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Utilization of sugarcane bagasse cellulose for producing cellulose acetates: Novel use of residual hemicellulose as plasticizer

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ABSTRACT

Sugarcane bagasse was fractionated to cellulose, hemicellulose and lignin by a proprietary steam explosion process, followed by downstream purifications, developed in our laboratory. The fractionated cellulose contained ~94% cellulose, about ~5% hemicellulose, traces of lignin (~0.2%), and ~1% ash. The cellulose was acetylated under heterogeneous conditions to obtain cellulose acetates. These were extensively characterized using FTIR, TGA, DSC, GPC, HPIC, WAXRD, and viscometry. The novel feature of this study was the utilization of the hemicellulose content (5%) of bagasse cellulose as an internal plasticizer. Through kinetic experimentation, we have demonstrated that the residual hemicellulose need not be considered as an impurity; rather it can be used in acetylated form as a plasticizer as well as a biodegradable additive for cellulose acetates made from slightly impure cellulose produced from non-wood origin. Our results therefore show how lignocellulosic agricultural wastes can be utilized to produce high value plastics.

1. Introduction

It is increasingly being realized that agricultural commodities are the key raw materials available to mankind for the sustainable production of numerous industrial and non-food consumer products such as fuels, paints, detergents, biodegradable polymers, textile fibers, fiber composites, and various other commodity and specialty chemicals. Research seeks to better understand properties of agricultural materials related to their quality, value, and processing characteristics and to develop innovative products and processes for conversion of agricultural materials to non-food products. While a question of ethics pervades the use of agricultural food materials for the production of chemicals, polymers and materials, the use of waste agricultural residues, produced in millions of tons quantities annually as waste, are not subject to these debates. Further, there is indeed a pressing need to value-add to these waste agricultural materials, as they are the most abundant source of organic raw materials available today. Even more importantly, the use of agricultural wastes is generally expected to ensure minimum carbon footprints in their utilization. Agricultural wastes are also relatively free from wide price fluctuations, and this is another major advantage of using this as a feedstock for value-added products, and justifies research and development efforts. For example, few commercial uses for the excess bagasse have been developed and its accumulation presents a waste problem for the sugar industry. The same is the case with wheat and rice straw, cereal straws, cotton stalks, etc.

One area where tremendous amount of research has been devoted pertains to the fractionation of agricultural biomass into its constituents, i.e., cellulose, hemicellulose, and lignin in what is best described as a bio-refinery. Each of these fractions can then be separately value-added by making industrially important derivatives. For example, cellulose can be converted cellulose esters, which have wide ranging applications as biodegradable plastics, textile fibers, films, etc. Extensive work has been reported in published literature on the synthesis of cellulose acetates form cotton linters and wood cellulose. In recent times, lignocellulosic agricultural materials as a source of cellulose are also being investigated with renewed vigor, considering the cost differential between the different raw materials.

Biswas, Shah, Lawton, and Willett (2006) have synthesized cellulose acetates from other agricultural residues like corn stalk, rice hulls, and wheat straws. Filho et al. (2000) have synthesized cellulose triacetate from sugarcane bagasse and reported water flux through membranes prepared from these materials. More recently, Cerqueira, Filho, and Meireles (2007) also reported the optimization of bagasse acetylation by varying acetic acid anhydride and catalyst volume and reaction and activation times. The effect of these variations on intrinsic viscosities and molecular weight of acetates have been reported. The same group reported that the lignin content of their bagasse cellulose was 3.84% (Viera et al, 2007). This level of purity is far less than the bagasse cellulose prepared by us in this work, wherein we obtained a lignin content of only

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0.2%. This low lignin content enabled us to evaluate accurately the role of residual hemicellulose present in the extracted cellulose as a plasticizer for cellulose ester films, thereby obviating the need for adding external plasticizers. Moreover, higher levels of lignin would lead to solubility problems as well as result in relatively opaque materials.

