degradation of C CA.

In comparison to C CA, DP CA exhibited a lower initial degradation temperature. Hence, it is expected that the initial degradation temperature of CPD CA (231.85°C) will also be lower than that of C CA, as it used the same production method as DP CA. However, when compared to DP CA, the cellulose acetate produced by CPD possessed higher initial degradation temperature and lower maximum degradation temperature. As can be observed from the DTG in Fig. 7, CPD CA showed two obvious peaks. This means that there are two steps of degradation in the material. CPD is not a kind of pure cellulose pulp, as it still contains lignin and hemicellulose, which will also be acetylated and thus will alter the thermal properties. It is proposed that the low temperature of

maximum degradation is due to the high hemicellulose contents, as hemicellulose in pulp reduces the thermal stability of CA (Shaikh et al. 2009).
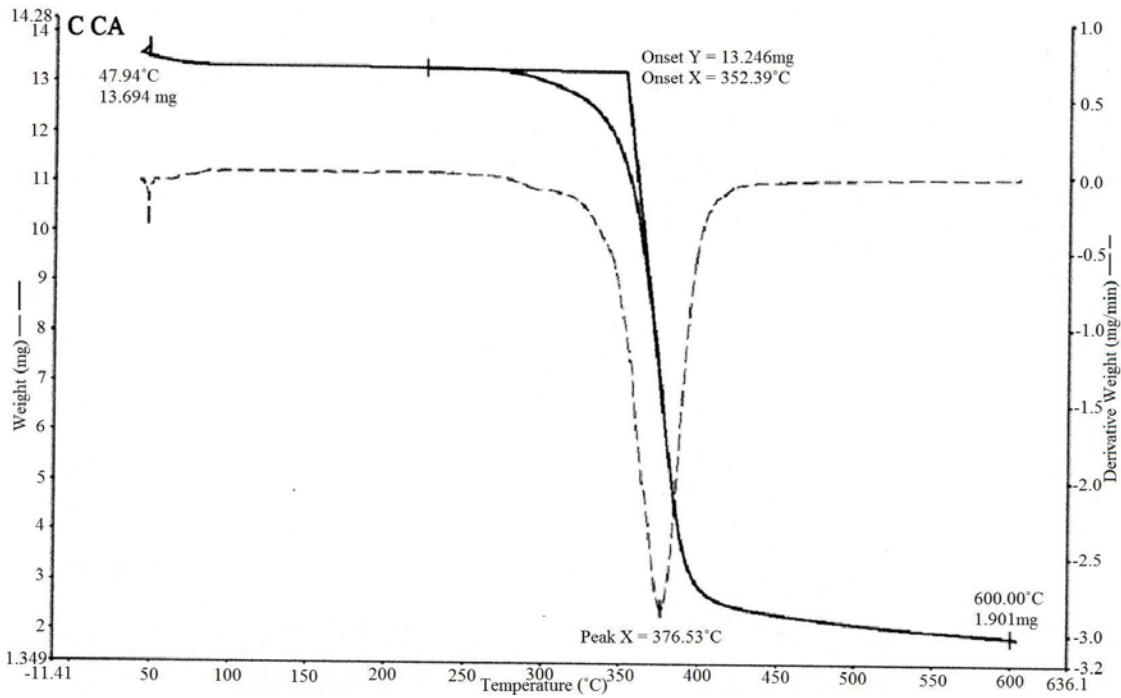
Fig. 5. Thermal degradation of commercial cellulose acetate (C CA)
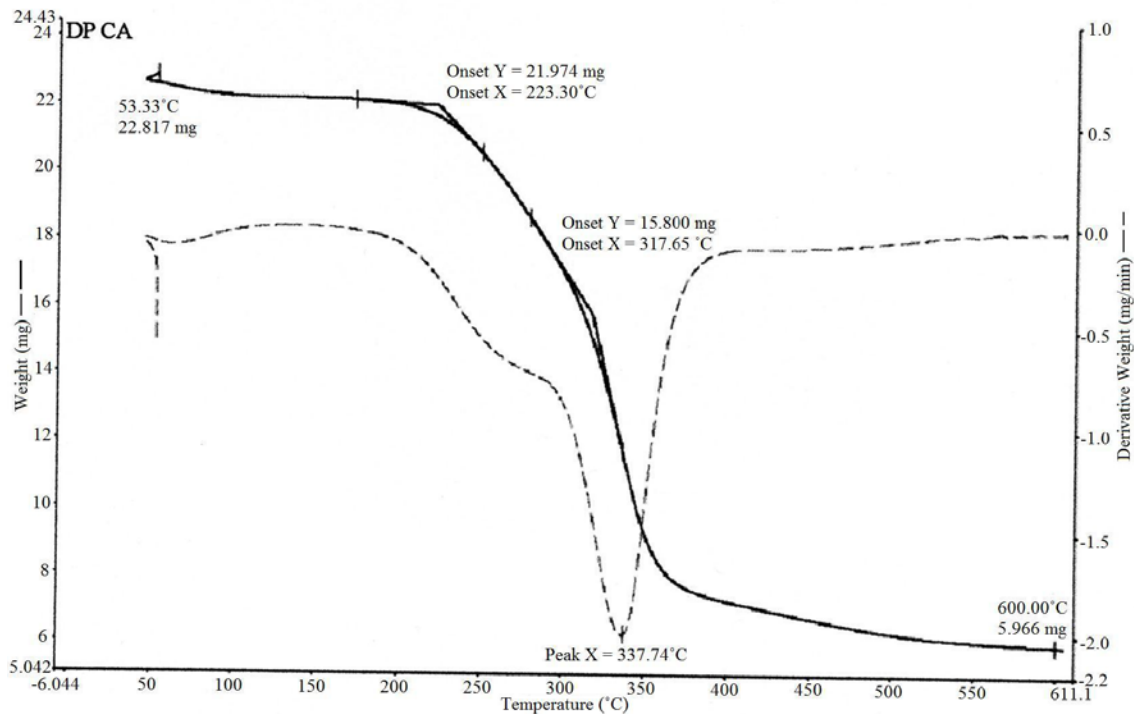
Fig. 6. Thermal degradation of cellulose acetate produced from dissolving pulp (DP CA)

