Glycerol-derived polyurethane nanocomposites containing cellulose nanowhiskers

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ABSTRACT. This work describes the synthesis of glycerol-derived polyurethane nanocomposite films containing unmodified cellulose nanowhiskers (CNW) or hexamethylene diisocyanate-modified cellulose nanowhiskers ([HDI]CNW) as a mechanical support. Cellulose was prepared from sugarcane bagasse using a delignification and whitening approach that is wholly free of chlorine. CNW's were obtained by acid hydrolysis in hydrochloric acid. The formation of nanocomposites was demonstrated by NMR, TEM, FTIR and WAXD. The films with different concentrations of CNW and [HDI]CNW were characterized by FTIR spectroscopy, and stress-strain measurements. The samples experienced plastic deformation as subjected to an increasing elongation load, and right after yield limit, they fractured without necking. In such a case, the limit tension, which is the maximum stress supported by the sample, matches with the rupture tension. Polyurethane nanocomposites with CNW (CNW-PU) showed values of modulus of elasticity and tensile strength higher than [HDI]CNW-PU.

Keywords: polyurethane, cellulose nanowhisker, sugarcane bagasse.

Nanocompósitos de poliuretanas derivadas de glicerol contendo nanocristais de celulose

RESUMO. Este trabalho descreve a síntese de filmes de nanocompósitos de poliuretanas derivadas do glicerol contendo nanowhiskers de celulose não modificados (CNW) ou nanowhiskers de celulose modificados com hexametileno diisocianato ([HDI]CNW) como reforço. A celulose foi preparada a partir do bagaço da cana-de-açúcar usando deslignificação e branqueamento livre de cloro. CNW's foram obtidos pela hidrólise em ácido clorídrico. A formação dos nanocompósitos foi demonstrada por RMN, MET, IV e DRX. Os filmes de nanocompósitos com diferentes concentrações de CNW e [HDI]CNW foram caracterizados por espectroscopia na região do infravermelho e medidas de tensão-deformação. As amostras apresentaram deformação plástica quando sujeitas a uma carga crescente de alongamento, e foram fraturadas logo após o limite de elasticidade, sem estiramento. Nesse caso, a tensão limite, que é a tensão máxima suportada pela amostra, coincide com a tensão de ruptura. Os nanocompósitos de poliuretana com CNW (CNW-PU) mostraram o módulo de elasticidade e resistência à tração superiores a [HDI]CNW-PU.

Palavras-chave: poliuretana, nanocristais de celulose, bagaço da cana-de-açúcar.

Introduction

Polymer-based nanocomposites involving materials from renewable sources have been the target of important scientific investigations aiming at preserving the environment and proving a better standard of life and social status. Currently, applications of naturally occurring modifiers, such as natural fibers, appear to be an innovative approach of a great scientific interest (BALZER et al., 2007; NECHWATAL et al., 2003; PLAYNE, 1984). The natural fibers are used in the 'in nature' or after-treatment forms. Brazilian fibers show great potential as modifier for thermoplastic polymers. The production of ethanol from sugarcane bagasse has proved to be a viable approach to displace petroleum-derived fuels on a global scale. The main waste from production of ethanol from sugarcane is bagasse. It is also the waste from production of biodiesel as obtained through a reaction route having ethanol as a basic insume.

Cellulose may be obtained from sugarcane bagasse (HENDRIKS; ZEEMAN, 2009; SILVA et al., 2009; YU et al., 2008). Cellulose whiskers with different levels of crystallinity may be obtained using a cellulose-hydrolyzing approach. The use of lignocellulosic fibers and cellulose whiskers, in the raw or modified forms, as a mechanical support for devices based on both natural and synthetic polymers has been the target of

current and growing investigations aiming at developing inorganic material-based biocomposites (NETO et al., 2007; PINTO et al., 2005).

Cellulose fibers, such as whisker (CW) or nanowhisker (CNW), may be modified by different processes (BRINCHI et al., 2013; FIORELLI et al., 2011). Some studies have demonstrated that the chemical treatments reduce fiber impurity, increase the effective fiber surface area, and significantly improve interfacial matrix/fiber adhesion. This is due to the binding of hydroxyls to other components (BLEDZKI; GASSAN, 1999; COLOM et al., 2003).

The combination of properties of whisker from sugarcane bagasse with highly versatile polymers such as polyurethane may be used to produce composites with specific properties. The nature of the fibers, which are rich in hydroxyls, suggests that they are particularly interesting in polyurethane-based systems, in which the hydroxyl groups at the fiber may form chemical bonds with $N = C = O$ groups from diisocyanates (MOHEBBY et al., 2009; WILPISZEWSKA; SPYCHAJ, 2007).

