

## Deinked and Acetylated Fiber of Newspapers

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**ABSTRACT:** Recently, the incorporation of lignocellulosic materials as reinforcing agents or as fillers in polymer composites has received an increased attention. Although natural fibers have a number of advantages over glass fibers, the strong polar character of their surface is a limiting factor, as compatibility with strongly apolar thermoplastic matrices is very low. Such problems of incompatibility may be overcome with fiber pretreatments, which can enhance compatibility, albeit having a negative impact on the economics. In this study, the newspaper is deinked and acetylated. The effect of esterification between the acetyl groups and the hydroxyl groups of the fiber was examined by Fourier transform infrared. X-ray diffraction and scanning electron microscopy were used to characterize the crystallinity and the surface morphology of the untreated deinked and acetylated fibers (newspaper). The thermal stability of deinked and acetylated fibers was slightly decreased. It was also shown that the deinking increased the crystallinity of newspaper fibers while acetylating decreased this crystallinity. Cellulose acetate is one of the most important cellulose derivatives and its main applications are its use in composites. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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### INTRODUCTION

In recent years, the incorporation of lignocellulosic materials as reinforcing agents or as fillers in polymer composites has received an increased attention. Lignocellulosic materials exhibit a number of attractive features including low density, low requirements on processing equipment, no abrasion during processing, abundance, and certainly biodegradability.<sup>1</sup>

The main advantage of lignocellulosic materials upon mineral fillers is their environmental friendliness. In general, polymer waste is disposed in large landfills causing serious problems on the environment, while biodegradable materials are envisaged to be an excellent alternative to tackle this problem, by reducing the waste volume. Hence, for these reasons it has not been surprising that the use of lignocellulosic materials in the production of composites has gained significant importance both in technical applications such as in automotive industry,<sup>2</sup> as well as in the packaging industry.

The main disadvantage encountered during the incorporation of natural lignocellulosic materials into polymers is the lack of good interfacial adhesion between the two components, which results in poor properties of the final material.<sup>3</sup> The polar

hydroxyl groups on the surface of the lignocellulosic materials have difficulty in forming a well-bonded interface with a non-polar matrix, as the hydrogen bonds tend to prevent the wetting of the filler surfaces.

Furthermore, the incorporation of lignocellulosic materials in a synthetic polymer is often associated with agglomeration because of insufficient dispersion, caused by the tendency of the fillers to form also hydrogen bonds with each other. This incompatibility leads to poor mechanical properties and high water absorption. Thus, to develop composites with good properties, it is necessary to improve the interface between the matrix and the lignocellulosic material. There are various methods for promoting interfacial adhesion in systems where lignocellulosic materials are used as fillers, such as esterification,<sup>4–10</sup> silane treatment,<sup>11,12</sup> graft copolymerization,<sup>13</sup> use of compatibilizers,<sup>14</sup> and treatment with other chemicals.<sup>15–17</sup> These methods are usually based on the use of reagents, which contain functional groups that are capable of bonding to the hydroxyl groups of the lignocellulosic material, while maintaining good compatibility with the matrix. Interfacial compatibilization improves the stress transfer between the two components and leads to the improvement of mechanical and physical properties of the

produced composites. However, the use of surface treatments has the disadvantage of increasing the cost of the final product. Esterification by means of acetylation is the chemical modification procedure, which has been studied the most.<sup>4–10</sup> In contrast, for deinked fibers, there are a limited number of studies.<sup>18,19</sup> Chemical modification with acetic anhydride, substitute the cell wall hydroxyl groups with acetyl groups (AG), rendering the surface more hydrophobic, and thus, more compatible to the polymer matrix.

The aim of this work was to study the deinking and effect of anhydride treatment on lignocellulosic (newspaper) materials, to produce biodegradable composites. In particular, the acetylation of old newspaper (ONP) and its effect on properties like the thermal stability, crystallinity, and surface morphology was investigated.

## EXPERIMENTAL

### Materials

**Newspaper.** ONPs were used as reinforcement for the preparation of matrix composites. The treatments applied on the fibers are reported, together with the indication of the relative letter associated to the series: Dienked newspaper (DNP), acetylated newspaper (ANP), and industrial cellulose (IC).

### Fibers Treatment

#### Deinked Newspaper

**Principle of deinking.** For DNP, it is necessary at first to remove the ink particles. Chemicals used in deinking newspaper are:

- Sodium hydroxide (NaOH) is used to improve detachment of the ink by raising the pH and by swelling the fibers;
- Surfactant (soap) used to unhook and stabilize the ink particles in solution, and prevents them from being redeposit on the fibers;
- Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is used to maintain a level of brightness of the pulp. It tends to yellow due to the action of sodium hydroxide on the lignin.

