

Nanocellulose reinforced polyurethane obtained from hydroxylated soybean oil

A Ivdre^{1,2}, V Mucci³, P M Stefani³, M I Aranguren³ and U Cabulis¹

¹Polymer Laboratory, Latvian State Institute of Wood Chemistry, Riga, LV-1006, Latvia

²Riga Technical University, Faculty of Material Science and Applied Chemistry, Institute of Polymer Materials, P. Valdena Street 3, Riga, LV-1048, Latvia

³Institute of Research in Materials Science and Technology (INTEMA), National University of Mar del Plata - National Research Council (CONICET), Mar del Plata, Argentina

E-mail: aiga.ivdre@gmail.com

Abstract. In this research, cellulose nanocrystals were successfully obtained from microcrystalline cellulose and dispersed in a polyurethane matrix. Cellulose nanocrystals were characterized by dynamic light scattering. Polyurethane matrix was prepared from hydroxylated soybean oil, tertiary amine catalyst and polymeric diphenyl diisocyanate. Nanocellulose reinforced polyurethane composites were successfully prepared with different concentration and good dispersion of cellulose nanocrystals. Thermal properties and tensile strength of the resulting films were evaluated and dynamic mechanical analysis was carried out. The glass transition temperature of the nanocomposites increased slightly by increasing concentration of nanocellulose. The highest tensile strength was found for the nanocomposite with 1 wt% of cellulose nanocrystals.

1. Introduction

Polyurethane (PU) has become one of the most widely used plastics for various applications such as thermal insulation, construction, automotive parts and seating materials, in forms of rigid, semi-rigid and flexible foams as well as elastomers. Polyols for PU production are derived mostly from petrochemical products but can be replaced by renewable materials. The use of renewable resources in materials has attracted great interest in both industrial and academic fields because of their environmental aspect and sustainability [1, 2]. Polyols from such a natural oils as soybean [3-4], castor [5-6], palm oils [7-8], rapeseed [9-12] and sunflower oils [12-13] for obtaining PU materials has been widely investigated.

Also, different natural fillers could be used to improve characteristics of PUR, to reduce production costs and to enhance the renewable content in the product. The three major chemical components of biomass, cellulose, hemicellulose and lignin are utilized in diverse fields, such as biofuels, biomaterials, including conventional composites and novel nanocomposites, and other value-added chemicals [14]. Cellulose is a carbohydrate building block obtained from many prevalent resources to include wood, hemp, ramie, cotton, and bacteria [15]. It constitutes the most abundant renewable polymer resource available today. Most studies found in the literature about biocomposites use cellulose as simple “filler” which in some cases contributes to enhance the rigidity but mostly embrittles the polymer [16]. Through different processes cellulose can be separated into nano-scale forms [17-18]. The main process for the isolation of cellulose nanocrystals (CNC) from cellulose fibers is based on acid hydrolysis. When cellulose fibers are subjected to acid hydrolysis, the fibers yield defect-free, rod-like crystalline residues called nanowhiskers [17]. CNC is often being regarded as the next generation renewable reinforcement for the production of high performance biocomposites. CNC have been the subject of a wide array of research efforts as reinforcing agents in nanocomposites due to their low cost, availability, renewability, light weight, nanoscale dimension, and unique morphology [1, 19].



The present paper describes a method for obtaining well dispersed nanocomposites from hydroxylated soybean oil and different concentration of CNC. The mechanical and thermal properties of obtained nanocomposite films were investigated and compared.

2. Experimental

2.1. Materials

Polyurethane was prepared from the reaction of 4,4'-diphenylmethane diisocyanate prepolymer, pMDI (Rubinate 5005, Huntsman Polyurethanes, USA) with an equivalent weight of 131 g/eq and Agrol 3.6 (Biobased Technologies, USA) as the polyol component. This polyol was a hydroxylated soybean oil, OH value = 120.8 mg KOH/g (measured according to DIN 53240 norm). Dibutyl tin dilaurate (DBTDL) (Alkanos S.A. Co.) was used as the catalyst for the reaction. Commercial microcrystalline cellulose from Sigma Aldrich (USA) was acid hydrolyzed to prepare CNC. Other reagents used were: sulfuric acid, acetone (from Cicarelli, Argentina).