A large variety of polyols are used in the production of polyurethane. Glycerol is an interesting polyol that may be used in polymers and composite synthesis since it is from biodisel subproduct, besides properties like hydrofobicity and trifunctionality (HU et al., 2012).

Currently, the use of glycerol in the industrial sector is addressed to cosmetics, soaps and pharmaceutical formulations (MOTA et al., 2009). A large amount of glycerol is used in the polymer industry (HU et al., 2012; SIVAIAH et al., 2012). For example, the production of alkyd resins requires 6% of the material available on the market (STUMBÉ; BRUCHMANN, 2004). The reaction of glycerol with diisocyanate through a polyaddition reaction between hydroxyl groups and isocyanates results in a highly branched polymer (ZHANG et al., 2004). The mechanical properties of the formed material can vary a great deal (from elastomeric to rigid solid) and depend on parameters such as branch degree, ratio of glycerol to diisocyanate, and chemical characteristics of diisocyanate (ZHANG et al., 2004).

The present work aims at the use of waste generated by the sugar industry and the production of biodiesel, and turn them into materials with unique characteristics adding economic value in a sustainable manner and contribute to increasing the economic viability of biodiesel as a renewable energy source global.

Material and methods

Synthesis of cellulose nanowhiskers (CNW)

The sugarcane bagasse (BSC), previously separated from its husk, was cut into smaller pieces and subsequently washed with water at room temperature while stirring. The samples were dried in an oven at 40°C for 7 days and then crushed with the use of a cutting mill, in the absence of light or humidity. After being washed and dried at room temperature, 100 g of crushed bagasse was submitted to a pre-treatment in water, hexane and toluene/ethanol (2:1) mixture for removal of impurities (MOHAN et al., 2006; ROGALINSKI et al., 2008; SUN et al., 2004). Each stage of the treatment was performed at 40°C for 3h, and in the interval of each stage, bagasse was filtered and dried in an air-circulating oven at 50°C for 20h. The yield of bagasse after the whole treatment was around 85%. For delignification and whitening, the material was submitted to a step-five treatment sequence: i) aqueous solution of 6% NaOH, mechanical stirring for 6h; ii) aqueous solution of 35% peracetic acid (PAA), 60°C, mechanical stirring for 22h; iii) aqueous solution of 45% PAA, 60°C, mechanical stirring for 24h; iv) aqueous solution 60°C, mechanical stirring for 6h; v) aqueous solution of 6% NaOH, 60°C, mechanical stirring for 18h. The yield of cellulose obtained after delignification and whitening processes (namely, whitened cellulose, Wcell) was of 40%. To obtain nanowhiskers using an acid hydrolysis approach, whitened cellulose was treated with hydrochloric acid (37% HCl) using a [cellulose/HCl] ratio of [1 g / 25 mL] at 45°C. After 1h of reaction, the system was cooled to 25°C and the sample was continually washed until a pH 3 was obtained. After hydrolysis, whitened cellulose was dialyzed using high retention seamless cellulose tubes with a cut-off of 12.000 Daltons until a neutral pH was reached. The yield of whitened cellulose nanowhisker (CNW) was of 61%, calculated as the average over three experiments.

Chemical modification of CNW with hexamethylene diisocyanate (HDI) for [HDI]CNW

Known amounts of CNW were added to 50 mL of tetrahydrofuran (THF) under reflux while stirring. After 5 min., 100 μL of dibutyltin dilaurate was added as catalytic agent, and right after, HDI was incorporated. After 72h of reaction, the product ([HDI]CNW) was filtered, washed with hot THF and dried at room temperature. The [CNW/HDI] ratios (wt wt^{-1}) used in the CNW-modifying reaction were [1:4], [1:6], [1:8]; [1:10] and [1:20].

Synthesis of polyurethane (PU) composites containing CNW (CNW-PU) by solvent casting

Pre-determined amounts of polyethylene glycol 1,000 (PEG-1000) and glycerol ([PEG/glycerol] ratio of [1:10] in wt wt^{-1}) were added to 25 mL of ethyl acetate at 50°C while stirring. Then, dibutyltin dilaurate (0.3% in relation to glycerol weight) and HDI ([NCO/OH] ratio of [1.6/1]) were incorporated. After 5 min. under vigorous stirring, the resultant mixture was poured on a glass mould that was left for 24h at room temperature to evaporate solvent. After that, a film with a thickness of 0.2 mm was formed.

