Elaboration and Characterization of Composites of Castor Oil-Based Polyurethane and Fibers from Alfa Stems

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ABSTRACT: Polyurethane (PU) based on castor oil and hexamethylene diisocyanate (HDI) was synthesized by a two-step method in the presence of dibutyltin dilaurate (DBTDL) as catalyst. The PU obtained was blended with various amounts of cellulose fibers extracted from alfa stems to prepare composite materials. The influence of cellulose fibers on the thermal and mechanical properties of different composites was demonstrated by means of several characterization techniques, such as thermomechanical, structural, and morphological analyses. The hydrogen bonding interaction and the possible formation of urethane links between PU and hydroxyl groups of cellulose provide a good fiber-matrix interface. The infrared absorption vibration of the N—H bond, which is 3336 cm^{-1} for pure PU, in fact shifts to 3319 cm^{-1} for a composite containing 25% of cellulose. Moreover, the variation of glass transition temperature, T_g, versus cellulose content is linear, for example, T_g of pure PU and of a composite containing 40% of cellulose is -35 and $-24°C$, respectively. Furthermore, the mechanical properties rise steadily up to 20 wt % of fibers and decrease beyond this value. The novelty of this article lies in the fact that over 95% of starting materials used are obtained from agro-resource. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 902–909, 2010

Key words: alfa stem; castor oil; polyurethane; cellulose fibers; composites

INTRODUCTION

Biodegradable polymers from renewable resources have been studied very extensively and developed as a result of both concerns related to environmental pollution from fossil plastic waste and the great importance of sustainable development.[1,2] Increasing concerns about the environment and sustainability are encouraging a growing worldwide research effort devoted to the understanding and use of renewable resources. The aim is to reduce the dependence on fossil fuels, which will rapidly be exhausted,[3,4] and to develop innovative technologies and competitive industrial products. Vegetable oils exist in abundance and are cheap renewable resources, which represent a major potential alternative source of chemicals suitable for developing environmentally safe and consumer-friendly products.

Today, the high-price of petroleum raw materials, scarcity of petroleum products, and severe environmental rules and regulations put pressure on synthetic polymer scientists to use natural renewable resources as feedstocks for the development of many industrially important polymers. These feedstocks, especially vegetable oils, are well accepted by synthetic polymer chemists for social, economic, and environmental reasons. Fortunately, many researchers now use renewable natural resources for the development of a large number of polymers.[5]

The unusual composition and chemistry of castor oil (CO) make it quite valuable for many applications, including the preparation of polyurethane (PU).[6] Approximately 90% of fatty acids in CO are ricinoleic acid. Ricinoleic acid—a monounsaturated, 18-carbon fatty acid—has a hydroxyl functional group at the 12th carbon; this is a very rare property for a natural fatty acid and is the main reason for the direct use of this oil as a hydroxyl-containing trifunctional monomer. Vegetable oils also have other advantages, such as renewability,[7] easy availability in a large quantity,[8] environmental friendliness,[9] biodegradability,[10] and overall low cost.[11]

Composite materials are made up of two or more solid phases: fibers (dispersed phase), which are

responsible for stress resistance, and a matrix (continuous phase), which is responsible for stress propagation. The great need for reinforced materials has created a demand for improvements in the mechanical properties of matrices. The use of natural fibers, such as bagasse of sugarcane, coir, sisal, jute, ramie, and pineapple leaf, to reinforce plastics offers a number of advantages over conventional materials because of their low-cost, biodegradability, flexibility, and low-gravimetric density. In addition, they are obtained from renewable sources, can improve properties and, at the same time, can produce materials that have low environmental impact.[12–14]

Of the various plants, alfa stems have good calorific value, identical to that of wood, making them an alternative to wood fuel and charcoal.[15] The chemical composition of alfa stems, such as any natural fiber, is mainly cellulose, hemicellulose, and lignin.[16–18] In a much smaller proportion, they also contain extractive protein and some inorganic compounds.[19] Chemical extraction processes are needed to isolate the cellulose before utilization; the best known is the Kraft method,[20] which is used for 90% of current extraction.

The aim of this study was to extract and characterize the cellulose from Moroccan alfa stems and use it as reinforcement in composite materials. This application is justified by the many advantages of cellulose fibers from alfa stems owing to its strength, toughness, lightness, availability, low- cost, renewability, and biodegradability. The first part of this study presents the characterization and properties of cellulose extracted from alfa stems. The second part focuses on the synthesis and characterization of the organic matrix of PU based on CO. Finally, the composites of synthesized PU and alfa cellulose fibers will be produced with different matrix-reinforcement ratios. Our objective was to determine the optimal composition for obtaining biodegradable materials with good thermal and mechanical performance.