2.2. Synthesis and characterization of CNC

Acid hydrolysis of microcrystalline cellulose was carried out to obtain CNC. 15 g of microcrystalline cellulose and 52.5 g of distilled water were mixed in a flask by mechanical agitation. Afterwards 97.5 g of sulfuric acid (98 wt%) was added drop by drop while controlling that the temperature of the mixture did not exceed 30 °C. Once all the acid was added, the solution was heated to 44 °C. When temperature reached 44 °C, synthesis was continued for 2 hours more. The mixture was mechanically agitated during all the time of the synthesis. Then, the solution was cooled down in refrigerator for 24 h. The resulting solution has a pH of about 1-2. Dialysis against distilled water was then performed to remove any free acid molecules from the dispersion. Spectra/Por molecular porous membrane with molecular weight cut-off range of 12000 to 14000 Da was used for dialysis. Dialysis was continued until the pH of solution reached constant pH (pH ~6). After dialysis, the solution was filtered using a specific filter cloth to obtain nanocrystals by removing the last oversized cellulose particles.

Concentration of CNC was determined by gravimetric analysis. Size of particles were determined by dynamic light scattering.

2.3. Preparation of nanocomposites

The CNC solution was centrifuged 4 times using a cycle of 30 minutes at 12 000 rpm. At the end of each cycle the supernatant was removed and replaced with acetone. After centrifugation CNC dispersion in acetone was mixed in well dried Agrol polyol. Ultrasonic irradiation with IKA T 18 Basic Ultra-Turrax was used to disperse particles and to obtain homogenous dispersion. Afterwards acetone was evaporated by keeping mixture in vacuum for 2 days at 40 °C temperature.

Nanocomposites were prepared by mixing Agrol and CNC dispersion with DBTDL (0.1 wt%) and pMDI at NCO / OH molar ratio of 1.2. Mixture was poured in a closed mould which was pre-heated at 80 °C temperature. Afterwards the mould with sample was placed in a press at 0.5 MPa pressure and at 80 °C temperature. After 2 h the mould was put in an oven at 80 °C temperature for 16 h. All samples were allowed to stay at ambient conditions for a 24 h before cutting them into test samples. The concentrations of added CNC were 0, 0.5, 1.0 and 2.0 wt% with respect to the total weight of the sample.

2.4. Characterization of nanocomposites

Tests of dynamic mechanical analysis (DMA) (frequency of 1 Hz, amplitude of 0.1% and a ramp rate of 5°C/min.), tensile strength, and thermogravimetric analysis were carried out to characterize the PU nanocomposites. Tensile strength tests were performed with a load cell of 500 N at 1 mm/min and results were averaged out from five test specimen data.

3. Results and discussion

3.1. Size distribution of CNC

Results of dynamic light scattering showed that size of CNC is in range from 33 to 950 nm (Figure 1).

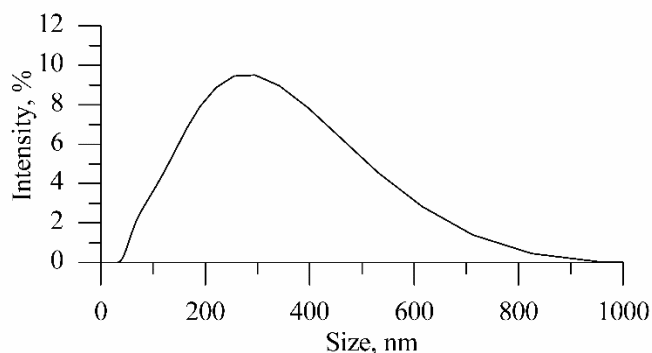


Figure 1. CNC particles size distribution

Size distribution showed peak at 295 nm, and the average size of CNC was ~200 nm which coincides with other publish results. Length of CNC can vary from 35 to 500 nm and width – from 3 to 48 [18, 20-21]. The size of CNC varies widely, depending on the source of the cellulosic material and the conditions (temperature, agitating, time etc.) under which the hydrolysis is performed [17].

3.2. Dynamic mechanical analysis and thermogravimetric analysis

Glass transition temperature (T_g) was measured from DMA results. Although there are several thermal techniques available to make T_g measurements, by far the most sensitive technique is DMA [22]. The maximum of the peak in the viscoelastic parameter $\tan \delta$ was used to define the T_g . As shown in Table 1, the T_g of the nanocomposites increased slightly, reaching 35 °C for sample with 2 wt% of CNC.

Table 1. Glass transition temperature and initial decomposition temperature of nanocomposites.

CNC content, wt%	T_g , °C	T_{in} , °C
0	31	303.8
0.5	31	307.7
1.0	33	307.6
2.0	35	307.7

Increase of T_g indicates a favourable fiber–matrix interaction and restriction of molecular mobility because of the strong association between CNC and the soft segment of the PU matrix [1]. Results of thermogravimetry showed that thermal stability of nanocomposites is not significantly affected by incorporation of CNC (Table 1). The initial decomposition temperature (T_{in}) of PU composites (~308 °C) was a little bit higher than the neat sample without CNC (~304 °C).