The ONP were cut into small pieces and added to an aqueous solution, at a concentration of 2% w/w. The chemicals used for the preparation of the aqueous solution and their addition rates, expressed on an oven dry paper weight basis, were the following: 2% w/w NaOH, 1% w/w H<sub>2</sub>O<sub>2</sub>, and 0.6% w/w surfactant agent. Impregnation of ONP lasted 180 min at constant temperature of 45°C. In the second step, the fibers were washed with distilled water until a neutral solution (pH = 7) was obtained. Finally, the fibers were dried at room temperature.

#### Acetylated Newspaper

Initially 10 g of sample (deinked newspaper) was placed in a round bottom flask with 250 mL acetic acid. The reaction was performed in a thermostatic bath at 35°C for 45 min under mechanical stirring. After that, 24 mL of acetic acid was added with 0.1 mL of concentrated H<sub>2</sub>SO<sub>4</sub> and the bath was maintained for more 1 h. After this step, the mixture was cooled at 18°C for slow addition of anhydride acetic (40 mL) with 0.6 mL concentrated H<sub>2</sub>SO<sub>4</sub> during 3 h under constant stirring. Temperature of 18°C was maintained for more 15 min and later

than, was slowly increased to 50–55°C to finalize the esterification process.

Then, this mixture was vacuum filtered to remove undissolved particles and water was added to the filtrate to stop the reaction and precipitate cellulose acetate (CA), which was filtered, washed with distilled water to remove acetic acid and dried at 70°C for 2 h.<sup>8</sup>

The degree of substitution (DS) of the produced materials was determined by a saponification reaction (Rodrigues Filho et al.<sup>20</sup>).

### Fiber Characterization

**Determination of the DS.** The DS of the material was determined to characterize it as CA. DS is the average value of AG, which replace the hydroxyl groups in the glucosidic units. DS was determined through a saponification reaction, as follows: 5.00 mL NaOH (0.25 mol L<sup>-1</sup>) and 5.00 mL ethanol were added to about 0.1 g CA, then, this mixture was left to stand for 24 h. After that, 10.00 mL HCl (0.25 mol L<sup>-1</sup>) was added to the system, which was left to stand for 30 min. Next, the mixture was titrated using a standard 0.25 mol L<sup>-1</sup> NaOH solution, using phenolphthalein as indicator. This procedure was repeated in triplicate.

$$\%AG = \frac{[(Vb_i + Vb_t)\mu_b - V_a]43 \cdot 100}{m_{ca}} \quad (1)$$

Equation (1) was used in order to determine the percentage of AG. Where %AG = percentage of AG; Vb<sub>i</sub> = NaOH volume added to the system; Vb<sub>t</sub> = NaOH volume spent in titration; μ<sub>b</sub> = NaOH concentration; V<sub>a</sub> = HCl volume added to the system; μ<sub>a</sub> = HCl concentration; 43 = molar weight of the AG; m<sub>ca</sub> = weight of CA sample. The acetyl content (AG%) was used to calculate the DS according to the following equation:

$$DS = \frac{(162.1AG)}{43.100 - (43 - 1).AG} \quad (2)$$

where 162 is the molecular weight of anhydroglucose unit, 43 is the formular weight of AG, and 1 is the atomic mass of hydrogen.

### Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectra were recorded using a SHIMADZU FTIR-8400S spectrophotometer with a resolution of 4 cm<sup>-1</sup>. Samples were finely ground and mixed with potassium bromide, KBr. The mixture was then compressed into pellet form. FTIR spectral analysis was performed within the wave number range of 400–4000 cm<sup>-1</sup>.

### Thermogravimetric Analysis

Thermogravimetric analysis (ATG) was performed to determine weight loss as a function of temperature. A sample of initial mass of 15–20 mg was introduced into a platinum crucible; the sample mass (ATG) variation was then measured as a function of temperature (or time), and the rates of mass loss (DTG) were determined by using a thermobalance under an inert nitrogen atmosphere up to 900°C, at a heating rate of 10°C min<sup>-1</sup>.

### Scanning Electron Microscopy

The effect of modification upon the fibers surface was examined using FEI CONTA 200 electron microscope. Prior to the analysis, the samples were coated with graphite (layer thickness = 20 nm) to avoid sample charging under the electron beam.

### X-Ray Diffraction

To assess the influence of the treatments on fibers crystallinity, X-ray diffraction (XRD) analysis was applied. A Siemens diffractometer, employing Cu-K ( $\lambda = 1.54059 \text{ \AA}$ ) radiation was used. The crystallinity index (CrI) of the fibers was calculated according to the Segal empirical method as follows (Tserki et al.<sup>5</sup>):

$$\text{CrI}(\%) = (I_{002} - I_{\text{am}})/I_{002} \times 100$$

where  $I_{002}$  is the maximum intensity of the 002 lattice diffraction of the cellulose crystallographic form (I) at  $2\theta = 22^\circ$  and  $I_{\text{am}}$  is the intensity of diffraction of the amorphous material at  $2\theta = 18^\circ$ .