2. Experimental

2.1. Preparation of bagasse cellulose

Our laboratory has developed a proprietary process for the extraction of 94% α-cellulose from sugarcane bagasse, and the process is under patenting (Varma, 2007). This bagasse cellulose contained ~94% α-cellulose, ~5% hemicellulose, ~0.2% lignin, and ~1% ash, and was found to be suitable for the production of cellulose esters and ethers, and the process is under commercialization. A pilot plant based on this process is running successfully.

2.2. Preparation of bagasse cellulose esters

Acetylation of bagasse cellulose was conducted using a process described elsewhere (Kuo & Bogan, 1997; Ozaki, Ogawa, & Sasai, 2004). Cellulose was dried in vacuum oven (30 mm) at 60 °C for 12 h. Twenty gram of this cellulose was taken in a three neck round bottom flask fitted with an overhead stirrer. To this was added 350 ml of glacial acetic acid. After the addition of acetic acid the reaction mixture was kept at 0–5 °C for 1 h; to this was added the acetylating mixture (135 ml acetic anhydride + 0.75 g sodium bisulphate + 0.5 ml sulfuric acid) over a period of half an hour, all the time maintaining the temperature from 0 to 5 °C in an ice-water bath. After 1 h the cold water from the bath was removed and the flask allowed to come to room temperature of ~30 °C; this process took about 3 h. At this stage the reaction mixture started to become viscous. In successive experiments, the reaction was carried out for 2, 4, 6, 8, 10, and 18 h, respectively. In each case, 1 h before the completion of the reaction time, a solution of 0.5 g sodium acetate in 10 ml glacial acetic acid was added to the reaction mixture and the stirring was continued for 1 h to remove the sulfate group substituent on the cellulose molecule.

The reaction mixture was now slowly poured into ~3 L of distilled water with constant stirring. Once the precipitation process was completed the product was filtered and washed with distilled water. The washings was continued till the product was free of acetic acid smell, it was also monitored by pH measurements until neutral pH was reached. Finally, the product was washed with acetone, filtered and dried in vacuum oven (30 mm pressure) at 60 °C for 6 h.

2.3. Casting of cellulose acetate films

Films with dimensions of 200 × 200 × 0.01 mm were prepared as follows:

5.75 gm of cellulose acetate (CA) was dissolved in 200 ml chloroform. This solution was stirred for 4–5 h, then filtered to remove any insoluble matter. A glass tray with dimensions of 21 × 21 cm was used for making the films. The tray was cleaned thoroughly, dried and kept in the oven set at 40 °C. The level of the tray was adjusted using leveling screws. The CA solution was slowly poured into the tray from one corner of the tray. The oven was closed and left undisturbed at 40 °C for 8 h. The film was exposed to 75 °C for 1 h. The thickness of the film was measured using a micrometer. Plasticized films of CA were made by adding 15 phr (i.e. parts per hundred of resin) of plasticizer (equal mixture of diethyl phthalate and triphenyl phosphate) during the dissolution stage. The thickness of the films was ~0.01–0.012 mm.

2.4. Methods

2.4.1. Determination of degree of substitution (DS) according to (ASTM D 871-96)

0.5 g of cellulose acetate samples were weighed accurately and transferred to a 250 ml flask; to each sample 20 ml of 75% aqueous ethanol was added and then heated for 30 min at 60 °C. Then 20 ml of 0.49 N NaOH solution was added to each sample and again heated at 60 °C for 15 ml/min. The same procedure was also done for a control system (not containing CA). The flasks were stoppered and allowed to stand at room temperature for 72 h.

The excess alkali in the sample and control was titrated with HCl (0.5 N) using phenolphthalein as indicator. An excess of acid was added (1 ml) and the alkali was allowed to diffuse from the regenerated cellulose overnight. The disappearance of the pink color indicated complete neutralization of the alkali. The small excess of acid was then back titrated with sodium hydroxide to a phenolphthalein end-point (i.e. until the solution had acquired faint pink color).

2.4.2. FTIR

A Perkin Elmer Spectrum 1 instrument was used. Spectra of CA in chloroform were recorded using KBr windows. Cellulose IR were recorded in KBr.

2.4.3. Thermogravimetry (TGA)

Thermal stability of CA was studied using TGA (Perkin Elmer TGA 7) with a heating rate of 10 °C/min under nitrogen atmosphere.

