Flow Properties of Natural Rubber Composites Filled with Defatted Soy Flour

Jeffrey A. Byars, Lei Jong

Cereal Products and Food Science Research Unit, National Center for Agricultural Utilization Research, Agricultural Research Service, United States Department of Agriculture, Peoria, Illinois 61604

ABSTRACT: The linear and nonlinear viscoelastic properties of natural rubber composites reinforced with defatted soy flour (DSF) were studied. DSF is an abundant, renewable commodity, and its rigid nature makes it suitable as a reinforcement phase in rubber composites. At small strain, the elastic modulus of a 30% filled composite was about 20 times higher than the unfilled rubber. Greater reinforcement was observed for carbon black filled composites than for DSF filled composites at filler concentrations of 10 and 20%. At high strain, values of the relaxation modulus dropped more rapidly for highly filled DSF composites. At high shear rates in a capillary viscometer, a small reinforcement effect remained for all composites, and lower die swell was observed for DSF composites. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 2049–2055, 2009

Key words: composites; defatted soy flour; elastomers; rheology

INTRODUCTION

In an effort to lower costs and reduce dependence on petroleum-based materials, a number of studies have investigated the use of renewable materials as replacements for carbon black (CB) as fillers in rubbers. The modulus enhancement of rubbers has been studied for materials such as crab shell chitin,[1] cocoa pod,[2] and rubber seed shell.[3] Recent work at our laboratory has considered the use of a range of soy-based materials for rubber reinforcement.[4–9] Soy protein isolate has been shown to be an effective filler in styrene–butadiene (SB) rubber composites. It was shown to increase the elastic modulus more than CB at the same filler weight fraction[4] and to maintain good structure recovery behavior up to three cycles of strain.[5] Composites prepared with soy protein concentrate, which includes soy carbohydrate, further increased the elastic modulus and improved the strain recovery.[8] Defatted soy flour (DSF) also improved the strain recovery behavior, and it increased the tensile stress and toughness of composites at high filler loading.[7]

Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

Correspondence to: J. A. Byars (jeffrey.byars@ars.usda.gov).

DSF is an abundant and inexpensive renewable commodity. It is less expensive than soy protein and soy protein concentrate, as the DSF must be further processed to obtain those materials. DSF is a soy product that remains after soybean oil is removed from soybean flakes. The composition of DSF includes soy protein, soy carbohydrate (insoluble carbohydrate), and soy whey (soluble carbohydrate). Structurally, soy protein is a globular protein, and its aggregates are similar to colloidal aggregates, but soy carbohydrate is a nonglobular and film-like material.[7] Dry DSF is a rigid material and has a shear elastic modulus of ∼ 3 GPa under ambient conditions. Because the high rigidity of a reinforcement phase is one of the requirements in rubber reinforcement, dry DSF is therefore a possible candidate for this application.[10]

Because of its low cost and proven effectiveness as a filler in SB rubbers, DSF is used in this study as a filler in natural rubber (NR) composites. Its effectiveness as a filler is assessed through comparisons to unfilled NR and to CB composites. It has previously been shown that DSF provides less reinforcement than CB in NR systems,[9] and both were lower than in the SB rubbers. Cofiller reinforced composites were shown to have improved recovery behavior at high-CB content. To begin to understand the processing characteristics of bio-based rubber composites, we examine here the flow behavior in large strain stress relaxation experiments, and the viscosity is measured at low shear rates in a parallel-plate geometry and at high shear rates in a capillary rheometer. The composites in this study were formed by freeze-drying, and

to focus on the role of the filler, no processing aids or other materials were added.

EXPERIMENTAL

Materials

The DSF used in this research is a spray dried powder (Nutrisoy 7B, Archer Daniels Midland, Decatur, IL). The DSF contains $\sim$ 53% soy protein and has a protein dispersibility index (PDI) of $\sim$ 90. An aqueous dispersion of CB N-339 (Sid Richardson Carbon Co., Fort Worth, TX) was prepared by dispersing $\sim$ 100 g of CB in water with the aid of a surfactant, sodium lignosulfonate (Vanisphere CB, Lignotech USA, Rothschild, WI). The weight fraction of the surfactant based on CB was 3%. The dispersion was homogenized with a Janke and Kunkel (Staufen, Germany) Ultra-Turrax T25 disperser with a 1 mm mixing head at 10^4 rpm for 1 h. The NR latex received had $\sim$ 60% solids and a pH $\sim$ 10. Sodium hydroxide (ACS grade, Fischer Scientific, Fairhawn, NJ) was used to adjust the pH. The glass transition temperature of crosslinked NR with 3 phr (parts per hundred parts of rubber) sulfur is $-56°C$ determined by G'' maximum. The volume weighted mean particle size of latex was $\sim$ 0.85 μm.