## RESULTS AND DISCUSSION

### Determination of the DS

The rate of AG, calculated from the average of three trials is 22.58%, slightly lower than that found by G. Rodrigues Filho et al.,<sup>20</sup> which is 31.9%, their study involves the recycling of newspapers in the form of CA.

In this study, we founded the DS = 1.10 for CAs. The DS of cellulose is the average number of hydroxyl groups that may be substituted on the glycosidic rings, and may take any value from 0 (cellulose) to 3 (completely substituted cellulose). DS affects various characteristics, such as the polymer crystallinity and solubility in different solvents. For example, pure cellulose (DS = 0) is insoluble in most common solvents, but upon increasing the DS of cellulose through formation of acetate esters or other derivatives, the solubilities in different types of solvents change.

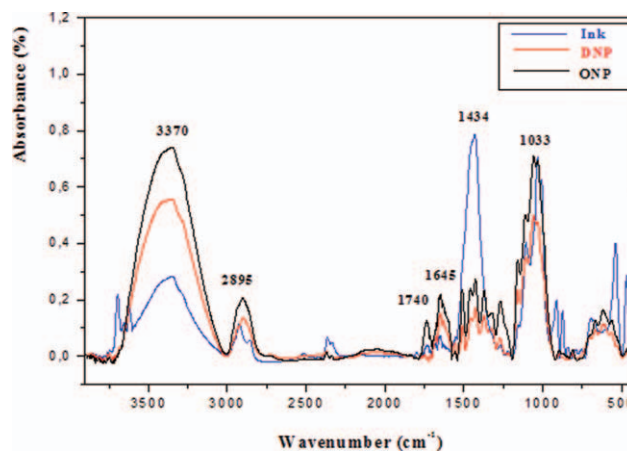
Thus, for microcrystalline cellulose, a DS close to 3.0 is already obtained in a short time reaction, while for newspaper cellulose the same DS was obtained after a long time.

### FTIR Analysis

**Deinked Fibers.** Figure 1 shows the FTIR spectra of the ink, newspaper before, and that after the deinking of the newspaper. From this figure, we see the characteristic band of hydroxyl groups of the newspaper fibers between  $3600$  and  $3200 \text{ cm}^{-1}$  and the area of this peak is more intense for ONP fibers. This is assigned to the decrease in the concentration of hydroxyl groups after deinking because the ink has an absorption band at  $3373 \text{ cm}^{-1}$ . This result is similar to that found by Ferrer and Vila<sup>21</sup> and after deinking, there is a reduction in the amount of lignin and hemicelluloses.

The decrease in the intensity of several bands showed that deinking eliminates an amount of lignin: at  $1740 \text{ cm}^{-1}$ , which can be assigned to the C=O of lignin, and at  $1520 \text{ cm}^{-1}$ , which can be attributed to C—C aromatic rings.

This result is consistent with the work of Carla da Silva Meireles et al.<sup>22</sup> and Tejado et al.<sup>23</sup> who found that the same bands



**Figure 1.** ATR-FTIR spectra of old, deinked fiber of newspapers and ink. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

( $1728$ ,  $1515$ , and  $1278 \text{ cm}^{-1}$ ) undergo a decrease in intensity after treatment with NaOH, lower intensities of the bands at  $1033$  and  $1060 \text{ cm}^{-1}$  that match the vibration of deformation C—O—C bonds of the cellulose and hemicellulose. Fávoro et al.<sup>24</sup> observed the disappearance of the bands at  $1730$  and  $1245 \text{ cm}^{-1}$ , attributed to vibrations group C=O and C—O, respectively, after the process of mercerization of sisal fibers, these groups are present in the structures of lignin and hemicellulose. We also observe the decrease of the band at  $1434 \text{ cm}^{-1}$ , which can be assigned to CH<sub>2</sub>OH group in ink, Senvaitiene et al.<sup>25</sup> noted the presence of a band between  $1380$  and  $1450 \text{ cm}^{-1}$  in the FTIR spectrum of the ink, which was attributed to CH<sub>2</sub>OH groups.

### Esterified Fibers

The assignments of the main infrared bonds for lignocellulosic materials are listed in Tables I and II. As seen in Figure 2, the treatment of newspaper fibers with acetic anhydride increased the absorbance in the regions  $1735$ – $1752 \text{ cm}^{-1}$  and  $1183$ – $1244 \text{ cm}^{-1}$ .<sup>24,26</sup> The absorbance in the region  $1735$ – $1752 \text{ cm}^{-1}$  is due to the esterification of the hydroxyl groups resulting in increased stretching vibration of the carbonyl (C=O) group. The band in the spectrum of untreated fiber near  $1740 \text{ cm}^{-1}$  is assigned primarily to the C=O stretching vibration of the carboxyl and AG in the “xylan” component of hemicelluloses and also to chemical groups of lignin. The appearance of the peak at around  $1740 \text{ cm}^{-1}$  for the treated fibers proves that AG is involved in an ester bond with the hydroxyl groups of the fibers. If the AG were in the form of acetic acid, then the stretching of C=O should have appeared below  $1720 \text{ cm}^{-1}$  in the case of dimers and about  $1760 \text{ cm}^{-1}$  in the case of monomers. In addition, due to the high reactivity of acetic anhydride it is almost unlikely that AG exist in this form. The esterification reaction is also confirmed by the absorbance observed at  $1183$ – $1244 \text{ cm}^{-1}$  (C—O stretching).