To prepare CNW-PU and ^{HDI}CNW-PU composites, the cellulose nanowhiskers were introduced as reinforcement in the proportion of 1, 2.5, 5 and 20% (wt wt^{-1}) with respect to glycerol weight. For this purpose, cellulose nanowhiskers were dispersed in 12 mL of ethyl acetate for 3h with the use of an ultrasonic bath 1440 A (Ondontobrás) by applying a frequency of 44 kHz.

Characterizations

FTIR spectra were recorded on a Bomen FT-IR model MB100 spectrometer in the spectral region of 4000 a 400 cm^{-1}. The samples were analyzed in photo-acoustic mode. Measures were performed in triplicate and a total of 128 scans were run for each spectrum to reach the resolution of 4 cm^{-1}.

NMR spectra were performed on Varian Mercury plus BB 300 MHz spectrometer equipped with a probe of 7 mm for Solid-state ^{13}C-CP/MAS NMR. The spectra were obtained by applying a frequency of 75.457 MHz for ^{13}C. The samples were placed in a 7 mm-diameter dimension silicon nitride rotor with a Kel-F cover. The spectrum of hexamethylbenzene (methyl signal at 17.3 ppm) was used as external reference.

The index of apparent crystallinity was determined through the resolutions of ^{13}C-CP/MAS NMR curves. Deconvolution was applied to spectral region of 92-80 ppm by the method of least squares curve-fitting with use of a WinSpec/32 software ver. 2.5.12.0 (Princeton Instruments). Lorentzian distribution function was applied for resolution of the bands, according to Equation 1.

$$IC_{NMR'}\% = \frac{100a}{(a+b)} \qquad (1)$$

where:

a and b are the sum of the integrals in the spectral region of 92-86 ppm and in the spectral region of 86-80 ppm, respectively.

Wide-angle X-rays diffraction (WAXD) patterns were recorded on a Siemens Kristaloflex 4-Difractometer equipped with a Ni-filtered Co-K$_\alpha$ radiation by applying an accelerating voltage of 40 kV and a current intensity of 30 mA. The WAXD data were collected in the scale of $2\theta = 5°\text{-}50°$ at a scanning speed of 1° min^{-1}.

Crystalline allomorphs were determined through the resolutions of the WAXD curves. The curves were deconvoluted without a base line by the method of least squares curve-fitting using Lorentzian distribution function, according to Equation 2.

$$IC_{RX} = \frac{1-h_{am}}{h_{cr}} = \frac{1-h_{am}}{h_{tot}-h_{am}} \qquad (2)$$

where:

h_{cr} is the maximum intensity (a.u.) of the WAXD signal for (002) crystalline plan at $2\theta = 22.5°$ and h_{am} is the maximum intensity (a.u.) of the WAXD signal for amorphous reflection $2\theta = 18°$.

The components of cellulose I and cellulose II were determined from three, four reflections by the deconvolution of the WAXD curves (OH et al., 2005). From sum of the integrals in the spectral region corresponding to the same crystalline system ($\sum A_{CI}$ for cellulose I and $\sum A_{CII}$ for cellulose II), the contributions of each allomorph were divided into IC$_{RX\text{-}CI}$ for cellulose I and IC$_{RX\text{-}CII}$ for cellulose II, according to Equation 3.

$$IC_{RX-CI} = \frac{\sum A_{CI}}{\sum (A_{CI} + A_{CII})} \times IC_{RX}$$
$$IC_{RX-CII} = \frac{\sum A_{CII}}{\sum (A_{CI} + A_{CII})} \times IC_{RX} \qquad (3)$$

The dimension of the crystallites $D_{(hkl)}$ was defined by applying Scherrer equation.

$$D_{(hkl)} = \frac{K\lambda}{\beta_{1/2} \cos\theta} \qquad (4)$$

where:

K is the shape factor approximately 0.92, λ is the X-ray wavelength typically 1.54 Å, $\beta\frac{1}{2}$ is the line broadening at half of the maximum intensity in radians, and θ is the Bragg angle.

For transmission electron microscopy (TEM) images, drops of stirred aqueous suspensions of CNW or ^{HDI}CNW were deposited on glow-discharged carbon coated TEM grids and the excess of water was

left to evaporate. The specimens were stained with 2% uranyl acetate and the TEM images were recorded on a JEOL JEM 1200FxII electron microscope by applying an acceleration voltage of 80 kV.