Preparation of composites

In this study, a freeze-drying and compression molding method is preferred because CB has a density of 1.72 g/cm^3 and tends to precipitate if a casting method is used. DSF was first dispersed in water at $\sim$ 10% concentration, pH $\sim$ 10, and 55°C for 1 h. The NR latex, already adjusted to pH 10, was then added to the cooled DSF dispersion and mixed homogeneously to form composites with three different filler contents (10 wt %, 20 wt %, and 30 wt %). The homogeneous composite mixtures were then quickly frozen in a rotating shell freezer (Labconco, Kansas City, MO) at about $-40°C$ and followed by freeze-drying in a freeze-dryer (Free-Zone 4.5, Labconco, Kansas City, MO). The moisture content of dried composite crumb is less than 2%. The composite crumbs were then compression molded into 3-mm thick sheets at 100°C and 29,000 psi for 30 min (Model 3389 Hot Press, Carver, Wabash, IN). The sheets were cut into pieces $\sim$ 3 mm $\times$ 5 mm $\times$ 10 mm. The samples were dried at 50°C for 3 days under vacuum before measuring their rheological properties.

Rheology

Small amplitude oscillatory shear flow measurements of the storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, and the viscosity $\eta(\dot{\gamma})$, were measured using an ARES-LSM rheometer (TA Instruments, New Castle, DE). Parallel plates with 8 mm diameter were used, and the typical sample height was 3 mm. The strain was 0.05%, and measurements were obtained at frequencies from 0.1 to 100 rad/s at temperatures from 80 to 200°C. To ensure that moisture loss did not change the samples over the course of the measurements, samples were annealed at 140°C for 2 h prior to other tests. Time–temperature superposition master curves were obtained using the instrument software Orchestrator V7.2.0.2. The relaxation modulus was measured as a function of strain at 120°C for strains from 0.01% to 50%. Fits of the linear viscoelastic spectra were obtained using a quasi-Newton algorithm with MathCad software (MathSoft, Cambridge, MA).

Viscosities were also measured by using a high-pressure capillary rheometer model Acer 2000 (TA Instruments, New Castle, DE). Measurements were carried out with capillary dies of diameter 2 mm, and L/D ratios of 15 and 5. The cubes of composites were loaded into the rheometer barrel and compressed at 180 MPa for 20 min under a constant temperature, while the die exit was blocked. The temperature range investigated was from 110 to 140°C, and the shear rate range was from 5 to 1000 s^{-1}. The instrument software was used to apply the Bagley correction to the data. Optical measurements of the extrudate diameter were also recorded.