The strong absorption between  $3400$  and  $3600 \text{ cm}^{-1}$  in all FTIR spectra is caused by the OH groups, as hydroxyl substitution is not high enough and these bands are always present. Rodrigues

**Table I.** Infrared Band Assignments for Lignocellulosic Materials

Wavenumber (cm <sup>-1</sup> )	Assignment
3200–3600	O–H stretching
2920	C–H and CH <sub>2</sub> stretching
1739	C=O stretching of carboxylic ester
1600–1650	1600–1650 H–O–H bending of absorbed water
1510	Benzene ring vibrations
1440–1460	C–H deformation (asymmetric) and aromatic skeletal vibrations
1375	C–H in-plane deformation (symmetric) for polysaccharides
1235–1270	C–O stretching
1168	C–O–C antisymmetric bridge stretching
1039	C–O stretching in cellulose and hemicelluloses
600	Out of plane OH bending

Filho et al.<sup>20</sup> made a chemical modification of newspapers fibers with acetic anhydride; they also found that the same absorption bands appear after acetylation. Luz et al.<sup>8</sup> worked on the chemical modification of cellulose fibers and cellulignin with acetic anhydride. The FTIR analysis confirmed the acetylation on the appearance of absorption bands at 1758 cm<sup>-1</sup>, 1380 and 1240 cm<sup>-1</sup>, which correspond to the groups (C=O) (C–CH<sub>3</sub>) and (C–O–C), respectively. The infrared spectra confirm the presence of AG, due to the absorption bands at 1752 cm<sup>-1</sup> (C=O), 1375 cm<sup>-1</sup> (–C–CH<sub>3</sub>), and 1244 cm<sup>-1</sup> (C–O).

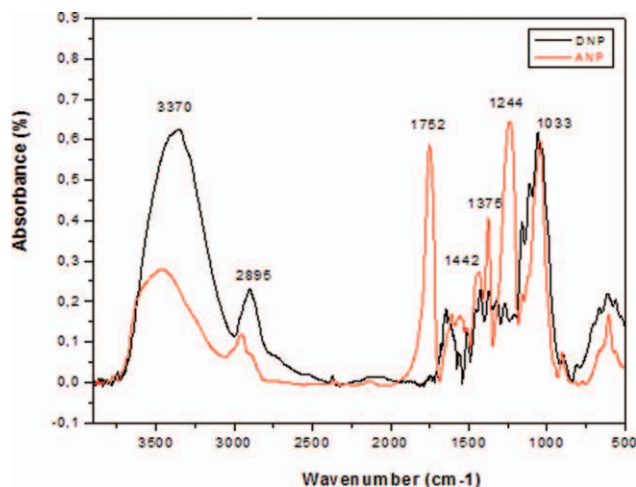
### X-ray Diffraction

Only the crystal polymorph I of cellulose was present in both untreated and esterified fibers, as it is usual for native cellulose. The XRD patterns of crude, deinked, esterified newspaper, and industrial cellulose fibers are given in Figure 3. As seen the patterns of IC fibers exhibit four well-defined peaks at 15.0, 16.49, 22.37, and 34.40 2θ. The 15.0 and 16.49 reflections correspond to the (1–10) and (110) crystallographic planes, respectively. The other two peaks at 22.37 and 34.40 correspond to the (200), and (023) or (004) planes, respectively.<sup>5</sup> When the cellulose content is high, as in the case of IC fibers, then at around 16° one may observe two peaks, but when the fiber contain high amounts of amorphous materials such as lignin, hemicelluloses, and amorphous cellulose, like the wood fibers, these two peaks are smeared, thus appearing as one broad peak.

The effect of chemical modification of lignocellulosic materials on their crystallinity has been investigated by various researchers. Shiraishi et al.<sup>27</sup> reported that esterification of cellulose with

**Table II.** Crystallinity Index of Different Fibers (ONP, DNP, ANP, and IC)

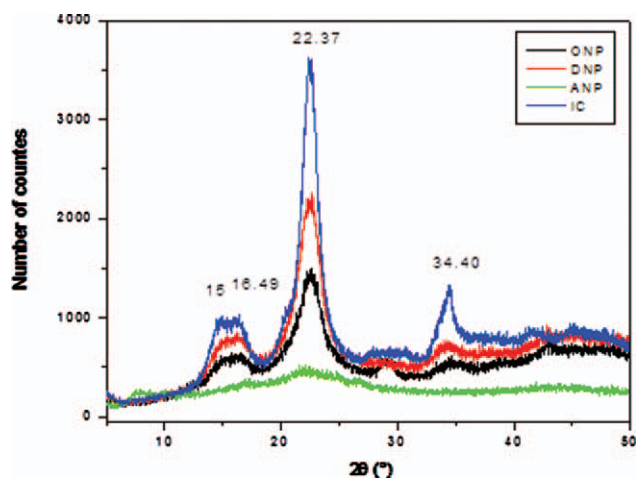
Fiber	ONP	DNP	ANP	IC
Crystallinity (%)	65	73	23	84.5



