

Synthesis of high-performance green nanocomposites from renewable natural oils

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ABSTRACT

This paper describes preparation and properties of *green nanocomposites* from renewable resources. The nanocomposites were synthesized by an acid-catalyzed curing of epoxidized natural oils in the presence of silane coupling agents. The resulting nanocomposites were transparent and highly glossy. Their hardness and Young's modulus of the nanocomposite coatings improved, as compared with those only from the epoxidized natural oils. Dynamic viscoelasticity analysis and TEM observation showed the homogeneous structure of the nanocomposites. The properties of the nanocomposites were strongly affected by the structure and feed ratio of the monomers.

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1. Introduction

Polymeric materials from renewable resources have attracted a lot of attention in recent years [1,2]. Using biomass as starting material contributes to global sustainability without depletion of scarce resources, because of their large potential to substitute petrochemical derivatives to bio-based ones in industries. Furthermore, the advantages of these bio-based materials are sometimes composting and biodegradability after their use. For decrease of carbon dioxide emission, there is also a great demand to develop high-performance bio-based polymers.

Natural plant and animal oil sources are found in abundance in the world; and hence, are expected as an ideal alternative chemical feedstock. Inexpensive triglyceride natural oils have been utilized extensively for coatings, inks, plasticizers, lubricants, resins and agrochemicals in addition to their applications in food industry [3–7]. Since most of oil-based polymeric materials do not show properties of rigidity and strength required for structural applications by themselves, these oils were used as a toughening agent to produce interpenetrating networks [8–10].

Recently, high-performance nanocomposites of organic polymers and silica by a sol–gel process have been developed, in which the inorganic phase is formed in situ in a polymer matrix [11–17].

For preparation of highly intermingled inorganic–organic nanocomposites, functional silane coupling agents such as 3-glycidopropyltrimethoxysilane (GPTMS), 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane (ECTMS), 3-aminopropyltrimethoxysilane, and 2-aminoethyl-3-aminopropyltrimethoxysilane are often used as modifier of organic polymer precursors [18–23].

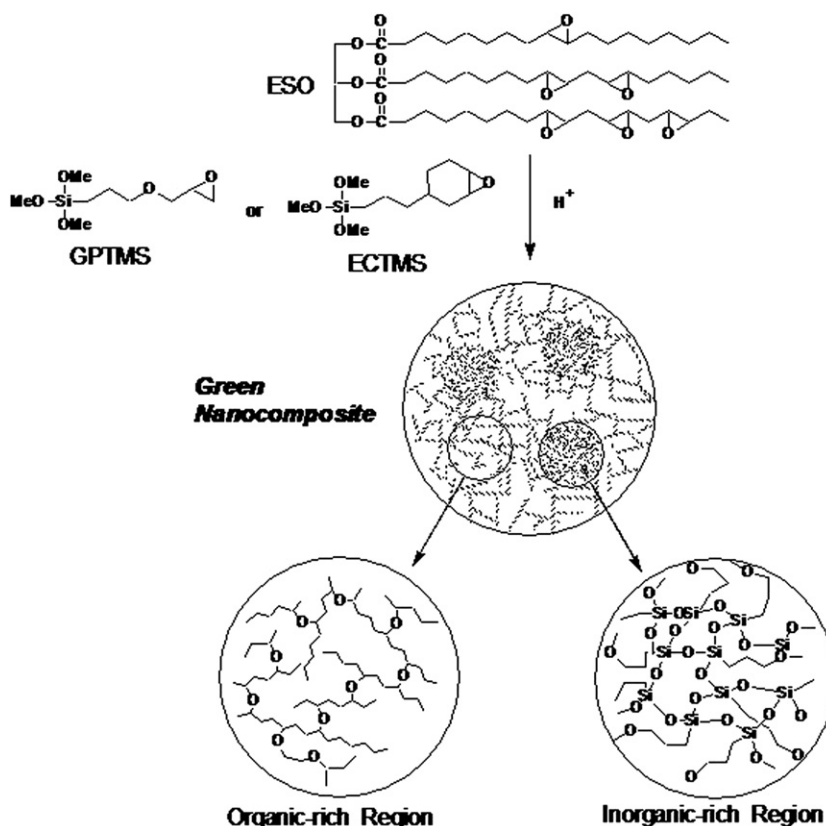
Inorganic–organic composites are of increasing interest as constituent of coating materials for a wide variety of applications since they offer the prospect of combining the mechanical toughness and flexibility of the organic component with the hardness and thermal stability of the inorganic component. Natural oil-based composites with good mechanical properties were prepared from an acrylate-modified soybean oil and natural fibers (flax and hemp fibers) [24]. Excellent gas barrier properties were found in laminated films of drying oil and Zein (corn) [25,26]. Organic–inorganic composite coatings were developed using plant oils and metal (Ti and Zn) oxides [27,28].