2.4.4. Differential scanning calorimeter (DSC)

TA instruments DSC Model Q100 was used for measurement of glass transition temperatures. 3–4 mg of the sample was crimped in aluminum pan and loaded along with reference pan without sample. The heating rate was 10 °/min, and heating was carried out up to 300 °C.

2.4.5. Gel permeation chromatography (GPC)

GPC studies were carried out using a Dionex GPC with RI detector, at room temperature. Shodex KF 803, 804, and 805 columns were used with HPLC grade chloroform as an eluent. The flow rate was 1 ml/min. A polystyrene calibration curve (20 samples of weight average molecular weights from 164 to 1.5 million) was used to estimate the molecular weights and polydispersity of CA samples. Sample preparation: 15–20 mg of CA was dissolved in 5 ml of Chloroform and 20 uL was injected.

2.4.6. Wide-angle X-ray crystallography (WAXRD)

WAXRD experiments were carried out with the sample in film form having a thickness of ~0.01 mm using a Rigaku, Japan, WAXRD instrument. The scanning speed was 4°/min, with a radiation of CuK-α. The samples were scanned from 2θ values of 5–40°.

2.4.7. High pressure ion chromatography (HPIC)

Dionex HPIC consisting of quaternary gradient pump, electrochemical detector and chromeleon software was used for the detection of carbohydrates detached from cellulose during the course of acetylation. A Dionex Carbopac PA 10 column was used for this purpose. The eluent used was 20 mM NaOH solution.

2.4.8. Viscosity measurements

Dilute solution viscosities were measured in 1% (w/v) solution of CA in dimethyl sulfoxide (DMSO) and chloroform using an Ubbelohde capillary viscometer at room temperature.

2.4.9. Mechanical properties

Tensile strength and modulus were determined on an Instron UTM instrument. The procedure of ASTM D 882-95a was used for this purpose. The load cell used was 1 KN with 5-mm/min crosshead speed. The test specimens were prepared from 100 µm thick film by cutting the films with a sharp knife. The dimensions were 150 mm length and 20 mm width.

3. Results and discussion

The properties of the cellulose acetates synthesized under the same reaction conditions but with different reaction times (2–18 h) are shown in Table 1. After 2 h the reaction product was still insoluble in anhydrous DMSO, and its DS was not measured. After 4 h reaction time, the product was soluble in DMSO and its DS was found to be 2.65, reaching the maximum value of 3.0 after 6 h. Thereafter, as the reaction time increased, the DS was found to be steady in the range of 2.8–2.9. Apparently, an equilibrium stage is reached. The intrinsic viscosities are seen to decrease as the reaction time increases, due to chain degradation under the acidic conditions.

Saka and Takanashi (1998) reported that the presence of hemicellulose in cellulose acetate gives false viscosity and turbidity to the solution. However, our 4 and 6 h samples show no turbidity in solution even though they contain hemicellulose acetate.

Fig. 1 shows FTIR spectra of various CA samples. All the samples show similar spectral features. The FTIR shows the reduction of OH frequency and appearance of C=O band at 1747 cm^{-1} (Heinze & Liebert, 2004; Rajini, Venkateswarlu, Rose, & Sastry, 2001). Complete disappearance of the OH peak is not seen even for the sample with DS 3.0, perhaps due to adhering moisture. The absence of band at 1760–1840 cm^{-1} and 1700 cm^{-1} confirms the absence of acetic acid and acetic anhydride.

Fig. 2 shows the DSC scans of various CA samples. The endotherm around 100 °C is attributed to evaporation of water. The 4 and 6 h samples have two endotherms at 215 and 285 °C, which could be due to outflow of xylan acetate present in these samples. The endotherm at 285 °C in 4 and 6 h could be due to the triacetate fusion process which has shifted to lower temperature (Filho et al., 2000; Saka & Ohmae, 1996). The intensity of this transition gets reduced with increased reaction time, since these endotherms are not seen in the DSC scans of 8–18 h samples, which is due to the removal of xylan acetate during the course of the reaction reaction. This was confirmed by HPIC studies (see later discussion).

