

EFFECT OF SOY PROTEIN AND CARBOHYDRATE RATIO ON THE VISCOELASTIC PROPERTIES OF STYRENE-BUTADIENE COMPOSITES

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ABSTRACT

When soy products including soy protein isolate, defatted soy flour, soy protein concentrate, and soy spent flakes were incorporated into rubber latex to form composites, they showed substantial reinforcement effects as measured by rheological and mechanical methods. It was observed that different reinforcement effects were obtained when these soy products have a different protein/carbohydrate ratio. In this study, soy protein and carbohydrate were mixed in different ratios as a co-filler and their effects on the viscoelastic properties of the composites were investigated. This study shows that the combination of soy protein (SP) and soy carbohydrate (SC) as a co-filler yields a composite modulus that can not be extrapolated from their single filler composites. The co-filler dominated by SP produced a stronger composite and the co-filler dominated by SC produced a weaker composite, when compared to SP or SC single filler composites. The recovery and stress softening experiments also indicated a synergistic effect of the co-filler.

1. INTRODUCTION

For practical applications (tires, seals, dampers, etc), carbon black derived from petroleum or natural gas is the dominating filler used to reinforce crosslinked rubber materials. Some renewable materials such as dry soy protein and carbohydrates are rigid and can be used as rubber reinforcements. Soy products including soy protein isolate (SPI) [1], defatted soy flour [2], soy protein concentrate [3], and soy spent flakes (SSF) [4] were incorporated into rubber latex to form composites that showed substantial reinforcement effects as measured by rheological and mechanical methods. It was observed that different reinforcement effects were obtained when these soy products have a different protein/carbohydrate ratio [2, 3]. In this study, soy protein and carbohydrate were mixed in different ratios as a co-filler and their effects on the viscoelastic properties of the composites were investigated. The polymer matrix used in this study was styrene-butadiene (SB) latex with a small amount of carboxylic acid containing monomer units. The carboxylated SB forms a crosslinked polymer matrix by the aggregation of ionic functional groups without the complication of covalent reactions.

2. EXPERIMENTS

Soy protein (SP) and soy carbohydrate (SC) used were SPI and SSF, respectively. The SPI contained ~90% soy protein, ~5% ash, and ~5% fat. SSF used was an insoluble carbohydrate that was obtained by removing soy protein and soluble carbohydrate from a defatted soy flour. SSF contained ~15% soy protein, which was factored into the calculation of SP to SC ratio. The small fraction of soy protein in SSF was not separable from the insoluble carbohydrate in the current separation process. SP and SC were first mixed at 1:4, 1:1, and 4:1 ratios in aqueous phase, and then mixed with carboxylated

styrene-butadiene latex at 20%, 30% and 40% filler concentration. The homogeneous composite mixtures were then quickly frozen in a rotating shell freezer at about $-40\text{ }^{\circ}\text{C}$, followed by freeze-drying in a freeze-dryer. The freeze-dried crumb was then compression molded in a plunge type mold. After compression molding, the samples were relaxed and further dried at $80\text{ }^{\circ}\text{C}$ and $140\text{ }^{\circ}\text{C}$ for 24 hours, respectively. Because water is a plasticizer for soy protein and carbohydrate and has an effect on their moduli, the additional drying ensures the samples are compared in dry state without the effect of moisture.

Both linear and non-linear viscoelastic properties in shear mode were studied with a control-strain rheometer. A Rheometric ARES-LSM rheometer (TA Instruments, Piscataway, NJ) with TA Orchestrator software v 7.1.2.3 was used for the dynamic mechanical measurements. To study thermal mechanical properties of the composites, temperature ramp experiments were conducted using torsion rectangular geometry with a heating rate of $1\text{ }^{\circ}\text{C}/\text{min}$ in a temperature range from $-70\text{ }^{\circ}\text{C}$ to $140\text{ }^{\circ}\text{C}$. When using torsion rectangular geometry, torsional bars with dimensions of approximately $40\text{ X }12.5\text{ X }5\text{ mm}$ were mounted between a pair of torsion rectangular fixtures and the dynamic mechanical measurements were conducted at a frequency of 0.16 Hz (1 rad/s) and a strain of 0.05 \% .

