



Polymer communication

Organic–inorganic nanomatrix structure and properties of related naturally occurring rubbery macromolecules



Seiichi Kawahara^{a, *}, Nurul Hayati Yusof^a, Kenshi Noguchi^a, Kenichiro Kosugi^a, Yoshimasa Yamamoto^b

^a Department of Materials Science and Technology, Nagaoka University of Technology, 1603-1, Kamitomioka-machi, Nagaoka, Niigata 940-2188, Japan

^b Department of Chemical Science and Engineering, Tokyo National College of Technology, 1220-2, Kunugida-machi, Hachioji, Tokyo 193-0997, Japan

ARTICLE INFO

Article history:

Received 20 April 2014

Received in revised form

14 July 2014

Accepted 20 July 2014

Available online 1 August 2014

Keywords:

Nanomatrix structure

Natural rubber

Silica

ABSTRACT

The outstanding mechanical properties of soft materials i.e. natural rubber are partly due to the organic–inorganic nanomatrix structure because numerous organic microparticles are dispersed in a small amount of an inorganic nanomatrix composed of inorganic nanoparticles and organic macromolecules. Here we form an organic–inorganic nanomatrix using graft-copolymerization of a vinyl monomer with an inorganic oxide precursor onto natural rubber particles with an average diameter of 1 μm dispersed in water. The inorganic oxide precursor is converted into inorganic oxide nanoparticles through hydrolysis and condensation, forming chemical linkages between natural rubber microparticles and inorganic oxide nanoparticles. Transmission electron microscopy indicates that the organic–inorganic nanomatrix is densely filled with inorganic oxide nanoparticles and the natural rubber microparticles are dispersed in the nanomatrix. This nanomatrix composite realizes both energetic elasticity and entropic elasticity of a soft material, opening a novel field of building block chemistry with respect to a pair of organic microparticles and inorganic nanoparticles.

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1. Introduction

An organic–inorganic nanomatrix composite is a novel nanocomposite, which conflicts with the conventional wisdom of a multi-component system with the island-matrix structure, which consists of both major components as the matrix and minor components as the dispersoid [1]. It is difficult to realize an antithesis of the island matrix structure, which is a soft material consisting of a dispersoid of the major component and a matrix of the minor component. Thus, much attention has focused on developing novel nanocomposites using a nanomatrix less than several tens nm thick. Here, we define a nanomatrix composite as “a nanocomposite consisting of organic particles as the major component and organic or inorganic matrices as the minor component”.

Upon observing the morphology of natural rubber, we first discovered an organic–organic nanomatrix structure in *Hevea brasiliensis*. Natural rubber particles with an average diameter of about 1 μm are well dispersed in a nanomatrix of non-rubber components, which has a thickness of about 15 nm (e.g., proteins

and phospholipids) [2,3]. Removing the proteins destroys the nanomatrix structure and significantly reduces the mechanical properties. For example, the storage modulus value without proteins is one-tenth of that of natural rubber [2]. Hence, the organic–organic nanomatrix plays a crucial role in the outstanding properties of natural rubber.

The discovery of the organic–organic nanomatrix structure stimulated the development of nanocomposites; for instance, as-casted films have been prepared by mixing inorganic nanoparticles (e.g., silica-nanoparticles [4–7] and carbon-nanosheets (graphene) [8–13]) with naturally occurring polymers (e.g., natural rubber in the latex stage) and subsequent coagulation. Although the morphology of the resulting films resembles a nanomatrix structure, the mechanical properties are poor. For example, the stress at break of rubber prepared from wet master batch is below 10 MPa. Thus, to achieve outstanding mechanical properties, the physical and chemical interactions between the natural rubber microparticles and the inorganic nanoparticles should be controlled.

When rubbery macromolecules are used as organic particles, the organic microparticles and inorganic nanoparticles must interact physically and chemically, which may suppress the active thermal movement of the rubbery macromolecules [14]. However,

* Corresponding author.

E-mail address: kawahara@mst.nagaokaut.ac.jp (S. Kawahara).

the chemical interactions may maintain the organic–inorganic nanomatrix as the island–matrix structure is formed by incorporating suitable chemical constituents into the rubbery macromolecules in water. One example of such interactions is graft-copolymerization of suitable monomers onto rubber particles in the latex stage and subsequent coagulation of the resulting latex forms a nanomatrix structure [15–18].

Graft-copolymerization of a vinyl monomer with an inorganic oxide precursor onto natural rubber particles in the latex stage and subsequent hydrolysis and condensation can form chemical linkages between natural rubber microparticles and inorganic nanoparticles. After coagulation of the resulting latex, an organic–inorganic nanomatrix structure is formed by joining natural rubber microparticles with inorganic oxide nanoparticles.

Herein we use vinyltriethoxysilane as a vinyl monomer with an inorganic oxide precursor to form an organic–inorganic nanomatrix structure. Specifically, vinyltriethoxysilane (0.50–1.50 mol/kg-rubber) is graft-copolymerized onto natural rubber microparticles, which are in the latex stage where the proteins have been removed via purification using urea and sodium dodecyl sulfate, with *tert*-butylhydroperoxide and tetraethylenepentamine as initiators (3.3×10^{-2} – 9.9×10^{-2} mol/kg-rubber). The sudden increase in pH to 12 due to the hydroxyl ion concentration of the latex indicates that hydrolysis and condensation of the grafted polyvinyltriethoxysilane form silica nanoparticles on the surface of the natural rubber microparticles and that the unreacted monomer may be incorporated into silica nanoparticles. Hence, we further investigate the morphology of natural rubber with the nanomatrix structure using a transmission electron microscope (TEM) as well as the relationship between the nanomatrix structure and mechanical properties (e.g., viscoelastic and tensile properties).