EXPERIMENTAL

Materials and syntheses

Reagents

Alfa plants were collected from Jerada in the east of Morocco in July, the recommended time for harvesting alfa plants. CO and 1,3-propanediol were purchased from Aldrich. Sodium hypochlorite (NaClO) solution (40 wt %), 1.6-hexamethylene diisocyanate (purity of 98%) (HDI), acetone (analysis grade), chloroform (analysis grade) ($CHCl_3$), methanol (analysis grade) (CH_3OH), diethyl ether, and dibutyl tin dilaurate (DBTDL) were also supplied by Aldrich. As HDI could dimerize at room temperature, it was stored in a refrigerator at $-10°C$. All reagents were used without before purification.

Determination of the moisture content in alfa stems

Twenty five grams of ground alfa stems was weighed into a 100 mL beaker. The beaker was placed in an oven for 5 h at 110°C. After this drying treatment, it was covered and cooled in a desiccator for 30 min. About 23.57 g (or 94.3 wt %) of dried Alfa was obtained.

Determination of the content of extractive substances

A cartridge containing 22 g of dried alfa stems was placed in an Soxhlet extractor equipped with a 1000 mL round bottom flask containing 600 mL of methanol/chloroform (1/2 v/v) mixture. The cellulose was extracted for 3 h. The filtrate was evaporated and dried under vacuum. 1.1 g of extractive substances (proteins and some inorganic compounds[19]) was obtained which corresponds to 5% of total dried alfa stems.

Extraction of cellulose in alkaline solution

After extractive substance elimination, 20 g of dried alfa stems was charged into a 250 mL round bottom flask, equipped with a reflux condenser and a magnetic stirrer, containing 120 mL of KOH solution 1*M*. The mixture was heated for 3 h at 100°C and was then immediately filtered. The residue was successively washed with 250 mL of NaClO solution (40 wt %), 200 mL of ethanol, and 200 mL of diethyl ether. The residue was then dried for 24 h at 60°C. As a result, 11 g of pure cellulose was recovered—a yield of 55%—thus indicating that alfa stems contained 47% of pure cellulose.

Synthesis of PU and composite preparation

CO (0.01 mol) and HDI (0.021 mol) were charged into a reactor equipped with mechanical agitation and a supply of nitrogen. The mixture was heated at 60°C for 10 min. DBTDL (0.05 wt %) was then added to the reaction mixture. The reaction was maintained at 90°C for 2 h. After cooling, the prepolymer was dissolved in acetone. 1,3-propanediol (0.01 mol; chain extender) was then added. After 10 min of stirring, various amounts of cellulose fibers of 0.6 mm in length were incorporated. The mixture was stirred for 20 min and poured into Petri dishes. The solvent was removed by evaporation at room temperature for 24 h and at 80°C for 72 h.

Techniques

Fourier transform infrared spectroscopy

The FTIR spectra were recorded on a FTIR 8400 SHI-MADZU between 4000 and 600 cm^{-1} with a resolution of 4 cm^{-1}. Samples were in film form with 20 scans for each sample.

Differential scanning calorimetry

DSC analyses were performed with a 204 F1 NETZSCH (Germany). Experiments were carried out under nitrogen with samples ranging from 15 to 20 mg. The temperature range of the first scan was between −80 and 250°C, with a heating rate of 10 K min^{-1}, followed by a cooling at 20 K min^{-1}. A second scan was immediately performed with a heating rate of 10 K min^{-1}. The glass transition temperature was taken at the midpoint of heat capacity change.

Thermogravimetric analyses

The TGA tests provide the mass loss of samples during heating. Measurements were performed on a TG 209 F3 NETZSCH 51(Germany). About 15 mg of the samples was placed in a ceramic pan and heated from 30 to 600°C under nitrogen purge with a temperature ramp of 10 K min^{-1}.

Mechanical properties

Mechanical tests were carried out with a machine of type MTS Adamel Lhomargy-DY35XL (France) equipped with a load of 500 N on dumbbell-shaped H3 samples (ISO 37, 34 mm long and 4 mm wide) at room temperature. The tensile speed was 10 mm/min. The Young's modulus, tensile, and elongation at break were calculated from stress-strain curves. For each sample, the mechanical properties at break were obtained from the average of tests on 10 specimens.

Scanning electron microscopy

The measurements were carried out in a scanning electron microscope JEOL JSM-6460LA (Japan) equipped with an energy dispersive (Si-Li) X-ray spectrometer. The electron beam was incident on the specimen perpendicular to the surface and the measurements were performed under the following conditions: primary beam energy of 5 keV, working distance of 10 mm, take-off angle of 30°, and residual pressure in the specimen chamber below 10^{-5} Torr. All samples were broken with liquid nitrogen and their facial fracture was analyzed.
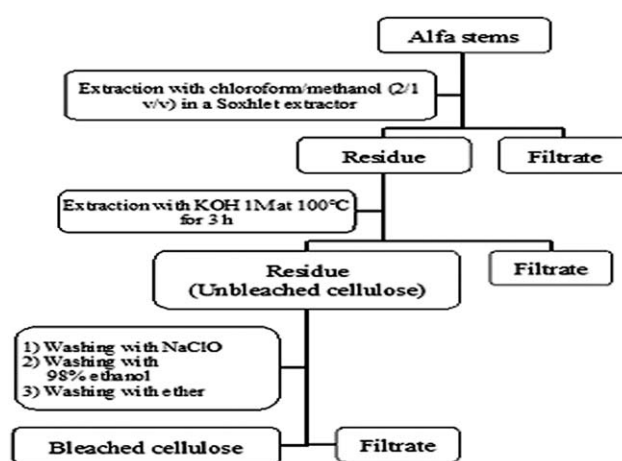

Figure 1 Different steps of cellulose extraction.