Previously, we reported *green nanocomposites* consisting of abundant natural resources, plant oils and clay [29–31]. An acid-catalyzed hardening of epoxidized plant oils in the presence of an organophilic montmorillonite produced triglyceride–clay nanocomposites with homogeneous structure, in which silicate layers of the clay were intercalated and randomly distributed in the polymer matrix.

Furthermore, *green nanocomposite coatings* from renewable plant oils have been developed by using functional silane coupling agents [32]. The curing of epoxidized plant oils in the presence of

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Scheme 1.

GPTMS produced transparent nanocomposite coatings, in which both oxirane groups of epoxidized plant oils and GPTMS were copolymerized to produce an organic polymer matrix, simultaneously forming a silica network. The covalent linkage between the organic and inorganic polymers controlled the nanocomposite structure in nanoscales, leading to improvement of coating properties. Furthermore, the nanocomposites showed good biodegradability in an activated sludge. An oxetane-containing silane coupling agent was also used as starting material for preparation of the *green nanocomposites* based on epoxidized plant oils [33]. This study deals with comprehensive results on synthesis and properties of *green nanocomposites* from epoxidized natural oils and silane coupling agents (Scheme 1).

2. Experimental

2.1. Materials

Epoxidized soybean and linseed oils (ESO and ELO) were gifts from Kao Co. and Daicel Chemical Industries, LTD., respectively. Epoxidized fish oil (EFO) was synthesized by lipase-catalyzed epoxidation of fish oil with hydrogen peroxide as an oxidant in the presence of a small amount of linoleic acid [34,35]. Thermally-latent cationic catalyst (a benzylsulfonium hexafluoroantimonate derivative, Sun Aid SI-60L) was provided by Sanshin Chemical Industry Co. Other reagents were commercially available and used as received.

2.2. Preparation of green nanocomposites

The following is a typical procedure for the preparation of the nanocomposite coating. To a mixture of ESO and GPTMS (total 2.0 g), thermally-latent catalyst (20 μ L) was added and the mixture

was coated using an applicator with slit thickness of 50 μ m on a glass plate and kept at 140 $^{\circ}$ C for 2 h. For evaluation of mechanical properties, a test piece of 1 mm thickness was prepared in a Teflon mold (17 mm $\times$ 40 mm $\times$ 1 mm) under the same conditions.

2.3. Measurements

Coating hardness was evaluated by a Fischerscope H100VS microhardness tester with test force of 40 mN. Dynamic viscoelasticity analysis was carried out by using a SEIKO EXSTAR 6000 with frequency of 1 Hz at a heating rate of 3 $^{\circ}$ C/min. Gloss value of coatings was measured at 60 $^{\circ}$ by a Horiba IG-330 gloss checker. FT-IR and UV–visible spectra were recorded on a Perkin–Elmer Spectrum One and a Hitachi U-2001 spectrometer, respectively. TG analysis was performed using a Seiko SSC/5200 apparatus for thermogravimetry/differential thermal analysis at a heating rate of 10 $^{\circ}$ C/min under nitrogen. Tensile properties were measured by a Seiko EXSTAR 6000. Transmission electron microscopy (TEM) and electron probe X-ray microanalysis (EPMA) image were obtained using a JEOL JEM-1220 at an accelerating voltage of 100 kV and a Horiba E-MAX 7000 at accelerating voltage of 10 kV, respectively. Scanning electron microscopy (SEM) image was obtained using Hitachi FE-SEM S-800 at accelerating voltage of 10 kV. 1 H NMR spectra were recorded on a Bruker DPX 400 spectrometer.

3. Results and discussion

3.1. Coating properties of green nanocomposites

The coating properties of green nanocomposites from epoxidized natural oils and oxirane-containing silane coupling agents were examined. In this study, three epoxidized triglycerides,

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