Determination of NCO content

The determination of free isocyanate content (NCO%) was performed by titrimetric analysis, based on ASTM D2572-97 using Equation 5.

$$NCO\% = [(B-V) \times N \times 0.0420] \times 100 (10) W \quad (5)$$

where:

NCO is the NCO content (in %), B is the consumed volume of HCl (in mL) for reference, V is the volume of HCl consumed by the sample (in mL), M is the normality of HCl solution (in $m$eq mL^{-1}), and W is the weight of the sample.

Stress-strain measurements for mechanical properties

The composite tensile strength and modulus assays were performed according to the ASTM D-882-10 test method. The samples were submitted to tensile tests in an Texture Expert machine equipped with 500-N load cell and operated at a constant cross-speed of 0.8 mm s^{-1}. Tensile properties were determined for eight samples of each composition (50 x 10 mm) conditioned at a relative humidity of approx. 58% (saturated solution of NaBr) and temperature ranging from 20 to 25°C for 21 days. The elongation of the specimens was determined on a 30 mm-length dimension extensometer.

Results and discussion

Characterization of CNW

Figure 1A shows the ^{13}C-CP/MAS NMR spectra of CNW and whitened cellulose. Both samples showed characteristic signals of glucose rings, which were identified as follows: C1 (105.1 ppm), C4 (89-82 ppm), C2 (74.9 ppm), C3 (74.9 ppm), C5 (74.9 ppm), and C6 (65-63 ppm). These are strong indicative of the attachment of glucose on cellulose. Figure 1B shows the application of deconvolution to the spectral region of 92 to 80 ppm in the NMR spectrum of CNW. It can be seen in Figure 2A the wide-angle X-rays diffraction (WAXD) patterns of BSC, WCELL and CNW. Figure 2B shows the application of deconvolution to the spectral region of 7.5-32.5° in the WAXD pattern.

The crystallinity indexes of CNW and whitened cellulose were obtained from ^{13}C-CP/MAS NMR spectra ((IC$_{RMN}$) Figure 1B)) and WAXD patterns ((IC$_{RX}$) Figure 2B)). The data were summarized in Table 1.

There was an increase in the apparent crystallinity of CNW, as a result of acid hydrolysis. The dimension of the crystallites in CNW is in the range of 3.2-4.4 nm.
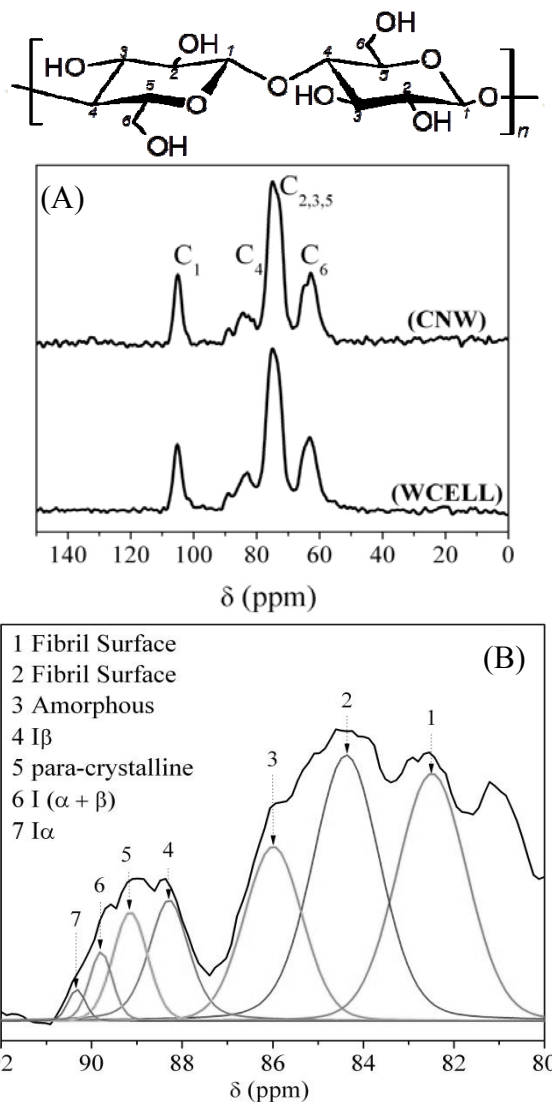

Figure 1. ^{13}C-CP/MAS NMR spectra of CNW and WCELL (A). Application of deconvolution to the spectral region of 92-80 ppm in the NMR spectrum (A) of CNW (B).

Table 1. Crystallinity indexes (IC), obtained from ^{13}C-CP/MAS NMR spectra and WAXD patterns, for whitened cellulose and CNW.