2. Experimental

2.1. Removal of proteins from natural rubber latex

The starting material was high ammonia natural rubber (HANR) latex. First, the deproteinized natural rubber (DPNR) latex in the presence of a surfactant, SDS, and urea was prepared. SDS (1.0 w/w %) was dissolved in distilled water and poured into ~60 w/w % total solid content (TSC) of HANR latex until 30 w/w % TSC of the latex achieved. Then 0.1 w/w % urea was added into diluted HANR latex, and the mixture was incubated for 1 h at room temperature while stirring. The mixture was subsequently centrifuged three times at 10,000 rpm, 15 °C for 30 min. The cream fractions collected after the second and third centrifugations were re-dispersed in 0.5 w/w % and 0.1 w/w % SDS solution, respectively. The final rubber cream fraction was then dispersed in a 0.1 w/w % SDS solution. The percentages of SDS and urea were based on the overall solution. Prior to determining the grafting efficiency, DPNR latex was diluted to 20 w/w % TSC and topped with 0.5 w/w % SDS.

2.2. Graft-copolymerization of vinyltriethoxysilane onto natural rubber particles in DPNR latex

Monomers along with *tert*-butylhydroperoxide (TBHP) and tetraethylenepentamine (TEPA) as initiators were used for graft-copolymerization of DPNR latex. The initiator and monomer were added sequentially after purging latex (200 g) with 20 w/w % DRC and 0.5 w/w % SDS with N₂ gas for one hour. After continuously stirring the reaction mixture for two hours at 200 rpm under a N₂ atmosphere at 353 K in a water bath, the unreacted monomer was removed with a rotary evaporator under a reduced pressure for about 30 min at 353 K. The reacted latex was poured in a petri dish and dried in an oven at 323 K for about two days (until dried) and

then transferred into a vacuum oven and dried for an additional three days at 323 K. Monomer conversion was determined by incinerating the resulting polymer above 1000 °C until only silica was recovered and the weight was constant. The percentage of monomer conversion was calculated by the weight ratio of formed silica to the gross polymer. The grafting efficiency was obtained by weight ratio of grafted polymer to gross polymer.

2.3. Material characterizations

The morphology at high magnification was observed by a transmission electron microscope (TEM), JEOL JEM-2100 at an accelerating voltage of 200 kV. Ultra-thin sections of the sample were prepared by a Richert-Nissei FC S-Ultracut at 183 K, and then the sections were placed onto the copper grid before being subjected to the electron beam of the TEM.

The tensile properties were measured according to JIS K6251. Film samples (~1 mm thick) were cut with a Dumbbell-shaped Type 7. Each test piece was stretched at a speed rate of 200 mm/min. Data was plotted in stress–strain curves.

Dynamic viscoelasticity was measured with Anton Paar Physica MCR 301. Parallel plates geometry of 12 mm diameter was used. Angular frequency range was from 0.1 to 100 rad s⁻¹. Temperature range was from –70 to 50 °C. The oscillatory strain amplitudes were within the range of linear viscoelasticity in all measurements.

3. Results and discussion

Fig. 1 shows conversion, monomer content, and grafting efficiency of vinyltriethoxysilane, which are estimated from the ratio (mol%) of the resulting polymer to the fed monomer, the ratio of the resulting polymer to rubber, and the ratio of the grafted polymer to the resulting polymer, respectively. As the monomer concentration increases at a constant initiator concentration, the conversion is constantly high, while the monomer content and grafting efficiency are increased. High grafting efficiency is obtained, which is more than 80%. This may be explained to be due to the triethoxysilyl group undergo condensation and hydrolysis, and vinyl group reacts with natural rubber. Since both groups are reacting during the polymerization, therefore high grafting efficiency is achieved. Consequently, the most suitable conditions for graft-copolymerization of vinyltriethoxysilane onto natural rubber using a water process are a vinyltriethoxysilane concentration of 1.05 mol/kg-rubber and an initiator concentration of 0.066 mol/kg-rubber.

Casting the grafted latex onto a Petri dish prepared an as-cast film of the resulting grafted natural rubber (i.e., DPNR-graft-PVTES). The bright and dark domains in the TEM images of the as-cast film represent natural rubber and colloidal silica, respectively, because the films are not stained with a reagent (Fig. 2). For the DPNR-graft-PVTES, the natural rubber particles (average diameter of about 1 μm) are well dispersed into the silica nanomatrix as a three-dimensional nanonetwork (Fig. 2b). The nanonetwork consists of colloidal silica nanoparticles with diameters between 5 and 150 nm, which differs from natural rubber (Fig. 2a) because the removal of proteins from natural rubber inhibits a nanophase-separated structure. The size of the colloidal silica depends upon both the vinyltriethoxysilane concentration and the initiator concentration. The colloidal silica particles become smaller when the initiator concentration increases at a vinyltriethoxysilane concentration of 1.05 mol/kg-rubber, but become larger when the vinyltriethoxysilane concentration increases at an initiator concentration of 0.066 mol/kg-rubber.

Fig. 3 shows the stress–strain curves for DPNR and DPNR-graft-PVTES. DPNR exhibits a typical stress–strain curve where the value

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