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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 when produced as inexpensive micro-fillers and, as expensive nanofillers, can completely replace carbon black without loss of tensile strength (TS) [2].

Our central hypothesis is that SI and ES rubber composites can meet or exceed the mechanical and dynamic mechanical properties of guayule NR compounds reinforced solely with SI. New markets are expected to open for hybrid filler-filled guayule rubber compounds.

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).

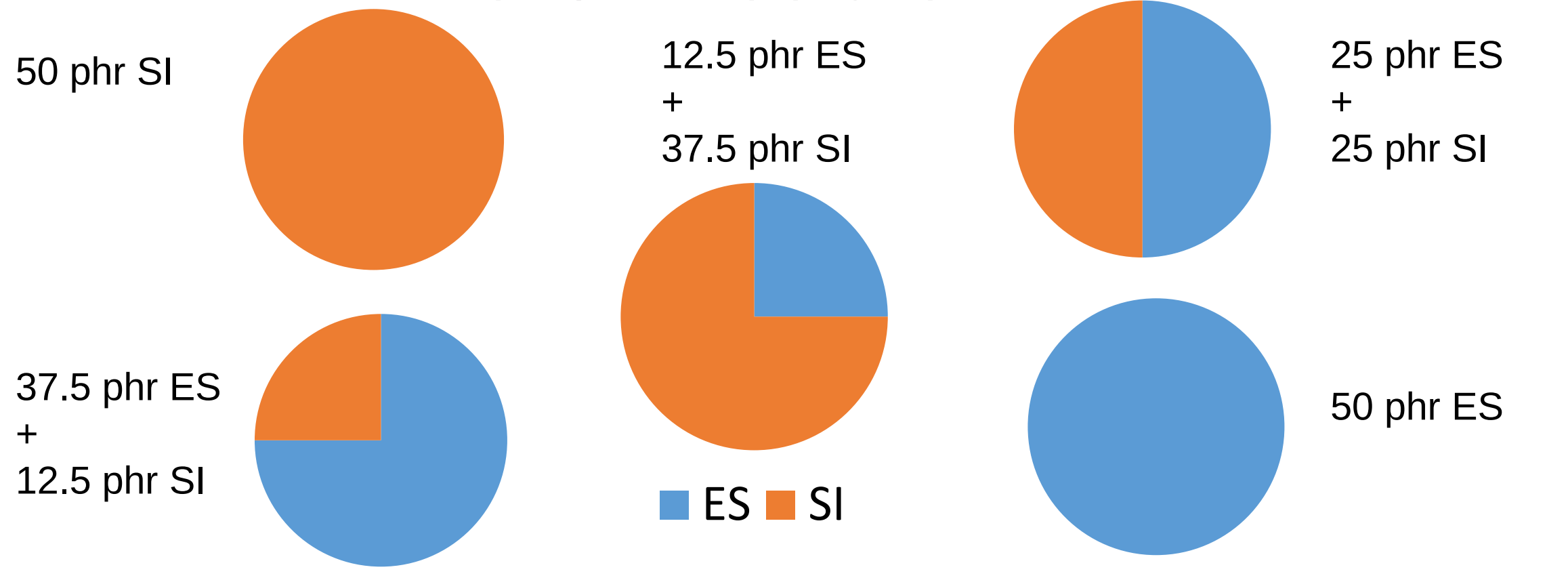


Fig. 1: Filler composition. Total content is 50 phr. Orange, SI; blue, ES

1 phr orange pigment (E-6580,Akrochem Corporation) or 0.5 phr of yellow pigment (GM Foam, Inc.) and 2 phr rutile TiO_2 (Rutile Titanum Dioxide, Akrochem Corporation) were added during compounding. The energy consumption of mixing GNR with other components was recorded.