RESULTS AND DISCUSSIONS

Cellulose extraction from alfa stems

Cellulose was extracted from alfa stems using the Kraft method[20] as illustrated in Figure 1. At first, the moisture content and the extractive products in alfa stems were determined. The moisture content was determined by a simple weighing of crushed alfa stems before and after drying at 110°C. The extractive products were then removed by Soxhlet extraction. The dry material content is 94.3%, which means a moisture content of 5.7%. The extractive material content of dry alfa stems is 5%. Both values obtained are consistent with those described in the literature[18] and indicate that alfa stems have a low-moisture content and low-extractive compound. Generally speaking, the term "cellulose extraction" is rarely used, instead "cellulose purification" or "cellulose enrichment" is more common. The latter term refers to the elimination of all contaminants that alfa stems may contain, such as aromatic compounds, pectin, or hemicellulose. In this process, hemicellulose and pectin are extracted by a hot alkaline solution. However, after the removal of pectin and hemicellulose, lignin is generally the residual contaminant which is strongly linked to cellulose. It can be removed by buffered solution treatment at 60°C, commonly known as bleach. The cellulose extraction efficiency determined under these conditions is 47%. This value is consistent with those described in the literature for Alfa stems[17,19] and other plant species.[21–23]

FTIR spectroscopy is an appropriate technique for studying changes introduced by any chemical treatment. Figure 2 outlines the FTIR spectra of alfa, commercial cellulose, and extracted cellulose. The interpretation of these spectra is based on data from the literature. The spectrum of alfa stems shows the presence of a band at 2858 cm^{-1} because of the elongation of aromatic C—H bonds of lignin.[24–27] The
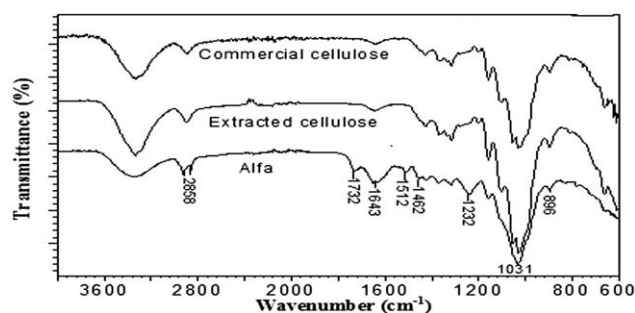
Figure 2 FTIR spectra of Alfa, extracted cellulose, and commercial cellulose.

band at 1732 cm^{-1} can be attributed to the vibration of the acetyl group of hemicellulose uronic ester or the carboxylic ester group of the ferulic ring and p-coumaric acid of lignin and/or hemicellulose.[28–31] Sun et al.[29] reported that the band at 1512 cm^{-1} is because of the C=C bond elongation of the lignin aromatic ring. The peak at 1643 cm^{-1} is attributed to the stretching vibration of water molecules in alfa stems.[32]

These bands are absent on the spectrum of extracted cellulose. This result indicates that the extraction of lignin and hemicellulose has been effective. In addition, the spectrum of extracted cellulose is identical to that of commercial cellulose. In these spectra, all characteristic absorption peaks of cellulose are present. The broad band at 3300 cm^{-1} corresponds to the stretching vibration of O—H bonds. The band at 2915 cm^{-1} characterizes the C—H stretching vibration of cellulose. The band at 1031 cm^{-1} is because of the elongation of C—O bonds in alcohol and ether functions.[33,34] There is also a small band at 896 cm^{-1} because of the C-1 group frequency or ring frequency and characteristic of β-glycosidic bonds between glucose units.[35]

Synthesis and characterization of PU and composites

The organic matrix studied is a PU based on CO and HDI with 1,3-propanediol as a chain extender. To control the distribution of CO along the polymer chain, segmented PU was synthesized by the two-step process of prepolymers. The first step in this synthesis was the condensation of CO and HDI. In the second step, the molar mass of PU prepolymer previously obtained was extended using 1,3-propanediol.