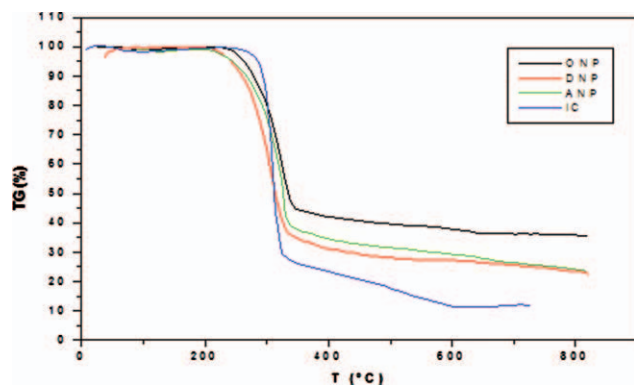
**Figure 2.** ATR-FTIR spectra of untreated and treated fibers of newspapers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

different chemical reagents takes place in the amorphous regions and proceeds at two different rates (rate of diffusion and rate of chemical reaction). The reagent first reacts with the chain ends on the surface of the crystallites, as it cannot diffuse into the crystalline region, resulting in the opening of some of the hydrogen-bonded cellulose chains. This procedure has as a result some new amorphous cellulose to be formed. The reagent then diffuses into this newly produced amorphous section, reacting with the cellulose and simultaneously generating more amorphous cellulose. These steps take place concurrently and depend on each other.

The crystallinity index was calculated according to the Segal empirical method described in the Experimental Section and the results are presented in Table II. As seen in Table II, the crystallinity index of the IC fibers is higher than other fibers.



**Figure 3.** XRD patterns of old, deinked, acetylated, and cellulose fibers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



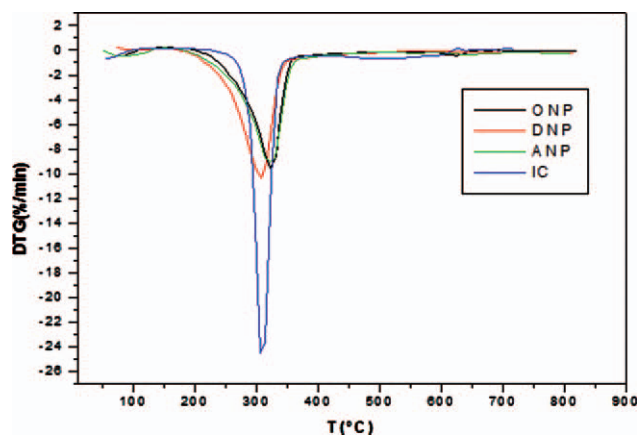
**Figure 4.** ATG thermograms of the different fibers (ONP, DNP, ANP, and IC). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Acetylated fibers decreased the crystallinity of newspaper fibers, several researchers<sup>28–32</sup> showed that the treatment of fiber with anhydride led to a reduction of crystallinity. However, Zafeiropoulos et al.<sup>33</sup> reported that acetylation increased the crystallinity of flax fibers, possibly due to an increased removal of the fiber amorphous constituents during the treatment.

Deinking increased crystallinity of newspaper fibers. Ghali et al.,<sup>34</sup> Islam et al.,<sup>35</sup> and Liu and Dai<sup>36</sup> found that treatment of the fiber with NaOH, leads to increased crystallinity. However, Beatriz A.P. Ass et al.<sup>37</sup> found that treatment of sisal fiber with NaOH led to the reduction of crystallinity.

### Thermogravimetric Analysis

The thermal stability of lignocellulosic materials used as filler or reinforcement in polymer matrix composites is of paramount importance. The manufacturing of composites requires the mixing of fibers/fillers and matrix at high temperatures, well above the melting point of the polymer matrices. A prolonged exposure of the natural fillers at such high temperatures raises question about the potential degradation of the fillers. Hence, it is imperative that one should determine the degradation profile of lignocellulosic materials prior to use in composites applications. Thermal analysis curves of old, deinked ANP and IC are presented in Figure 4. As seen at lower temperatures the thermal stability was in the following order IC > ONP > deinked newspaper > ANP, while at  $\approx 300^\circ\text{C}$  the order is reversed. This behavior can be explained on the basis of material composition. Degradation of the polysaccharides, hemicelluloses and cellulose, starts at temperatures of 220 and 290°C, respectively, while lignin