	IC$_{RMN}$	IC$_{RX-CI}$	IC$_{RX-CII}$	IC$_{RX}$
		(%)		
WCELL	18	52	19	71
CNW	20	53	23	76

Figure 3 shows the TEM micrographs of CNW. Although agglomerates of crystalline nanostructures are observed, they suggest the formation of nanowhiskers.
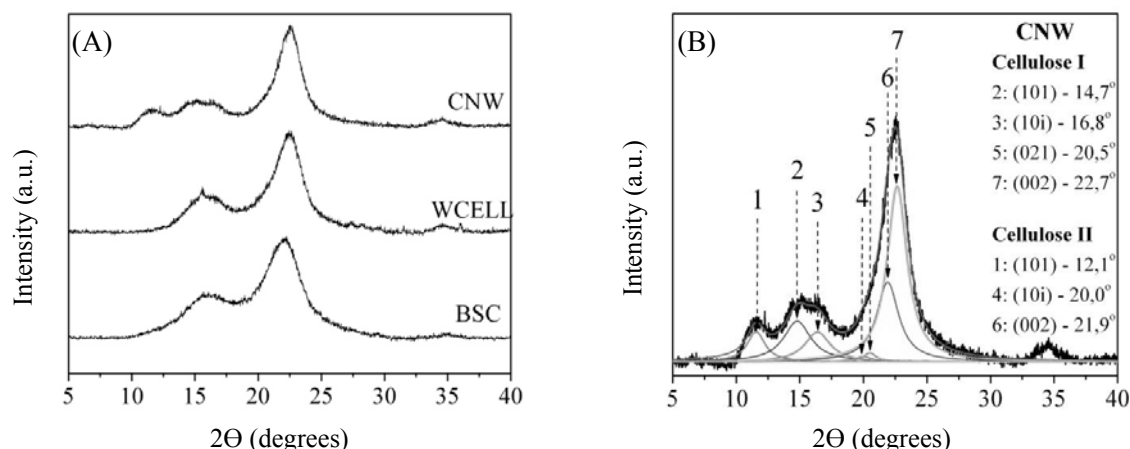
Figure 2. (A) Wide-angle X-rays diffraction (WAXD) patterns of BSC, WCELL and CNW. (B) Application of deconvolution to the spectral region of 7.5-32.5° in the WAXD pattern (A) of CNW (B).
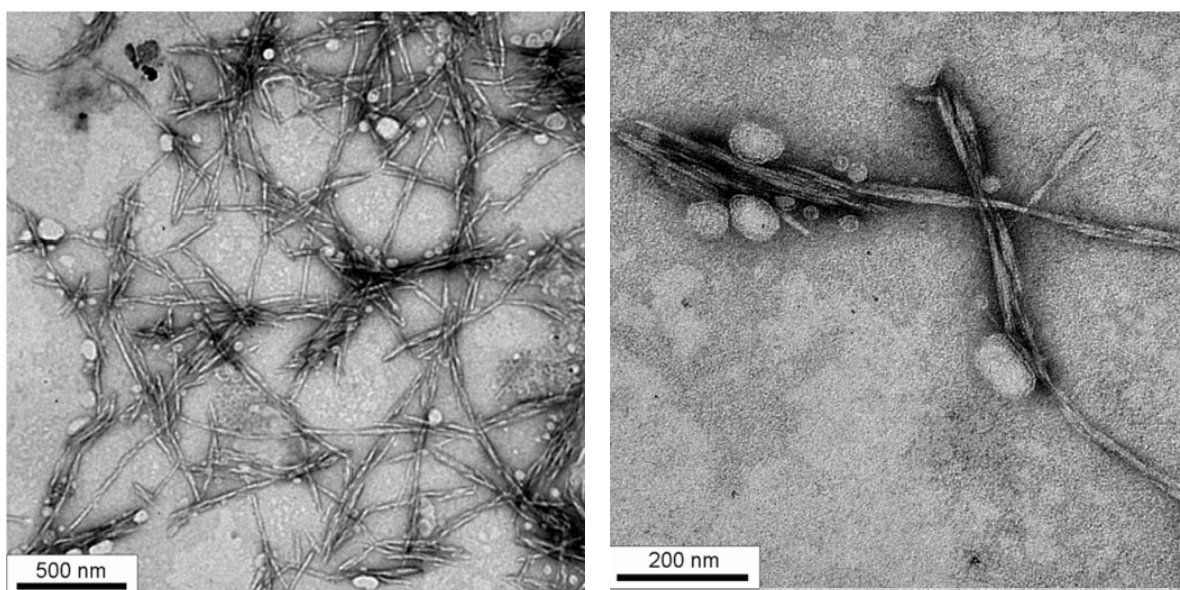

Figure 3. Transmission electron microscopy (TEM) micrographs of CNW.