From Figs. 8 and 9, it can be observed that the initial degradation temperatures for cellulose acetates produced from pretreated CPD decreased in comparison to CPD CA. Both ACPD CA and OCPD CA started to degrade at around 226°C, and their maximum degradation temperatures are 339.43°C and 266.31°C, respectively.
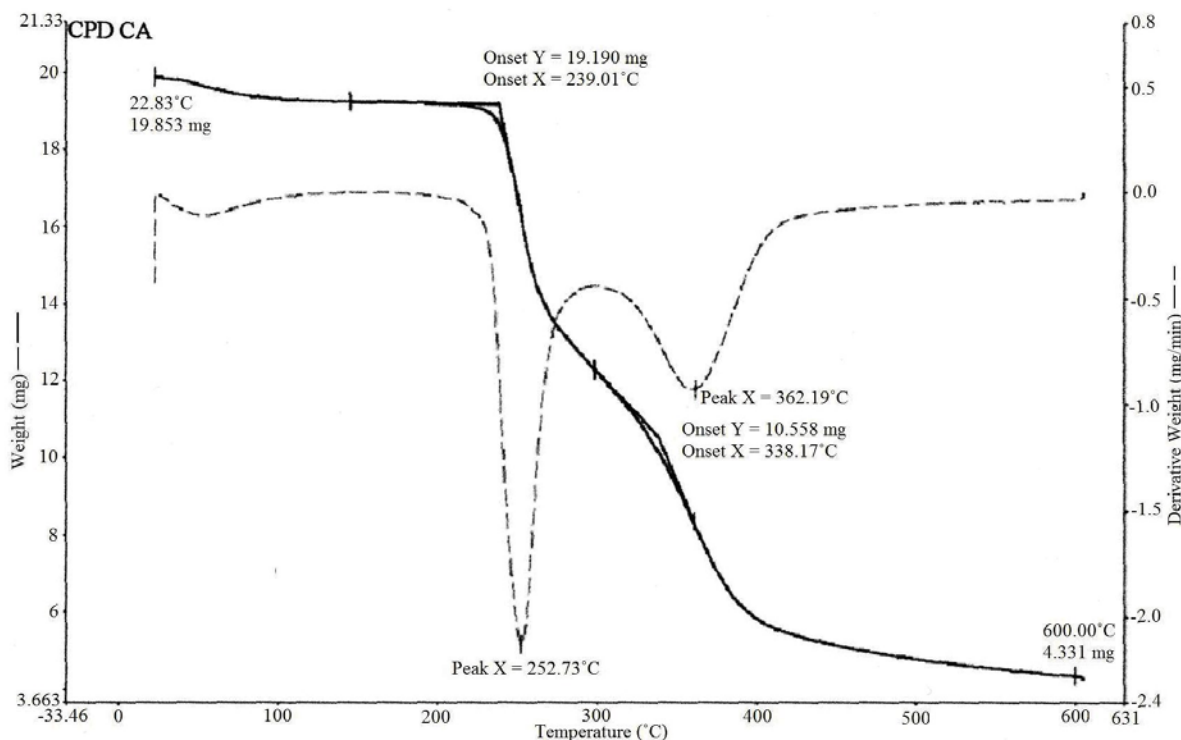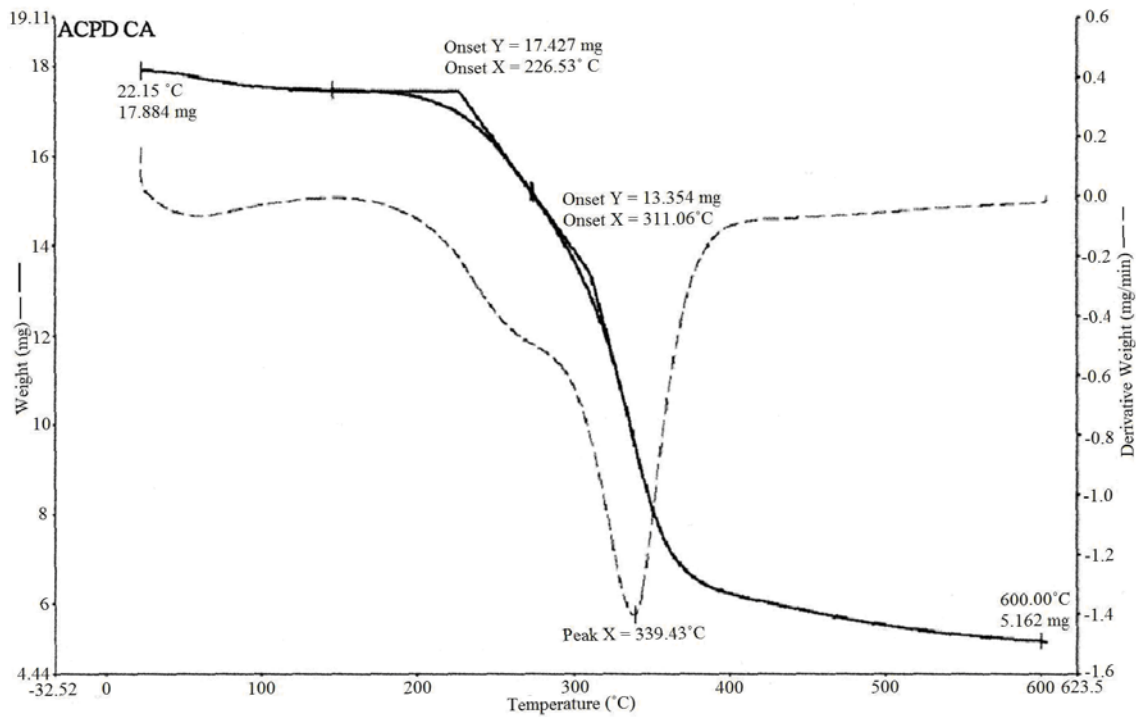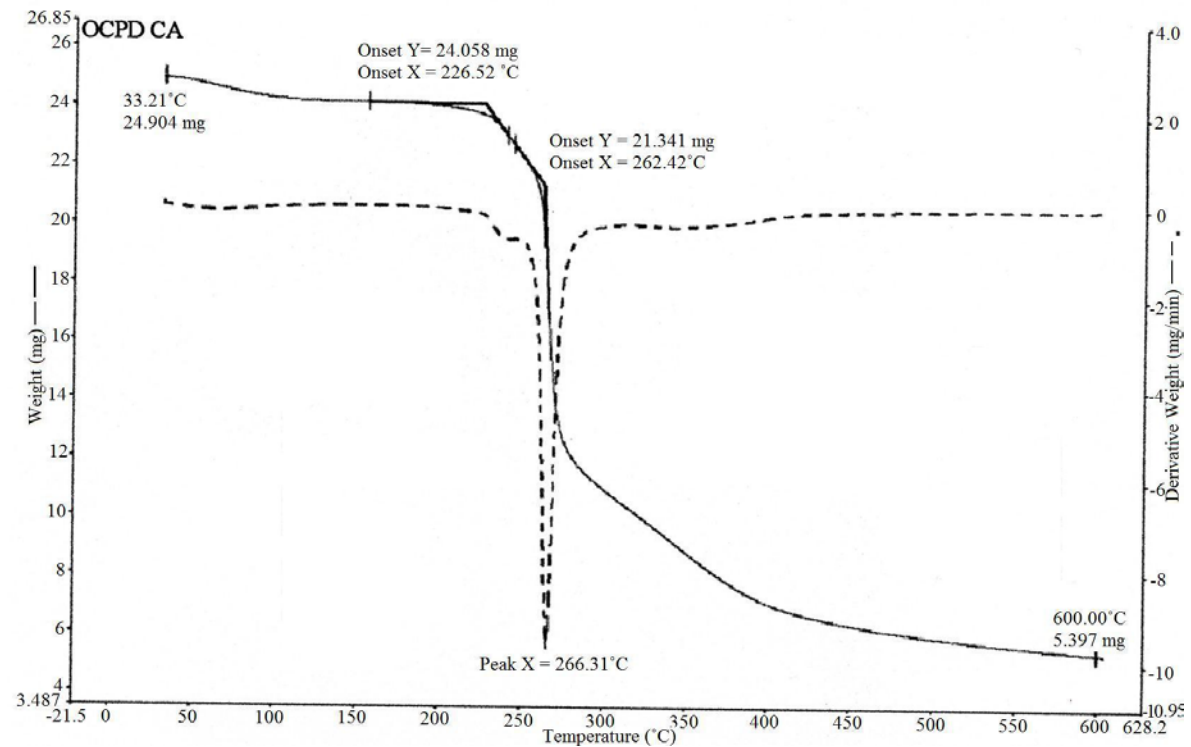

