Rubber composites reinforced by soy spent flakes†

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Abstract: Soy spent flakes (SSF) is a plentiful renewable material from the waste stream of commercial soy protein extraction. SSF contains mostly soy carbohydrate and a small fraction of soy protein. Dry SSF is a rigid material and has a shear elastic modulus of ~4 GPa. Aqueous dispersions of SSF were blended with styrene-butadiene (SB) latex to form rubber composites. Soy carbohydrate increased the tensile stress in the small strain region, but also decreased the elongation at break. The shear elastic modulus of the composites showed an increase in the small strain region, consistent with the stress–strain behavior. The SSF composites showed a slightly better modulus recovery than the protein composite after eight cycles of strain sweep. In the small strain region, the shear elastic modulus of 30% filled composites at 140°C was about 160 times greater than that of the unfilled elastomer, showing a significant reinforcement effect caused by SSF. Compared with soy protein isolate, the recovery behavior after eight cycles of dynamic strain suggests that SSF composites have a slightly stronger filler–rubber interaction. In general, SSF composites gave a slightly higher composite strength compared with the protein composites, but at a much lower cost.

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INTRODUCTION

Soybean can be processed into soybean oil and defatted soy flour (DSF). Soy spent flakes (SSF) is mostly an insoluble carbohydrate after most of the soy protein and soy whey, a soluble carbohydrate, are removed from defatted soy flour. SSF is a by-product or residue in the commercial extraction process of soy protein isolate (SPI). It is an abundant and inexpensive renewable material, but it has little commercial value at this time. The composition of SSF includes approximately 12% cellulose, 17% pectin, 14% protein and 53% insoluble polysaccharide.1 SSF is desirable to be used in the as-is form from the commercial process without further separation so that its cost is comparable to inorganic fillers. SSF has the lowest cost among soy products such as DSF, soy protein concentrate (SPC) and SPI, whereas SPI has the highest cost.

Many investigations in recent years have reported the modulus enhancement of rubbers by natural materials, for example oil palm wood,2 crab shell chitin3 and bamboo fiber.4 From the perspective of renewable materials and environmental reasons, soy protein and other soybean products have been investigated as a component in plastic and adhesive applications5–9 but have rarely been investigated as a reinforcement component in elastomers. Attempts to use protein in rubber latex can be traced back to the 1930s. A few patents10,11 had claimed the use of protein in rubber composites. For example, Lehmann and coworkers12 had demonstrated the use of casein (milk protein) in natural rubber latex to achieve approximately a four-fold increase in the modulus. Protein as an additive in rubber materials has also been claimed to improve the anti-skid resistance of winter tire treads.13–15 In rubber reinforcement, factors such as aggregate structure, effective filler volume fraction, filler–rubber interaction and elastic modulus of filler clusters have an important impact on the modulus of rubber composites.16

Dry SSF is a rigid material and has a shear elastic modulus of ~4 GPa (Fig 1) under ambient conditions. Because the high rigidity of a reinforcement phase is one of the requirements in rubber reinforcement, dry SSF is therefore a possible candidate for this application. One objective in this research was to explore the use of this material in rubber reinforcement for certain applications. Another objective was to compare...
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Figure 1. Elastic ($G'_0$) and loss ($G''_0$) moduli of four soy products: soy spent flakes (SSF), defatted soy flour (DSF), soy protein concentrate (SPC), soy protein isolate (SPI). Arrows indicate the regions of glass transition.

the reinforcement effect of SSF with SPI in order to understand the effect of their disparate structure.