Figure 3 highlights the FTIR spectra of CO, Alfa cellulose fiber, pure PU matrix (PU100), and composites with 15% (PU85) and 25% (PU75) of alfa cellulose. The FTIR spectrum of PU100 shows the absorption bands at 3336, 1740, 1690, and 1530 cm^{-1} characteristic of elongation of the N—H link, elongation of the ester carbonyl group of CO, stretching

vibration of C=O in urethane groups, and out-of-plane distortion of N—H bonds, respectively.[36] Moreover, the band at 1240 cm^{-1} characteristic of the valence vibration of C—N and the deformation of N—H bonds of the urethane group[37] is also present.

In the FTIR spectra of composites, the band characteristic of the stretching vibration of N—H bonds at 3336 cm^{-1} shifts to 3321 cm^{-1}, and 3319 cm^{-1} for PU85 and PU75, respectively. In addition, this band is larger in composites than in pure PU. These results indicate the presence of hydrogen bonds between N—H bonds of the PU matrix and O—H groups of cellulose. There is also an intensification of the valence vibration band of C=O in urethane groups at 1690 cm^{-1} and the band at 1031 cm^{-1} because of stretching vibration of C—O bonds in alcohol and ether functions of cellulose. The greater the percentage of cellulose embedded in composites, the more intense these bands are. First, the peak intensification at 1690 cm^{-1} could be attributed to the presence of hydrogen bonds between the C=O groups of CO and O—H groups of cellulose. This vibration is at 1740 cm^{-1} in the free form and shifts to 1690 cm^{-1} in the bound form. Second, another explanation could be proposed; it is possible to attribute the increase observed in the peak at 1690 cm^{-1} to the formation of urethane groups from a slight residual NCO function and the OH of cellulose. All these results show clearly the existence of secondary interactions and/or covalent bonds between the matrix and cellulose fiber.

Composite properties

Thermal properties

The DSC second scan thermograms of PU and composites are shown in Figure 4. The composition and the glass transition temperature (T_g) of all samples are reported in Table I. An increase in the alfa
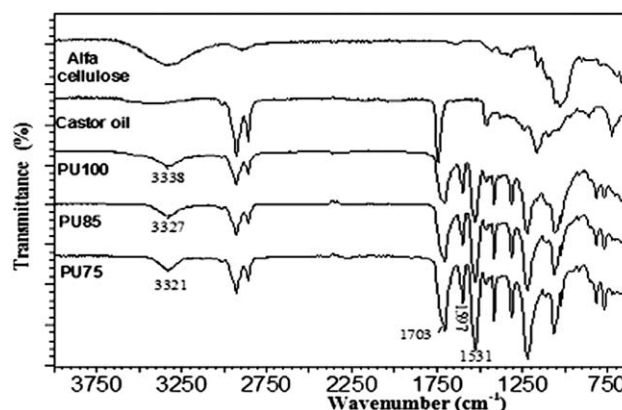

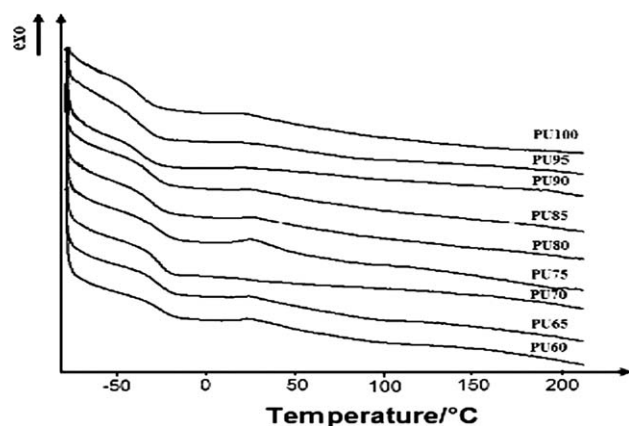**Figure 3** FTIR spectra of castor oil, pure PU, and composites PU85 and PU75.

Figure 4 Second scan DSC thermograms of different composites.

cellulose percentage leads to an increase in T_g. T_g of pure PU and PU60 (40% of cellulose) is – 35.1 and – 24.1°C, respectively. Moreover, T_g of composites rises steadily with the amount of cellulose (Fig. 5). In general, the increase in T_g of PU flexible segments indicates the presence of interactions between the matrix and reinforcement due to hydrogen bonding and/or covalent bonding, both enhance the compatibility between the matrix and reinforcement. The presence of hydrogen bonding and possible urethane bonding between the PU matrix and cellulose fibers has been previously seen in FTIR spectra. However, at this stage of study we cannot explain with certainty the origin of the small exothermic peak at 25°C. It could perhaps be a crystallization peak of flexible segments.

