Reinforcement of guayule natural rubber with silica and egg shells

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ABSTRACT

Because of the increased concerns about carbon footprint, the replacement of carbon black is becoming more and more important to the US rubber industry. One alternative filler gaining popularity is silica (SI). SI-filled tires have lower rolling resistance and therefore save more fuel per mile than carbon black-filled tires with similar reinforcement. Furthermore, the color of SI is pale, so SI-filled rubber can be easily dyed colors other than black. Egg shells (ES) are a byproduct of the food industry. Each year, 571,200 metric tons of ES waste is produced. ES are mostly composed of calcium carbonate, which is a common non-reinforcing filler. However, previous research showed that ES have a significant reinforcing effect in guayule rubber compounds. The pale color of ES, like SI, allow the dye-ability of rubber products. As an alternative source of natural rubber (NR), guayule is highly important for US NR self-sustainability ($2.1B of NR was imported in 2014), as it can be grown domestically. In this research, ES and SI mixtures proved synergistic, and mechanical properties match or exceed the properties of current rubber products reinforced with SI. ES also reduced the power needed to mix the compound, and improved filler dispersion, composite wet-grip and rolling resistance. These new products will reduce carbon footprint and, in the case of complete carbon black replacement, will add dye-ability to rubber, opening new consumer markets for colored products.

INTRODUCTION

NR is one of the most important materials in the world. Guayule is NR-producing shrub native to Mexico and southwest Texas and its rubber does not induce latex allergies (Fig. 4(a)), including the widespread and life threatening Type I latex allergy. However, as a new crop, mechanical properties, dynamic mechanical properties, and polymer-filler interactions of its rubber, are not yet fully understood.

SI is one of the most important and widely used fillers in rubber products. However, SI is neither bio-based nor renewable. Sustainable rubber fillers are greatly desired by the rubber industry. ES waste produced from the US food industry is mainly landfilled [1], which is neither economic nor eco-friendly. Initial research has demonstrated that waste ES can partially replace carbon black and offer lower cost, increased abrasion resistance and reduced rolling resistance. ES can also provide uniform dispersion (Fig. 1), and the color of ES is pale, so SI filled rubber can be easily dyed colors other than black.

MATERIALS AND METHODS

Sample preparation

Guayule natural rubber (GNR) was used as the rubber matrix. Rubber fillers are 50 parts per hundred rubber (phr). SI was gradually replaced by ES until no SI remained (50 phr to 0) (Fig. 1).

RESULTS

Mechanical and Physical Properties

A synergetic effect of ES and SI on TS was clearly seen (Fig. 2(a)), with ratios of 50:50 ES:HS supporting enhanced TS. The surface polarities of ES and SI particles are different, so adding ES to SI helps breakdown the aggregated structure of SI, leading to a more uniform dispersion of ES and SI which may explain the superior TS. In contrast, EB was determined by the ES content, whereas M300 (softness) and hardness were determined by SI (Fig. 2(a)), and no evidence of interaction between the two fillers was apparent for these two mechanical properties. Tg reduced with increasing ES indicating that the rubber molecules became more flexible at higher ES levels, which may be explained by reduced crosslink density which is directly linked to EB (Fig. 2(b)). In contrast, the silane coupling agent increased interactions between the rubber molecules and the SI, so the crosslink density increased with increasing content of SI, directly affecting EB and M300 (Fig. 2(b)).

Energy-related Properties

As increasing ES and decreasing SI were incorporated into rubber composites, the predicted rolling resistance and the average mixing energy reduced (Fig. 2(b)). Thus, less electricity was needed during rubber compounding, and energy loss was reduced during dynamic deformation (lower fuel consumption for vehicles). The hybrid filler filled GNR showed higher predicted wet traction, so hybrid filled GNR can provide stronger grip between rubber products and substrate. The higher predicted wet traction resulted from more flexible rubber molecules with ES addition (Fig. 2(b)).

CONCLUSIONS

ES and SI synergistically reinforce GNR composites. Compared to single filler (ES or SI) GNR composites, the advantages of the hybrid filler are:

- Improved TS and EB;
- Relatively low energy consumption during manufacturing, and low energy loss under dynamic deformation, meaning higher fuel-efficiency;
- Relatively low Tg and high wet traction makes the ES/SI filled GNR usable under low temperatures and slippery conditions;
- The low price of ES reduces the cost of ES/SI GNR composites;
- ES filler may reduce the carbon footprint of rubber industry.

Future work will focus on other filler loading levels, and more filler combinations will be tested to see if the properties of GNR can be further improved.

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REFERENCES