The 8–18 h CA samples shows an exotherm around 200 °C. In previous studies this exotherm was attributed to crystallization of a fraction of the CA during the scan (Filho et al., 2000). This exotherm is absent in the 4 and 6 h samples. The 8–18 h reaction time samples show an endotherm above 290 °C. This endotherm resembles the previously reported data (Filho et al., 2000; Zugenmaier, 2004), indicating that crystallanity increases with reaction time

Table 1
Properties of various cellulose acetates synthesized in the laboratory

CA Sample	DS	Intrinsic viscosity dl/gm[*]	MW	Mn	Mw/Mn	Tg °C	Peak Temp °C	TS (MPa) (Avg of 5 specimen)	TM (MPa) (Avg of 5 specimen)
CA 18 h	2.9	2.3	215804	125601	1.71	148	378	Could not be tested	
CA 10 h	2.8	2.5	191494	106497	1.8	136	383	Could not be tested	
CA 8 h	2.8	2.6	195165	68611	2.84	156	372	Could not be tested	
CA 6 h	3.0	2.8	164532	77768	2.11	139	367	40	2791
CA 4 h	2.6	3.1	129849	17066	7.62	146	365	61	2913
CA 2 h	–	Insoluble	–	–	–	–	–	–	–

[*] Polymer dissolved in DMSO and measurements carried out at 3 °C.

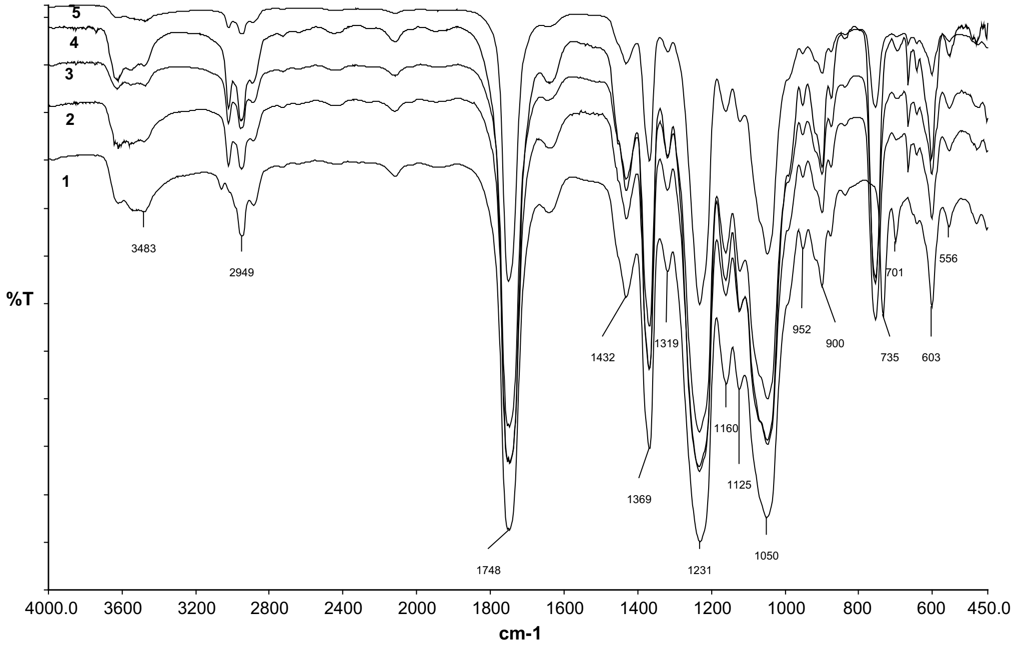

Fig. 1. FTIR of various cellulose acetate samples (1) 4 h reaction, (2) 6 h reaction, (3) 8 h reaction, (4) 10 h reaction, (5) 18 h reaction.