Figure 4A shows the FTIR spectra of CNW, and [HDI]CNW synthesized using different [HDI/CNW] ratios. The characteristic band of –NH groups at 3337 cm^{-1} in the spectra of [HDI]CNW overlaps with the band of –OH groups. The band appearing at the spectral region of 3000-2790 cm^{-1} was attributed to –CH$_2$ groups of HDI and –CH groups of cellulose. The band at 2262 cm^{-1} was associated to free –NCO groups. The bands at 1578 cm^{-1} and 1256 cm^{-1} were attributed, respectively, to –CN stretching (amide II) and –NH deformation (amide III) vibrations.

The bands at 772 cm^{-1} and 734 cm^{-1} in the spectrum of Figure 4A (b to h), corresponded to –NH out-of-plane deformation (amide), are characteristics of urethane bond (NH–CO–O–), a strong evidence of the reaction of CNW with HDI.

The bands at 1703 cm^{-1} (C=O of urethane) and 1622 cm^{-1} (C = O of urea) (RATH et al., 2008; ZIA et al., 2008) in the same figure are additional evidences of the [HDI]CNW formation and can be better visualized in Figure 4B.

Figure 5 shows the ^{13}C-CP/MAS NMR spectra of CNW, and [HDI]CNW synthesized using different [HDI/CNW] ratios. The signals at 31 ppm and 42 ppm in the spectra of [HDI]CNW were attributed to CH$_2$ groups of HDI and the signal at 160 ppm was corresponded to C = O groups of cellulose. The characteristic signals of C = O groups were detected at 155 ppm (urethane) and 165 ppm (urea) and the pattern of which sample can be better distinguished at Figure 5B. The difference between the chemical shifts of C = O groups of urethane and urea is only

2 ppm (δ_{urea} 160.1 ppm, $\delta_{urethane}$ 162.1 ppm) (JAISANKAR et al., 2009). This could explain the overlap of both signals at 160 ppm.
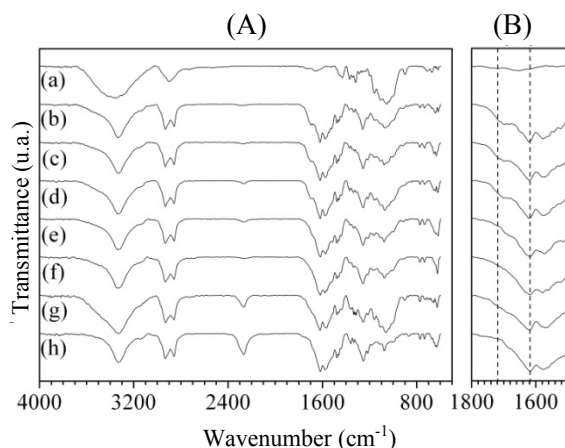

Figure 4. (A) FTIR spectra of CNW (a), [HDI]CNW [2/1] (b), [HDI]CNW [4/1] (c), [HDI]CNW [6/1] (d), [HDI]CNW [8/1] (e), [HDI]CNW [10/1] (f), [HDI]CNW [20/1] (g), and HDI-HDI (h). The numbers inserted in square brackets indicate the [HDI/CNW] ratio. (B) Corresponding FTIR spectra shown in the spectral region of 1800 cm^{-1} to 1500 cm^{-1}.

The characteristic signals of cellulose gradually reduce (comparatively to the signals of HDI) when the amount of HDI in the reaction increases. In the spectrum of [HDI]CNW [20/1], they may not be differed from signals of HDI-HDI, suggesting that the products of secondary reactions are in amount higher than modified cellulose.
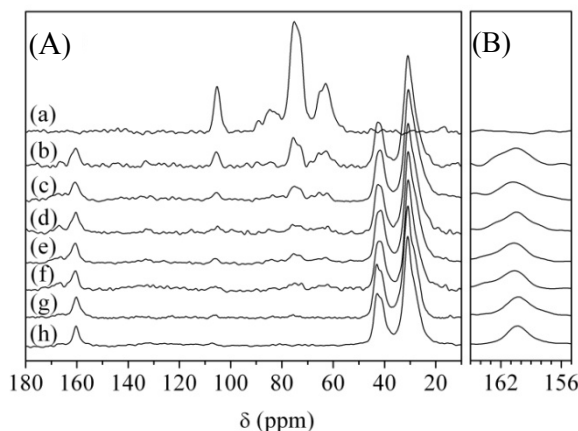

Figure 5. (A) ^{13}C-CP/MAS NMR spectra of CNW (a), [HDI]CNW [2/1] (b), [HDI]CNW [4/1] (c), [HDI]CNW [6/1] (d), [HDI]CNW [8/1] (e), [HDI]CNW [10/1] (f), [HDI]CNW [20/1] (g), and HDI-HDI (h). The numbers inserted in square brackets indicate the [HDI/CNW] ratio. (B) Corresponding ^{13}C-CP/MAS NMR spectra shown in the spectral region of 165 ppm to 155 ppm.

