



# Reinforcement effect of soy protein nanoparticles in amine-modified natural rubber latex



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## ABSTRACT

Mechanical properties of natural rubber reinforced with soy protein nanoparticles are useful for various rubber applications. However, the properties is further improved by improving interactions between soy protein and rubber. A novel method is used to modify particle surface of natural rubber latex by grafting with diallylamine. The improved polymer-filler interactions caused tensile stress at 300% elongation to match that of carbon black, which is a breakthrough for organic fillers. The grafting was demonstrated with infrared and particle size measurements. The size of natural rubber latex particles increased 8% after the grafting and the infrared spectra showed an increase of amine groups in coagulated NR latex. The curing rate of modified NR reinforced with soy protein matches that of carbon black composite. With the addition of 10% soy protein nanoparticles, the tensile strength of natural rubber and modified natural rubbers increased from 9 to 15 MPa to 19–25 MPa. Both dynamic mechanical strain and swelling measurements indicate modified natural rubber composites have a higher degree of polymer-filler interaction. The change of reinforcement factors with filler fraction can be described by modified Mooney model that includes anisotropic reinforcement elements. Tan $\delta$  at 60 °C indicates the modified composite has a better rolling resistance than carbon black.

## 1. Introduction

Natural rubber (NR) composites have many applications in molded objects such as tire treads, seals, automobile belts, and hoses. Fillers used in NR include different types of fillers that have different particle size and surface energy for different applications. To improve the rubber strength, nano-sized filler and suitable interactions between filler and rubber matrix usually lead to an improvement in the modulus of rubber (Wang, 1998; Leblanc, 2002). Both carbonized organic materials and inorganic particles have been used as fillers in rubber products. The major fillers are carbon black and silica of various aggregate size and surface treatments. Carbon black is currently the dominant filler for rubbers. It is produced by burning nonrenewable sources such as petroleum oil or natural gas with undesirable emissions as byproducts.

The advantages of using natural fillers are well known as sustainable, biodegradable, and light weight. A number of efforts have indicated that the mechanical properties of NR can be improved with natural fillers such as fibers (Favier et al., 1995; Cao et al., 2007), cellulose (Jacob et al., 2004; Geethamma et al., 2005), biomass carbon

(Jong, 2013a), and starch (Wu et al., 2004). Lignin was also used to reinforced rubber and showed practically useful mechanical properties (Jiang et al., 2013; Datta et al., 2017; Ikeda et al., 2017). We have studied the effect of soy protein nanoparticles in NR and showed its reinforcement effect (Jong, 2015). Dry soy protein is rigid with a storage modulus of  $\sim 1$  GPa (Jong, 2005) and therefore can reinforce rubbers. With global soybean production approaching 340 million metric tons, it provides a stable material source for industrial applications.

However, NR composites reinforced with hydrophilic bio-fillers (Jiang et al., 2013; Datta et al., 2017; Ikeda et al., 2017) are often soft compared with carbon black and are reflected in lower tensile stress at 100–300% strain. Although the increase of modulus can be achieved by increasing crosslinking density and filler concentration, they often have adverse effect on tensile strength and elongation. To solve this problem, interactions between rubber and filler can be increased to restrict the movement of polymer chains, but still allow the mobility under high stress so that concentrated local stress under larger load can be redistributed to prevent premature rupture of rubber composites. To this end, NR can be modified to contain some hydrophilic functional

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groups to improve the interactions between NR and hydrophilic fillers. Direct modification of natural rubber latex with hydrophilic monomers has been reported in several publications. Dimethylaminoethyl methacrylate has been used to modify natural rubber (Kangwansupamonkon et al., 2005; Lamb et al., 2001; Kangwansupamonkon et al., 2004) and the modified NR was used to improve compatibility with starch particles (Rouilly et al., 2004). Methacrylamide (Burfield and Ng, 1978a,b,c) has also been used to modify natural rubber latex.

However, the grafting of diallylamine to NR to improve the mechanical properties of soy protein nanocomposites has not been studied. In this study, rubber particles in NR latex was modified using diallylamine and free-radical initiator to impart hydrophilic amine functional groups onto a portion of NR on the surface of latex particles so that improved coupling through hydrogen and ionic bonds between NR and hydrophilic bio-fillers such as soy protein nanoparticles can be achieved. The composites were melt-processed using traditional rubber compounding process. These latex and modified natural rubber composites were characterized to understand their structures and evaluate their properties. With the improved mechanical properties of these rubber composites, they have potential to be used in tire tread, seals, rubber belts, and damping applications.

## 2. Experimental

### 2.1. Materials

Soy protein (SP) (trade name Ardex F) in powder form was from Archer Daniels Midland Company (Decatur, IL). The composition of SP is consisted of ~90% protein, ~5% ash, and ~5% fat. The NR latex with ~61% solids and a pH ~10 was from Centrotech Rubber USA, Inc. (Chesapeake, VA). Calcium hydroxide was from Fisher Scientific (Waltham, MA). Diallylamine was purchased from Alfa Aesar (Ward Hill, MA). *tert*-butyl hydroperoxide as initiator and tetraethylene pentamine as activator were from Sigma-Aldrich (St. Louis, MO). Carbon black (CB) N339 and rubber curing accelerator, N-cyclohexyl-2-benzothiazolesulfenamide, were from Akrochem Co. (Akron, OH). Sulfur, zinc oxide, 2,2'-Methylenebis(6-*tert*-butyl-4-methylphenol), and stearic acid were from Alfa Aesar (Ward Hill, MA).

