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Superior reinforcement of ethyl-co-vinyl acetate rubber composites by using nano-sized starch filler: The role of particle size and reactive compatibilization

Pengwu Xu[a], Xiyuan Zhao[a], Deyu Niu[a], Martin Hoch[b], Piming Ma[a,*], Weifu Dong[a], Mingqing Chen[a], Yogesh Deshmukh[c,1]

[a] The Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, 1800 Lihu Road, Wuxi 214122, China
[b] ARLANXEO High Performance Elastomers (Changzhou) Co. Ltd., Shanghai Branch, 150, Hubin Road, Shanghai 200021, China
[c] Department of Biobased Materials, Faculty of Humanities and Sciences, Maastricht University, P. O. Box 616, 6200MD Maastricht, The Netherlands

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ABSTRACT

Nano-sized starch (NSt) was reported as reactive filler to reinforce ethylene-co-vinyl acetate rubber (EVM) by using epoxy-functionalized EVM (GMA-EVM) as compatibilizer together with 3-(2-aminoethylamino) propyl dimethoxy methyl silane (KH602). This resulted in EVM/GMA-EVM/NSt nanocomposites having significant improved properties. The improvement is attributed to the small starch particle size and chemical compatibilization. The tensile strength (*Ts*) was increased from 9.2 to 18.7 MPa when 20 phr (per hundred rubber by weight) of the GMA-EVM compatibilizer is incorporated. Compared to EVM/NSt, the EVM/GMA-EVM/NSt nanocomposites possess stronger interfacial interaction between fillers and the matrix according to morphology and crosslink density analysis. Besides the crosslink of EVM and GMA-EVM chains created by dicumyl peroxide (DCP), under the aid of KH602, extra chemical bonding was generated between: (a) GMA-EVM chains, (b) GMA-EVM and NSt. Thus, strong reinforcement of EVM was obtained. These interesting results provide a new insight to make robust rubbers which may create new applications for rubbers and natural fillers.

1. Introduction

In the past decades, due to the environmental issues and petroleum resource shortages, polymers from renewable resources become extremely important [1]. Starch, as one of the renewable and biodegradable natural polymers, is derived from plentiful resources at a low cost such as roots, seeds, fruits and blocks of higher plants. It has attracted great attention from research and industrial community [2]. Although starch is difficult to melt owing to the abundant intermolecular hydrogen bonding and the poor thermal decomposition temperature, it is widely used as environmentally friendly cheap filler in polymers. To melt starch, plasticizers such as glycerol have to be incorporated to make composites which are referred to thermal plastic starch, viz. TPS. Currently, starch is mainly used in plastic industry to make cheap biodegradable packaging [3]. In rubber industry, modified starch was reported as a reinforcing agent [4,5]. It is manifested that modified starch could endow tire with evolutionary properties, i.e., lower rolling resistance, noise and carbon dioxide emission. However, compared to the tire reinforced by silica, the tire reinforced by starch, which was accordant with the "green tire" concept [6], was limited by the poor compatibility between starch and rubber, and the subsequent coarse morphology in the final composites.

Generally, size and interfacial bonding of filler in a rubber matrix are the key factors for rubber reinforcement. The application of native starch as a reinforcing agent is limited due to its large diameter and poor dispersion. With the development of nanotechnology, lots of researches have been conducted on nano-sized starch (NSt). Starch nanocrystals (~200 nm) prepared by using the methods of phosphoric acid hydrolysis was reported. The nanocrystal starch was then blended with nature rubber (NR) latex to prepare NR/Starch nanocomposites [7]. This research confirmed that nanocrystal starch could disperse in NR latex uniformly leading to improved properties of the NR/starch composites. It was reported previously that NR was reinforced significantly by filling with 20 wt% of nanocrystal starch, e.g., the modulus was increased by 75 times due to the formation of starch network in the NR matrix [8]. In spite of these remarkable results, there are still

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* Corresponding author.
E-mail address: p.ma@jiangnan.edu.cn (P. Ma).
[1] Current address: Wavin Innovation and Technology, Rollepaal 20, 7701BS, Dedemsvaart, the Netherlands.