Previously, globular soy protein aggregates were used to reinforce styrene-butadiene (SB) rubber and indicated a significant reinforcement effect in the small strain region. The rubber matrix used in this study was an SB rubber with a small amount of carboxylic acid-containing monomer units. The carboxylated SB formed a crosslinked rubber by the aggregation of ionic functional groups without the complication of covalent reactions. Previous studies have indicated the importance of interaction between filler and matrix. Soy protein contains a significant amount of carboxylic acid and substituted amine group. Soy carbohydrate can also interact with carboxylic functional groups in SB matrix through hydrogen bonding and ionic interaction. Although ionic interactions can occur between these soy products and the carboxylated SB, the condensation reactions do not occur under the alkali condition between the carboxyl groups of SB and the major functional groups such as hydroxyl, carboxyl, thiol, amine and amide groups in SSF. Structurally, Soy protein is a globular protein and its aggregate is similar to colloidal aggregates, but soy carbohydrate is a non-globular and film-like material. For practical applications, the issue of moisture sensitivity in some applications is always associated with natural materials, but it may be improved through product formulation or selective applications. For example, SSF may be used as an ingredient in multilayered structures, in coated objects, in high temperature applications or in a rubber part used in greasy/oily environments where the moisture effect is minimal.

The rubber composites investigated here were prepared by casting films from the dispersion of SSF and carboxylated SB latex. To give some background on the rubber matrix of this composite, the properties of carboxylated SB rubber will be described briefly. Carboxylated SB rubber is classified as an ion-containing polymer. Its viscoelastic properties are affected by molecular weight, degree of crosslinking, glass transition temperature ($T_g$), copolymer composition, the number of ionic functional groups, the size of ionic aggregation, the degree of neutralization, and the size of the neutralizing ions. Previous studies have also shown honeycomb-like structures in the film of carboxylated latexes due to a higher concentration of carboxylic acid groups on the particle surface. Mechanically, the elastic modulus of base rubber is not significant when compared with the modulus of the filler network in highly filled elastomeric composites.

EXPERIMENTAL

Materials

SSF was obtained from DSF, a spray-dried powder (Nutrisoy 7B) from Archer Daniels Midland Company, Decatur, IL, USA. The DSF was first dispersed in water at pH 10 and 45°C for 1 h, followed by centrifuging at 3000 rpm for 10 min at 15°C to separate insoluble SSF. The SSF obtained was washed with water and centrifuged again to obtain the final product. SPC was obtained by coagulating an 11% DSF dispersion at pH 4.5 followed by centrifuging at 3000 rpm for 10 min. The process was repeated a further three times and the resulting paste with a solid content of 22% was used to prepare rubber composites. The SPI used in this research was a slightly enzyme-hydrolyzed SPI (PRO-FAM 781, Archer Daniels Midland Company), which contained more than 90% protein, ~6% ash and ~4% fat. Sodium hydroxide, used to adjust pH, was ACS grade. The carboxylated SB latex was a random copolymer of styrene, butadiene and small amount of carboxylic acid-containing monomers (CP 620NA, Dow Chemical Company, Midland, MI, USA). The $T_g$ of the carboxylated SB latex was ~10°C, determined by DSC. The styrene/butadiene ratio, estimated from the $T_g$ values of a series of commercially available carboxylated SB, was about 65/35. The dried latex is not known to be soluble in any solvent or combination of solvents. The latex received had ~50% solids and a pH ~ 6. The volume-weighted mean particle size of the latex was ~0.18 μm.

Preparation of elastomer composites

SSF in a paste form from the centrifuge step mentioned above was added to SB latex, already adjusted to pH 9, and mixed homogeneously. The composites of SSF and carboxylated SB latex were prepared...
by first casting a dispersion of the blend onto an aluminium mold (17 cm × 19 cm × 1.3 cm) covered with a Teflon® release sheet (BYTAC, Saint-Gobain Performance Plastics, Wayne, NJ, USA) and then allowing them to dry at 75°C for 72 h. After drying at low temperature, the samples were removed from the mold and annealed at 110°C and 140°C for 24 h, respectively. Dry composites containing 10% to 30% by weight of SSF were prepared. The film of 100% carboxylated SB rubber was prepared by adjusting the pH of latex to 9 and drying under the same conditions as that of the SSF/SB composites. The soy protein composites (SPI/SB) were also prepared by the same procedure. The dried carboxylated SBR film contained less than 0.3% moisture and the dried SSF/SB and SPI/SB composites had moisture contents of less than 0.8% as measured by a halogen moisture analyzer (HR73, Mettler-Toledo, Columbus, OH, USA) at 105°C for 60 min. For the 100% SSF and SPI, torsion bars could not be made by the casting method. The freeze-dried powder was compression-molded at 44 MPa and 140°C for 2h. After compression molding, the samples were relaxed at 140°C for 24 h. The density of soy products and composites was measured by using a density bottle with a low-viscosity poly(dimethylsiloxane) as the immersion liquid.

