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A novel interpenetrating polymer network of natural rubber/regenerated cellulose made by simple co-precipitation

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ABSTRACT

A novel interpenetrating polymer network (IPN) structure consisting of natural rubber (NR) and cellulose was successfully prepared using a simple co-precipitation process. Cellulose was first dissolved in the aqueous alkali/urea system, and then it was mixed with NR latex. The mixed NR/cellulose solution was co-precipitated with ethanol. During the fast co-precipitation process, both rubber network and cellulose network were formed and interpenetrated simultaneously. Scanning electron microscopy (SEM) clearly demonstrated that the two networks could be interlaced to form a full-IPN structure. This simple method provides a new insight into the fabrication of novel IPNs from cellulose and broadens the potential applications of cellulose in rubber compounds.

1. Introduction

Natural rubber (NR) is widely used in many applications and products. It is a bio-based material derived from rubber trees as latex. Cellulose, the most abundant polymer on Earth, is renewable, biodegradable, as well as non-toxic [1], and can be used as an attractive reinforcing filler for various polymer matrices. Recently, many academic papers regarding preparation of NR/cellulose compounds have been published [2–4]. Usually, two kinds of cellulose filler (cellulose nanocrystals and microfibrillated cellulose) are widely investigated as rubber filler. However, the studies devoted to the preparation of rubber/regenerated cellulose (RC) composites is scarce [5,6].

The aqueous alkali/urea system at low temperature is a green chemical medium to dissolve cellulose [7–10] and NR is available in the latex form. Also, ethanol could act as flocculating agent for both cellulose aqueous alkali/urea solution [11] and NR latex. Therefore, a simple approach to prepare NR/cellulose hybrids is proposed in this study through the co-coagulation of the rubber/cellulose mixed aqueous system using ethanol as the co-flocculating agent. To the best of our knowledge, this kind of rubber/cellulose hybrid has seldom been reported. The results showed that this novel NR/cellulose hybrid could have a typical full-IPN structure. The thermal stability and crystallinity of cellulose in the hybrids were also studied.

2. Experimental

2.1. Materials

Natural rubber latex (type: CENTEX FA, Full Ammonia, pH 10–11, dry rubber content 59–61%) was kindly provided by Centrotrade Deutschland GmbH (Eschborn, Germany). Microcrystalline cellulose powder was purchased from Sigma-Aldrich (USA). Urea (purity ≥ 99.5%, BioScience-Grade) and NaOH were purchased from Carl Roth (Karlsruhe, Germany). Ethanol and other agents were bought from local sources.

2.2. Samples preparation

The preparation route for NR/cellulose hybrids is shown in Fig. 1. Cellulose was first dissolved in NaOH/urea aqueous system at low temperature as reported elsewhere [10] to form a 4 wt% transparent cellulose solution. The cellulose solution was subjected to centrifugation at 5000 rpm for 10 min at 0 °C to promote the degasification and to exclude the slightly remaining undissolved fraction. A desired amount of cellulose solution was immediately dropped into the diluted NR latex (the solid content

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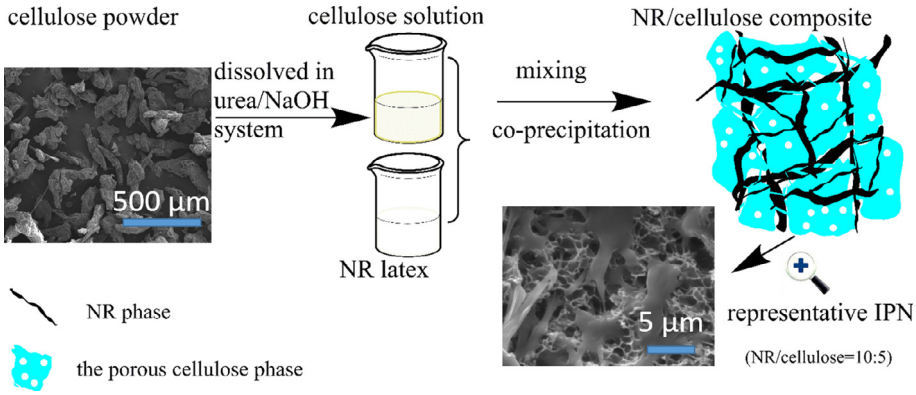

Fig. 1. Preparation route for NR/cellulose hybrids.

was 30%) under stirring to obtain a uniform cellulose/NR mixture solution at room temperature. The mixture solution was co-precipitated by adding ethanol. The resulting white NR/cellulose sediment was washed with deionized water to remove urea and NaOH and it was dried in a oven at 50 °C until a constant weight was obtained.

