A New Composite from Cellulose Industrial Waste and Elastomeric Polyurethane

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ABSTRACT: Cellulose fiber waste from the white cellulose pulp purification process produced by the company Nipo Cellulose-Brazil (CENIBRA) was used in the preparation of composites with polyurethane. An elastomeric polyurethane based on polyether poly(tetramethylene glycol) and 4,4-diphenylmethane diisocyanate was used as polymeric matrix. Structural, thermal, and morphological characterization of the composites was carried out by infrared spectroscopy, thermogravimetry, differential scanning calorimetry, and scanning electron microscopy. The results indicate that interfacial interaction between the cellulose fiber residue and the polyurethane matrix occurs and that cellulose waste is a promising reinforcement for polyurethane composites. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 336–340, 2005

Key words: composites; renewable resources; cellulose waste; vegetal fibers; polyurethane

INTRODUCTION

The replacement of synthetic fibers for vegetal fibers in polymeric composites has attracted the attention of many researchers in recent times.[1,2] The use of vegetal fibers as a composite reinforcement can result in a material that combines good mechanical properties with low specific mass and smaller environmental impact compared to a totally synthetic material.[3–6] Among the natural fibers, cellulose fiber can be one of the main sources of the future as it is the most abundant organic compound in nature.[7,8] Curvelo et al.[9] showed that thermoplastic composites reinforced with cellulose fibers have superior mechanical properties compared to the thermoplastic non-reinforced materials.

Polyurethanes are versatile polymers largely employed in products that require high chemical and abrasion resistance.[10] The compatibility between polyurethane and microcrystalline cellulose was investigated by Ryabov et al.[8] Environmental degradation of the composites was also observed by these authors.

The aim of this study was to investigate the structural and thermal properties of a polymeric composite based on an elastomeric polyurethane reinforced with industrial waste cellulose fibers.

EXPERIMENTAL

The polyether poly(tetramethylene glycol) (PTMG), molar mass 1.000 g mol^{-1} and 4,4-diphenylmethane diisocyanate (MDI), both from Aldrich, were used as received. Dichloromethane and *N,N*-dimethylformamide (DMF) were used as solvents. The vegetal fiber used is an industrial waste from the cellulose pulp purification process called cellulose residue (CR). This residue was provided by the cellulose company Nipo-Brasileira S.A. (CENIBRA, Belo Oriente, Minas Gerais, Brasil), which produces white short cellulose fiber pulp. This cellulose waste, among other residues from CENIBRA, was previous characterized in our laboratory.[11]

Ground MDI was dissolved in DMF and added to cellulose fiber dispersed in dichloromethane. Then, the catalyst dibutyltin dilaurate was introduced. A solution of PTMG/dichloromethane was added to the mixture MDI/cellulose fiber. The reaction was stirred for 1 h and finally the solvent was removed from the mixture. The CR fiber was used in the ratios of 3 and 5% to the polymeric matrix mass. The composites were named PUCR3 and PUCR5 (which means polyurethane-cellulose residue in the concentration of 3 and 5 wt %). These concentrations allowed a homogeneous dispersion of the fibers in the matrix in our experimental conditions.

The structural study of PUCR3 and PUCR5 composites was carried out by using Fourier transform infra-

red spectroscopy by total attenuated reflectance (FTIR-ATR) and the study of the thermal properties was performed with thermogravimetry (TG) and temperature-modulated differential scanning calorimetry (TMDSC). Scanning electron microscopy (SEM) was used for morphological characterization. For FTIR-ATR analysis, the spectrometer FTIR-GX Perkin–Elmer with horizontal ATR (crystal of zinc selenate) was used in the spectral range from 4000 to 500 cm^{-1}. TG measurements were obtained with a Mettler Toledo Star System apparatus. TG measurements were conducted at 10°C min^{-1} in atmospheric air between ambient temperature and 750°C. TMDSC analysis was performed in an MTDSC 2920 TA Instruments apparatus. DSC curves were obtained in He atmosphere with a heating rate of 3°C min^{-1} and amplitude modulation of 0.5°C every 50 s between -100 and 220°C. The morphological study of the composites was carried out with a JEOL JSM-8404 scanning microscope. The samples were immersed in liquid nitrogen and broken. The fractured surfaces were coated with a fine gold layer.

RESULTS AND DISCUSSION

FTIR-ATR spectra for polyurethane (PU), cellulose fiber residue (CR), and composites PUCR3 and PUCR5, with 3 and 5 wt % of fiber, respectively, are presented in Figures 1 and 2 in different spectral regions. Table I presents tentative FTIR band attributions.