Scanning electron microscopy
The morphology of SSF and SPI aggregates was examined by SEM using a JEOl (Tokyo, Japan) JSM-6400V instrument. Images of these soy products were obtained by casting onto an aluminium substrate was based on the Mie scattering theory and had a blue light wavelength of 405 nm. The measurement with the red light wavelength of 632.8 nm and the volume-weighted mean diameter of 0.17 μm obtained for the SSF/SB composite film contained less than 0.3% moisture and the dried SSF/SB and SPI/SB composites had moisture contents of less than 0.8% as measured by a halogen moisture analyzer (HR73, Mettler-Toledo, Columbus, OH, USA) at 105°C for 60 min. For the 100% SSF and SPI, torsion bars could not be made by the casting method. The freeze-dried powder was compression-molded at 44 MPa and 140°C for 2h. After compression molding, the samples were relaxed at 140°C for 24 h. The density of soy products and composites was measured by using a density bottle with a low-viscosity poly(dimethylsiloxane) as the immersion liquid.

Particle size measurements
The mean particle size and distribution of SSF and SPI aggregates were measured by using a Horiba (Kyoto, Japan) LA-930 laser scattering particle size analyzer with the red light wavelength of 632.8 nm and the blue light wavelength of 405 nm. The measurement was based on the Mie scattering theory and had a measurement range of 0.02-2000 μm. The volume-weighted mean diameter of 0.17 μm obtained for the SB latex was in good agreement with the particle size value of 0.18 μm supplied by Dow Chemical Company.

Stress–strain measurements
The stress–strain measurements were conducted by using an Instron 4201 (Instron Corporation, Canton, MA, USA) with Instron Series IX software control. All samples were measured in the dry state without conditioning and the sample size was approximately 12.5 mm × 60 mm × 3 mm. All measurements were conducted at a speed of 50 mm min⁻¹ under the ambient condition of 23°C.

Dynamic mechanical measurements
For all strain sweep experiments, the oscillatory storage and loss moduli, \( G'(\omega) \) and \( G''(\omega) \), were measured using a Rheometric (TA Instruments, New Castle, DE, USA) ARES-LSM rheometer with a torsional rectangular geometry. A rectangular sample with dimensions of approximately 12.5 mm × 20 mm × 3 mm was inserted between the top and bottom grips. The gap between the fixtures was 5–6 mm to achieve a strain of ~15%. A sample length shorter than 5 mm is not desirable because of the shape change from the clamping at both ends of the sample. The frequency used in the measurements was 1 Hz. The oscillatory storage and loss moduli were measured over a strain range of approximately 0.007% to 15%. The actual strain sweep range was limited by sample geometry and motor compliance at large strain, and transducer sensitivity at small strain. Although harmonics in the displacement signal may be expected in nonlinear material, a previous study showed the harmonics are not significant if the shearing does not exceed 100%.

In torsion geometry, torsional bars with dimensions of approximately 40 mm × 12.5 mm × 3 mm were mounted in the torsion rectangular fixtures and the dynamic mechanical measurements were conducted at a frequency of 0.16 Hz (1 rad s⁻¹) and a strain of 0.05%.

