



Processing and mechanical properties of natural rubber/waste-derived nano filler composites compared to macro and micro filler composites



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ABSTRACT

Nano-sized fillers produced from renewable materials can generate high performance natural rubber (NR) composites while reducing dependency on petroleum. We made NR composites, with both hevea and guayule NR, containing nano-scale waste-derived fillers as complete and partial replacements of carbon black. The effect of nano-filler type and loading on composite mechanical properties was analyzed and compared to previous results with micro and macro fillers. Also, processability of the compounds was investigated. Reinforcement of both NRs was achieved by nano-sized waste-derived fillers, even with complete replacement of carbon black. Increases of up to 2.4 and 1.8 times higher tensile and tear strength, respectively, were achieved in some of the composites compared to the unfilled compound. Better relative reinforcement was obtained in guayule than in hevea rubber due to different rubber macromolecular structure and the strength of the rubber-waste filler interactions. Composites containing waste-derived fillers as co-fillers with carbon black displayed uncommon combinations of properties not achieved with single conventional reinforcing fillers. Furthermore, significant reductions in power consumption during mixing, up to 10% in hevea and 19% in guayule composites, were obtained even by replacement of a small portion of carbon black in the composites. Despite increased interest in nano-sized particles, micro-sized fillers are effective reinforcing fillers when used as partial replacements of carbon black, and can be produced at a much lower cost than nano-sized particles.

1. Introduction

Fillers are extensively used polymer additives, considered essential to attainment of product performance (Leblanc, 2002). Currently the main two commercially used reinforcing fillers are carbon black (CB) and silica. Since the early 1900s, CB has been the most widely used and studied reinforcing filler for rubber composites (Fröhlich et al., 2005; Tohsan and Ikeda, 2014). However, CB is a non-renewable resource derived from petroleum. Furthermore, increased tire production along with reductions in CB production capacity due to increasing environmental regulations in North America and Europe, is likely to lead to CB shortfalls and price rises by 2020 (Moore, 2015; Pourriahi, 2016).

Silica has gained increasing attention as a reinforcing filler since the early 1990s, particularly in the tire industry due to improvements it confers in dynamic-mechanical properties such as lower rolling resistance at equal wear resistance and improved wet grip compared to CB composites (Rattanasom et al., 2007; Stöckelhuber et al., 2010). The use of silica in rubber compounds also has positive impact on the sustainability of the tire industry, due to increased fuel economy and

decreased CO₂ emissions achieved as result of tires' low rolling resistance. Nevertheless, the production of silica requires the use of harsh chemicals and high temperatures (Byers, 2001). Moreover, compounding natural rubber (NR) with silica requires the use of expensive coupling agents to overcome unacceptably strong filler–filler interactions and improve compatibility with NR (Choi et al., 2003; Kato et al., 2014; Murakami et al., 2003). Furthermore, 36% of the silica demand is related to non-rubber products (Notch consulting Inc., 2015), which limits current availability for the rubber industry.

New fillers are desired that can offer similar or better reinforcing and processing properties to CB but be derived from more sustainable sources. Increasingly, research is focusing on the utilization of waste-derived, renewable materials as alternative fillers for elastomers (Abraham et al., 2013; Barrera and Cornish, 2016, 2015; Gopalan Nair and Dufresne, 2003; Intharapat et al., 2013; Ishak and Bakar, 1995; Pasquini et al., 2010; Visakh et al., 2012). This field of research is driven by concerns about environmental footprint, sustainability in manufacturing, and the rising cost of treatment and disposal of high volume waste materials.

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Particle size is an important morphological characteristic affecting the utility of alternate fillers as reinforcing agents (Leblanc, 2002). Smaller particles have more surface area per unit weight than bigger particles. Greater surface area facilitates more interfacial contact between the filler and the polymer, which increases the effectiveness of reinforcement (Bandyopadhyay-Ghosh et al., 2015; Szeluga et al., 2015). However, the strength and nature of interactions between the polymer and the filler depends on other filler characteristics such as surface activity (Kohls and Beaucage, 2002). Differences in surface activity result from the presence of chemical groups and structural heterogeneities (Byers, 2001; Fröhlich et al., 2005; Leblanc, 2002), and can be quantified in terms of surface energy of the filler (Cordeiro et al., 2011; Nardin et al., 1990). Big particles (> 40 µm) also act as localized stress points, generating flaws within the composite that can initiate failure (Byers, 2001; Samsuri, 2013). Hence, research efforts on alternative filler sources have focused on nano particles for the manufacture of high performance polymer composites (Angellier et al., 2005a; Bitinis et al., 2013; Visakh et al., 2012).

Nevertheless, important drawbacks have been associated with the use of nano particles, including the complexity and high cost of their production compared to macro and micro size particles, and composite processability issues (Abraham et al., 2011; Byers, 2001; Fang et al., 2014; Peddini et al., 2014). The mixing of rubber compounds is a very complex operation. Despite advancements in composites technology, the dispersion of nano particles in the polymer matrix remains a challenge, particularly for non-CB composites. The higher surface area, and active surfaces of these particles, favor interaction between the particles leading to agglomeration that reduces composite performance (Chao and Riggleman, 2013; Donnet and Custodero, 2013; Kueseng and Jacob, 2006). To achieve homogeneous dispersion of nanoparticles in rubber, complex mixes are required that often involve high power consumption, increasing processing costs (Szeluga et al., 2015).