PU polymerization in the presence of cellulose fiber can be confirmed by the characteristic absorption bands of the urethane unit and by the presence of bands of different conformations of this unit. Polyurethanes based on polyethers can have four different hydrogen bond interactions: three interactions of urethane units occur between the N—H group and C=O (type I), N—H, and the alkoxy oxygen (type II), and between N—H groups (type III), while type IV conformation is established between the N—H group and the oxygen of the ether group of the flexible segment.[12,13]

The structure and nature of the matrix–fiber interface play an important role in the mechanical and physicochemical properties of composites.[14] The existence of covalent bonding and/or secondary interactions between the matrix PU and the fiber CR can be observed in the spectra of composites polyurethane/cellulose residue, PUCR3 and PUCR5, in the 4400- to 2000-cm^{-1} spectral range (Fig. 1). PU presents N—H absorption bands with bonded hydrogen at 3290 cm^{-1}. The FTIR spectra of the composites exhibit the band relative to the PU —NH group shifted to regions of higher wavenumber, being observed at 3309 cm^{-1} for PUCR3 and at 3307 cm^{-1} for PUCR5. For composite PUCR5, this band is also larger than the PU absorption at 3290 cm^{-1}. This result is an indication of
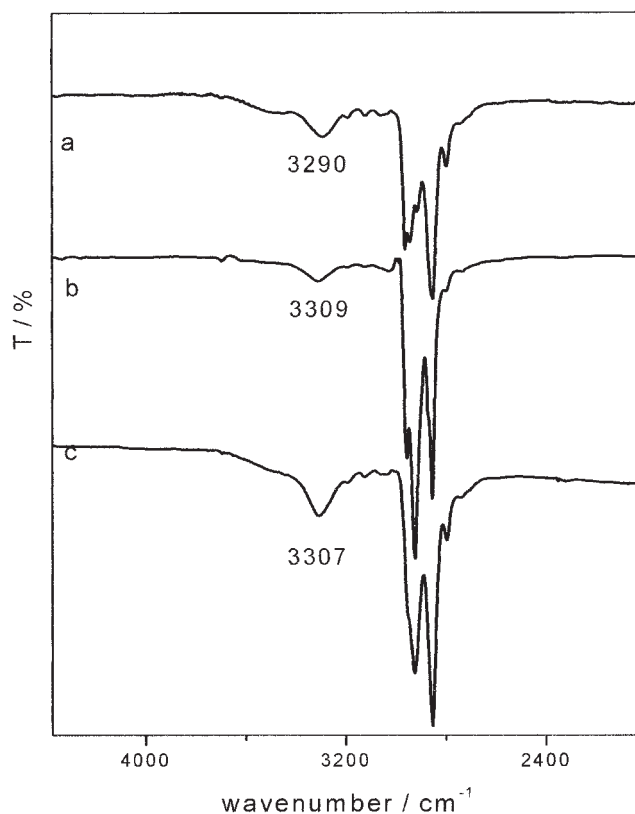

Figure 1 FTIR of (a) polyurethane (PU), (B) polyurethane/cellulose residue with 3 wt % of fiber (PUCR3), and (c) polyurethane/cellulose residue with 5 wt % of fiber (PUCR5) in the 4400 to 2000 cm^{-1} spectral region.

hydrogen interaction between cellulose fiber N—H and O—H groups.

Two other important pieces of information can be obtained from FTIR spectra, as follows: (1) an intensification of the band in the form of a shoulder characterized in the case of PU at 1708 cm^{-1} is observed in both composite spectra (Fig. 2). This intensification is attributed to the stretching of C=O with hydrogen bond interactions. (2) Also for the composites, the band at 1667 cm^{-1} associated with the stretching of C=O and the deformation of N—H with hydrogen bond interactions type 1 disappears.

Besides these observations, it should be mentioned that there is a reduction in the composite spectral relative intensity of N—H symmetrical deformation absorption at 798 cm^{-1} of PU.

These results indicate the occurrence of interfacial interactions between the polymeric matrix and the cellulose fiber. The observations that (1) C=O stretching with hydrogen bond interaction (1708 cm^{-1}) is better defined, and (2) the N—H symmetrical deformation (798 cm^{-1}) is reduced allow us to draw the conclusion that hydrogen bond interactions between C=O of PU and O—H of cellulose occur.