RESULTS AND DISCUSSION
Thermal mechanical properties of soy products
Figure 1 shows the dynamic shear moduli of SSF, SPC, DSF and SPI at various temperatures. SSF has the highest elastic modulus, whereas SPI has the lowest. The increase in elastic modulus is roughly proportional to the density of soy products. The densities of the soy products measured were 1.50 g cm⁻³ (SSF), 1.41 g cm⁻³ (DSF), 1.35 g cm⁻³ (SPC), and 1.30 g cm⁻³ (SPI). Soy carbohydrate is denser than soy protein aggregates, as shown in Fig 2. SPI is a globular protein aggregate, but SSF is a film-like material. The loss modulus (Fig 1) of SSF has a glass transition at about 65°C. DSF and SPC also contain soy carbohydrate and show a glass transition in a similar temperature range, but SPI does not have a transition in this region. For rubber reinforcement, SSF has an advantage over SPI because of its greater rigidity, but other factors such as the strength of filler network and filler–rubber interaction also have to be considered.
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Aggregate size of SSF
Because the composite is formed from the dispersion of SSF and latex, the size distribution data of SSF can improve understanding of the composite structure. The aggregate size measurements were conducted in water under ultrasonic dispersion, and the size distribution curves are shown in Fig 3. After both the SSF and SPI dispersions were subjected to the same ultrasonic dispersion for 1 h, the SPI aggregates were significantly reduced in size, whereas the size distribution of SSF only changed slightly. This suggests the protein-embedded SSF aggregates are strong and resilient in water. This effect is expected to strengthen the filler network in the small strain region. The particle size data also shows that SSF dispersion is dominated by the large particles in terms of volume or weight (Fig 3(b)), but it also contains many smaller particles (Fig 3(a)). The disparity between the number- and volume-average size indicates a significant heterogeneity in the SSF dispersion. The small and large size aggregates contribute differently to the rubber reinforcement. The modulus of the composite is proportional to the weight or volume fraction of soy products. Therefore, the larger particle aggregates increase the composite modulus through the effect of volume fraction. The large number of smaller aggregates, although occupying a smaller volume fraction, can also contribute substantially to the composite modulus through their greater surface area for filler–rubber interaction, and lead to an increase in the volume fraction of immobilized rubbers. The volume fractions of filler and immobilized rubber make up the effective volume fraction of the filler. The comparison between SPI and SSF shows that SSF had a larger aggregate size in both number- and volume-averaged particle size. This indicates that SPI has a greater surface area and therefore could interact with more rubber molecules. The factor of this size difference will be discussed later in the sections of shear elastic modulus and stress softening effect.

Stress–strain behavior
Figure 4 shows the stress–strain behavior of SSF and SPI composites at ambient conditions. Compared with SPI at the same weight fraction, SSF composites showed a higher modulus in the small strain region, but the elongation at break was also lowered. Comparing the tensile stress at break for both composites, the SSF composites showed a slightly lower value for the 10 % composite and a similar value for the 20 % composite. The toughness estimated from the area under the stress–strain curve is similar to the tensile stress at break because a lower elongation at break compensates...
for the higher tensile stress of the SSF composites in the small strain region. This indicates that SSF and SPI have a similar ultimate strength in the composites, but SSF has a significantly higher composite strength at the lower strain region (5–30 %). This also shows that the soy carbohydrate significantly changes the rigidity of the composite, which gradually displays a more brittle than elastic behavior as the SSF concentration increases. Such behavior has also been reported for SSF/polyurethane composites.\(^\text{24}\) The small strain behavior is consistent with that measured by dynamic mechanical methods and will be investigated further in the following sections. In general, the stress–strain behavior suggests that the filler loading in these rubber composites is an important parameter to adjust in order to obtain different material characteristics for different applications.