The aim of this study was to evaluate power consumption during mixing of different waste-derived fillers with hevea and guayule rubber, and compare resultant mechanical properties of the nanocomposites to composites made with CB, and micro and macro sized waste-derived particles.

2. Materials and methods

2.1. Materials

Hevea NR (grade SMR-20) and natural rubber latex (NRL, grade Centex), purchased from Centrotech (Chesapeake, Virginia), were used to manufacture hevea rubber composites. Guayule rubber (GNR) was obtained by drying guayule natural rubber latex (GNRL) extracted as described (Cornish, 1996). GNR and GNRL were used to prepare guayule rubber composites. Compounding chemicals, namely zinc oxide, stearic acid, sulfur, the vulcanization accelerator butyl benzothiazole sulfonamide (TBBS), and CB N330 (mean particle size: 108 nm, SD: 31.42 nm), were purchased from HB chemicals (Twinsburg, OH). The waste filler raw materials were generously donated as follows: eggshells (ES) by Michael Foods (Gaylord, MN), carbon fly ash (CFA) by Cargill Salt (Akron, OH), processing tomato peels (TP) by Hirzel Canning Co & Farms (Toledo, OH), and guayule bagasse (GB) was generated as a co-product of latex extraction from shrubs generously donated by PanAridus LLC (Casa Grande AZ).

2.2. Preparation of waste-derived nano-fillers

Raw materials were dried and ground to macro particle size (300 µm > d > 38 µm) as described (Barrera and Cornish, 2015). Nano-sized ES, TP and CFA particles were made by wet-milling the macro sized particles using a five liter ball mill, U.S. Stoneware (East Palestine, OH) for 5–8 days. Nano-sized GB particles were prepared by wet-milling with simultaneous hydrolyzation using a sulfuric acid

solution (40%) at room temperature for 2–3 days. The GB dispersion was then centrifuged at 8000 rpm for 10 min using a J2-MC high speed centrifuge, Beckman Coulter (Indianapolis, IN). The solution was decanted and the precipitated particles re-suspended in deionized water. Centrifugation and resuspension was repeated three times to quench hydrolysis.

Aqueous dispersions (1:3 w:v) of each filler were sonicated for 30 min at 35% amplitude using a high intensity ultrasonic processor VCX750, Sonics & Materials (Newtown, CT) to break apart aggregates. Intervals of 10 s on and 5 s off were used to avoid over-heating. Particle size distributions were determined using a Particle size analyzer LA-950V2, Horiba Scientific (Irvine, CA). In addition, primary particle length and width were determined using ImageJ software from TEM micrographs.

2.3. Rubber nanocomposites manufacture

Aqueous filler dispersions were added to latex (NRL or GNRL) (1:1 v:v) under constant mixing using a magnetic stirrer. Latex coagulated during the mixing process was collected and allowed to rest overnight, during which time the rubber exuded most of the entrained water. The samples of coagulated rubber with nano fillers dispersed throughout, were then passed once through a two-roll EEMCO lab mill, roll diameter 15.24 cm and 33.02 cm face width (Rubber City Machinery Corporation, Akron, OH), and dried at 50 °C. The resulting materials were used as master batches for compounding with various amounts of unfilled solid rubber (guayule or hevea) and CB to achieve specific waste-derived filler concentrations (5, 10, 20 or 35 phr) (parts per hundred rubber). Total combined filler loading (CB plus waste-derived nano filler) was 35 phr. A standard compounding formulation was used for all the composites (Table 1). Composites containing 35 phr of CB N330 with no other filler were used as reference materials for both NRs, and unfilled compounded rubber was used as a second reference.

CB and compounding ingredients were mixed into the rubber composites through mastication using a Farrel BR lab mixer (Rubber City Machinery Corporation, Akron, OH). The mixing protocol can be summarized in three steps: (1) rubber was added into the mixer and allowed to knead; (2) fillers and stearic acid were added in the mixing chamber. In these two first steps, roto speed was 6.3 rad/s; (3) sulfur and remaining compounding ingredients were added, and rotor speed was increased to 9.4 rad/s. Power required for the mixing of each rubber composite in the lab mixer was recorded using a Pro-server Ex software v 1.3., Pro-face Digital Electronics Corporation (Osaka, Japan). The hot mix was discharged from the mixer, then milled and cured. The processing conditions for rubber compounding and curing were as previously described (Barrera and Cornish, 2015).

2.4. Materials characterization

2.4.1. Mechanical properties

Tensile properties and tear strength were measured according to ASTM D412 and ASTM D624, respectively (ASTM International, 2013a, 2012), along the grain direction at a crosshead speed of 500 mm/min at 23 °C. Testing was performed using a tensiometer (Model 3366, Instron,

Table 1
Compounding formulation used to prepare natural rubber composites.

Material	Quantity (phr)				
Natural rubber	100				
Carbon black	35	30	25	15	0
Filler	0	5	10	20	35
Sulfur	3.5				
Zinc Oxide	5				
Butyl benzothiazole sulfonamide (TBBS)	0.75				
Stearic acid	1				

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