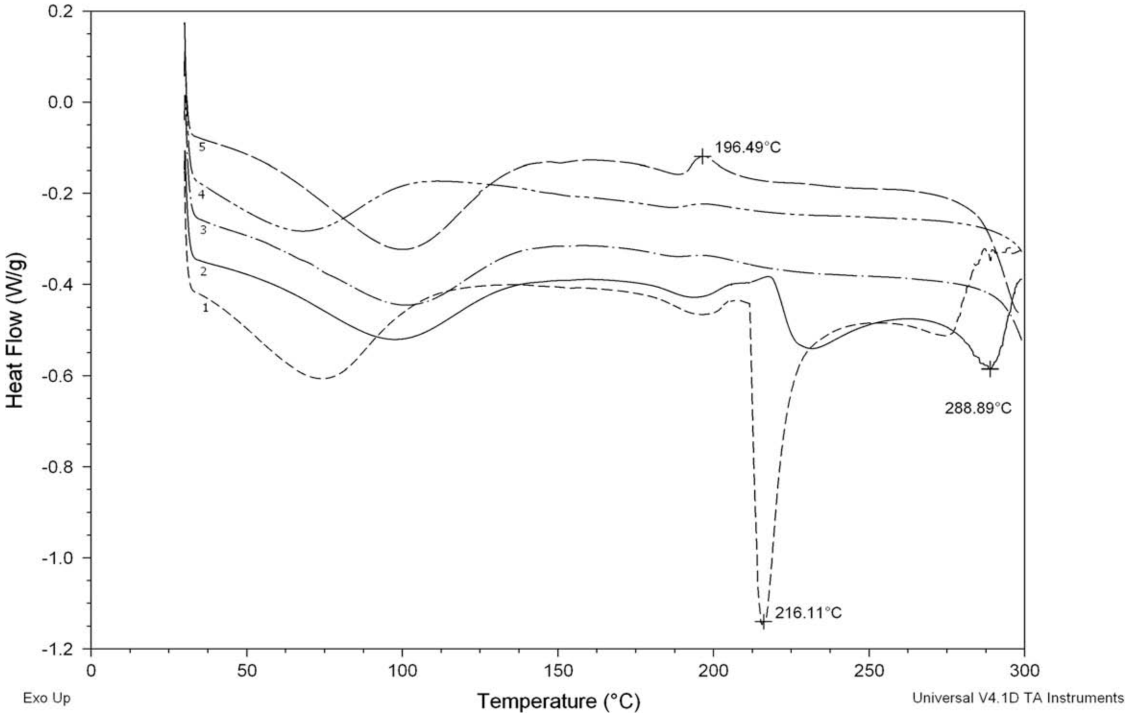

Fig. 2. DSC of cellulose acetate Samples: (1) 4 h Reaction, (2) 6 h reaction, (3) 8 h reaction (4) 10 h reaction, (5) 18 h reaction time.

at 300 °C. This clearly shows the effect of reaction time on the thermal properties of cellulose acetates. The change in crystalline nature of the samples exposed to long durations (48 h), as reported by Filho et al. (2000), Filho et al. (2008), has thus been confirmed by our observations. We have obtained the same product in 8–18 h as compared to 48 h reported by Filho et al. (2000), by our synthetic procedure.

3.1. TG analysis

Fig. 3 shows the TGA curves of various CA samples prepared in our laboratory.

The thermal degradation of cellulose esters is known to take place in various steps such as removal of water and solvents (between 50 and 150 °C), deacetylation at 320 °C and thermal pyrolysis of the cellulose skeleton at 370 °C (Huang & Li, 1998). The thermal stability of CA increases with acetylation reaction time and reaches a maximum at 8 h reaction time. The thermal stability also depends on molecular weight and crystallinity of the polymer. Generally, lower the molecular weight or lower the crystallinity, the easier the degradation of the polymer. We also have observed a similar pattern in our samples.

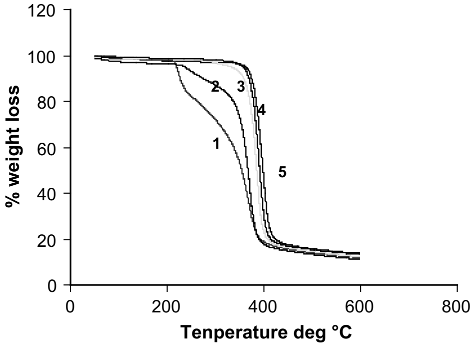

Fig. 3. TGA curves of various cellulose acetate: (1) 4 h, (2) 6 h, (3) 8 h, (4) 10 h, (5) 18 h, reaction time.