**Shear elastic modulus**

As shown in Fig 5, the addition of SSF dispersion into SB rubber caused a significant reinforcement effect in the rubber plateau region. The reinforcement effect was proportional to the SSF content. Comparing SSF and SPI filled composites at all concentrations, the SSF composites had a slightly higher modulus in the rubber plateau region. The elastic moduli of 100 % SSF and SPI are also shown in the top portion of Fig 5. SSF prepared under the same conditions as those of SPI showed a significantly higher elastic modulus. Both rigidity and filler–rubber interaction of SSF can account for the higher elastic moduli of its composites in the small strain region. In rubbers with the same filler fraction, it is known that smaller particles should have a greater reinforcement effect than larger particles because their effective volume fractions are larger owing to a greater surface area and a greater amount of immobilized rubbers.\(^\text{16}\) The fact that SSF has larger particle size but has a higher composite strength in the small strain region indicates that the filler network strength is a dominating factor for these composites. This can also be understood from the polymer blends consisting of rigid and soft phases, where the mechanical strength increases drastically when the minor rigid phase becomes continuous as its volume fraction reaches a percolation threshold.\(^\text{25}\)

In the rubber plateau region, the elastic moduli of SSF and SPI composites were plotted against the weight and volume fraction of fillers (Fig 6). The SSF had a slightly higher reinforcement effect than the SPI in the concentration range studied and the difference between the moduli of SSF and that of SPI was similar for all concentrations. From the slope of elastic modulus versus volume fraction, it was observed that the modulus of SSF composites increased with filler concentration, similarly to that of SPI composites. The slope of the plots in Fig 6(b) is ~2.7 for SSF composites and ~2.6 for SPI composites. Overall, SSF showed a slightly stronger effect in the reinforcement of elastomers, but has a much lower cost than SPI.

**Stress softening effect**

The stress softening effect occurs in most filled elastomers. It is defined as the extent to which the stress needed to deform the filled rubber at a given elongation is reduced during the second cycle of deformation. The effect is also called the Mullin effect
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The stress softening effect is generally considered to be caused by filler-related structures and therefore can yield some insight into the filler structures. The stress softening effect of 100 % SB rubber, 30 % SSF-filled rubber composite (30/70 SSF/SB) and 30 % SPI-filled rubber composite (30/70 SPI/SB) is shown in Fig 7. Similar to carbon black or silica filled elastomers, the SSF and SPI composites show a significant decrease in the shear elastic modulus after the first strain cycle. At 80 °C, the strain sweep curves for both 30/70 SSF/SB and SPI/SB composites become more reproducible after the four cycles of dynamic strain. 100 % SB rubber also showed a stress softening effect, but its contribution to the stress softening effect of the composites was not significant. This is obvious by comparing the differences between the first and the eighth strain cycle of shear elastic modulus in Fig 7(a) and (b). The contribution to the stress softening effect from the rubber is less than 0.5 % in the stress softening effect of 30/70 SSF/SB or 30/70 SPI/SB composite. The stress softening effect in SSF/SB composites is caused mostly by the contribution from the SSF-related structures such as the SSF network and SSF–rubber interactions. The increasing extent of strain (deformation) in the first four strain cycles is likely to cause the filler network to break down and possibly the polymer chains to detach from the filler aggregates. In this respect, the current SSF/rubber composites are no different from the well-known carbon black filled rubber composites. After four strain cycles, filler-related network structures can be broken and reformed and this is a sign of reaching an equilibrium condition. The mechanism of agglomeration and de-agglomeration of fillers is based on the elasticity of filler immobilized rubber network for his extensive studies on this phenomenon.

**Figure 6.** Elastic moduli of SSF and SPI composites at the small strain region plotted against weight and volume fractions. The measurements were conducted at 0.16 Hz and 140 °C.

**Figure 7.** Strain sweep experiments at 80 °C: (a) 100 % SB; (b) 30/70 SSF/SB composite; (c) 30/70 SPI/SB composite.

and not on the elasticity of the filler network, because the rigid filler network is broken when it is deformed beyond the small strain region. However, the filler network needs to bridge again after the retraction of the rubber network to have a 100% recovery of small strain modulus. The strength recovery of the deformed composite therefore depends on both the elasticity of the filler-immobilized rubber shell around the fillers and the re-bridging capability between the fillers. That is, the original interactive forces such as ionic bonding, hydrogen bonding or van der Waals forces between the broken filler structure, need to be re-established for a complete modulus recovery. The network structure of the immobilized rubber shell around the filler network is a reflection of filler structure and therefore can be characterized by the filler structure. The immobilized rubber network is similar to rubber with a higher crosslinking density and therefore has a better memory to return to its original shape when compared with a rubber with a lower crosslinking density. A stronger interaction between filler and rubber matrix has been shown to be effective in improving modulus recovery.28