**Figure 5.** DTG Thermograms of the different fibers (ONP, DNP, ANP, and IC). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

nin degrades at a lower temperature,  $\approx 200^\circ\text{C}$ . However, at higher temperatures lignin appears to be more heat resistant than hemicelluloses and cellulose, due to its low degradation rate.<sup>38,39</sup>

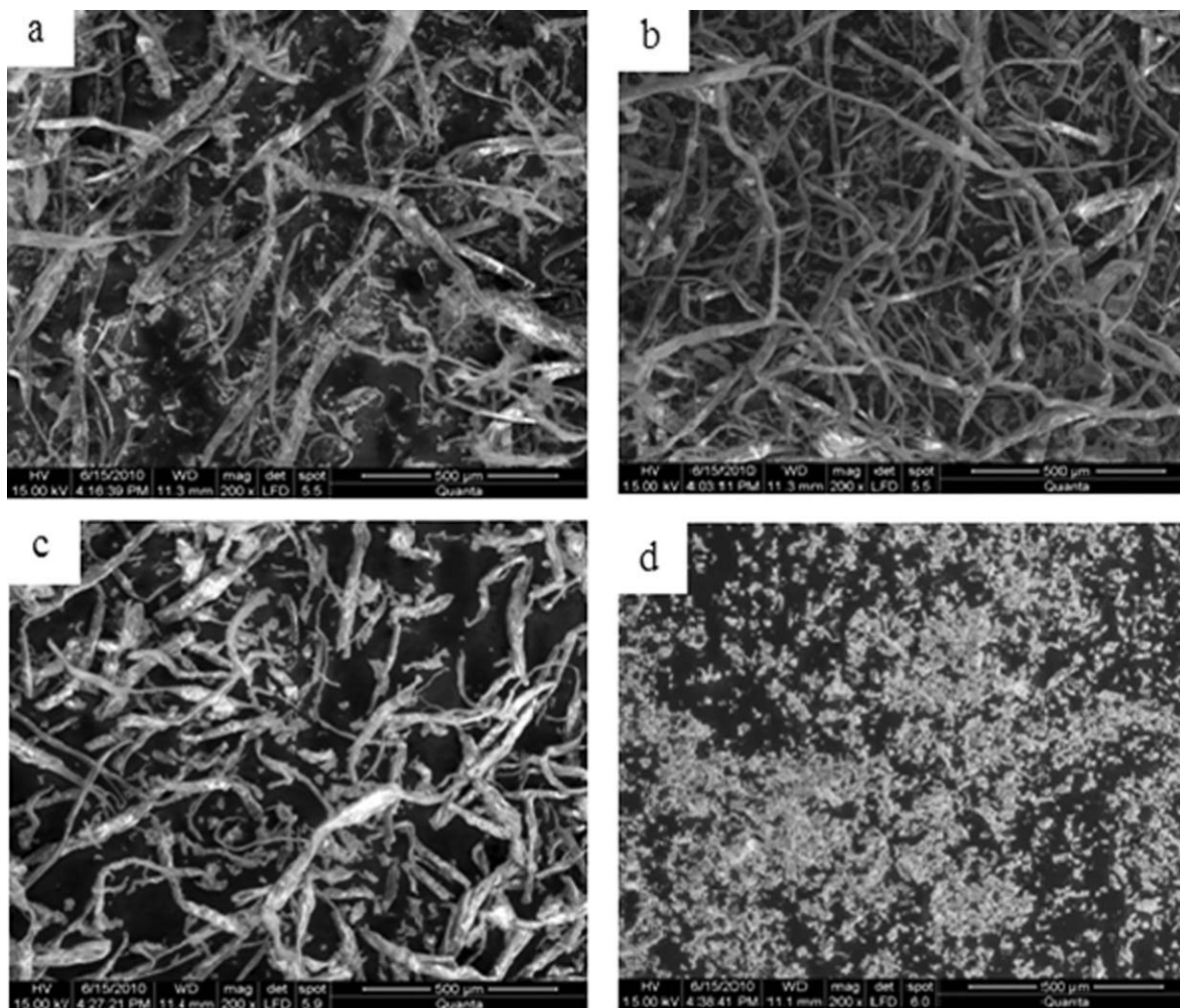
Therefore the weight loss between 180 and 220°C is mainly due to hemicelluloses decomposition and the parallel slow decomposition of lignin, while the weight loss between 300 and 450°C is attributed to cellulose and lignin decomposition (release of phenolic monomers). At temperatures higher than 450°C, there is evaporation of the volatile components. Thus, at low temperatures ANP is less stable than ONP, because of the high lignin and hemicelluloses content, while IC is more stable due to higher cellulose content. However, at  $\approx 300^\circ\text{C}$ , the thermal stability order of the materials is reversed, because lignin, as already mentioned, at higher temperature is more heat resistant than hemicelluloses and cellulose.

