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Reinforcement of transparent ethylene-co-vinyl acetate rubber by nanocrystalline cellulose

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ABSTRACT

Ethylene-co-vinyl acetate rubber/nanocrystalline cellulose (EVA/NCC) nanocomposites were prepared by solution mixing and static vulcanization in the presence of peroxide. The gel content and crosslink density of the nanocomposites were decreased with increasing NCC loading. However, mechanical properties of the EVA were considerably enhanced, e.g., the tensile strength and the storage modulus were increased by around 75% and 50%, respectively, when 2 phr of the NCC was incorporated. Such significant reinforcement is ascribed to a uniform dispersion of the NCC, the formation of NCC network and the strong EVA–NCC interactions as confirmed by morphology observation (SEM and AFM) and dynamic mechanical thermal analysis (DMA). Moreover, the presence of the NCC did not compromise obviously the optical clarity and the thermal decomposition temperature of the EVA. The highly reinforced ethylene-co-vinyl acetate rubber with high transparency may broaden its application range.

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1. Introduction

Environmental awareness has been deeply rooted in people's mind due to the sustainability issue and the pollution of environment. Consequently, development and utilization of biopolymers from renewable resources are highly encouraged to protect the ecological and environmental quality [1].

Cellulose is one of the renewable and biodegradable biopolymers derived from abundant natural plants. Although cellulose cannot be processed directly via conventional techniques such as extrusion and injection molding because the thermal decomposition temperature of cellulose is even lower than its melting point and the molar

mass is far too high, some advantages such as low price and density, high modulus and strength make cellulose promising as biomass filler in polymer technology. For such application, both microcrystalline cellulose (MCC) and nanocrystalline cellulose (NCC) were used to make (partially) bio-based and biodegradable composites [2–5]. NCC was first prepared by Nickerson and Habrle using hydrochloric acid and sulfuric acid as a mixing solvent in 1947 [6], which has been regarded as an ideal green reinforcing agent for polymeric materials because of its large specific area, nanoscales and rod-like geometry.

In literatures, mechanical properties of plastics such as poly(lactic acid) [2,5], poly(caprolactone) [3] and polyamide [4] were modified by using different types of NCC. However, the affinity between the NCC and the polymer matrices was not so good leading to a poor dispersion of NCC and a limited reinforcing effect. The mechanical properties of poly(caprolactone)/NCC composites could

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be further improved by modification of NCC, e.g., grafting with poly(caprolactone) [7].

Reinforcement of rubber is more crucial in comparison with plastics since non-crystalline synthetic rubber generally exhibits very low tensile strength (1–3 MPa) [8]. The conventional reinforcing agent i.e., carbon black (CB) could greatly enhance rubber's mechanical properties such as modulus, tensile strength, tear strength and abrasion resistance [9,10]. However, the production of oil-based CB is a highly energy consumption process accompanied by pollution of the environment. With the development of nanotechnology, ultra fine mineral fillers such as clay and calcium carbonate (CaCO₃) were used to reinforce rubber [11,12]. To achieve reinforcing effect, high loading (e.g., 30–60 phr) of the mineral fillers is required which, undesirably, increased the density of rubber compounds. Carbon nanotubes (CNTs) with low density, large specific area and fiber-like geometry were then received considerable attention as a new type of nano-filler [13]. Indeed, the tensile strength of both nitrile-butadiene rubber (NBR) and styrene-butadiene rubber (SBR) was remarkably increased in the presence of a small amount (3–7 phr) of CNTs in combination with a surface treatment [13,14]. However, the high production cost, the agglomeration and the black nature of virgin CNTs restricted their industrial application range. The bio-based and biodegradable NCC possesses similar physical and mechanical features as CNTs but low in cost. Furthermore, it can be used to make transparent rubber compounds with designable color [15–17]. It was reported that a small percentage of NCC could already improve the mechanical properties of natural rubber (NR) [18]. In another study, the tensile modulus of SBR was also significantly enhanced by the addition of cellulose nanofiber [17].