For the loss modulus under cyclic strain, the energy dissipation process of SPI composites became less pronounced and the maximum was shifted to lower strain amplitudes. The structure responsible for the energy dissipation process was obviously reduced after the first four cycles. The loss maximum of the SSF composite, however, showed a different behavior. An original broad loss maximum was narrowed and shifted slightly to lower strain amplitude, but its magnitude did not decrease and it remained at a similar modulus value. The exact energy dissipation process is not known for this observation, but it may involve the friction of broken filler structure under oscillatory strain. In the first strain cycle, the ratio of the loss modulus at maximum to the loss modulus value at 0.01% strain was ~1.3 for the SSF composite (Fig 7(b)) and ~1.1 for the SPI composite (Fig 7(c)). Comparing the SSF composite with the SPI composite, the magnitude of loss maximum in the SPI composite was slightly less pronounced than the SSF composite, suggesting that the SSF composite may have had a slightly stronger structure.

The extents of shifting in the position of loss maxima in Figs 7(b) and (c) were also different. At 80°C, the SPI/SB composite in Fig 7(c) showed a loss maximum at 1.2% strain in the first cycle, whereas the SSF/SB composite in Fig 7(b) had a loss maximum at 0.32% strain in the first cycle. In the eighth cycle, the loss maximum of the SPI composite occurred at 0.3% strain and that of the SSF composite was at 0.14% strain. The SPI composite had 0.9% shifting in the position of loss maximum compared with 0.18% in the SSF composite. A greater extent of shifting in loss maximum towards lower strain at the eighth cycle in the SPI composite may indicate that the SPI-related network structure was slower to recover than that of the SSF composite within the same period. On the other hand, that the position of loss maximum for the SSF composite occurred at a lower strain suggests that the SSF composite was more brittle than the SPI composite; that is, the structure was more easily broken at a smaller extent of deformation.

At 140°C a similar phenomenon was observed, as shown in Fig 8. This observation was consistent with the recovery curves shown in Fig 8. The percentage
of recovery is defined here as the fraction of the initial elastic modulus (first cycle), but not the recovery from the modulus at the eighth cycle. The modulus recovery includes both the instant recovery during the strain experiment and the recovery during high-temperature conditioning (140°C, 24 h) after the experiment. The SSF composite recovered 60% of its initial elastic modulus, the 30/70 SPI/SB composite recovered 52%, and the 20/80 SPI/SB composite recovered 59%. Thus the SSF composite had a slightly better modulus recovery than the SPI composite under the same conditions. This is not an effect of filler volume fraction. The volume fraction of SSF in the 30/70 SSF/SB composite was smaller than that of 30/70 SPI/SB composite because the density of SSF (1.5 g cm⁻³) is greater than that of SPI (1.3 g cm⁻³). The 20/80 SPI/SB composite had a smaller filler volume fraction than the 30/70 SSF/SB composite, but its loss modulus and recovery curve (Fig 8(c)) showed the same trend as that of 30/70 SPI/SB composite (Fig 8(b)). It has previously been shown that a stronger filler-rubber interaction could yield a better recovery behavior. Therefore, a stronger SSF-rubber interaction in the SSF composites compared with that of the soy protein might explain these recovery behaviors. However, the detailed mechanism of molecular interaction between the filler and rubber in these composites requires a separate study because of the complicated composition and structure of these soy products.

The recovery curve of elastic modulus in Fig 8(a) also indicates that the SSF composite did not recover its $G'_{0}$ in the small strain region ($\sim 0.01\%$) from the destruction of the eighth strain cycle after the high-temperature conditioning. This suggests that the re-bridging between fillers after the destruction was not as good as in the SPI composite. That is, the SSF filler structure was brittle and did not recover once it was broken. Beyond the linear viscoelastic region, the recovery curve of the SSF composite showed a similar behavior to that of the SPI composite.