The whole FTIR data set can also support the conclusion that there are new urethane units in the com-
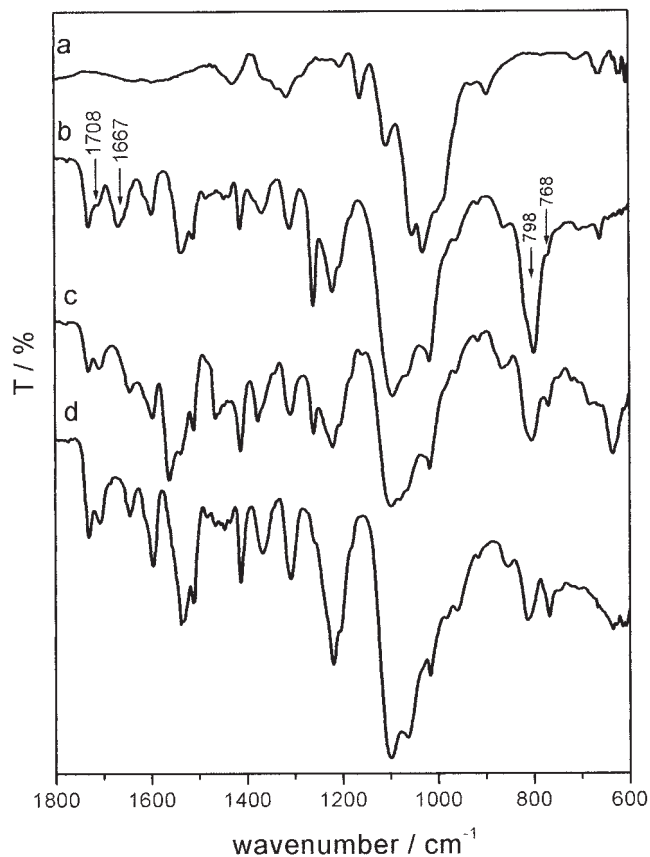
Figure 2 FTIR of (a) cellulose residue fiber (CR), (b) polyurethane (PU), (c) polyurethane/cellulose residue with 3 wt % of fiber (PUCR3), and (d) polyurethane/cellulose residue with 5 wt % of fiber (PUCR5) in the 1800 to 600 cm^{-1} spectral region.

posites associated with the formation of covalent bonds between the cellulose residue fiber and the polymeric matrix. However, this conclusion should be studied in more detail later.
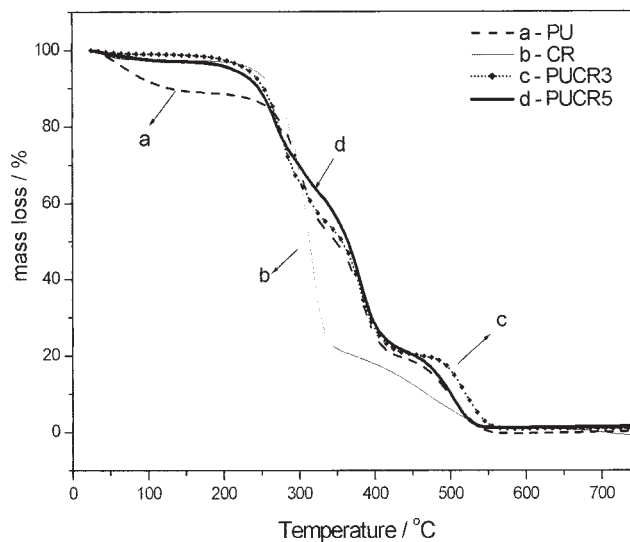

Figure 3 Thermogravimetric curves in air for (a) polyurethane (PU), (b) cellulose residue fiber (CR), (c) polyurethane/cellulose residue with 3 wt % of fiber (PUCR3), and (d) polyurethane/cellulose residue with 5 wt % of fiber (PUCR5).

Three stages of polymer decomposition can be observed in TG curves in atmospheric air (Fig. 3). Table II presents the peak temperatures and the total mass loss for PU, CR, and the composites. Polyurethane presented loss of volatiles at low temperature (solvent evaporation) and three stages of polymer degradation with mass losses of 37, 33, and 19% of the initial mass. The third stage can be attributed to the oxidation of polyurethane decomposition products and their evaporation, which justifies the absence of decomposition residue above 600°C.

