

Preparation and properties of carboxylated styrene-butadiene rubber/cellulose nanocrystals composites

Xiaodong Cao^a, Chuanhui Xu^a, Yuhong Liu^a, Yukun Chen^{b,c,*}

^a School of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, China

^b The Key Laboratory of Polymer Processing Engineering, Ministry of Education, China (South China University of Technology), Guangzhou 510640, China

^c School of Mechanical and Automotive Engineering, South China University of Technology, Guangzhou 510640, China

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ABSTRACT

A series of carboxylated styrene-butadiene rubber (XSBR)/cellulose nanocrystals (CNs) latex composites were successfully prepared. The vulcanization process, morphology, dynamic viscoelastic behavior, dynamic mechanical property, thermal and mechanical performance of the XSBR/CNs composites were investigated in detail. The results revealed that CNs were dispersed uniformly in the XSBR matrix and formed a strong filler–filler network. The dynamic mechanical analysis (DMA) showed that the glass transition temperature (T_g) of XSBR matrix was shifted from 48.45 to 50.64 °C with 3 phr CNs, but decreased from 50.64 to 46.28 °C when further increasing CNs content up to 15 phr. The composites exhibited a significant enhancement in tensile strength (from 16.9 to 24.1 MPa) and tear strength (from 43.5 to 65.2 MPa) with loading CNs from 0 to 15 phr. In addition, the thermo-gravimetric analysis (TGA) showed that the temperature at 5% weight loss of the XSBR/CNs composites decreased slightly with an increase of the CNs content.

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1. Introduction

In general, most of rubbers were reinforced with various fillers for their industry applications. Up to date, various reinforcing agents, such as clay (Kim, Seo, & Jeong, 2003; Kuan, Ma, Chuang, & Su, 2005; Lee & Lin, 2006; Lee, Hwang, & Liu, 2006), multi-wall carbon nanotubes (Bokobza, Rahmani, Belin, Bruneel, & El Bounia, 2008; Kuan, Ma, Chang, Yuen, et al., 2005; Kwon & Kim, 2005), carbon black (Dupres, Long, Albouy, & Sotta, 2009) and silica (Thongsang, Sombatsompop, & Ansarifard, 2008), have been used to enhance the mechanical and abrasion properties of cured rubbers. However, they are more or less charged with using the depleting petroleum resources or natural gas for their manufacture, directly or indirectly causing an increase in the carbon footprint and contributing to the accumulation of green house gases. Therefore, with the gradual drying up of petroleum and the higher demand of environmental protection, reinforcements from bio-based renewable resources are receiving increased attention in the scientific community. Tremendous efforts were focused on the development of new materials as viable alternatives that could replace conventional reinforcements in the rubber industry.

Polysaccharides have been used for a wide range of applications such as food, packaging, agricultural chemicals, and biomedical devices. Starch, as one of the most promising biodegradable materials, has been creatively used as reinforcing filler in rubbers to lower the rolling resistance and reduce the use of carbon black amount (Wu, Qi, Liang, & Zhang, 2006). Cellulose, as a most abundant biorenewable material in the world, has been utilized extensively as textile fibers, chemical precursors and food additives etc. In recent years, there has been an increased application of cellulose nanocrystals (CNs) as the load-bearing constituent in the development of new and inexpensive polymer nanocomposite materials (Helbert, Cavaille, & Dufresne, 1996; Sturcova, Davies, & Eichhorn, 2005). As compared to other inorganic reinforcing fillers, CNs have many additional advantages, including positive ecological, wide variety of fillers available throughout the world, low density, low energy consumption in manufacturing, ease for recycling by combustion, high sound attenuation, and comparatively easy processability due to their nonabrasive nature, which allows high filling levels, in turn resulting significant cost savings (Azizi Samir, Alloin, & Dufresne, 2005; Podsiadlo et al., 2005). Since the first announcement of using cellulose nanocrystals from tunicin (an animal cellulose) as a reinforcing phase in a matrix of latex by Favier, Chanzy, and Cavaille (1995) the use of CNs from various sources such as cotton (Fengel & Wegner, 1984), tunicate (Mathew & Dufresne, 2002; Terech, Chazeau, & Cavaille, 1999), algae (Revol, 1982; Hanley, Giasson, Revol, & Gray, 1992), bacteria (Grunert & Winter, 2002; Tokoh, Takabe, Fujita, & Saiki, 1998), ramie (Lu,

* Corresponding author at: School of Mechanical and Automotive Engineering, South China University of Technology, Guangzhou 510640, China.
Tel.: +86 20 87110804; fax: +86 20 85293483.

E-mail address: cyk@scut.edu.cn (Y. Chen).

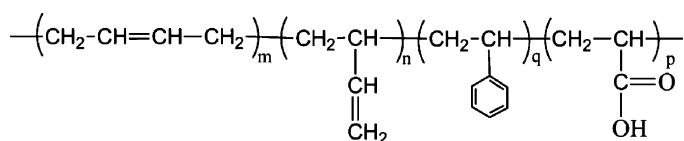
Weng, & Cao, 2006) and wood (Araki, Wada, Kuga, & Okano, 1998; Beck-Candanedo, Roman, & Gray, 2005), for the preparation of high performance composite materials based on a wide range of polymers matrices have been investigated widely (Cao, Habibi, & Lucia, 2009; Cao, Habibi, Magalhaes, Rojas, & Lucia, 2011; Chen, Liu, Chang, Cao, & Anderson, 2009; Magalhaes, Cao, & Lucia, 2009). To the best of our knowledge, however, research on CNs as filler for reinforcing of rubber can hardly be found in the literatures (Bai & Li, 2009; Bendahou, Kaddami, & Dufresne, 2010; Xu, Gu, Luo, & Jia, 2012).