Phenomenological description of strain experiment

The reduction of shear elastic modulus with increasing strain is a familiar phenomenon, as reported by Payne on carbon black filled rubbers in the early 1960s. Later, Kraus proposed a phenomenological model based on Payne's idea of filler networking. The model is based on the aggregation and de-aggregation of carbon black agglomerates. In this model, the carbon black contacts are continually broken and reformed under a periodic sinusoidal strain. Based on this kinetic aggregate forming and breaking mechanism at equilibrium, the elastic modulus was expressed as follows:

$$\frac{G'(y)}{G'_{0}} = \frac{1}{1 + (y/y_c)^{2m}}$$

where $G'_{\infty}$ is equal to $G'(y)$ at very large strain, $G'_{0}$ is equal to $G'(y)$ at very small strain, $y_c$ is a characteristic strain where $(G'_{0} - G'_{\infty})$ is reduced to half of its zero-strain value, and $m$ is a fitting parameter related to filler aggregate structures. Equation (1) has been shown to describe the behavior of $G'(y)$ in carbon black filled rubber reasonably. The loss modulus and loss tangent, however, do not have a good agreement with experiments, mainly because of the uncertainty in the formulation of loss mechanism. Recently, Huber and Vilgis also modelled the Payne effect and gave a similar expression as the Kraus model, but with a physical interpretation of the fitting parameter $m$ in the Kraus model. Based on the cluster—cluster aggregation (CCA) model, Huber and Vilgis obtained $m = 1/(C - d_f + 2)$, where $C$ is a connectivity exponent related to the minimum path along the cluster structure and $d_f$ is the fractal dimension of clusters. Therefore, the fitting parameter $m$ has a physical meaning related to filler structures or filler immobilized rubber structures (a reflection of filler structure). Protein composites can be described by the CCA model. However, the SSF structure consisting of soy carbohydrate embedded with small amounts of protein aggregates may no longer fit the definition of particle aggregates (Fig 2). Therefore, it may not be suitable to use a fractal-like description for the SSF composites. Nonetheless, an empirical fit is useful to show the difference in their strain behaviors (Fig 9 and Table 1) between the SSF and SPI composites. In general, the fitting parameter $m \approx 0.3$ for SSF composites suggests a more rapid and continual breaking up of filler structure as the strain increased, whereas $m \approx 0.5$ for SPI composites suggests a more elastic filler structure; that is, the filler structure of the SPI composite was breaking at a lower rate as the strain increased.

CONCLUSION

SSF was incorporated at various levels into carboxylated SB elastomers. Compared with SPI, SSF increased the tensile stress of the composites in the small strain region, but decreased the elongation at break. Both tensile strength at break and toughness were increased when SSF content was 20%, but remained the same or less when SSF content was 10%. Structurally, SSF had a bigger aggregate size than SPI. In the rubber plateau region, a significant increase in the shear elastic modulus of dry composites was observed when compared with the unfilled rubber. The observed significant reinforcement effect in SSF composites was studied by dynamic temperature sweep experiments and compared with SPI composites. At the same weight fraction of filler, SSF showed a slightly higher reinforcement effect than SPI in the rubber plateau region. The composites were also studied in dynamic strain sweep experiments to understand the filler-related structures. Both SSF and SPI structures showed a similar
Table 1. Fit parameters of shear elastic modulus

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<th>Composition</th>
<th>4th cycle</th>
<th>8th cycle</th>
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<th>$G'_0$ (MPa)</th>
<th>$G'_{\infty}$ (MPa)</th>
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<td>15/85</td>
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<td>0.27±0.02</td>
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*Measured at 140°C.

REFERENCES

Figure 9. The 8th cycle of the strain sweep experiments at 140°C and 1 Hz: (a) 15/85 SSF/SB composite; (b) 30/70 SSF/SB composite. The solid lines are the fit from the Kraus model.

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