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some limitations in the application of starch due to its incompatibility with hydrophobic rubber matrices. The agglomeration of starch nanoparticles will be observed during processing. Hence the interface where starch nanoparticles exist is often the potential weak region in nanocomposites, resulting in an adverse impact on the final performance [9]. Moreover, the research reported in literature are limited to the rubber matrices. Ethylene-co-vinyl acetate rubber (Levapren® EVM) with a vinyl acetate content of 40 wt% to 90 wt% is a specialty synthetic rubber which is widely applied in cables, sealing and automotive industry due to its excellent flexibility, oil and weather resistance [10,11]. The disadvantage of EVM rubber is the low tensile strength around 2 MPa at room temperature. Lately, mechanical properties of EVM were improved by inorganic nano/macro fillers such as montmorillonite and silica, and organic fillers such as cellulose and starch [12–15]. Microcrystalline cellulose (MCC) and nanocrystalline cellulose (NCC) as reinforcing fillers were also introduced in EVM technology. With incorporation of 7.5 wt% MCC or 2 wt% NCC, the tensile strength (*Ts*) of EVM was enhanced up to ~20 MPa with a crosslink of EVM phase [13,16]. Besides, the barrier properties of EVM could be improved by celluloses microfibers as well [17]. Compared with normal fillers, nano-sized particles such as NCC demonstrated a better reinforcing effect without significantly compromising transparency of the EVM. In our previous research, EVM rubber with 50 wt% of gelatinized micro-sized starch was reactively blended with maleic anhydride (MA) and benzoyl peroxide (BPO) leading to a *Ts* of 6 MPa of the resulting EVM/starch composites. Nevertheless, the effect of starch nanoparticles and interfacial improvement on the properties of EVM has not been reported yet.

In this paper, we intend to explore highly reinforced EVM composites by construction of a secondary crosslink network and strong interfacial bonding using an epoxidized EVM rubber (GMA-EVM) and 3-(2-aminoethylamino) propyl dimethoxy methyl silane (KH602). We assume that the successful use of starch particles critically depends not only on size-reduction but also on a suitable chemistry for interfacial coupling and rubber matrix crosslinking. Therefore, in this work we provided a new facile route to make nano-starch-reinforced rubbers, which may be suitable for industrial applications, such as medical devices and children's toys. The effect of starch particle size and interfacial improvement on the reinforcement of EVM was studied in detail and the structure-property relationship was further investigated.

2. Experiment

2.1. Materials

Ethylene-co-vinyl acetate rubber (EVM) with a vinyl acetate content of 50 wt% and a Mooney viscosity of 16 MU, ML1 + 4, 100 °C and epoxy-functionalized EVM (GMA-EVM) with a vinyl acetate content of 60 wt% and a Mooney viscosity of 16 MU, ML1 + 4, 100 °C were provided by Arlanxeo Deutschland GmbH. Micro-sized potato starch (MSt) with an initial moisture content of 10 wt% was obtained from Aladdin, Shanghai, China (CAS: 9005-82-7). The silanes 3-(2-aminoethylamino) propyl dimethoxy methyl silane (KH602) and dicumyl peroxide (DCP, half-life of decomposition is around 1.0 min at 170 °C) were purchased from Aladdin, Shanghai, China. Nano-sized starch (NSt) was prepared in the laboratory by means of reverse titration [18]. Chloroform, ethanol and dimethyl sulfoxide (DMSO) were supplied by Sinopharm Group Chemical Reagent Co., Ltd., China.