To study the stress softening effect, strain sweep experiments were conducted using a torsional rectangular geometry to measure the oscillatory storage and loss moduli, $G'(\omega)$ and $G''(\omega)$. The shear strain-controlled rheometer is capable of measuring the oscillatory strain down to $3\text{ X }10^{-5}\text{ \%}$ strain. The rheometer was calibrated in terms of torque, normal force, phase angle, and strain using the instrument's standard procedure. A rectangular sample with dimensions of approximately $12.5\text{ X }20\text{ X }5\text{ mm}$ was inserted between the top and bottom fixtures. The gap between the fixtures was $\sim 10\text{ mm}$ in order to achieve a strain of $\sim 15\text{ \%}$. 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 is limited by sample geometry and motor compliance at large strain, and transducer sensitivity at small strain. The data that was out of the transducer range was rejected. Although harmonics in the displacement signal may be expected in a non-linear material, a previous study [5] indicated that the harmonics are not significant if the shearing does not exceed 100 \% . Each sample was conditioned at $140\text{ }^{\circ}\text{C}$ for 30 minutes to reach an equilibrated dimension and then subjected to 8 cycles of dynamic strain sweep in order to study the stress softening effect. The delay between strain cycles was 100 seconds. After the first four cycles, they began to reach equilibrium. The data from the eighth cycle is taken as an equilibrated strain sweep and presented in Figure 3.

To measure the recovery behaviours at $140\text{ }^{\circ}\text{C}$, G_0' of the samples was first measured at 0.05 \% strain and 0.16 Hz (1 rad/s). Then, the samples were subjected to a large strain of 10 \% for 30 seconds and followed by periodic measurements of G' at 0.05 \% strain and 0.16 Hz (1 rad/s) to record the recovered modulus.

3. RESULTS AND DISCUSSION

3.1 Temperature dependent modulus

Figure 1 shows co-filler composites with a different ratio of SP to SC at three filler concentrations (20%, 30%, and 40%) along with their constituents (SPI, SSF, and SB)

for comparison. Despite the different co-filler ratios, the composites show similar temperature dependent behaviours as that of SB polymer. As temperature increased, their moduli showed an initial drop due to the glass transition of SB polymer, followed by reaching a rubber plateau region. However, the composites dominated with SP filler (SP:SC=4:1) show a greater temperature dependent behaviour in a higher temperature region of 120 to 140 °C, where they showed a more significant decrease of moduli with increasing temperature (Figure 1 (a)).