Fig. 7. Thermal degradation of cellulose acetate produced from carton box paper dust (CPD CA)

For ACPD CA (Fig. 8), besides a slight increment in the maximum degradation temperature, it only showed a shoulder at around 200°C to 300°C instead of a sharp peak, as indicated by the DTG of CPD CA. As hemicellulose in pulp reduces the thermal stability of CA, thus it is suggested that the CA synthesized by using acid pretreated pulp, which contains less hemicellulose, is capable of increasing the maximum degradation of the resultant cellulose acetate.

On the other hand, the DTG of OCPD (Fig. 9) showed a small shoulder at around 200°C to 250°C and only one sharp peak at 266.31°C. The oxygen-alkali pretreatment managed to remove more lignin content in the pulp in comparison to acid pretreatment. However, the hemicellulose content in OCPD was still higher than ACPD. Hence, it is suggested that the low degradation temperature is owing to the hemicellulose content remaining in the pulp (Shaikh et al. 2009).

Fig. 8. Thermal degradation of cellulose acetate produced from acid pretreatment carton box paper dust (ACPD CA)

Fig. 9. Thermal degradation of cellulose acetate produced from oxygen-alkaline pretreatment carton box paper dust (OCPD CA)

CONCLUSIONS

1. FTIR spectra illustrated the viability of producing CA from packaging carton box paper dust, although degree of substitution of cellulose acetate for paper dusts was lower than commercial cellulose acetate (CA).
2. Simple pretreatments with either acid or oxygen-alkaline are capable of modifying the carton box paper dust's properties to approach acetylating pulp properties. The cellulose acetate produced from pretreated pulps gave better results in terms of DS and thermal degradation.
3. Although the degree of substitution was lower, the thermal property of cellulose acetate produced from acid-pretreated paper dust was better than that of oxygen-alkaline pretreated paper dust.
4. The x-ray diffraction revealed that both acid and oxygen-alkaline pretreatment increased the crystallinity, but decreased the size of crystallites of carton box paper dust. The crystallinity of cellulose acetate was lower than that of paper dust.

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REFERENCES CITED

Barkalow, D. G., Rowell, R. M., and Young, R. A. (1989). "A new approach for the production of cellulose acetate: Acetylation of mechanical pulp with subsequent isolation of cellulose acetate by differential solubility," *Journal of Applied Polymer Science* 1009-1018.

Cao, Y., Wu, J., Meng, T., Zhang, J., He, J., and Li, H. Q. (2007). "Acetone-soluble cellulose acetates prepared by one-step homogeneous acetylation of cornhusk cellulose in an ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl):," *Carbohydrate Polymer* 69, 665-672.

Cerqueira, D. A., Rodrigues Filho, G., and Meireles, C. S. (2007). "Optimization of sugarcane bagasse cellulose acetylation," *Carbohydrate Polymer* 69, 579-582.