The TGA curves, which show the effect of fiber content are presented in Figure 6. Composites are less thermally stable than pure PU, which indicates the low-thermal stability of natural fibers. In the presence of natural fibers, samples begin to degrade at lower temperatures. At 5% of mass loss, the degradation temperature of composites decreases as the percentage of incorporated cellulose increases (Table II). It shifts from 285°C for PU100 to 233°C for PU70. Similarly, the temperature at 70% of mass loss shifts from 322 (PU 100) to 314°C (PU70). The same tend-
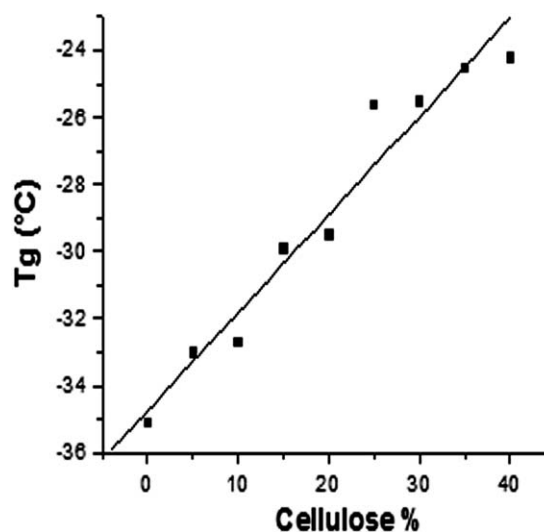

Figure 5 T_g of different composites versus cellulose percentage.

ency is observed for the temperature at 90% of mass loss. Furthermore, for example at 280°C, the mass loss increases with cellulose content, 3.94% for PU100 and 13.29% for PU70. Meanwhile at high temperatures, the residual mass increases as the percentage of cellulose rises (Fig. 6). Beyond 400°C, PU degrades strongly, whereas cellulose is more thermally stable.

The TGA results obtained have shown that below 400°C, composite materials are less stable than pure PU because of the lower thermal stability of natural fibers. However, at high temperatures, the presence of natural fibers delays the decomposition of PU by forming a protective layer, which slows down its degradation. Puglia et al.[38] have shown that the thermal stability of composites Mater-Bi® (thermoplastic polycaprolactone and starch-based polymer blends) is slightly affected by the presence of cellulose fibers with a small shift of the degradation at higher temperatures.

Morphological properties

The facial fracture images of PU100 [Fig. 7(a)], PU90 [Fig. 7(b)], PU70 [Fig. 7(c)], and PU60 [Fig. 7(d)]
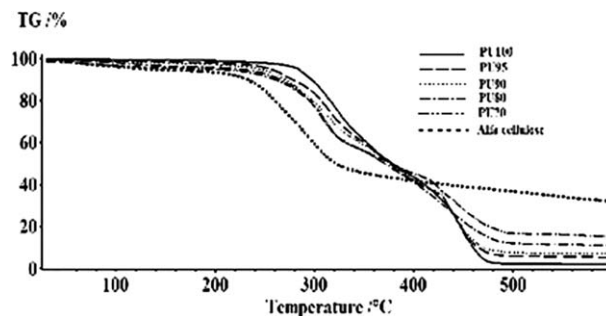
TABLE I
Cellulose Percentage and T_g of Pure PU and Different Composites

Samples	Cellulose (wt %)	T_g (°C)
PU100	0	−35.1
PU95	5	−33
PU90	10	−32.7
PU85	15	−29.9
PU80	20	−29.5
PU75	25	−25.6
PU70	30	−25.5
PU65	35	−24.5
PU60	40	−24.2

Figure 6 ATG thermograms of pure PU and different composites.

Samples	Temperature at 5% of mass loss (°C)	Temperature at 70% of mass loss	Temperature at 90% of mass loss	Percentage of mass loss at 280°C
PU100	285	322	461	3.94
PU95	258	335	466	10.16
PU90	248	319	473	12.54
PU80	235	311	–	13.16
PU70	233	314	–	13.29
Cellulose	185	282	–	28.84

were recorded and analyzed. The PU100 matrix seems homogeneous but the fracture unexpectedly provoked a lamellar morphology. The clusters of alfa cellulose fibers can be clearly seen in composite samples. Furthermore, Figure 7(b) shows a hole in the matrix because of the fiber loss that occurred when the sample was broken for analysis. In addition, the presence of PU is noted on the fiber surface [Figs. 7(c,d)]. This result can be attributed to a good adhesion at the fiber-matrix interface which is because of hydrogen bonding and possible covalent bonding between two phases, as seen previously in FTIR and DSC results.

Mechanical properties

The properties of composites reinforced by natural fibers depend on many parameters, such as fiber volume fraction, fiber-matrix adherence, transfer of force to the fiber-matrix interface, and fiber orientation. Most studies conducted on the natural fiber-based composites include a study of mechanical properties depending on fiber content, effect of different fiber treatments, and coupling agent use.[38–42] Other aspects of the prediction of modulus and resistance behavior were also studied using some predefined templates for biphasic systems and a comparison with experimental data.[42]

The properties of the matrix and fiber play an important role in the enhancement of composite mechanical properties. Indeed, the tensile strength is more sensitive to the properties of the matrix, whereas the Young's modulus depends on the properties of the fibers. To improve tensile strength, a high interface, low concentration, and good orientation of fibers are recommended. Meanwhile the wetting of fibers in the matrix and the high-fiber content determine the resistance modulus. The matrix/fiber ratio is very important when determining fracture properties. In the composites reinforced by short fibers, the critical length of a fiber is required to develop key conditions for obtaining optimal properties of composites. Fibers of a length less than the critical value are not successful due to the rupture of bonds at the interface under low loads. In the oppo-

site case, fibers that are longer than the critical length can be deformed under loads leading to high-strength composites. Oksman and Clemons[43] have noted that many dispersed small fibers generally increase resistance properties, whereas larger fibers improve the mechanical properties. Furthermore, this was confirmed by Sanadi et al.[44] who identify small fibers that improve rigidity and large fibers that improve the tensile strength.