Material characterization

- The mechanical properties (TS, elongation at break (EB), modulus at 300% strain (M300) and hardness) of each rubber compound were measured, according to ASTM D412. All tests have at least three replications.
- The tan δ and glass transition temperature (T_g) were measured by a dynamic mechanical analyzer. The rolling resistance (energy loss during dynamic strain) and wet traction (grip on wet pavement) were estimated by the tan δ at 60 °C and 0 °C.
- Swelling tests were conducted using toluene as solvent, and the Flory–Rehner equation was used to calculate crosslink density.
- The filler-filler and filler-polymer structures were evaluated by scanning electron microscope (SEM).

Data analysis

The mechanical properties (TS, EB and M300) were predicted by fitting the data into linear regression models. Significance level was 0.05, and all parameters were significant by analysis of variance (ANOVA). No studentized residuals were >3 or <-3, so no outliers occurred. Quantile plots showed normal distributions of data. Lack of fit tests showed no significance. All data were coded to make them dimensionless. The ES weight fraction of rubber filler is denoted *x*, and the unit is % (Table 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. T_g 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)).

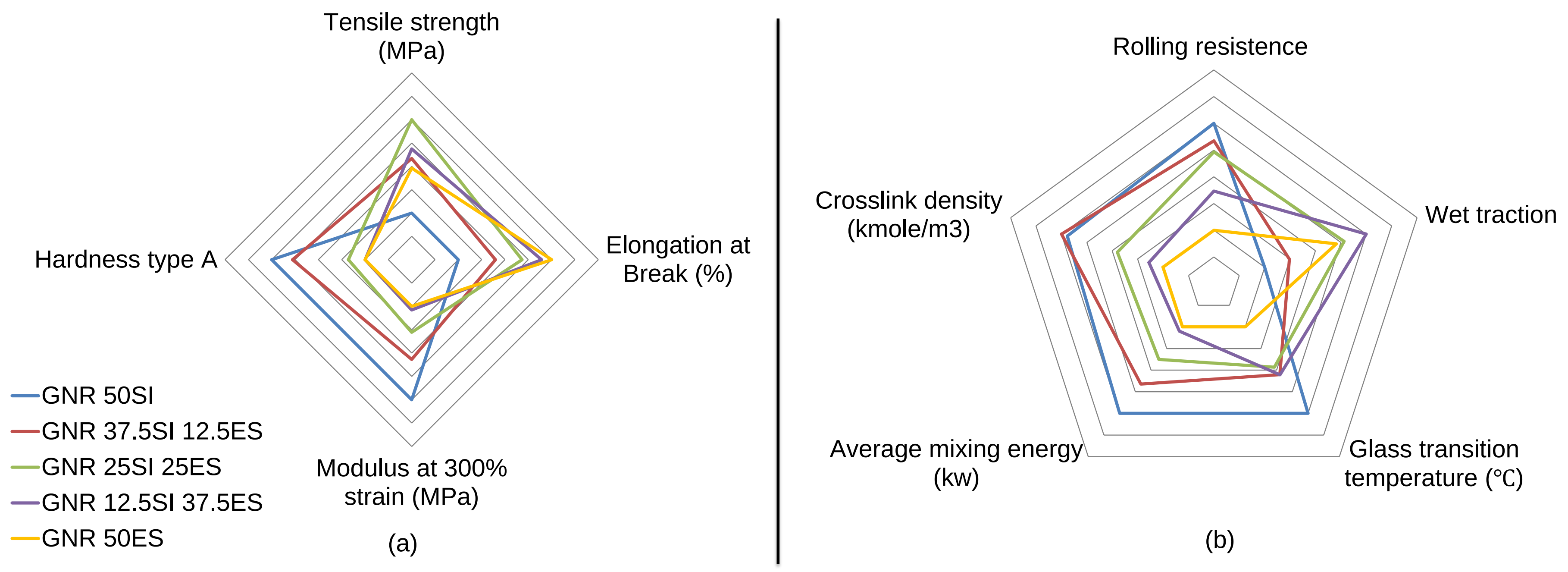


Fig. 2: Mechanical properties of guayule rubber composites with ES replacement: (a) TS, EB, M300 and hardness; (b) rolling resistance, wet traction, T_g *and average mixing energy consumption*

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)).