De Souza, I. J., Bouchard, J., Methot, M., Berry, R., and Argyropoulos, D. S. (2002). "Carbohydrates in oxygen delignification. Part 1: Changes in cellulose crystallinity," *Journal of Pulp and Paper Science* 28(5), 167-170.

Fan, X., Liu, Z.-T., and Liu, Z. W. (2010). "Preparation and application of cellulose triacetate microspheres," *Journal of Hazardous Materials* 177, 452-457.

Fritz, A., and Cant, J. (1986). *Consumer Textiles*, Oxford University Press, Melbourne.

Fu, S., and Lucia, L. A. (2003). "Investigation of the chemical basis for inefficient lignin removal in softwood kraft during oxygen delignification," *Industrial & Engineering*

Chemistry Research 42, 4269-4276.

He, J., Cui, S., and Wang, S.-Y. (2008). "Preparation and crystalline analysis of high-grade bamboo dissolving pulp for cellulose acetate," *Journal of Applied Polymer Science* 107, 1029-1038.

Hinck, J. F., Casebier, R. L., and Hamilton, J. K. (1985). *Pulp and Paper Manufacture-Sulfite Science and Technology*, O. V. Ingruber, M. J. Kocurek, and A. Wong (eds.), The Joint Textbook Committee of the Paper Industry, Atlanta.

Liao, R.-J., Tang, C., and Yang, L.-J. (2008). "Thermal aging micro-scale analysis of power transformer pressboard," *IEEE Transactions on Dielectrics and Electrical Insulation* 15(5), 1281-1287.

Liu, Z.-T., Fan, X., Wu, J., Zhang, L., Song, L., Gao, Z., Dong, W., Xiaong, H., Peng, Y. and Tang, S. (2007). "A green route to prepare cellulose acetate particle from ramie fiber," *Reactive & Functional Polymers* 67, 104-112.

Matsumura, H., and Saka, S. (1992). "Cellulose triacetate prepared from low-grade wood pulp. I. Insoluble residue in acetylation solution," *Mokuzai Gakkaishi* 38, 270-276.

Regiani, A. M., Frollini, E., Marson, G. A., Arantes, G. M., and El Seoud, O. A. (1999). "Aspects of acylation of cellulose under homogeneous solution conditions," *Journal of Polymer Science, Part A: Polymer Chemistry* 37, 1357-1363.

Rodrigues Filho, G., Monteiro, D. S., Meireles, C. S., Assunção, R. M. N., Cerqueira, D. A., Barud, H. S., Ribeiro, S. J. L., and Messadeq, Y. (2008). "Synthesis and characterization of cellulose acetate produced from recycled newspaper," *Carbohydrate Polymers* 73, 74-82.

Roncero, M. B., Torres, A. L., Colom, J. F., and Vidal, T. (2005). "The effect of xylanase on lignocellulosic components during the bleaching of wood pulps," *Bioresource Technology* 96, 21-30.

Samios, E., Dart, R. K., and Dawkins, J. V. (1997). "Preparation, characterization and biodegradation studies on cellulose acetates," *Polymer* 38(12), 3045-3054.

Shaikh, H. M., Pandare, K. V., Nair, G., and Varma, A. J. (2009). "Utilization of sugarcane bagasse cellulose for producing cellulose acetates: Novel use of residual hemicellulose as plasticizer," *Carbohydrate Polymers* 76, 223-229.

Tanghe, L. J., Genung, L. B., and Mench, J. W. (1963). "Section V. Cellulose esters: Preparation, properties, reaction, and analyses: Cellulose acetate," *Method in Carbohydrate Chemistry*, R. L. Whistler, J. W. Green, J. N. Bemiller, and M. L. Wolfram (eds.), Academic Press, New York.

Ueda, K., Saka, S., Funaki, Y., and Soejima, S. (1988). "Characterization of acetone-insoluble substances in cellulose acetate as prepared by an acetylation/ripening process from wood pulps," *Mokuzai Gakkaishi* 34(4), 346-353.

Yang, Z., Xu, S., Ma, X., and Wang, S. (2008). "Characterization and acetylation behavior of bamboo pulp," *Journal of the International Academy of Wood Science* 621-632.

Zugenmaier, P. (2004). "Characterization and physical properties of cellulose acetates," Macromolecular Symposia 208, P. Rustemeyer (ed.), Wiley-VCH, Heidelberg.