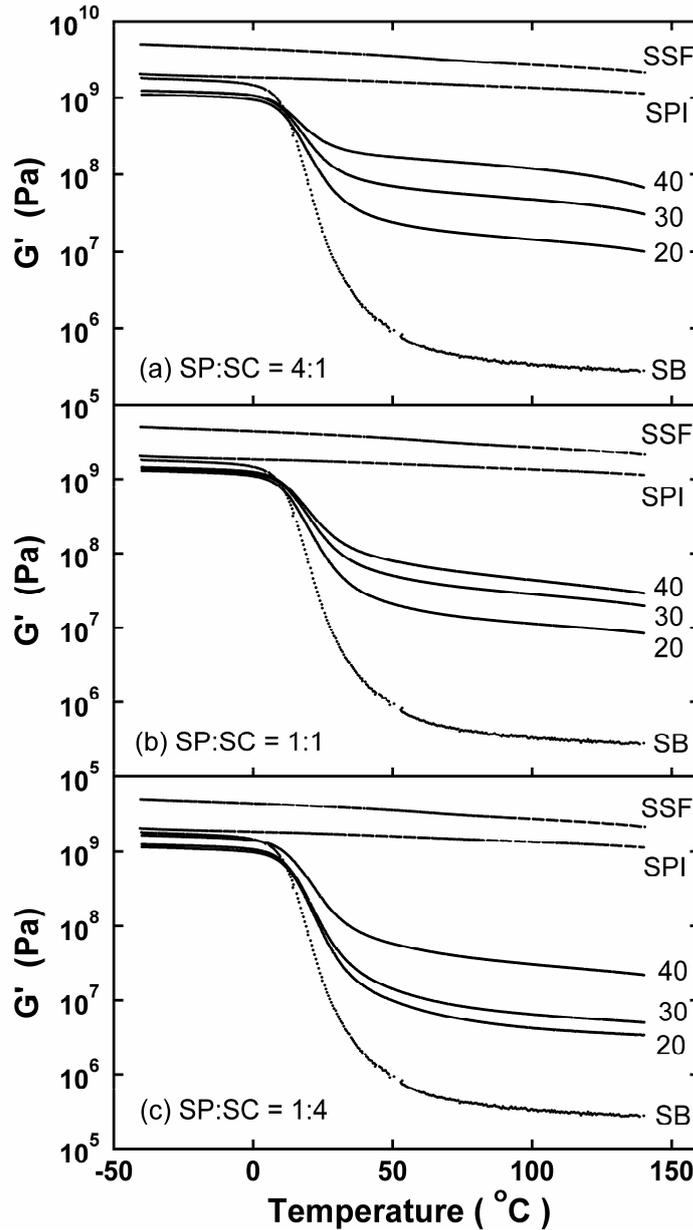


Figure 1: Thermal mechanical properties of soy composites with different co-filler ratios.

Compared to the polymer matrix SB, soy fillers show a significant reinforcement effect in increasing the composite moduli. For example, at 140 °C, a 40% filled composite (SP:SC=4:1) has a 240-fold increase in elastic modulus compared to SB matrix. To compare the effect of co-filler ratios at different filler concentration in rubber plateau

region, the shear elastic moduli at 140 °C such as those shown in Figure 1 are plotted against filler concentration in Figure 2. The results show that the combination of SP and SC does not yield a reinforcement effect that can be extrapolated from either SPI or SSF reinforced composites. This is an indication that different filler related network structures were formed as the co-filler ratio varies, likely arising from a different extent of filler-filler and filler-polymer interactions. It is also interesting to note that the elastic moduli of co-filler composites were much higher than that of SPI or SSF filled composites when the co-filler was dominated by SP (SP:SC=4:1). On the other hand, the elastic moduli of co-filler composites were lower than that of SPI or SSF filled composites when the co-filler was dominated by SC (SP:SC=1:4). Another observation in Figure 2 is that the logarithmic plots of SSF and SP:SC=1:4 composites are not linear, indicating that filler aggregate sizes in these composites were larger so that their percolation thresholds were shifted to a higher filler concentration.

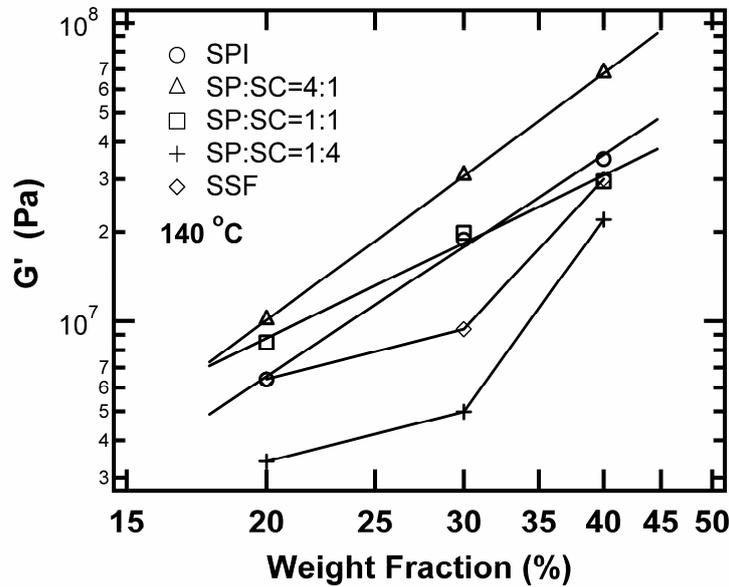


Figure 2: Elastic moduli of soy composites with different filler concentrations at 140 °C.