Data analysis

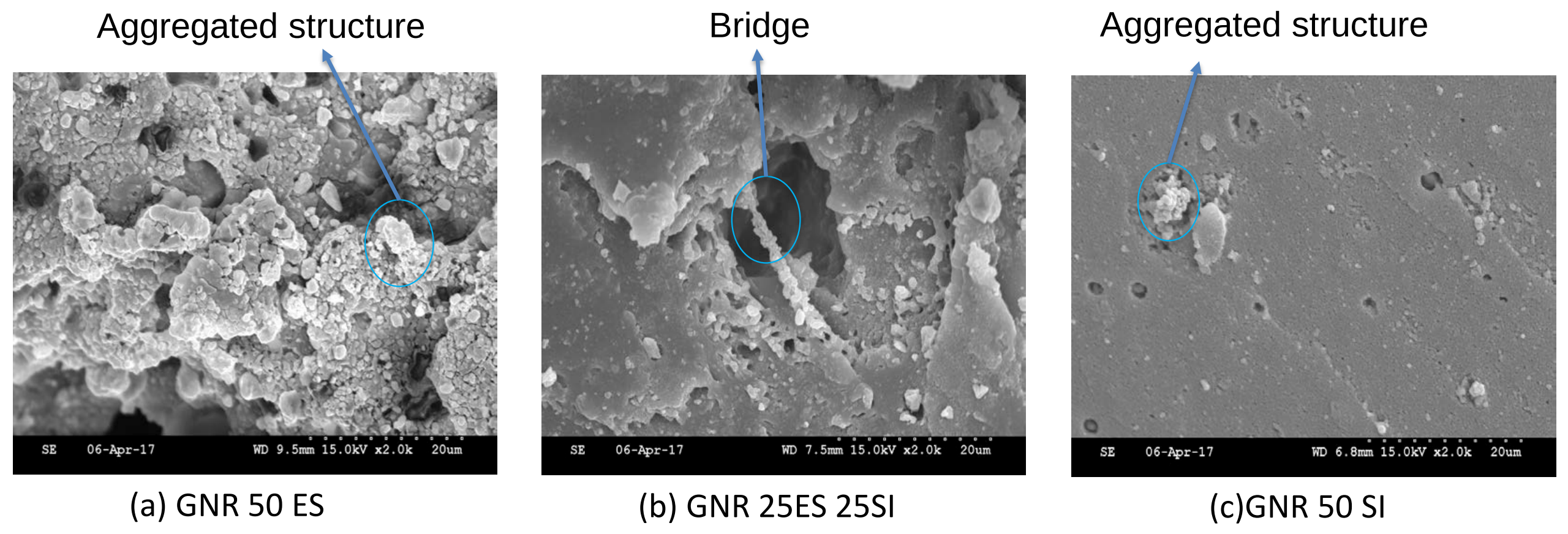
As ES content increased from 0% to 100%, the second order regression equation (Table 1) predicted that TS reached a maximum at 58% ES (of total filler). Although only 69% variance was explained (Table 1), the synergetic effect of the hybrid filler on TS was still significant. In contrast, nearly 100% of the variance was explained by the regression equations for EB and M300. Both properties exhibited monotonic behavior across the range of 0-100% ES content. EB increased monotonically, and M300 decreased monotonically with increasing ES content and decreasing SI content, resulting from the changes in crosslink density (Fig. 2(b)).

Table 1. Models for predicting mechanical properties

Predicted properties	Regression equation	R^2
TS (MPa)	$Y = 20.64 - 1.22 \times x + 0.4 \times x^2$	0.688
EB (%)	$Y = 669.38 - 32.63 \times x + 87.29 \times x^2$	0.988
M300 (MPa)	$Y = 4.11 - 1.99 \times x + 0.58 \times x^4$	0.997

Scanning Electron Microscopy

The fracture surface of 25 phr ES and 25 phr SI, revealed “bridge” structures formed by the edges of the fracture (Fig. 3(b)). The filler particles appeared to reinforce these “bridges”, which may explain the superior TS of 25 phr ES and 25 phr SI filled GNR (Fig. 2(a)). In addition, the aggregated structures, formed by single fillers during deformation, may create the defects which cause material failure. Fewer aggregated structures occur in the mixed fillers (Fig. 3(a,c)).