The 4 h samples show two weight loss regions, one at 221 °C and the other at 365 °C, The first one at 221 °C diminishes with time of acetylation and completely disappears after 8 h. This transition could be due to the xylan acetate degradation (Saka & Ohmae, 1996). This means higher the content of hemicellulose in the pulp lower will be the thermal stability of the CA (Abou-State Amine, Fahmy, and Safy El-Din, 1984). This transition disappears when the reaction times are increased, which is due to removal of the hemicellulose acetate due to hydrolysis and dissolution during the reaction workup. The onset temperatures of 4 and 6 h show two onset of degradation temperatures due to the presence of acetylated cellulose and acetylated hemicellulose, while the 10 and 18 h samples show a single onset of degradation temperature (as only cellulose acetate is present). This was further confirmed by the mechanical property measurements (see later discussions on mechanical properties).

3.2. Gel permeation chromatography and high pressure ion chromatography

As indicated in Table 1 the MWD of the samples decreased with acetylation reaction time. This may be due to the detachment of xylan acetate from the molecule during the reaction. This is also reflected in the thermogravimetric analysis at 221 °C, which is the appearance of xylan diacetate peak (Saka & Takanashi, 1998). The elution time for these samples is between 18 and 29 min. The samples having higher MWD values show a greater fraction of low molecular weight product. With increased reaction time (8–18 h) the xylan acetate fraction gets detached from the cellulose and washed away during reaction work up, as explained earlier. This was also confirmed by High-pressure ion chromatography. The acetylation mixture of two reactions (6 and 18 h) was precipitated in 500 ml of water, 10 ml filtrate was diluted to 100 ml and injected into the HPIC column. The remaining filtrate was extracted with chloroform and concentrated to get dry solid. Fig. 4 shows

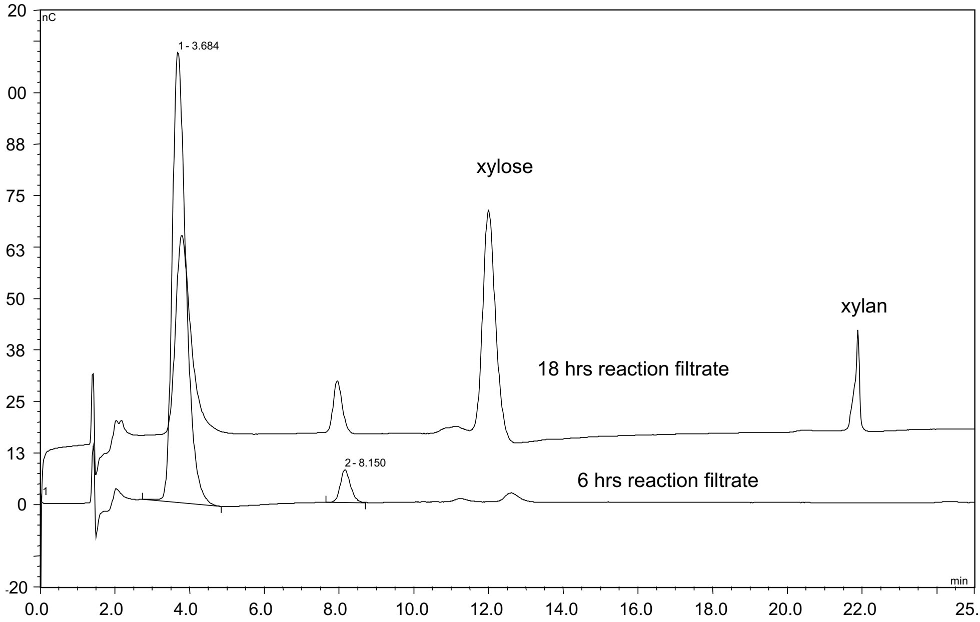

Fig. 4. HPIC chromatograph of the filtrate, showing the presence of xylose and xylan: Top: 18 h reaction and bottom: 6 h reaction.

the HPIC graphs of the two filtrates. It can be seen from the HPIC that the 6 h sample shows a very small amount of xylose and no detection of xylan, while the 18 h filtrate shows considerable amount of xylose and also xylan.