### 2.2. Modification of natural rubber

A method by Hourston and Romaine (Hourston and Romaine, 1990) to modify NR latex with unsaturated monomer was used to modify NR latex with diallylamine. The NR latex (490 g) was diluted with 100 g of a 0.26% ammonium hydroxide solution in a closed glass reactor under nitrogen atmosphere. Diallylamine at 5 wt% of dry rubber in 300 g of a 0.26% ammonium hydroxide solution was added to the reactor and mixed for 30 min. *tert*-butyl hydroperoxide as initiator at 1 wt% of rubber was then added and mixed for 15 min. Finally, tetraethylene pentamine as activator at 0.5 wt% of rubber was added and the temperature was raised to 50 °C. The reaction under constant stirring was allowed to proceed for 24 h. A different batch using the same condition was also prepared, but with the initiator at 0.3 wt% of rubber and the activator at 0.2 wt% of rubber. To examine the NR crosslinking by the free radical initiator, NR latex was also modified with *tert*-butyl hydroperoxide at 1 wt% of rubber under the same reaction condition. The modified rubber with the higher amount of initiator is designated as H and that with the lower amount of initiator is designated as L in this report. The NR modified with the initiator only is designated as Init.

### 2.3. Preparation of soy protein particles and composites

SP dispersion was prepared by hydrolyzing SP powder in distilled water at 9.3% concentration, and heated at 60 °C for 1 h under stirring. The batch weight was 1.93 kg. Calcium hydroxide at 2.2% concentra-

tion based on the dry weight of SP was used in the hydrolysis. Before using microfluidizer to reduce the particle size of SP, the dispersion was homogenized for 30 min at 8000 rpm. The pressure used in the operating the microfluidizer (M-100P, Microfluidics, Newton, MA) was 159 MPa. The dispersion was passed through a diamond (200 µm) and a ceramic interaction chamber (80 µm) three times. Cold flowing water was used to keep the exiting dispersion at about 30 °C. To prepared mixture of SP particles and NR latex, they were mixed at pH 10 for 30 min at room temperature with a solid content of ~15%. Water was removed from the mixture by freeze-drying. To compare the differences between the modified and unmodified NR latexes, four composites containing 10, 20, 30, and 40% SP were prepared with each latex.

The dry mixture of SP and NR was compounded with rubber chemicals in a Brabender mixer (ATR Plasti-corder, C.W. Brabender Instruments, Inc., South Hackensack, NJ). Rubber chemicals added were weighted in terms of phr (parts per hundred parts of rubber). The same formulation was used for all samples: 100 phr natural rubber, 1 phr anti-oxidant, 5 phr zinc oxide, 2 phr stearic acid, 2 phr sulfur, and 2 phr accelerator. The material volume is 70% of the mixing bowl volume. All components were added at once except sulfur and accelerator, and then mixed for 15 min at 60 rpm. After the mixing, sulfur and accelerator were added and mixed for 3 min at 80 °C. The composites with 10, 20, 30, and 40 wt% SP filler in the composites were compression molded at 5 MPa and 160 °C for 15 min, which was beyond full cured times for all samples.

### 2.4. Characterization of particles and latex modification

SP particle size was measured in water with a Horiba LA-930 laser scattering particle size analyzer (Horiba Instruments, Irvine, CA), which is equipped with both long (632.8 nm) and short wavelength (405 nm). An accumulation of 20 scans was obtained for the measurement of volume and number-weighted mean diameters and size distribution. The SP dispersion was also filtered through a 0.7 µm glass microfiber filter (WHATMAN GF/F) in order to measure the fraction and particle size of the dispersions less than 0.7 µm. The solid contents of the dispersions before and after filtration were also measured to determine the amount of particles passed through the filter. The latex modification was monitored with infrared absorption of the NR and modified NR films using ATR (Attenuated Total Reflectance) mode (Thermo Nicolet iS10 FT-IR, Waltham, MA). The measurement range was 650–4000 cm<sup>-1</sup> for 100 scans at a spectral resolution of 4 cm<sup>-1</sup>.

### 2.5. Measurements of mechanical properties

An Instron tensile testing machine (Instron, Norwood, MA) was used to measure stress-strain properties with a 1 kN load cell and at the crosshead speed of 500 mm/min. Dumbbell test specimens was based on ISO 37-2. The samples have a thickness of ~2 mm and the test was repeated five times for each composite. For elastic materials, the use of extensometer is required. The elongation was measured by using an Instron AutoX750 automatic extensometer. Linear viscoelastic properties were studied with a strain-controlled rheometer (ARES-G2, TA Instruments, Piscataway, NJ). The samples had a dimension of 50 × 12.5 × 5 mm and used in a torsion rectangular geometry. The variation of modulus with temperature was measured at a heating rate of 1 °C/min and within a range from -68 to 140 °C. For curing studies, a rubber compound before curing was compressed to form a circular disk of 25 mm in diameter and storage modulus was measured over time using serrated parallel plate fixture at 160 °C. The strain sweep experiments were conducted with a sample size of 25 × 12.5 × 5 mm at four temperatures (-15, 0, 25, and 60 °C) in a strain range of 0.01% to 100% and at a frequency of 1 Hz.

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