The derivatives of the thermogravimetric curves (DTG) of old, deinked, ANP and IC are given in Figure 5. From the diagrams, the main decomposition temperature\* (Td) was obtained for the four types of fiber.

According to other studies acetic anhydride treatment does not significantly influence material thermal stability. Unchanged, slightly decreased, or increased thermal stability has been reported.<sup>1,5,8</sup> Moreover, it seems that material stability is directly related to the type of reagent used for the treatment.

**Table III.** TG-DTG Results of Different Fibers (ONP, DNP, ANP, and IC)

Sample	On set degradation temperature (°C)	Maximal temperature of the first stage of decomposition (°C)	Maximal rate of the first stage of decomposition (%/min)	Mass loss in the first stage of decomposition (%)	Residue (%)
ONP	230.8	322.8	9.53	35.42	35.55
DNP	223.3	307.2	10.28	43.50	22.71
ANP	212.2	322.0	9.07	43.33	23.45
IC	264.0	305.9	24.49	28.86	11.92



**Figure 6.** SEM micrographs of old (a), deinked (b), acetylated (c), and IC fibers (d).

Esterification of the lignocellulosic materials with succinic anhydride led to decreased thermal stability.<sup>40</sup>

In this study, as seen from Figures 4 and 5 and Table III, we can see that IC decomposes more quickly with a top speed of degradation of  $24.48\% \text{ min}^{-1}$  followed by the DNP fiber with a speed of  $10.28\% \text{ min}^{-1}$ , ONP fiber with a speed of  $9.53\% \text{ min}^{-1}$  and at the end ANP fiber at a speed of  $9.07\% \text{ min}^{-1}$ .

#### Scanning Electron Microscopy

Scanning electron micrographs of ONP (a), deinked newspaper (b), acetylated newspaper (c), and IC fibers (d) are shown in Figure 6. The micrographs 6 (a) show that the ONP is covered with an unevenly distributed layer, as seen the surface of the esterified newspaper 6 (c) became rather smoother as compared with that of untreated newspaper 6 (b). Removal of substances, which usually cover the surface of lignocellulosic materials<sup>6,8,36</sup> and replacement of surface hydroxyl groups by AG,<sup>11</sup> could explain the formation of material surface during esterification.

SEM micrographs of IC showed cylindrical shape fibers, ONP, deinked newspaper, and ANP fibers are long.

#### CONCLUSION

Natural fibers are considered as potential replacement for synthetic fibers in composite materials. Although natural fibers have advantages of being low cost and low density, they are not totally free of problems. A serious problem of natural fibers is their strong polar character, which creates incompatibility with most polymer matrices. In this work, it was demonstrated the viability of producing CA from the chemical recycling of newspaper.

Chemical modification of fibers by acetylation and deinking was carried out. Esterification and deinking reaction was confirmed by FTIR. Deinking increased the crystallinity of newspaper fibers while acetylating decreased this crystallinity.

#### REFERENCES

1. Tserki, V.; Matzinos, P.; Kokkou, S.; Panayiotou, C. *Compos. A* **2005**, *36*, 965.
2. Bledzki, A. K.; Gassan, J. *Prog. Polym. Sci.* **1999**, *24*, 221.
3. Frisoni, G.; Baiardo, M.; Scandola, M. *Biomacromolecules* **2001**, *2*, 476.