3.3. Tensile strength and elastic modulus

Klemm *et al.* [23] found that the optimal enhancement of mechanical properties usually occurs at the point at which just enough reinforcing agent has been added to establish connectivity. For nanocellulose reinforced segmented PU films, Auad *et al.* obtained approximately 53% increase in tensile modulus by the addition of just 1.0 wt% CNC [24]. Li *et al.* investigated cellulose nano whiskers as a reinforcing filler in PU foams. Results showed that tensile modulus decreases by adding 0.5 wt% cellulose nano whiskers but increases by adding 1 wt% [3]. Also, Floros *et al.* investigations showed that tensile strength do not increase linearly by adding cellulose-based fibers to PU matrix. The best results were

obtained with 0.5 wt% and 1.0 wt% CNC in the PU, but nanocomposite samples with CNC content beyond 1.0 wt% showed a negative effect on mechanical properties [25]. The mechanisms responsible for the improved mechanical performance are likely related to the nature of the nanoparticle and PU matrix.

Results of tensile strength and elastic modulus of our investigation are presented in Figure 2.

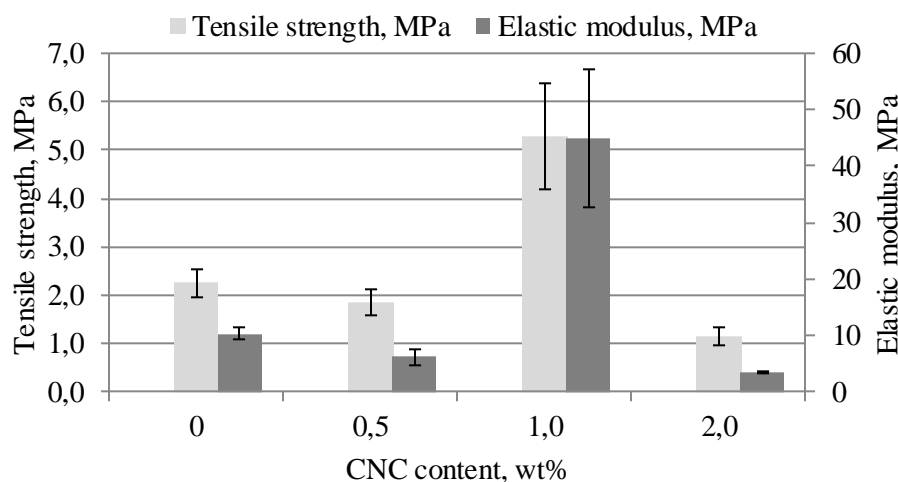


Figure 2. Tensile strength and elastic modulus of PU composites

In our study the tensile strength and elastic modulus increased more than 2 times and 4 times respectively by adding 1 wt% CNC in PU matrix reaching 5.3 MPa of tensile strength and 45 MPa of elastic modulus. However, samples with 0.5 wt% and 2.0 wt% CNC showed worse performance in mechanical properties than sample without CNC. Character of the change of tensile strength and elastic modulus coincides with other authors results described previously. Nanocrystals added in low concentration behave as point of failure in the composite, and probably interfere in the PU formation, since OH in the cellulose can also react with the isocyanate. At about 1 wt% of CNC the percolation of the system is reached, a network of touching crystals interpenetrates the PU matrix and the properties are much improved, although with a large dispersion of the results which is understandable because of the critical concentration (percolation threshold). Higher concentrations of the crystals result in agglomeration (concentrations above percolation) and thus the properties drop again, since the sample becomes heterogeneous and agglomerates are stress concentrators and point of failure for the material.

4. Conclusions

The objective of this study was to prepare PU composites with CNC and to examine how the concentration of CNC affects the final properties of PU composites. CNC were successfully obtained from microcrystalline cellulose by acid hydrolysis and dispersed in a PU matrix based on hydroxylated soybean oil. Nanocellulose reinforced PU composites were successfully prepared with different concentration (0 – 2 wt%) and good dispersion of CNC.

T_g of the nanocomposites increased slightly, reaching 35 °C for sample with 2 wt% of CNC. Results of thermogravimetric analysis showed that thermal stability of nanocomposites is slightly increased by incorporation of CNC. Results of tensile strength and elastic modulus showed that 1 wt% of CNC is the optimal concentration to improve mechanical properties of PU. The tensile strength increased more than 2 times comparing with neat sample without CNC.

Overall, results indicated that CNC can improve final properties of PU composites based on hydroxylated soybean oil. Further investigations are required to explore CNC effect onto other properties of PU composites.

5. Acknowledgments

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6. References

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