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Cellulose nanocrystal reinforced oxidized natural rubber nanocomposites

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ABSTRACT

Natural rubber (NR) latex particles were oxidized using $KMnO_4$ as oxidant to promote the insertion of hydroxyl groups in the surface polyisoprene chains. Different degrees of oxidation were investigated. Both unoxidized and oxidized NR (ONR) latex were used to prepare nanocomposite films reinforced with cellulose nanocrystals (CNCs) by casting/evaporation. The oxidation of NR was carried out to promote chemical interactions between the hydroxyl groups of ONR with those of CNCs through hydrogen bonding. The effect of the degree of oxidation of the NR latex on the rheological behavior of CNC/NR and CNC/ONR suspensions, as well as on the mechanical, swelling and thermal properties of ensuing nanocomposites was investigated. Improved properties were observed for intermediate degrees of oxidation but they were found to degrade for higher oxidation levels.

1. Introduction

According to its versatility and application volume natural rubber (NR) is one of the most important elastomers with interesting strength, elasticity, flexibility, resilience, and abrasion resistance. Latex from rubber tree (*Hevea brasiliensis*) is virtually the source of all commercial NR and its first description appeared almost 500 years ago, during the first European expeditions to America. This biopolymer has a great economic and social importance, being practically the only rubber used until the mid-20th century. Today, NR is used in 50 thousand different products (as adhesives, tires, gloves, condoms, coatings, etc.) and its applications are still in expansion (Rippel & Galembeck, 2009; Steward, Hearn, & Wilkinson, 2000). It is extracted as a white emulsion composed of cis-1,4-polyisoprene nanoparticles that usually exhibit a diameter of 100 nm or more. The dispersion is stabilized by phospholipids, carbohydrates, proteins and metal ions (Ballauff, Bolze, Dingenouts, Hickl, & Pötschke, 1996; Sansatsadeekul, Sakdapipanich, & Rojruthai, 2011). The drying or coalescence stage causes compaction, deformation and inter-diffusion of the individual latex particles. This phenomenon gradually improves the latex homogeneity and mechanical properties (Steward et al., 2000).

The mechanical properties of NR can be improved and tailored by crosslinking (Gopalan Nair & Dufresne, 2003) and addition of reinforcing fillers of varying chemistry and aggregate size/aspect ratio to suit the application concerned, among which cellulose nanocrystals (Abraham et al., 2013; Bras et al., 2010; Gu, Li, Jia, Luo, & Cheng, 2009; Gu, Lin, Luo, & Jia, 2012; Pasquini, Teixeira, Curvelo, Belgacem, & Dufresne, 2010; Xu, Gu, Luo, & Jia, 2012; Xu, Gu, Luo, Jia, & Yan, 2015). Moreover, due its high flexibility and low stiffness, NR is a perfect matrix to be used as a model system to study the effect of filler reinforcement. The use of filler as reinforcing agent is largely explored in materials science. Nanoparticles such as carbon nanotubes, ceramics and natural fibers (Bendahou, Kaddami, Espuche, Gouanvé, & Dufresne, 2011; Müller, Laurindo, & Yamashita, 2009; Pötschke, Bhattacharyya, Janke, & Goering, 2003; Zhao, Morgan, & Harris, 2005) can impart specific properties to the polymeric matrix. Not only the mechanical properties (Azizi Samir, Alloin, & Dufresne, 2005; Goffin et al., 2011; He et al., 2006), but also the crystallinity (Camarero-Espinosa, Boday, Weder, & Foster, 2015) and the permeability (Belbekhouche et al., 2011; Follain et al., 2013) of the matrix can be altered when adding nanofiller. Carbon black is the conventionally used filler in many applications of NR. It is produced from petroleum oil and is carcinogenic. Its use has therefore to be reduced through substitution with more eco-friendly components to reduce the health hazards and

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environmental issues. In this context, natural and renewable materials such as polysaccharide nanoparticles appear as a perfect option for the production of new light weight green composites (Lin & Dufresne, 2013a).

Among polysaccharides, cellulose is the most abundant material and cellulosic nanomaterials can be extracted from many natural resources as nanofibrils (Jonoobi et al., 2015; Lavoine, Desloges, Dufresne, & Bras, 2012) or nanocrystals (CNC) (Dufresne, 2013; Mariano, El Kissi, & Dufresne, 2014). The latter is generally obtained by an acid hydrolysis process of the cellulosic fiber (Lin & Dufresne, 2014a; Roman & Winter, 2004), which causes depolymerization and solubilization of the amorphous regions. The extracted highly crystalline domains can be used as reinforcing agent (Silva & d'Almeida, 2009), in biomedical applications (Lin & Dufresne, 2014b), coatings (Poaty, Vardanyan, Wilczak, Chauve, & Riedl, 2014), and hydrogels (Lin & Dufresne, 2013b), among other applications, due to their high modulus, low density, dimensional stability and ability for surface modification (Habibi, 2014; Siqueira, Bras, & Dufresne, 2010). Nanoscale fillers and concomitant high specific surface area are instrumental in imparting improved mechanical performance to NR at low volume contents (Dufresne, 2010). However, the efficiency of CNC on composite mechanical properties is strongly dependent on its dispersion and interactions with the matrix. These interactions can also change the rheological behavior of the latex particle/CNC suspension, which is relevant for coating applications (Grüneberger, Künniger, Zimmermann, & Arnold, 2014; Vardanyan et al., 2014).