To obtain good impact resistance, an optimal fiber-matrix interaction is essential. The degree of fiber adhesion and the energy absorption mechanism are examples of parameters that can influence the impact resistance of composites enhanced with short fibers.[45] The mechanical properties vary and increase linearly with the composition according to the rule of mixtures. However, this linear dependence of the fiber content is no longer valid for a large fiber
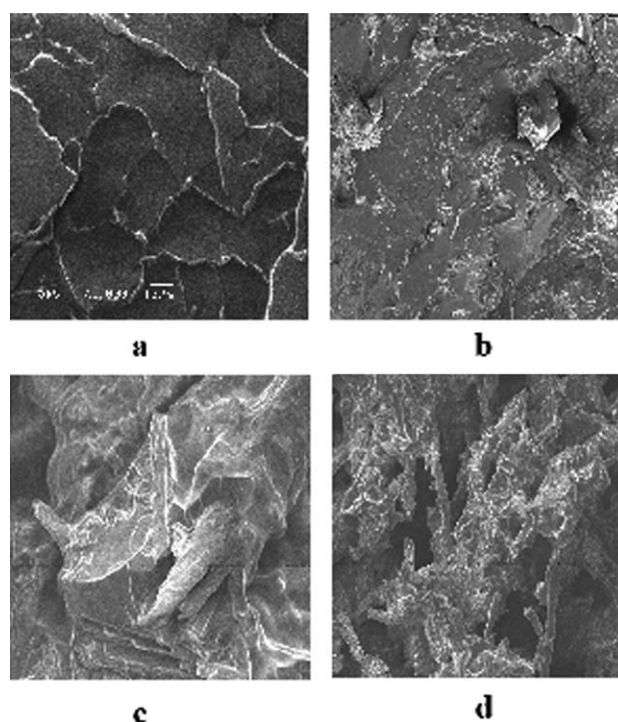

Figure 7 Facial fracture images (a): PU100, (b): PU70, (c): PU90, and (d):PU60.
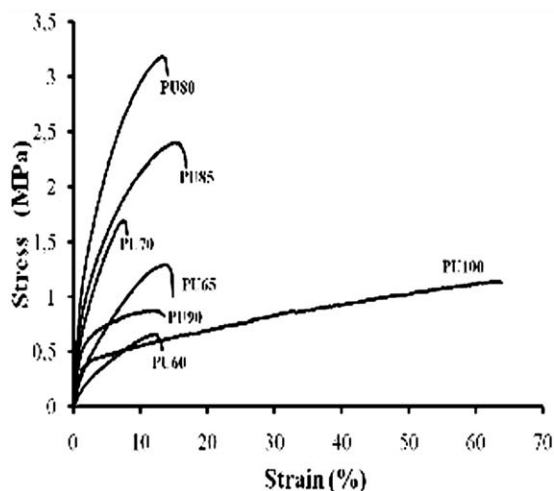
Figure 8 Stress-strain curves of pure PU and various composites.

Figure 9 Young's modulus (●), deformation (■), and stress (▲) at break versus cellulose percentage.

percentage. This is probably because of the lack of total fiber immersion in the polymer matrix.