Carboxylated styrene-butadiene rubber (XSBR) is a copolymer of styrene, butadiene and a small amount of acrylic acid and it has the excellent cohesive strength, good physical and chemistry stability. The carboxyl groups introduced by acrylic acid are potential functionality for the formation of hydrogen bonding with fillers such as silica, clays and halloysite nanotubes (HNTs) (Du, Guo, Lei, Liu, & Jia, 2008). In the present work, we attempt to fabricate CNs via acid hydrolysis of cotton linter with concentrated sulfuric acid, and then use the resulting CNs to reinforce XSBR matrix for preparation of a nanocomposite material with improved performance. As we all know, for preparation of a nanocomposite material with high mechanical properties, the major problem is the uniform dispersion of fillers in the matrix and a strong interfacial combination between the fillers and the matrix. In this case, the abundant hydroxyl groups on the surface of CNs make them possible to form strong hydrogen bonds with the carboxyl groups of XSBR. Considering that the nature of serious aggregation of CNs when they are dried, XSBR/CNs composites were prepared by mixing a water suspension of CNs with the water based XSBR latex directly. As expected, the CNs showed significant reinforcing effects on XSBR. The morphology, structure and properties of the resulting nanocomposites were investigated by scanning electron microscopy (SEM), dynamic mechanical analysis (DMA), rubber process analysis (RPA), thermal gravimetric analysis (TGA) and mechanical properties tests carefully.

2. Experimental and method

2.1. Materials

Cottonseed linter was supplied by Hubei Chemical Fiber Manufacture, China. Concentrated sulfuric acid (98%) was purchased from Sigma-Aldrich Corporation and used as received without further purification. Sulfur, zinc oxide, stearic acid, accelerators, and other additives were of industrial grade and used as-received. Carboxylate butadiene-styrene (XSBR) latex with 48% solids was obtained from Quanzhou Deli Chemical Co., Ltd. (DL659, Fujian, China), which is a random copolymer consisting of 33 wt% butadiene, 64 wt% styrene and 3 wt% of carboxylate functional monomer. The chemical structure of XSBR is shown as below.



2.2. Preparation of cellulose nanocrystals

The cottonseed linter pulp (30 g) was cut into small pieces, and then mixed with sulfuric acid aqueous solution (250 mL, 64 wt%) under vigorous stirring at 60 °C for 2 h. Subsequently, the suspension was washed with water by successive centrifugation and dialyzed against deionized water until the pH of the suspension was neutral. Finally, a stable suspension with a solid content of 5.0 wt%

was obtained through 10 min ultrasonic treatment, which then was stored in a refrigerator before use.

2.3. Preparation of XSBR/CNs composites

A desired content of CNs suspension was mixed with XSBR latex and stirred vigorously at room temperature for 30 min, and then the mixture was dried under reduced pressure at 60 °C until a constant weight was obtained. The compounding of XSBR/CNs with other ingredients was carried out on a two-roll mill. The rubber compound sheets were then compressed and vulcanized at 170 °C in an electrically heated hydraulic press for their optimal cure time (t_{90}) respectively, which was derived from curing curves. By changing the contents of CNs over the range of 0 phr, 3 phr, 5 phr, 10 phr and 15 phr, a series of nanocomposite sheets with a thickness of around 1 mm were prepared and coded as XSBR, XSBR-3N, XSBR-5N, XSBR-10N, and XSBR-15N respectively. In addition, the other components of the XSBR/CNs nanocomposites were fixed as follows (phr): XSBR 100, sulfur 1.5, zinc oxide 5, stearic acid 2, N-cyclohexylbenzothiazole-2-sulphenamide 1.5 phr, sulfenamide 2,2'-dibenzothiazole disulfide 0.5.

2.4. Curing characteristics

The curing curves at 170 °C were recorded in a M2000 Rheometer (Gotech Testing Machines Inc., Taiwan). The relative curing degree was represented by the variation between the maximal torque value (M_H) and the minimal torque value (M_L) of the curing curve.

2.5. Dynamic mechanical analysis (DMA)

The dynamic mechanical behaviors of the XSBR/CNs nanocomposites were determined by a dynamic mechanical analyzer (DMA242C NETZSCH; Germany) in tension mode. The temperature program was run from –100 to +150 °C using a heating ramp of 5 °C min⁻¹ at a fixed frequency of 10 Hz. The samples were prepared as a cut strip with the size of 8 mm × 1 mm × 6 mm (length × thickness × width).

2.6. Morphological studies

EVO18 SEM (NEISS, Germany) was used to observe the phase morphology of XSBR/CNs composites. The cryogenically fractured surfaces of the specimens were sputter-coated with gold prior to analysis.

2.7. Crosslink density measurement

The apparent crosslink density was determined by equilibrium swelling experiments. To calculate the crosslink density, five weighed test pieces of rubber were immersed in toluene at about 23 °C for 72 h in sealed dark vials. Then, the samples were blotted with tissue paper to remove the excess of solvent and immediately weighed on an analytical balance. Finally, the samples were dried in a vacuum oven for 48 h at 60 °C until a constant weight was reached. The volume fraction of rubber swollen in the gel, V_r , which was used to represent the crosslink density of the samples, was determined by the following equation:

$$V_r = \frac{m_0\varphi(1-\alpha)\rho_r^{-1}}{m_0\varphi(1-\alpha)\rho_r^{-1} + (m_1 - m_2)\rho_s^{-1}} \quad (1)$$

where m_0 is the mass of the sample before swollen, m_1 and m_2 are the masses of the swelled sample before and after drying, respectively, φ is the mass fraction of rubber in the vulcanizates, α is the

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