3.2 Stress softening effect

Payne [6-8] reported the reduction of shear elastic modulus with increasing strain on carbon black filled rubbers in the early 1960s. Later Kraus [9] proposed a phenomenological model based on Payne's postulation 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 continuously broken and reformed under a periodic sinusoidal strain. Based on this kinetic aggregate forming and breaking mechanism at equilibrium, elastic modulus was expressed as follows:

$$\frac{G'(\gamma) - G'_\infty}{G'_0 - G'_\infty} = \frac{1}{1 + (\gamma/\gamma_c)^{2m}} \quad (1)$$

where G'_∞ is equal to $G'(\gamma)$ at very large strain, G'_0 is equal to $G'(\gamma)$ at very small strain, γ_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 behaviour of $G'(\gamma)$ in carbon black filled rubber reasonably well [10]. The loss modulus and loss tangent, however, do not have good agreement with experiments [11], mainly due to the uncertainty in the formulation of a loss mechanism.

The physical meaning of m in the Kraus model may be obtained from the recent studies by Huber et al. [12], who modelled the Payne effect based on the cluster-cluster aggregation (CCA) model. They 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). The fitting of reversible strain sweep data to the Kraus model is shown in Figure 3.

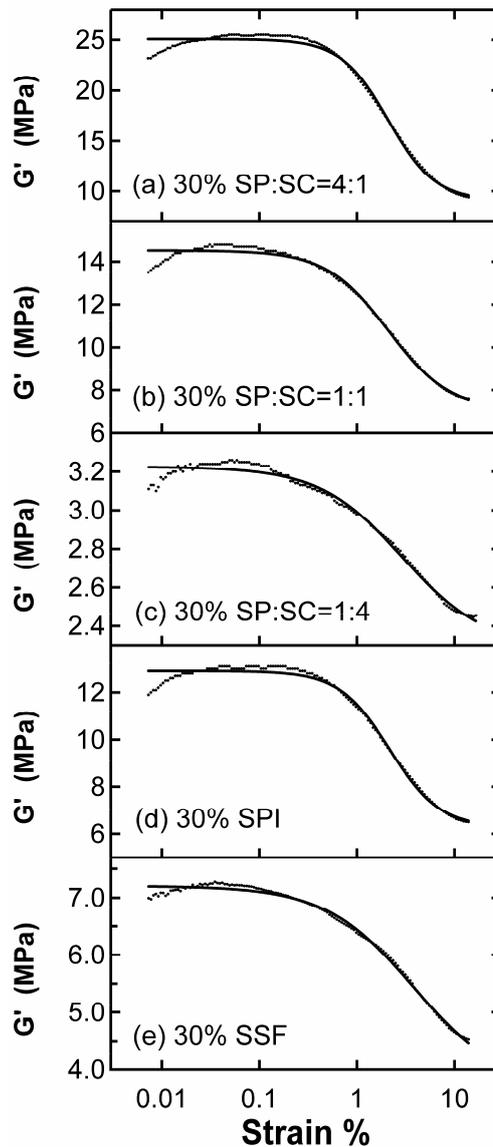


Figure 3: The composites with 30% filler. The 8th cycle of strain sweep experiments at 140 °C and 1 Hz. Solid lines are the fit from the Kraus model.

The model fit and standard deviation of the fit coefficients in Table 1 were based on 99.73% confidence level using Igor Pro 6.0 software. In general, a smaller fitting parameter m indicates a continuous decrease of G' with increasing strain and suggests a smoother and continuous breaking up of filler network structure as the strain is increased. On the other hand, a larger m indicates a more elastic structure at lower strains, which does not yield until a certain strain is reached. When m values are similar between two composites, it was observed that a smaller γ_c value was related to a composite that is less elastic and breaks down substantially at smaller strains [2-4]. The characteristic strain γ_c therefore has a physical meaning associated with the brittleness of the composite structures. From Figure 3 and Table 1, the fitting using the Kraus model was generally acceptable except when a significant G' maximum occurred in the small strain region, which gave rise to a greater uncertainty in m values (Table 1).

Table 1. Fitting parameters of shear elastic modulus¹.