In Table 2 it is described the %NCO data for [HDI]CNW. There was an increase in free NCO content of 0.26% to 1.84%. [HDI]CNW [2/1] showed

better free NCO result (0.56%), owing to lower amount of HDI used in its synthesis.

Table 2. Percentages of free NCO for [HDI]CNW.

	[HDI]CNW					
	[2/1]	[4/1]	[6/1]	[8/1]	[10/1]	[20/1]
Average	0.56	0.46	0.26	0.59	0,85	1.84
SD* (%)	± 0.08	± 0.08	± 0.07	± 0.01	± 0.08	± 0.31

*SD: Standard Deviation

CNW-PU nanocomposites

The formation of CNW-PU composites and PU films issued from glycerol occurs by an addition reaction between hydroxyl groups on glycerol and isocyanate groups on HDI, forming urethane bonds. A proposed schema of a hyperbranched polymer that is the product of such a reaction is shown in Figure 6. PEG was added to CNW-PU formulation because it is also a source of hydroxyl groups and acts as a plasticizer.
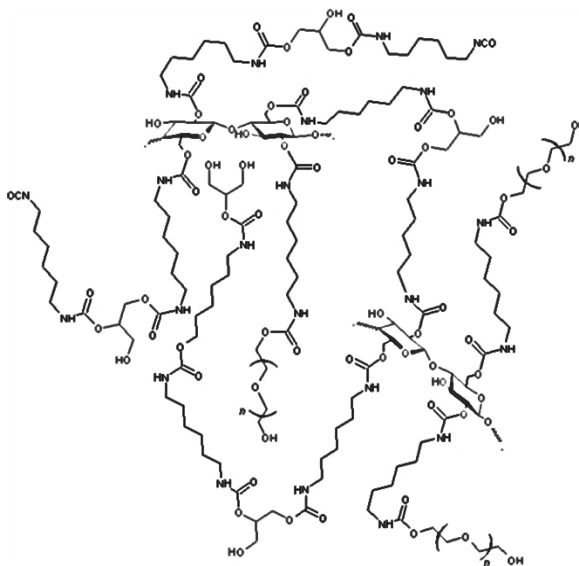

Figure 6. Schema of a hyperbranched polymer that is the product of reaction between hydroxyl groups on glycerol and isocyanate groups on HDI.

Figure 7 shows the FTIR spectra of PU, CNW-PU and [HDI]CNW-PU. The bands corresponding to axial deformation of free N = C = O groups at 2262 cm^{-1} were absent in the spectra of CNW-PU and [HDI]CNW-PU, indicative of the reaction of isocyanate groups on HDI with hydroxyl groups on glycerol.

The bands of cellulose were not detected in the spectra of CNW-PU1, CNW-PU2.5, and CNW-PU5. However, in the spectrum of CNW-PU20, which is the cellulose-richer sample, the characteristic bands appear at 1370 cm^{-1} (C-H deformation) and 1320 cm^{-1} (O-H in-plane vibration). The absence of characteristic bands of