(a) GNR 50 ES (b) GNR 25ES 25SI (c)GNR 50 SI

Fig. 3: SEM results of fracture surfaces: (a) GNR 50 phr ES; (b) GNR 25 phr ES+25 phr SI; (c) GNR 50 phr SI

Dye ability

The cured dumbbells (Fig. 4(b)) demonstrated that SI and ES filled rubber can be dyed yellow and orange. The carbon black filled GNR is black.

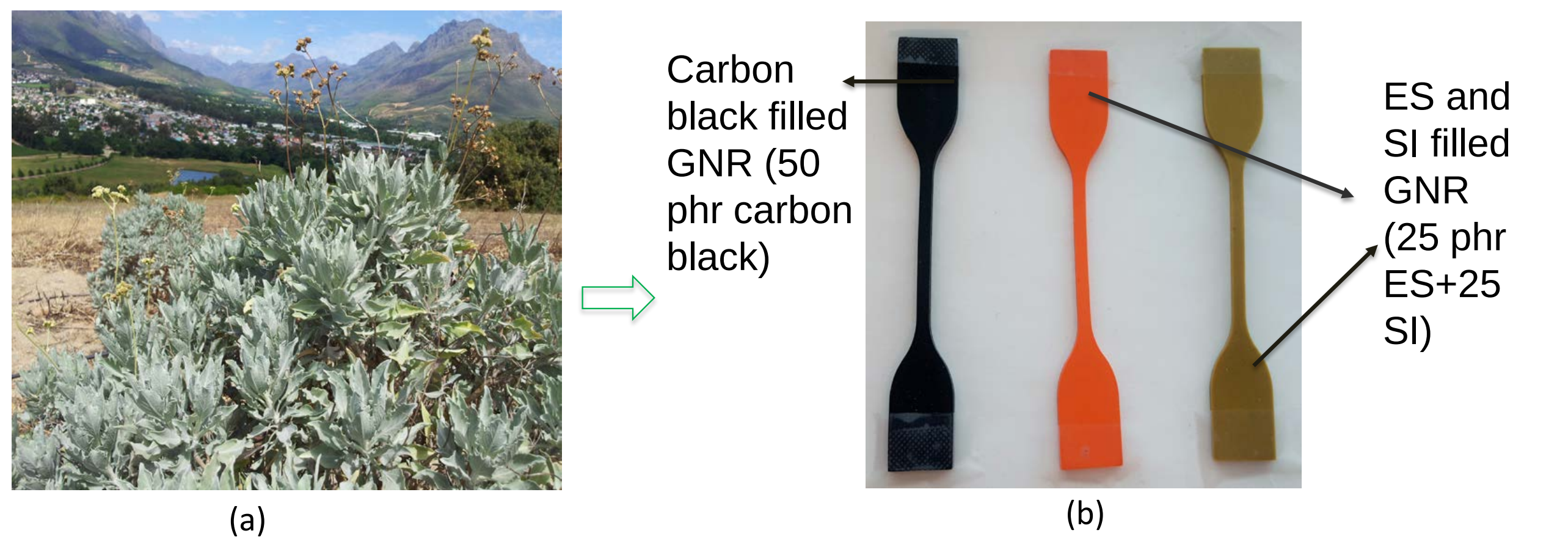


Fig. 4: (a) guayule; (b) cured rubber compounds filled with carbon black or SI and ES

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 mixing, and low energy loss under dynamic deformation, meaning higher fuel-efficiency;
- Relatively low T_g 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.

The ES/SI filled GNR composites exhibit excellent mechanical and energy-saving properties, and likely reduce cost. This material may open new markets for high performance, colored rubber products.

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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