



Influence of protein hydrolysis on the mechanical properties of natural rubber composites reinforced with soy protein particles



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ABSTRACT

For natural rubber applications, the reinforcing fillers are used to improve the mechanical properties of the rubber. Soy protein particles have been shown to reinforce natural rubber. The hydrolysis conditions of soy protein are studied to understand its effect on the particle size and size distribution, and their subsequent effect on the mechanical properties of natural rubber. The reinforced and crosslinked rubber composites showed an improvement on modulus, tensile strength, and toughness compared to natural rubber. The composites reinforced with less hydrolyzed soy protein and the composites prepared under alkali condition had greater tensile strength, modulus, and toughness, while the composites reinforced with highly hydrolyzed soy protein and the composites prepared under acidic condition had greater elongation. The highly hydrolyzed soy protein was found to decrease the total crosslinking density and decrease the modulus at larger strain region. The structure-properties of the composites were characterized with stress-strain, dynamic frequency sweep, transmission electron microscopy, and swelling experiments.

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1. Introduction

Natural materials have advantages of being renewable, sustainable, light weight, carbon neutral, and biodegradable. Proteins from reliable raw material sources such as soybean and wheat are desirable feedstocks for commercial applications because of the stability of their supply. Soy protein is a low cost raw material and was found to have substantial reinforcement effect in natural rubber (NR) (Jong, 2013) because soy protein is rigid in dry state with a storage modulus of ~1 GPa (Jong, 2005). The properties of soy protein are altered when heated above denaturation temperature and/or hydrolyzed under alkali/acidic condition (Damodaran, 1988; Jiang et al., 2009; Akkermans et al., 2007). These heating and hydrolysis steps change the protein particle size, size distribution, and particle-particle interactions, which in turn change the mechanical properties of NR composites reinforced with these soy protein particles. To develop an all natural and renewable rubber composites,

NR is chosen as rubber matrix. NR is a major rubber raw material mainly produced from Hevea trees (Greve, 2000) in Asia and Africa as well as from Guayule shrubs (Pearson et al., 2013) in the United States. NR latex is a natural polymer of isoprene, mostly *cis*-1,4-polyisoprene (Roberts, 1963; Archer et al., 1963) and its stereoregularity contributes to the strain-induced crystallization as well as good green and tensile strength. The composition of NR also includes a small percentage (up to 5% of dry mass) of other materials, such as proteins, fatty acids, carbohydrates, phospholipids, and inorganic salts (Greve, 2000; Archer et al., 1963). For practical applications, NR is reinforced with different types of fillers that have different particle size and surface energy to enhance its mechanical properties for applications such as seals, automobile belts, hoses, tire treads, and numerous molded objects. Conventional fillers include both carbonized organic compounds and inorganic particles. The major fillers represent these two categories are carbon black and silica of various aggregate size and surface treatments. Carbon black dominates the rubber filler market and is produced by the combustion of petroleum oil or natural gas with a yield less than 50% and generates carbon dioxide as the main by-product. The environmentally friendly natural fillers have been under development and the mechanical properties of NR have been enhanced with natural fillers such as cellulose (Cao et al., 2007; Favier et al., 1995) and starch (Wu et al., 2004; Qi et al., 2006; Angellier et al., 2005).

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For filler reinforcement, filler size and filler surface properties are important factors to improve the strength of rubber. Generally, small filler size and proper interactions between filler and rubber matrix tend to improve the rubber modulus (Wang, 1998; Leblanc, 2002). In this study, soy protein was hydrolyzed under different hydrolysis conditions and microfluidized to reduce particle size and homogenize the size distribution. The dispersion was then blended with natural rubber latex and dried. The dried mixture was melt-processed with other rubber chemicals using traditional rubber compounding process. The NR composites filled with highly hydrolyzed soy protein were compared with the NR composites filled with less hydrolyzed soy protein. A comparison was also made between the composites prepared under alkali condition and the composites prepared under acidic condition. These soy protein reinforced natural rubbers were characterized with stress-strain method, dynamic frequency sweep, transmission electron microscopy (TEM), and swelling experiments to evaluate and understand their structure-properties.

2. Experimental

2.1. Materials

The soy protein isolate (SP) (trade name Ardex F) used in this research was a spray dried powder (Archer Daniels Midland Company, Decatur, IL). The SP contained ~90% protein, ~5% ash, and ~5% fat. The NR latex used was Centex LATZ obtained from Centrotrade Rubber USA, Inc. (Chesapeake, VA). The glass transition temperature, determined by G'' maximum, of a crosslinked NR with 2 phr (parts per hundred parts of rubber) sulfur was -60°C . The NR latex received had ~61% solids and a pH ~10. Carbon black used in this study was N-339 (Vulcan M from Cabot Corporation, Alpharetta, GA), which was an aggregate (Lyon and Burgess, 1985) that consisted of ~39 nm primary particles. The aggregates had a surface area of ~91 m²/g. Rubber curing accelerator, *N*-cyclohexyl-2-benzothiazolesulfenamide (CBTS), was purchased from Akrochem Co. (Akron, OH). Rubber compounding ingredients including antioxidant (2,2'-Methylenebis(6-*tert*-butyl-4-methylphenol)), sulfur, stearic acid, and zinc oxide were purchased from Sigma-Aldrich (St. Louis, MO).