Tanghe, Rebel, and Brewer (1970) reported the presence of a pre-hump attributed to the xylan acetate and showed the separation of this pre-hump; however, in our samples we did not observe the pre-hump, instead we observed a broad molecular weight distribution which narrowed down when the acetylation time was increased. The GPC curve of the samples reacted for more than 8 h showed lowest the MWD. This means during the acetylation reaction after 8 h the hemicellulose is almost completely removed during the workup. It is seen from Fig. 5 that the FTIR spectrum of the chloroform extracted solids from the reaction workup filtrate are very similar to the FTIR spectra of pure xylan acetate, thus confirming the xylan acetate separation during reaction.

3.3. X ray diffraction study

The XRD study of the heterogeneous acetylation reaction of cellulose studied by Doyle and Pethrick (1987) indicated the presence of crystallinity in the triacetate. The changes in structure at various levels of organization, which occur during acetylation of cellulose linters using heterogeneous conditions, have been reported in their paper.

We also found changes in the crystalline nature of CA's of different reaction times. Fig. 6 and 7 show the WAXRD of CA samples. Filho et al. (2000) has reported a 2θ of ~20. However, all our CA

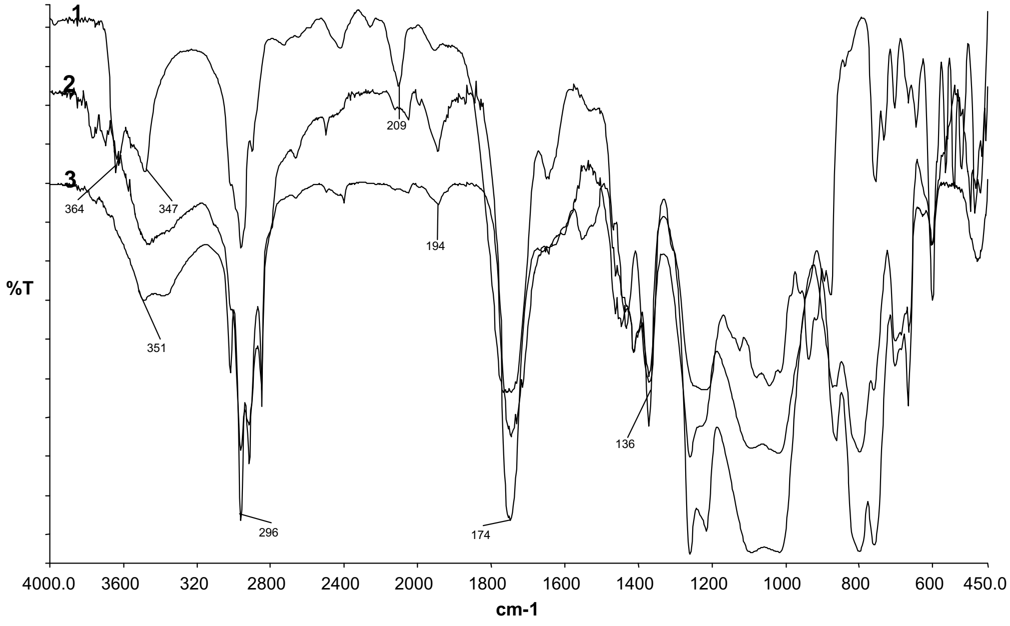

Fig. 5. FTIR of the (1) Xylose acetate, (2) 6 h reaction filtrate, (3) 18 h reaction filtrate.