2.3. Characterizations

X-ray diffraction (XRD) tests were performed on the composite powder at room temperature with a fixed time mode with a step interval of 0.02° and Cu-Kα radiation (40 kV, 40 mA) using a diffractometer (X'Pert PROMPD, PAN analytical, Netherlands). Scanning electron microscopy (SEM) observations were conducted on a Quanta 250 FEI microscope with an acceleration voltage of 10 kV in high vacuum mode. NR and NR/RC samples were cut with a razor blade in order to examine their cross-section, and the surfaces were sputter coated with Au/Pd before any observation. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-6 equipment under N_2 atmosphere with a heating rate of 10 °C/min in the range of 30 °C to 700 °C.

3. Results and discussion

Fig. 2 shows the XRD patterns obtained for the various materials. It is obviously noticed that native cellulose (NC) powder shows the typical cellulose I structure. After the dissolution–gelation–precipitation process in urea/NaOH system, RC shows the typical cellulose II structure, which was in agreement with a previous report [10]. NR does not show any diffraction peak and displays typical behavior of fully amorphous polymer. It is characterized by a broad hump located around 19°. The diffractograms for NR/RC mixtures consist in the superimposition of the diffractograms of NR and RC attesting that mixing does not change the crystalline structure of RC. However, the diffraction peak at 12.1° of RC is hardly visible and probably drowned by the signal corresponding to NR.

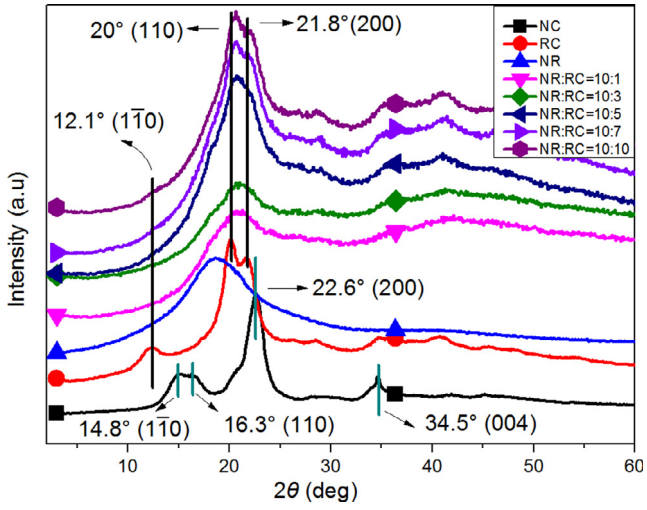

Fig. 2. XRD patterns for the NR/cellulose composites.

SEM images for the various materials are shown in Fig. 3. The RC phase shows a microporous structure, in agreement with a previous report [11], while the NR phase is a tight, non-microporous structure. There is an obvious IPN structure in the NR/cellulose mixtures. For example, for the NR:RC = 10:1 sample, a sea-island morphology is clearly identified, the NR and RC occurring as the continuous phase and disperse phase, respectively. The structure formed in the blend is at the micrometer scale instead of nanoscale, which is more like a quasi-interpenetrating polymer network (quasi-IPN). However, for the NR/RC = 10:10 sample, both RC and NR display a continuous phase. NR network and RC network are entangled and interpenetrated to form a fully-IPN structure. SEM clearly demonstrates the existence of IPN structure in the NR/RC blends.

The thermal stability of NR, RC and NR/RC blends was investigated through TGA (Fig. 4). Fig. 4 (a) shows that $T_{50\%}$ for NR/RC samples decreased when increasing the RC content due to the lower thermal stability of RC. Also, it is observed that the char residue increased with the increase in RC content because of the higher char residue for neat RC compared to NR. As shown in Fig. 4(b), the DTG curves for highly RC loaded samples (NR:RC = 10:5, 10:7, 10:10) obviously exhibit two peaks (two T_{max} values), the one occurring at lower temperatures (T_{max1}) is associated to RC and the second at higher temperatures (T_{max2}) corresponds to NR. The T_{max1} peaks became stronger when increasing the RC content. Obviously, the thermal stability for NR/RC blends gradually deteriorates when enriching the material in RC due to its lower thermal stability compared to NR.

4. Conclusions

We prepared a novel interpenetrating polymer network consisting of NR and RC by a simple co-precipitation method. XRD shows that the crystallinity of RC is not affected by NR. TGA shows that the thermal stability of the hybrids decreases when increasing the RC content, and SEM definitely evidenced the existence of IPN structure in the NR/RC blends. In this unique hybrid architecture, the rigid RC network interlaced and entangled with the soft NR network, and we could tailor the resilience/stiffness of the