4. Ibrahim, M. M.; Alain Dufresne; El-Zawawy; Agblevor, F. A. *Carbohydr. Polym.* **2010**, *81*, 811.
5. Tserki, V.; Zafeiropoulos, N. E.; Simon, F.; Panayiotou, C. *Compos. A* **2005**, *36*, 1110.
6. Bertoti, A. R.; Luporini, S.; Esperidião, M. C. A. *Carbohydr. Polym.* **2009**, *77*, 20.
7. Fávoro, S. L.; Lopes, M. S.; Vieira de Carvalho Neto, A. G. R.; Rogério de Santana, R.; Radovanovic, E. *Compos. A* **2010**, *41*, 154.
8. Luz, S. M.; Del Tio, J.; Rocha, G. J. M.; Gonçalves, A. R.; Del'Arco, J. A. R. *Compos. A* **2008**, *39*, 1362.
9. Alix, S.; Philippe, E.; Bessadok, A.; Lebrun, L.; Morvan, C.; Marais, S. *Bioresour. Technol.* **2009**, *100*, 4742.
10. Zhang, W.; Zhang, X.; Liang, M.; Lum, C. *Compos. Sci. Technol.* **2008**, *68*, 2479.
11. Abdelmouleh, M.; Bouffi, S.; Belgacem, M. N.; Durate, A. P.; Ben Saleh, A.; Gandini, A. *Int. J. Adhes. Adhes.* **2004**, *24*, 43.
12. Abdelmouleh, M.; Boufi, S.; Belgacem, M. N.; Dufresne, A. *Compos. Sci. Technol.* **2007**, *67*, 1627.
13. Kalia, S.; Kaith, B. S. *Express Polym. Lett.* **2008**, *2*, 93.
14. Kaci, M.; Djidjelli, H.; Boukerrou, A.; Zaidi, L. *Express Polym. Lett.* **2007**, *467*.
15. Djidjelli, H.; Benachour, D.; Boukerrou, A.; Zefouni, O.; Véga, J. J. M.; Farenc, J.; Kaci, M. *Express Polym. Lett.* **2007**, *1*, 846.
16. Djidjelli, H.; Boukerrou, A.; Founas, R.; Rabouhi, A.; Kaci, M.; Farenc, J.; Vega, J. J. M.; Benachour, D. *J. Appl. Polym. Sci.* **2007**, *103*, 3630.
17. Islam, M. S.; Pickering, K. L.; Foreman, N. J. *Compos. A* **2010**, *41*, 596.
18. Baroulaki, I.; Karakasi, O.; Pappa, G.; Tarantili, P. A.; Economides, D.; Magoulas, K. *Compos. A* **2006**, *37*, 1613.
19. Nassar, M. A.; Abdelwahab, N. A.; Elhalawany, N. R. *Carbohydr. Polym.* **2009**, *79*, 417.
20. Rodrigues Filho, G.; Monteiro, D. S.; Meireles, C. d. S.; Nascimento de Assuncao, R. M.; Cerqueira, D. A.; Barud, H. S.; Ribeiro, S. J. L.; Messadeq, Y. *Carbohydr. Polym.* **2008**, *73*, 74.
21. Ferrer, N.; Vila, A. *Anal. Chim. Acta* **2006**, *555*, 161.
22. Meireles, C. d. S.; Rodrigues Filho, G.; Ferreira, M. f., Jr.; Cerqueira, D. A.; Assunção, R. M. N.; Ribeiro, E. A. M.; Poletto, P.; Zeni, M. *Carbohydr. Polym.* **2010**, *80*, 954.
23. Tejado, A.; Peña, C.; Labidi, J.; Echeverria, J. M.; Mondragon, I. *Bioresour. Technol.* **2007**, *98*, 1655.
24. Fávoro, S. L.; Ganzerli, T. A.; de Carvalho Neto, A. G. V.; da Silva, O. R. R. F.; Radovanovic, E. *Express Polym. Lett.* **2010**, *4*, 465.
25. Senvaitiene, J.; Beganskiene, A.; Kareiva, A. *Vib. Spectrosc.* **2005**, *37*, 61.
26. Peres de Paula, M.; Lacerda, T. M.; Frollini, E. *Express Polym. Lett.* **2008**, *2*, 423.
27. Shiraiishi, N.; Matsunaga, T.; Yokota, T. *J. Appl. Polym. Sci.* **1979**, *24*, 2347.
28. Marcovich, N. E.; Reboredo, M. M.; Aranguren, M. I. *Thermochim. Acta* **2001**, *372*, 45.
29. Safou-Tchiam, R.; Bernard de Jeso; Akagah, A. G.; Petraud, G. S. M. *Ind. Crops Prod.* **2007**, *26*, 173.
30. Wojnarovits, L.; Foldvry, Cs. M.; Takacs, E. *Radiat. Phys. Chem.* **2010**, *79*, 848.
31. Fan, X.; Liu, Z. T.; Liu, Z. W. *J. Hazard Mater* **2010**, *177*, 452–457.
32. Tronc, E.; Hernández-Escobar, C. A.; Ibarra-Gómez, R.; Estrada-Monje, A.; Navarrete-Bolaños, J.; Zaragoza-Contreras, E. A. *Carbohydr. Polym.* **2007**, *67*, 245.
33. Zafeiropoulos, N. E.; Williams, D. R.; Baillie, C. A.; Matthews, F. L. *Compos. A* **2002**, *33*, 1083.
34. Ghali, L.; Msahli, S.; Zidi, M.; Sakli, F. *Mater. Lett.* **2009**, *63*, 61.
35. Islam, M. S.; Pickering, K. L.; Foreman, N. J. *Compos. A* **2010**, *41*, 596.
36. Liu, X. Y.; Dai, G. C. *Express Polym. Lett.* **2007**, *299*.
37. Beatriz, A. P. Ass.; Ciacco, G. T.; Frollini, E. *Bioresour. Technol.* **2006**, *97*, 1696.
38. Masud, S. H.; Lawrence T. D.; Amar K. M.; Manjusri M. *Compos. Sci. Technol.* **2006**, *66*, 1813.
39. Hornsby, P. R.; Hinrichsen, E.; Trivedi, K. J. *Mater. Sci.* **1997**, *32*, 443.
40. Liu, C. F.; Sun, R. C.; Zhang, A. P.; Ren, J. L.; Wang, X. A.; Qin, M. H.; Chao, Z. N.; Luo, W. *Carbohydr. Res.* **2007**, *342*, 919.