For composites polyurethane/cellulose residue, PUCR3 and PUCR5, the TG curves in Figure 3 show that the presence of fiber in the polymeric matrix

TABLE I
Absorption Bands, in cm^{-1}, of in the Infrared Region of the Cellulose Residue (CR) Fiber, Polyurethane (PU) Matrix, and Composites with 3 and 5 wt % of fibers, PUCR3 and PUCR5, and Their Respective Attribution Attempts[12,13,17–19]

CR	Attribution	PU	PUCR3	PUCR5	Attribution
3334	νOH	3290	3309	3307	νN—H
2930–2855	νC-H	2936–2852	2960–2790	2925–2790	νC—H
1427	δCH$_2$	1667	—	—	νC=O and δN—H with hydrogen bond interaction-type I
1370–1250	δC—H, νC—O, and νC—C	1600–1500	1600–1500	1600–1500	δ aromatic ring
1160	δC—O—C	1400	1400	1400	δC—H
1106	C—O secondary alcohol vibration	1367	1375	1366	ν of —O—CO—CH
1054, 1031	νC—O or δC—O of ether and ester	1310	1307	1308	νC—N
898	δC—H of cellulose (β-anomeric linkage)	1219	1219	1220	δN—H with hydrogen bond interaction-type III
700–600	δC—O or glucose ring vibration	1102	1100	1098	ν of C—C(=O)—O
		1065	1065	1063	ν of O—C—C
		798	803	808	δN—H
		768	768	768	δ of C—H

TABLE II
Temperature of Maximum Degradation Rate (T_d) and Percentual Total Mass Loss of Cellulose Residue (CR), Polyurethane (PU), and Composites with 3 and 5 wt % of fiber, PUCR3 and PUCR5

Samples	T_d (°C)			Total mass loss (%)
CR	295	426	—	97
PU	300	380	500	100
PUCR3	295,335[a]	400	538	99
PUCR5	264,305[a]	379	500	99

[a] Thermal event split.

TABLE III
Heat Capacity (C_p) and Glass Transition (T_g) of Cellulose Residue (CR), Polyurethane (PU), and Composites with 3 and 5 wt % of fiber, PUCR3 and PUCR5

Sample	T_g (°C)	C_p/(Jg^{-1} °C^{-1})		
		25°C	100°C	175°C
CR	—	1.15	1.44	1.70
PU	−47	1.46	1.62	1.80
PUCR3	−50	1.73	2.01	1.84
PUCR5	−52	1.64	1.84	2.03

reduced solvent retention. Four peaks of degradation are observed in the DTG of the composites (Fig. 4), with an overlap of the first and second peaks. The three main events observed in the DTG of the composites can be associated with the decomposition of PU and cellulose with some shifts in peak temperatures. Nevertheless, the second mass loss peaks at 335 and 305°C for PUCR3 and PUCR5, respectively, Table II, may be an indication of the formation of a new phase due to PU–CR fiber interactions. In the literature, different mechanisms are proposed for the first stage of PU decomposition associated with the urethane scission.[15,16] The split of the first thermal degradation event in two peaks is a good indication of a new phase involving the urethane link in the interface with the possible covalent matrix–fiber bonding.

In both composites, the decomposition residue at 750°C corresponds to 1% of the initial mass. The formation of this residue is probably due to the oxidation of metals from the fiber.[11]

Through the TMDSC experiment, it was possible to determine the values of glass transition (T_g) attributed to the flexible segments of polyurethane, as well as values of heat capacity at constant pressure (C_p) for all samples studied. Table III presents T_g values for composites PUCR3 and PUCR5 at −50 and −52°C, respectively. The decrease in this event temperature in relation to the value observed for polyurethane PU (−47°C) can indicate an increase in the mobility of the flexible segment related to the presence of fiber in low concentration.

Table III shows the values of heat capacity for PU and CR samples, and for the composites at the temperatures of 25, 100, and 175°C. Both composites presented C_p values higher than the original components at all temperatures. This is an indication that the introduction of the fiber into PU increased the number of possibilities of movements of the chain segments (above T_g). This increase in mobility can be seen as due to new phases and interfaces and the ensuing increased disorder of the system.