The stress-strain curves of composites are shown in Figure 8 and the numerical values of data are collected in Table III. The results outline a decrease in strain at break and a marked improvement in the Young's modulus when the cellulose content in the composites increases up to 20%. Beyond this value, the modulus decreases. The modulus increases by 21% for the composite PU95 where the amount of incorporated cellulose is 5%, and by 83% for a cellulose content of 10% (PU90). The cellulose contents of 15 and 20% lead to a modulus increase of 176 and 234%, respectively. Figure 9 shows clearly the dependence of mechanical properties on cellulose content. Indeed, the Young's modulus reaches a maximum value with 20% of cellulose and has the lowest value with 40%. Furthermore, the stress at break depends to some extent on cellulose content. However, it is very low with cellulose content of more than 35%. In the majority of cases, the increase in the percentage of reinforcement improves the mechanical performance of composites. However, a
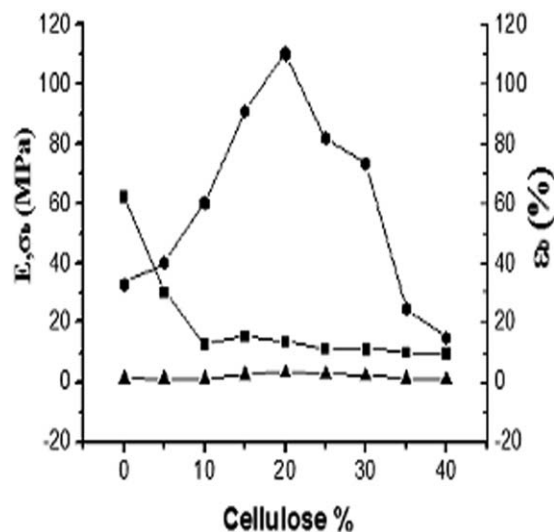
large amount of fibers implies that adherence is more difficult, which leads to a decrease in features in some cases. It should also be emphasized that there is a reinforcement content beyond which major difficulties appear, particularly in the manufacturing method. It is actually quite rare to find reinforced polymers containing a percentage of wood superior to 50–60%, at which many difficulties appear in molding and these difficulties increase in the order: compression, extrusion, injection. Klason et al.[46] observed that beyond 50%, the material becomes rough and presents surface cracks. A large amount of fibers also creates problems when mixing components. Moreover, the increase in fibers content could provoke a number of drawbacks, notably the hygroscopic properties and degradability of composites as well as their low elongation and low impact resistance.

CONCLUSIONS

PU based on CO and HDI was synthesized by a two-step method. Cellulose fibers were extracted from alfa stems. Composites were then prepared with different percentages of alfa cellulose fibers. The results of all characterization techniques converge to the fact that both thermal and mechanical properties of the composites are improved by the presence of Alfa cellulose fibers. Moreover, this improvement shows a linear dependence on the percentage of fiber incorporated up to 20%. Beyond this value, the mechanical properties of composites decline. However, the facial rupture images illustrate a good interface because of hydrogen bonding and possible covalent bonding between fiber and matrix.

TABLE III
Mechanical Properties of Pure Pu and Different Composites

Samples	Deformation at break (%)	Young's modulus (MPa)	Stress at break (MPa)
PU100	62.59 + 20.78	33.02 + 6.05	1.26 + 0.26
PU95%	30.23 + 8.3	40.32 + 2.84	0.93 + 0.16
PU90	12.63 + 2.65	60.37 + 9.36	0.99 + 0.27
PU85	15.42 + 1.81	91.21 + 7.13	2.44 + 0.18
PU80	13.48 + 1.73	110.14 + 3.33	3.17 + 0.28
PU75	10.9 + 4.44	82.06 + 9.03	2.55 + 0.65
PU70	10.89 + 3.27	73.64 + 9.09	2.04 + 0.60
PU65	9.91 + 2.16	24.49 + 3.63	1.02 + 0.18
PU60	9.65 + 1.13	14.61 + 1.97	0.69 + 0.05

To enhance further mechanical properties and to increase the fiber content, a fiber surface treatment should be used to favor the matrix-fiber interaction at the interface. Likewise, an improvement in processing would be desirable to homogeneously disperse fibers in the matrix.