2.2. Hydrolysis and microfluidization of soy protein

9% SP in distilled water was first heated at 60°C for 1 h under stirring at pH 10. The dispersion was further homogenized at 10^4 rpm for 15 min to ensure that it will not clog the orifice of microfluidizer before it was fed to a microfluidizer (M-100P, Microfluidics, Newton, MA) equipped with a diamond interaction chamber (200 μm) and a ceramic interaction chamber (80 μm), and operated at a pressure of 159 MPa. The dispersions were passed through the microfluidizer and the samples were collected after 10 cycles. The temperature of the dispersion was controlled by a continuous stream of cold water flowing through a water container, where an outlet coil was immersed. The SP dispersion was blended with natural rubber latex at pH 9.8 and freeze-dried. Four composites containing 10, 20, 30, and 40% SP were prepared. For the preparation of highly hydrolyzed SP, the heating condition was 95°C for 3 h at a starting pH of 11.5. For the composites prepared under acidic condition, the alkaline mixture of soy protein dispersion and NR latex was coagulated with dilute sulfuric acid at pH 4.5 and freeze-dried.

2.3. Particle sizing

The mean particle size and distribution of protein aggregates were measured using a Horiba LA-930 laser scattering particle

size analyzer (Horiba Instruments, Irvine, CA) with a red light wavelength of 632.8 nm and a blue light wavelength of 405 nm. An emulsion sample was drop-wise added to circulating distilled water, which had been adjusted to the same pH as that of the emulsion. A volume and number weighted mean diameter and size distribution of particles were recorded after 20 scans. Particles with a hydrodynamic radius less than 100 nm were measured with a Wyatt QELS (Wyatt Technology, Santa Barbara, CA). Aqueous dispersions were filtered through a 100 nm filter and measured in a scintillation vial using the principles of dynamic light scattering.

2.4. Composite formation

A Brabender mixer (ATR Plasti-corder, C.W. Brabender Instruments, Inc., South Hackensack, NJ) equipped with a pair of Banbury blades was used to mix all components. The mixing bowl has a volume of 75 ml and it was filled to 70% for all sample preparations. All formulations have the same mixing volume calculated from the components' densities. The dried natural rubber blends with SP prepared as described in the previous section was fed into the Brabender internal mixer along with other ingredients (antioxidant, rubber, zinc oxide) at 80°C , and mixed at 60 rpm for 20 min, which included 5 min of feeding time. Other ingredients measured in terms of phr (parts per hundred parts of rubber) are the same in all formulations: 100 phr natural rubber, 1 phr anti-oxidant, 2 phr stearic acid, 3 phr zinc oxide, 1 phr accelerator, and 2 phr sulfur. The mixture was then cooled to 80°C , followed by the addition of sulfur and accelerator, and mixed for 3 min. The composites with 10, 20, 30, and 40 wt% filler in terms of total weight of the filler and rubber were prepared. The final compounds were compression molded in a window-type mold at 5 MPa and 160°C for 15 min. Although different samples might have slightly different curing time, a fixed curing time beyond the full cure for all the samples was used to provide the same thermal history for all the samples under the comparison.

2.5. Transmission electron microscopy

A composite was cryogenically cut into thin slices with a microtome, stained, and placed on a lacey carbon grid. The specimens were imaged at room temperature using a 120 kV Philip 420T TEM in the Materials Characterization Laboratory at Pennsylvania State University (University Park, PA).

2.6. Stress-Strain measurements

The compounded rubber samples were molded into ring test specimens with a ring shape mold, which has an inner and outer diameter of 26 and 30 mm, respectively. The ring sample has a thickness of 3 mm. The calculation of tensile strength and elongation are described in ASTM D412, where the tensile strength is calculated as the force divided by the cross-sectional areas from the two legs of a ring and the percent elongation is the sum of elongation from the two legs of a ring divided by the mean circumference of the ring. The experiment was conducted using a ring tensile test fixture made by Instron (Instron, Norwood, MA) based on the specifications in ASTM D412. Stress-strain measurements were conducted with an Instron 55R1123 tensile testing machine equipped with a 1 KN load cell and operated at a crosshead speed of 500 mm/min.

2.7. Swelling measurements

Swelling experiments were conducted by immersing weighted samples in toluene for 48 h at 25°C . After removing the excess solvent on the surface and measuring the swollen weight of the samples, they were dried in a vacuum oven for 24 h at 50°C . Volume

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