2.2. Preparation of EVM/NSt and EVM/GMA-EVM/NSt nanocomposites

EVM (or EVM/GMA-EVM) and starch were compounded in a Haake mixer (Polylab-OS R600, Germany) at 65 °C for 10 min at a rotor speed of 50 rpm. Then, curing agent (DCP or DCP/KH602) was incorporated in and the composites were kept mixing for another 10 min to obtain homogeneous GMA-EVM/NSt (or EVM/GMA-EVM/NSt) nanocomposites. The vulcanization was performed by using a hot press machine at 170 °C for 10 min. The dimension of the molded nanocomposites is 10 × 10 × 2 mm^3, and the molded samples were used for characterizations. EVM/MSt composites were prepared in the same way for comparison.

2.3. Characterizations

Mechanical Properties: Tensile properties of the EVM/MSt, EVM/NSt and EVM/GMA-EVM/NSt composites were measured using a universal tensile tester (Instron5967, USA) at a tensile speed of 500 mm/min at 23 °C according to GBT529-2008. Five replicates of each sample were tested whose dimension were 25 × 4 × 2 mm^3 and the averaged values were presented. The permanent set (S_p) of each sample was measured 3 min after fracture and could be calculated using Eq. (1).

$$S_p = (L_1 - L_0)/L_0 \times 100\% \tag{1}$$

where L_0 and L_1 are respectively the original and final length. The Shore A hardness (*HA*) of the nanocomposites was measured via a hardness tester (Dirk LX-A, China) according to GB/T 531.1-200.

Fourier Transform Infrared (FTIR): The FTIR analysis on NSt and NSt-g-GMA-EVM copolymer was performed on a Nicolet 6700 FTIR spectrometer in a transmission mode in the wavenumber range of 400–4000 cm^{-1} with the resolution of 1 cm^{-1} and 128 scans.

Scanning Electron Microscopy (SEM): The phase morphology of the EVM/MSt, EVM/NSt and EVM/GMA-EVM/NSt composites were characterized by SEM (S-4800, HITACHI, Japan). Before characterization, the composites were cryo-fractured in liquid nitrogen and then coated with a thin gold layer. The accelerating voltage was 3 kV for characterization.

Transmission Electron Microscope (TEM): The morphology of EVM/NSt and EVM/GMA-EVM/NSt nanocomposites was characterized by TEM (JEOL-JEM-2100, Japan) with an accelerating voltage of 200 kV. At −80 °C, ultra-thin sections of the nanocomposites were obtained by ultramicrotomy using glass knives. The samples were then laid on TEM grids to observe the micro-morphology.

Crosslinked Structure Analysis: The crosslinked structures of EVM/GMA-EVM/NSt nanocomposites were characterized by using swelling equilibrium experiments, and the procedures can be found in our previous publication in detail [13].

According to Huggins and Flory-Rehner theory [19–21], the average molecular weight between crosslinks ($\overline{M}_c$) of a perfect network can be calculated using Eq. (2)

$$\overline{M}_c = -V_1\rho_P \frac{\phi_P^{1/3} - \phi_P^{1/2}}{\ln(1-\phi_P) + \phi_P + \chi_1\phi_P^2} \tag{2}$$

where $\overline{M}_c$ is the average molecular weight between crosslinks, ρ_P is the polymer density, χ_1 is the Flory-Huggins interaction parameter between polymer and solvent [22], ϕ_p is the polymer volume fraction, and V_1 is the molar volume of solvent. Here, $\chi_1 = 0.033$. Crosslink density (υ_e) quantizes the number of elastically effective chains per unit volume according to Eq. (3) [23].

$$\upsilon_e = \rho_P N/\overline{M}_c \tag{3}$$

where N is Avogadro's number (6.02 × 10^{23} mol^{-1}).

Dynamic Mechanical Analysis (DMA): The dynamic mechanical properties and thermal behavior of EVM/NSt and EVM/GMA-EVM/NSt nanocomposites were measured by DMA (Q800, TA Instruments, USA) in a tensile-film mode. The samples (4 × 4 × 2 mm^3) were characterized from −60 °C to 40 °C at a frequency of 1 Hz under a nitrogen atmosphere. The constant amplitude and the temperature ramp were respectively 20 μm and 3 °C/min. The storage modulus (*E′*) and loss factor (*tanδ*) were recorded as a function of temperature.