The hydrophobic NR matrix and hydrophilic CNC are inherently incompatible and insufficient molecular scale interactions can restrict the overall performance of the material. Moreover, CNC aggregates can lead to poor dispersion in the matrix and act as stress concentrator, resulting in poor properties of the composite. The conventional way to tailor and control the interfacial adhesion and interactions is the chemical grafting of specific moieties on the surface of CNC able to interact with the matrix. Another strategy, much less investigated, consists in modifying the matrix polymeric chains in contact with the filler. In the present study, oxidation of the NR latex particles (using $KMnO_4$ as oxidant) was performed to promote the insertion of hydroxyl groups in the surface polyisoprene chains. These groups were expected to create hydrogen bonding between the NR chains and CNC, as reported in a study aiming in improving the compatibility of blends composed of NR and starch (Trovatti, Carvalho, & Gandini, 2015). The effect of the degree of oxidation of the NR latex on the rheological behavior of CNC/NR suspensions, and on the mechanical, swelling and thermal properties of ensuing nanocomposites was investigated.

2. Experimental

2.1. Materials

Potassium permanganate ($KMnO_4$) was purchased from Sigma Aldrich. Cellulose nanocrystals (CNCs) with 1.1% sulfur content were purchased from the University of Maine as an 11% aqueous suspension. The natural rubber (NR) latex was kindly received from Centrotrade Deutschland GmbH (Eschborn, Germany). It contained spherical particles with an average diameter around 300 nm and its solid content was about 60 wt%.

2.2. NR oxidation

The NR latex suspension was oxidized with a $KMnO_4$ solution. An aqueous 0.125 mol L^{-1} $KMnO_4$ solution was prepared by dissolving solid $KMnO_4$ in water. The NR latex suspension was diluted by adding 10 mL water to 3 g of NR (dry basis). The $KMnO_4$ solution was diluted to 0.0125 and 0.00125 mol L^{-1} and added dropwise to the diluted NR latex suspension under gentle stirring to oxidize the double bond present in the isoprene (2-methyl-1,3-butadiene) monomer. The characteristic color change of the solution from pink to brown and the precipitation of solid MnO_2 indicated that the oxidation reaction was completed. NR samples with different degrees of oxidation were prepared and the oxidation level was expressed as –OH groups borne by NR chains normalized to CNC particle amount. This ratio will be described in sequence.

2.3. Preparation of nanocomposite films

Firstly, the CNC suspension was dialyzed against water for one week to ensure neutral pH and removal of any possible salt present in the material. Then, the suspension was sonicated for 5 min to improve the nanoparticle dispersion. The oxidized NR latex suspension was mixed with the CNC suspension in the desired amount (we fixed the CNC content to 5 wt%) to obtain the final nanocomposite. This CNC content was lower than the percolation threshold to have direct information on the filler–matrix interactions and avoid interference of the formation of a network. The volume of the suspension was adjusted to 25 mL and it was magnetically stirred for 6 h to improve the homogenization. The mixture was cast on aluminum plates, dried in oven with air circulation at 40 °C for 24 h and ensuing films were conditioned in desiccators containing silica gels for 4 days before testing. Reference CNC-free films consisting of unoxidized and oxidized NR, as well as unoxidized NR nanocomposite films were also prepared using the same protocol.

2.4. Characterization

2.4.1. Atomic force microscopy (AFM)

AFM images were obtained on a Nanoscope IIIa microscope from Veeco Instruments. A drop of a 0.01 wt% diluted CNC suspension was loaded on a mica substrate and imaged in tapping mode with a silicon cantilever. The nanocrystal dimensions were estimated from 50 measurements analyzed using ImageJ software.

2.4.2. UV–visible spectroscopy (UV–Vis)

To evaluate the presence of Mn in the medium, absorbance was evaluated before and after oxidation. The tests were performed with a Shimadzu UV 2401-(PC) UV–Vis spectrophotometer within a wavelength range 300–700 nm.

2.4.3. Dynamic light scattering

NR latex suspensions with a concentration of 0.1 wt% and different degrees of oxidation were analyzed using Particle Size Analyzer VASCO equipment. The average diameter and polydispersity index (PDI) of the particles were determined.

2.4.4. Fourier transform infrared spectroscopy (FTIR)

Infrared spectra were recorded on a FTIR Perkin-Elmer Spectrum One spectrometer. Samples were analyzed using a spectral width ranging from 600 to 4000 cm^{-1} with a 4 cm^{-1} resolution and an accumulation of 32 scans. All analyses were carried out in the ATR mode at room temperature.

2.4.5. Zeta potential (ξ)

NR suspensions with concentration around 0.01 wt% were analyzed on an equipment model DTS0230 from Malvern Instruments. To avoid the effects of ionic strength and pH during measurements, all the concentrated solutions were diluted in an aqueous standard solution with pH 10, ionic strength 5 mmol and 180 μS/cm conductivity. This solution was prepared by the addition of diluted NaOH solution and solid NaCl into distillated water.