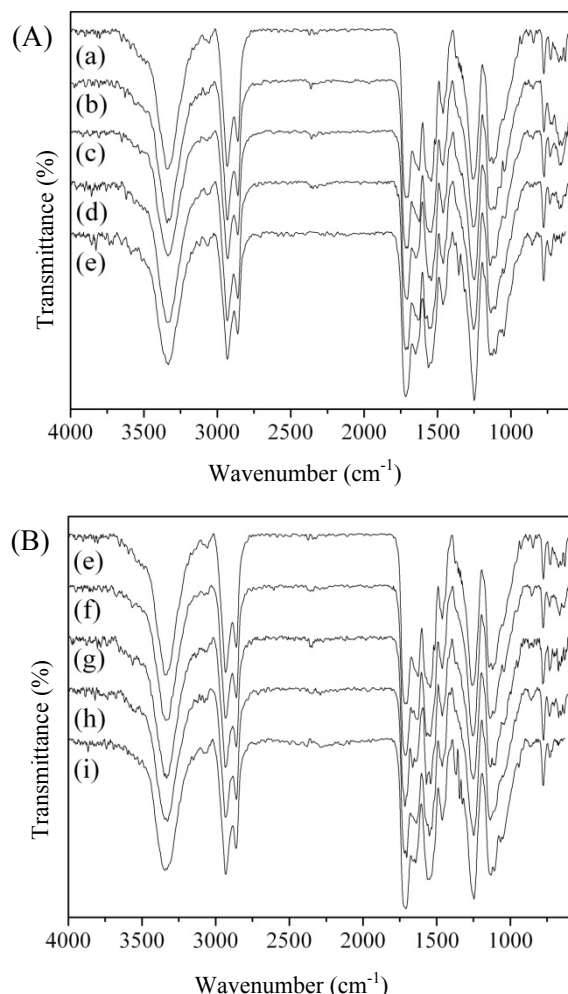whisker was attributed to a very small quantity of this material in the sample.

Figure 7. (A) FTIR spectra of PU (a), CNW-PU1 (b), CNW-PU2.5 (c), CNW- PU5 (d), and CNW-PU20 (e). (B) FTIR spectra of [HDI]CNW-PU1 (f), [HDI]CNW-PU2.5 (g), [HDI]CNW-PU5 (h), and [HDI]CNW-PU20 (i).

Figure 8 shows the applied stress versus the strain of PU, CNW-PU and [HDI]CNW-PU. The data generated from the correlation of the stress to the strain indicated materials of fragile structures when they were under an applied load. The samples experienced plastic deformation as subjected to an increasing elongation load, and right after yield limit, they fractured without necking. In such a case, the limit tension, which is the maximum stress supported by the structure of the sample, matches with the rupture tension.

The dispersion of the nanowhiskers in the polymer device can be a tensile strength-limiting factor. For example, when the nanowhiskers are well dispersed, the mechanical properties improve. But, if the nanowhiskers are agglomerated, a high stress

concentration may be created and mechanical properties may be decreased. CNW-PU20 and [HDI]CNW-PU20 showed values of E and T lower than other compositions.
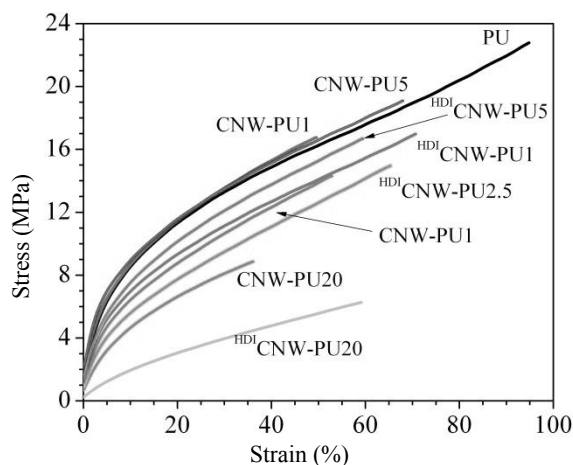

Figure 8. Applied stress versus the strain of PU, CNW-PU1, CNW-PU2.5, CNW- PU5, and CNW-PU20, [HDI]CNW-PU1, [HDI]CNW-PU2.5, [HDI]CNW-PU5, and [HDI]CNW-PU20.

Furthermore, CNW-PU showed values of E and T higher than [HDI]CNW-PU. CNW-PU5 showed the highest values of E, T, L, and toughness, comparatively to other nanocomposites. It also showed values of E slightly higher than PU.

Conclusion

Glycerol-derived polyurethane nanocomposites containing unmodified cellulose nanowhiskers or hexamethylene diisocyanate-modified cellulose nanowhiskers as mechanical support were developed. The cellulose was prepared from sugarcane bagasse using a delignification and whitening approach. The cellulose nanowhiskers were obtained by acid hydrolysis in hydrochloric acid. The data generated from the correlation of the stress to the strain indicated materials of fragile structures when they were under an applied load. The samples experienced plastic deformation as subjected to an increasing elongation load, and right after yield limit, they fractured without necking. In such a case, the limit tension, which is the maximum stress supported by the structure of the sample, matches with the rupture tension. CNW-PU5 and [HDI]CNW-PU5 showed values of E and T lower than other compositions. Furthermore, CNW-PU showed values of E and T higher than [HDI]CNW-PU. CNW-PU5 showed the highest values of E, T, L, and toughness, comparatively to other nanocomposites.

Acknowledgements

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