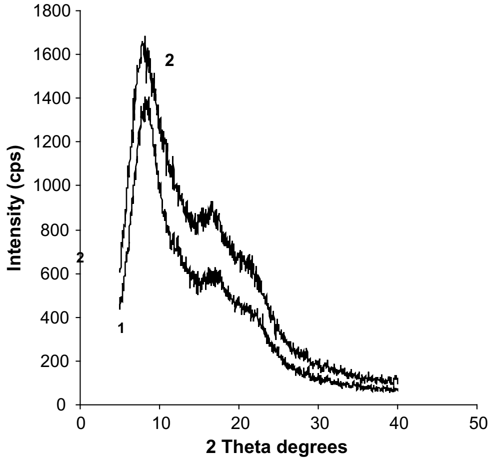

Fig. 6. XRD curves of cellulose acetate: (1) 4 h reaction and (2) 6 h reaction.

samples show a strong intensity peak at 2θ of 8.2°, and other weak diffractions at 2θ of 11.9, 16.8, and 21.5. These values correspond to the structure of cellulose triacetate (Kono, Numata, Nagai, Erata, & Takai, 1999). Fig. 6 indicates clearly that 4 and 6 h samples have very similar crystallinity. However, 8, 10, and 18 h sample also have similar crystallinity and are brittle in nature (Fig. 7).

3.4. Mechanical characterization

The tensile properties of CA films were measured (ASTM D 882-95a) on 0.010–0.012 mm thick film. Five specimen of each sample were tested. Table 1 shows the tensile strength and modulus of various CA samples. The 8–18 h samples could not be cut into notch free specimens, hence they could not be tested without plasticizer. These samples showed tensile strength of 14 MPa after addition of 15% plasticizer (equal mixture of diethyl phthalate and triphenyl phosphate). The 4 and 6 h samples have good tensile properties without addition of external plasticizer. The tensile strength of these samples is three to four times higher than 8–18 h samples in which the hemicellulose content is absent. This confirms the presence of hemicellulose acetate in the 4 and 6 h samples of CA, which is shown to function like a plasticizer.

Tensile strengths of commercial CA films is about 100–140 MPa (Peter Zugenmaier, 2004) which are higher than our values. This can be due to the different origin of cellulose, its molecular weight, and purity, in addition to different methods of film preparation. Thus, we conclude that the higher strength CA materials have less thermal stability due to the presence of xylan acetate, however, these xylan acetates are responsible for better mechanical properties as they function as plasticizers. Thus, it stands proved by careful analysis of CA reaction products (DSC, TGA, and mechanical properties) as well as analysis of washings from the CA reaction product (FTIR and HPIC) that only the CA sample obtained from 4 and 6 h reaction times contained hemicellulose acetate, while the CA products with reaction times greater than 6 h resulted in the detachment of the hemicellulose acetate and its loss in the washings.

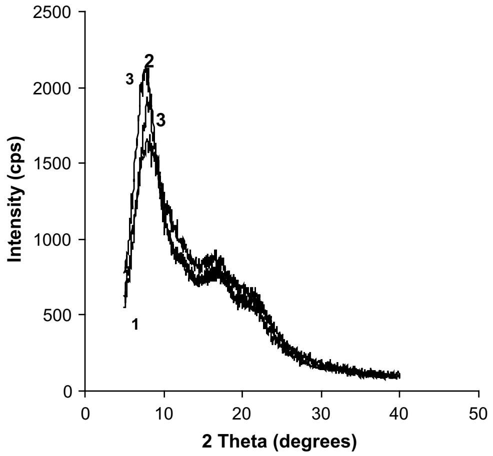

Fig. 7. XRD curves of cellulose acetate: (1) 8 h, (2) 10 h and (3) 18 h reaction.

4. Conclusions

From the above studies, we conclude that cellulose acetate reaches a DS of 3 in 6 h of acetylation time by the synthetic procedure reported in this paper. Increased reaction time improves the solubility in chloroform, due to removal of xylan acetate from the triacetate. This was confirmed by HPIC analysis, DSC, TGA and GPC and intrinsic viscosity. However, films made from these higher reaction time samples (samples with 8 h and above reaction time) could not be tested for mechanical properties as they could not give notch free specimen. For the 4 and 6 h samples of CA, the xylan acetate is not fully removed. This residual xylan acetate functioned as a plasticizer for the CA samples; therefore they exhibited good mechanical properties without addition of external plasticizer. Xylan acetate is also a biodegradable material, so this can be an added advantage of this plasticizer.

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