SEM images of the fractured surface of composites PUCR3 and PUCR5 are presented in Figure 5. Both composites presented fibers dispersed in the polymeric matrix without expressive agglomeration. The images indicate a good adhesion between the polyurethane matrix and the CR fiber as independent and unattached fibers are not observed at the fractured surface. In the case of PUCR5, a highly porous matrix was obtained, probably due to experimental difficulties observed in the stages of cellulose dispersion or solvent drying.
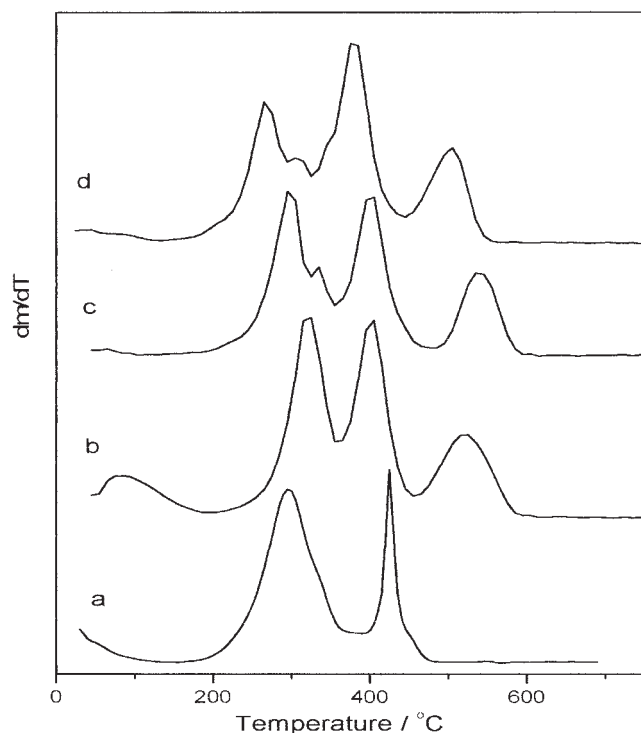

Figure 4 First derivative of the thermogravimetric curve (DTG) in air for (a) cellulose residue fiber (CR), (b) polyurethane (PU), (c) polyurethane/cellulose residue with 3 wt % of fiber (PUCR3), and (d) polyurethane/cellulose residue with 5 wt % of fiber (PUCR5).

CONCLUSIONS

The following FTIR-ATR results for the PU/CR fiber composites are presented: (1) the displacement of the
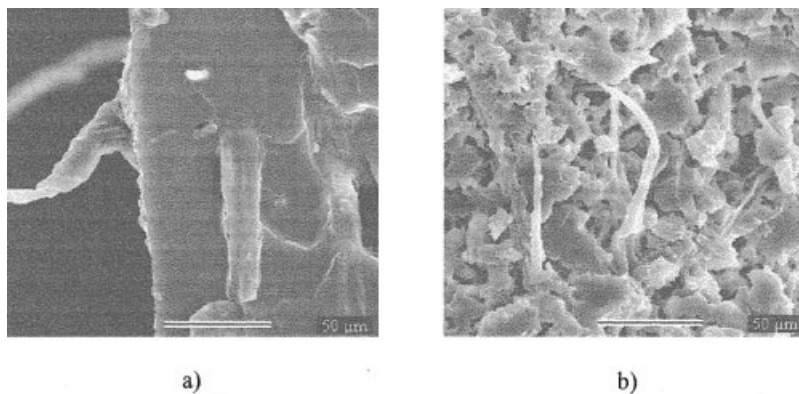
Figure 5 Scanning electron microscopy images with scale bar of 50 μm for the composites (a) polyurethane/cellulose residue 3 wt %, PUCR3, and (b) polyurethane/cellulose residue 5 wt %, PUCR5.

N—H group symmetrical stretching of the polymeric matrix to regions of higher wavenumber; (2) the absence of the deformation band of urethane type I; (3) a higher intensity of the band at 1708 cm^{-1} associated with the stretching of C=O of the urethane unit with hydrogen bond interactions; and (4) the reduction of the relative intensity of the deformation band of N—H at 798 cm^{-1}. These results suggest the existence of hydrogen bond interactions, and even covalent linkage, between cellulose residue fibers and the polymeric matrix.

The formation of a new phase due to interactions between PU and CR fiber is shown in the results of the thermal characterization of composites polyurethane/cellulose residue, PUCR3 and PUCR5, through the split of the first degradation event exhibited in the DTG curves, and the increase in mobility of the system after the introduction of CR fibers, characterized by the C_p data obtained in TMDSC.

The presence of fibers in the fractured surface of the composites without the pull-out effect, as observed through SEM micrographs, added morphological evidence of interfacial interaction between the cellulose residue fiber and the polyurethane matrix to the structural and thermal characterization results.

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