Ethylene-co-vinyl acetate (EVA) is a commodity copolymer which can be either thermoplastic or rubber depending on the vinyl acetate (VAc) content. It shows typical rubbery behavior when the VAc content is between 40 and 90 wt% (such as LEVAPREN® EVM) with excellent flexibility, transparency, weather resistance, oil resistance and good affinity with filler and pigment [19]. However, the application range of vulcanized EVA rubber is still confined because of its very low tensile strength at room temperature. To serve as a valuable specialty rubber, EVA has to be reinforced for utilization. Its mechanical properties could be improved by inorganic fillers, e.g., silica and montmorillonite (MMT) [20–22]. In our previous work, thermoplastic EVA/starch (50/50, wt/wt) master batches were fabricated with a reduction in material cost and reasonable tensile strength [23]. The compatibilized EVA/starch (50/50, wt/wt) master batches were further compounded with poly(lactic acid) and poly(hydroxyalkanoates) to make biocompostable materials [24,25]. In addition, MCC or NCC as potential reinforcing fillers were also explored in EVA system. The tensile strength of EVA was enhanced up to 22 MPa by incorporation of 7.5 wt% MCC in combination with a crosslinking of EVA phase [26], on the other hand, the tensile strength of un-cured EVA was only increase to 3 MPa by addition of 7.5 wt% NCC [27]. Besides the improvement in mechanical properties, the barrier properties of EVA could also be enhanced

by incorporation of celluloses microfibers [28,29]. To increase the compatibility between EVA and celluloses, surfactant such as poly(ethylene glycol ether) and reactive compatibilization were applied [30,31].

The primary objective of this paper is to prepare highly reinforced EVA/NCC nanocomposites with fine dispersion of NCC and transparency. The chemical structures, morphology and properties of the NCC and the EVA/NCC nanocomposites were well investigated by means of gel analysis, X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), dynamic mechanical analysis (DMA) and mechanical test. The structure–property relationships were studied.

2. Experiment

2.1. Materials

Rubber grade EVA (Levapren®500) with vinyl acetate (VAc) content of 50 wt% was provided by Lanxess Chemical Co., Ltd., Qingdao, China. Microcrystalline cellulose (MCC, with a purity of ≥96%) and chemicals such as dicumyl peroxide (DCP, purity ≥99.5%) with typical half-life time of 1 min at 171 °C, chloroform (purity ≥99.5%) and N,N-dimethylformamide (DMF, purity ≥99.5%) were supplied by Sinopharm Group Chemical Reagent Co., Ltd., China.

2.2. Preparation of nanocrystalline cellulose

Nanocrystalline cellulose (NCC) was made from acid hydrolysis of microcrystalline cellulose (MCC) in sulfuric acid (64 wt%) at 45 °C for 30 min following the reported procedures in the literature [32,33]. The suspension was washed with deionized water until approximate neutral by successively centrifugal (10,000 rpm, 8 min), then the excess sulfuric acid was neutralized by addition of a small amount of NaOH solution. The NCC was finally obtained after freeze-drying of the suspension, which was used for characterization and blending with EVA.

2.3. Preparation of EVA/NCC nanocomposites

Aggregation of NCC may easily occur during melt compounding with hydrophobic polymer due to the high specific surface energy and hydrophilic feature of NCC. Thus, EVA/NCC nanocomposites with NCC content of 0–5 phr (per hundred rubber) respectively were prepared from solution blending and static vulcanization with the following procedures: EVA and DCP were first dissolved in chloroform forming a 15 wt% solution, and NCC was ultrasonically dispersed in DMF forming a suspension. The DCP content was fixed at 3.0 phr. The EVA/DCP solution and NCC suspension were blended at room temperature with magnetic stirring for 2 h to obtain homogeneous EVA/NCC/DCP mixtures. Then the mixtures were completely dried at 45 °C under vacuum condition. The EVA/NCC nanocomposites were finally obtained by static vulcanization using a hot compression molding machine at 170 °C and 10 MPa for 6.5 min. The dimension

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