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Two different incorporation routes of cellulose nanocrystals in waterborne polyurethane nanocomposites

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ABSTRACT

The renewability, availability and low-cost of eco-friendly cellulose nanocrystals (CNC), have gaining attention for nanocomposites preparation due to their unique properties in the nanoscale and their water dispersibility, becoming a suitable reinforcement in waterborne polyurethane (WBPU) dispersions. Thereby, a WBPU matrix with a high hard segment content (about 48 wt%) was synthesized resulting in a dispersion of low particle size with a narrow distribution analyzed by means of dynamic light scattering and visually stable over 6 months. The CNC reinforcement isolated from microcrystalline cellulose via acid hydrolysis lead to CNC with a high length/diameter aspect ratio of about 31, determined by atomic force microscopy. In the nanocomposites preparation, two incorporation routes were designed for analyzing the influence of CNC disposition in the nanocomposites films: the classical mixing by sonication or *in-situ* adding CNC in water during particles formation step. The influence of CNC addition route and their disposition in the final properties of nanocomposites were analyzed by Fourier transform infrared spectroscopy, differential scanning calorimetry, thermogravimetric analysis, dynamic mechanical analysis, atomic force microscopy and dynamic water contact angle, observing considerable variations by adding 1 and 3 wt% of CNC. The reinforcement addition route influenced the WBPU–CNC interactions, which resulted more effective by the alternative *in-situ* incorporation method. The CNC incorporation restricted the crystallization of soft domains, in a higher extend in nanocomposites prepared by *in-situ* route, and improved the thermomechanical stability. The studied CNC incorporation routes lead to different dispositions of CNC in the matrix, resulting in different mechanical performance, providing a suitable stress transfer in the nanocomposite and diverse hydrophilic behavior, comparing with the WBPU matrix.

1. Introduction

Segmented polyurethanes are block copolymers with alternating hard and soft segments that separate in microphases due to the incompatibility between both segments [1]. The hard segment (HS) provides usually the rigidity and strength to the polymer whereas the soft segment (SS) confers flexibility. Thereby, considering the variety in the chemical

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constituents and composition, it is possible to synthesize specific polyurethanes with particular properties [2], opening a wide range of application fields. Conventional polyurethanes are solventborne systems, but the environmental awareness has promoted the development of waterborne polyurethane (WBPU) systems by the addition of internal emulsifiers [3], avoiding the use of organic solvents and obtaining stable water dispersions over months. With the purpose of synthesizing new environmentally friendly materials, WBPU has been employed in the preparation of nanocomposites. The chance to disperse hydrophilic reinforcement in WBPU, has focused attention in water dispersible entities, such as cellulose derivatives. Cellulose is the most abundant renewable biopolymer which has attracted great attention due to the availability, low cost, non-toxicity, biocompatibility and biodegradability. Cellulose is produced principally in nature by plants like cotton, jute or flax, different marine animals as tunicates, and in invertebrates, fungi, algae, bacteria, and amoeba (protozoa) in lower quantities [4,5]. Cellulose can be used in different dimensions, from macroscopic to nanoscale, and diverse assemblies such as fibers or crystals [6]. Among these, it is worth noting the relevance of cellulose nanocrystals (CNC) which are gaining importance in diverse application fields [4,7]. The isolation of the crystalline ordered regions of cellulose lead to obtaining those highly crystalline nanoentities, possessing unique properties in the nanoscale dimension, modulated by isolation hydrolysis process [8] and origin of cellulose [5]. The high length/diameter aspect ratio and high specific mechanical properties are focusing the attention of CNC in nanocomposites field [9]. Several strategies have been used in order to prepare cellulose well dispersed nanocomposites, such as melt blending or solvent casting. In the former case, it is difficult to obtain the adequate cellulose dispersion in the matrix and high temperatures could degrade nanocellulose nanocrystals [10]. By solvent-casting, the slow evaporation of the solvent promotes the formation of hydrogen bonds and rigid networks, resulting in high thermomechanical stability and mechanical reinforcement in the nanocomposites. Diverse types of polymers have been used for nanocellulose nanocomposites preparation [11]. The use of nonpolar polymers requires an appropriate organic dispersion medium or the use of surfactant or surface chemical modification of nanocellulose in order to obtain a suitable polymer matrix dispersion. Instead, the use of aqueous polymer dispersions ensures the compatibility between the polymer and nanocellulose in water, facilitating the good dispersion for homogeneous nanocomposites preparation without requiring chemical modifications or surfactants [10]. The chance to disperse hydrophilic CNC in WBPU, has focused their attention in WBPU–CNC nanocomposites. There are different works analyzing the final properties of CNC reinforced WBPU [12], but few works consider CNC addition strategy and its effect in the final disposition of CNC in the matrix. Thereby, in this work the synthesis of WBPU dispersion and the isolation of CNC have been carried out for the preparation of nanocomposites considering CNC addition protocol. Therefore, two CNC incorporation routes were designed for the analysis of CNC arrangement in the WBPU matrix: the classical mixing by sonication after WBPU synthesis and the alternative *in-situ* during the WBPU synthesis process. The effect of CNC addition as well as the incorporation procedure has been analyzed in the final properties of the nanocomposites.

2. Experimental

2.1. Materials

CNC were isolated from microcrystalline cellulose (MCC) powder supplied from Aldrich and sulfuric acid (H_2SO_4) (96%) was provided from Panreac. For WBPU synthesis, poly(ε-caprolactone) diol (PCL) ($\bar{M}_w$ = 2000 g mol^{-1}), purchased from BASF was chosen as soft segment and 1,4 butanediol (BD), supplied from Aldrich as chain extender, being dried in a rotary evaporator at 50 °C for 4 h. Isophorone diisocyanate (IPDI) was kindly supplied from Bayer, and dibutyl tin dilaurate (DBTDL) was purchased from Aldrich. 2,2-Bis(hydroxymethyl)propionic acid (DMPA) purchased from Aldrich and used as internal emulsifier, was dried at 55 °C for 4 h under vacuum. Hydranal-molecular Sieve 0.3 nm (water adsorption capacity of 15%), supplied by Fluka, and previously dried at 55 °C under vacuum for 1 day was employed for dehydration of triethylamine (TEA), both provided from Aldrich. N,N-dimethylformamide (DMF) and tetrahydrofuran (THF), were also provided by Aldrich.

2.2. Isolation of cellulose nanocrystals

CNC were isolated from microcrystalline cellulose via sulfuric acid hydrolysis removing the amorphous regions of cellulose. The isolation was carried out following previously reported method [13]. Briefly described, MCC were mixed with H_2SO_4 (64 wt%) at 45 °C for 30 min. The suspension was diluted with deionized water and after washed by centrifugation, the suspension was subjected to a dialysis process against deionized water until pH remained constant around 5–6. Thus, CNC dispersion with about 0.5 wt% concentration was obtained.

2.3. Synthesis of waterborne polyurethane

WBPU with a HS content of about 48 wt% was synthesized by two step polymerization process with the PCL:IPDI:DMPA:BD molar composition of 0.5:3.15:0.5:2 considering PCL as SS and IPDI, DMPA and BD as HS. According to previously published protocol [14], the reaction was carried out in a 250 mL four-necked flask placed in a thermostatized bath and equipped with a mechanical stirrer, thermometer, condenser and nitrogen inlet. The progress of each reaction step was determined by