Composition	Best fit ² m	γ_c (%)	G'_0 (MPa)	G'_∞ (MPa)
30% single filler				
SPI	0.84 ± 0.11	2.16 ± 0.22	12.9 ± 0.10	6.28 ± 0.36
SSF	0.48 ± 0.05	3.77 ± 0.87	7.20 ± 0.04	3.69 ± 0.35
30% Co-filler				
SP:SC = 4:1	0.89 ± 0.10	2.10 ± 0.17	25.1 ± 0.20	9.05 ± 0.72
SP:SC = 1:1	0.68 ± 0.08	2.10 ± 0.26	14.5 ± 0.11	7.04 ± 0.47
SP:SC = 1:4	0.51 ± 0.08	2.92 ± 0.77	3.23 ± 0.02	2.29 ± 0.11

1. The data are from the 8th strain cycle measured at 140 °C.
2. Best fit of shear elastic modulus vs. strain with the Kraus Model.

m values of 30% filled composites in Table 1 are in the range of 0.5-0.9. Compared SPI to SSF filled composites, their m values indicate the filler-related network structure of SPI filled composite is more elastic, while that of SSF filled composite is more brittle. The composites with different SP to SC ratios have m values between that of SPI and SSF composites, and their m values also have a decreasing order from 0.89 to 0.51 as their SC filler content is increased, indicating their filler-related network structure becomes more brittle with the increasing SC content.

3.3 Recovery behaviours

The recovery behaviours of 30% filled composites are shown in Figure 4, where the composites were subjected to a deformation stimulus and allowed to recover from it. SP dominated composites showed a better recovery behaviour. Especially, the composite with a co-filler ratio of 4:1 showed a recovered modulus greater than the original modulus ($G'/G'_0 > 1$), indicating a structure rearrangement resulting from the application of 10% strain. In general, SP increases the elasticity of the composites, while SC imparts brittleness to the composites. The recovery experiments indicated that the co-filler with an increasing SP content yielded a better recovery behaviour compared to SPI or SSF filled composites.

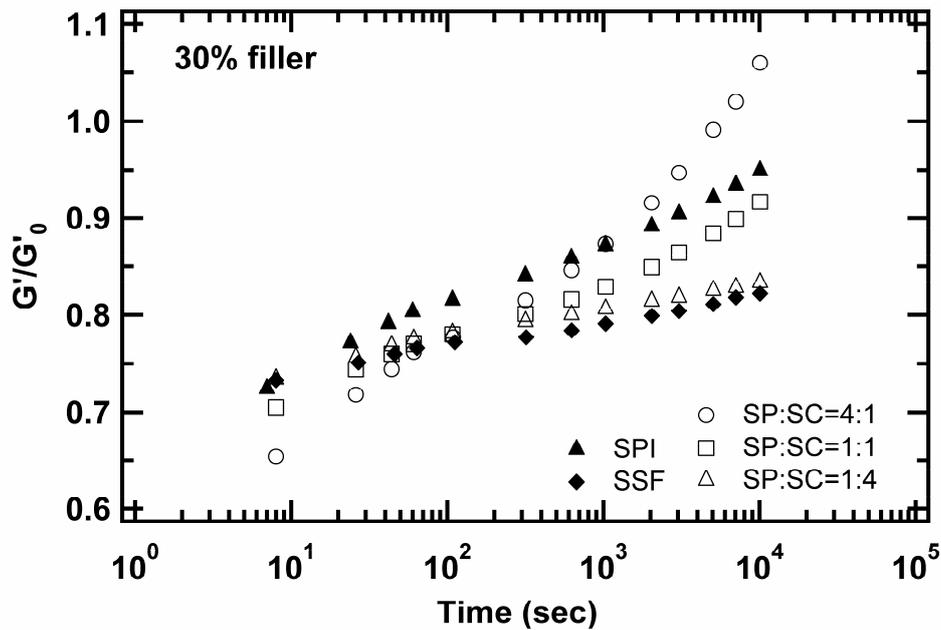


Figure 4: Modulus recovery of 30% filled soy composites measured at 140 °C.

4. CONCLUSIONS

This study shows that the combination of soy protein and soy carbohydrate as a co-filler yields a composite modulus that can not be extrapolated from their single filler composites. The co-filler dominated by SP produced a stronger composite and the co-filler dominated by SC produced a weaker composite, when compared to SPI or SSF filled composites. The recovery and stress softening experiments also indicated a synergistic effect of the co-filler.

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