References

1. Choi, E. J.; Kim, C. H.; Park, J. K. Macromolecules 1999, 32, 7402.
2. Gao, S.; Nishinari, K. Biomacromolecules 2004, 5, 175.
3. Sperling, L. H.; Manson, J. A. J Am Oil Chem Soc 1983, 60, 1887.
4. Sperling, H. L.; Manson, J. A.; Linne, M. A. J Polym Mater 1984, 1, 54.
5. Gast, L. E.; Schneider, W. J.; Cowan, J. C. J Am Oil Chem Soc 1968, 45, 534.
6. Zlatanic, A.; Lava, C.; Zhang, W.; Petrovic, Z. S. J Polym Sci Part B: Polym Phys 2004, 42, 809.
7. John, W. C.; Bogart, V.; Gibson, E.; Copper, S. L. J Polym Sci Polym Phys Ed 1983, 21, 65.
8. Frontini, P. M.; Rink, M.; Pavan, A. J Appl Polym Sci 1993, 48, 2023.
9. Zhang, C.; Feng, S. Polym Int 2004, 53, 1936.
10. Martin, D. J.; Meijs, G. F.; Gunatillake, P. A.; Mccarthy, S. J.; Renwick, G. M. J Appl Polym Sci 1997, 64, 803.
11. Chu, B.; Gao, T.; Li, Y.; Wang, J.; Desper, C. R.; Byrne, C. A. Macromolecules 1992, 25, 5724.
12. De Araujo, C. R.; Mothé, C. G. Second International Symposium on Natural Polymer and Composites (ISNAPOL/98), SP, Brazil, 1998, p 123.
13. Mothé, C. G.; De Araujo, C. R. 26th Conference North American Thermal Analysis (NATAS), Cleveland, USA, 1998, p 260.
14. Mothé, C. G.; De Araujo, C. R. Thermochim Acta 2000, 358, 321.
15. Administration des eaux et forêts et de la conservation des sols. Correspondance de la CIOR, Ref. 16364, Rabat 1995, 1–30.
16. Ben Brahim, S.; Ben Cheikh, R. Compos Sci Technol 2007, 67, 140.
17. Bessadok, A.; Marais, S.; Gouanve, F.; Colasse, L.; Zimmerlin, I.; Roudesli, S.; Metayer, M. Compos Sci Technol 2007, 67, 685.
18. Hattalli, S.; Benaboura, A.; Ham-Pichavant, F.; Nourmamode, A.; Castellan, A. Polym Degrad Stab 2002, 75, 259.
19. Rowell, R. M.; Young, R. A.; Rowell, J. K. Paper and Composites from Agro-Based Resources, Ed Rowell, R. M., Ed.; Lewis publishers: Boca Raton, USA, 1997.
20. Krassig, H.; Schurz, J. "Cellulose", Ullmann's Encyclopedia of Industrial Chemistry, 6th ed.; Wiley, 2003, Vol. 6, p 593.
21. Hamad, W. Cellulosic Materials: Fibers, Networks and Composites; Kluwer Academic Publishers: The Netherlands, 2002.
22. Bhattacharya, D.; Germinario, L. T.; Winter, W. T. Carbohydr Polym 2008, 73, 371.
23. Zuluaga, R.; Putaux, J. L.; Cruz, J.; Vélez, J.; Mondragon, I.; Gañan, P. Carbohydr Polym 2009, 76, 51.
24. Gañan, P.; Cruz, J.; Garbizu, S.; Arbelaiz, A.; Mondragon, I. J App Polym Sci 2004, 94, 1489.
25. Gañan, P.; Zuluaga, R.; Vélez, J.; Mondragon, I. Macromol Biosci 2004, 4, 978.
26. Xu, F.; Sun, J. X.; Geng, Z. C.; Liu, C. F.; Ren, J. L.; Sun, R. C.; Fowler, P.; Baird, M. S. Carbohydr Polym 2007, 67, 56.
27. Xu, F.; Zhou, Q. A.; Sun, J. X.; Liu, C. F.; Ren, J. L.; Sun, R. C.; Curling, S.; Fowler, P.; Baird, M. S. Process Biochem 2007, 42, 913.
28. Sain, M.; Panthapulakkal, S. Ind Crops Prod 2006, 23, 1.
29. Sun, X. F.; Xu, F.; Sun, R. C.; Fowler, P.; Baird, M. S. Carbohydr Res 2005, 340, 97.
30. Sun, R. C.; Sun, X. F.; Liu, G. Q.; Fowler, P.; Tomkinson, J. Polym Int 2002, 51, 117.
31. Xiao, B.; Sun, X. F.; Sun, R. C. Polym Degrad Stab 2001, 74, 307.
32. Olsson, A. M.; Salmén, L. Carbohydr Res 2004, 339, 813.
33. Paiva, M. C.; Ammar, I.; Campos, A. R.; Cheikh, R. B.; Cunha, A. M. Compos Sci Technol 2007, 67, 1132.
34. Alemdar, A.; Sain, M. Bioresour Technol 2008, 99, 1664.
35. Pappas, C.; Tarantilis, P. A.; Daliani, I.; Mavromoustakos, T.; Polissiou, M. Ultrason Sonochem 1999, 5, 163.
36. Sun, J. X.; Sun, X. F.; Zhao, H.; Sun, R. C. Polym Degrad Stab 2004, 84, 331.
37. Yeganeh, H.; Hojati-Talemi, P. Polym Degrad Stab 2007, 92, 480.
38. Puglia, D.; Tomassucci, A.; Kenny, J. M. Polym Adv Technol 2003, 14, 749.
39. Garcia, Z. F.; Martinez, E.; Alvarez, C. A.; Castano, V. M. Reinforc J Plast Compos 1995, 14, 641.
40. Tobias, B. C. Proceedings of the International Conference on Advanced Composite Materials; Minerals, Metals and Materials Society (TMS); Warrendale, PA, 1993; p 623.
41. Vollenberg, P. H.; Heiken, D. Polymer 1990, 30, 1652.
42. Felix, J. M.; Gotenholm, P.; Schreiber, H. P. Polym Compos 1993, 14, 449.
43. Oksman, K.; Clemons, C. J Appl Polym Sci 1998, 67, 1503.
44. Sanadi, A. R.; Caulfield, D. F.; Jacobson, R. E.; Rowelltg, R. M. Ind Eng Chem Res 1995, 34, 1889.
45. Mukharjea, R. N.; Pal, S. K.; Sanyal, S. K.; Phani, D. K. Polym J Mater 1984, 1, 69.
46. Klason, C.; Kubat, J.; Stromval, H. E. Int J Polym Mater 1984, 10, 159.