RESULTS AND DISCUSSION

The effect of fillers on the linear viscoelastic properties of NR composites is shown in Figure 1. The storage modulus, G', and the loss modulus, G'', are shown as functions of frequency, ω, at 120°C. All measurements were conducted at a strain of 0.05%, which was within the linear viscoelastic region for all materials. The reinforcement effect of the fillers is shown by the increase in the modulus values with the addition of DSF or CB to NR. At the highest loading of 30%, the DSF increases the modulus values by a factor of $\sim$ 20 over those of the NR. In the SB composites previously studied,[7] 30% DSF increased the modulus by 500 times, indicating that there is less effective interaction between the fillers and the rubber matrix in this system. The modulus values obtained here with parallel plates were about a factor of two lower than those previously reported[9] for measurements with a torsion rectangular geometry. The samples in this study were cut from sheets that were compression molded at a lower temperature and for a shorter time than in the previous work. However, the trends in the data were the same for the two methods. At 1 rad/s at 120°C, the elastic modulus of the 30% DSF sample
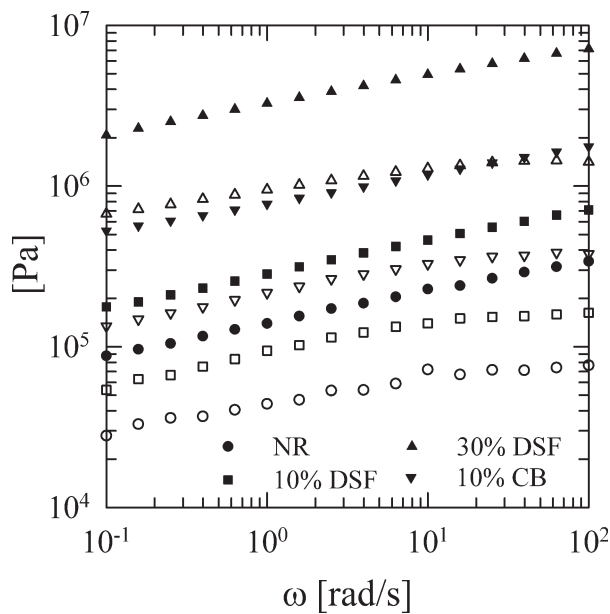
Figure 1 Linear viscoelastic properties of natural rubber and filled composites at 120°C. The storage modulus (G') is shown by solid symbols, and the loss modulus (G'') is shown by open symbols.

was 23.5 times higher than for NR, whereas the ratio was 22.9 for the measurements in the torsion rectangular geometry. In this case, CB is also the more effective reinforcement filler at a given weight concentration. The 10% CB material had modulus values about three times higher than the 10% DSF material, and the 20% CB was similar to the 30% DSF (data not shown). This is also in contrast to the SB composites, where soy proteins were more effective. Because the NR already forms a network without the presence of the fillers, there is no qualitative change in the frequency dependence of the modulus values upon the addition of fillers. In noncrosslinked polymer systems, the addition of fillers decreases the frequency dependence of the modulus values, especially at low frequencies.[11]

Similar measurements of the moduli were conducted at temperatures from 80 to 200°C, depending on the material. For the relatively short time at high temperatures (~ 15 min at each temperature), no oxidative crosslinking was observed, as has been shown to occur at longer times in SB systems.[5] The principle of time–temperature superposition[12] was applied to create the master curves at a reference temperature of 140°C shown in Figure 2 for 20 and 30% DSF materials. In this manner, materials can be characterized over a wide range of frequencies outside the limits of the rheometer at a single temperature. Both composites show similar behavior over the broad range of frequencies, with the 30% sample showing a slight change in the frequency dependence of the storage modulus at the lowest frequen-

cies. Figure 2 was constructed by shifting the data for each temperature along the frequency axis to superimpose it with the data for the reference temperature. The amount of the frequency shift for each temperature is given by the shift factor, a_T. The flow activation energy, E_a, can be calculated from an Arrhenius fit of the shift factors, and these values are given in Table I. The flow activation energy has much higher values for the highly filled DSF
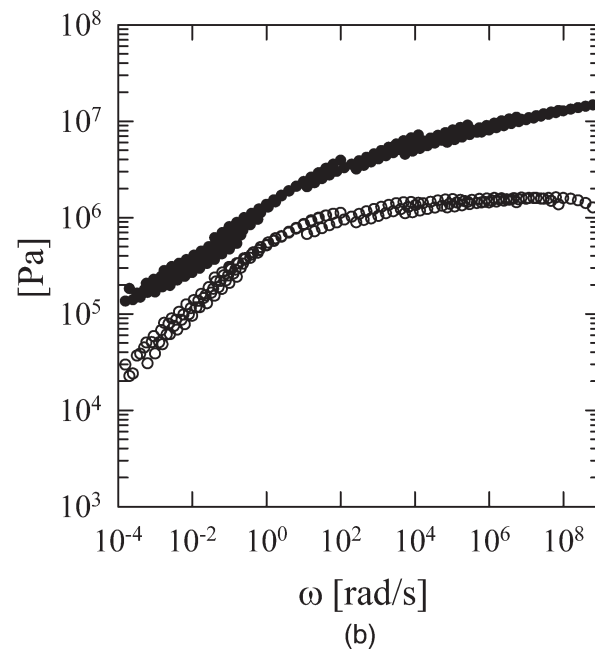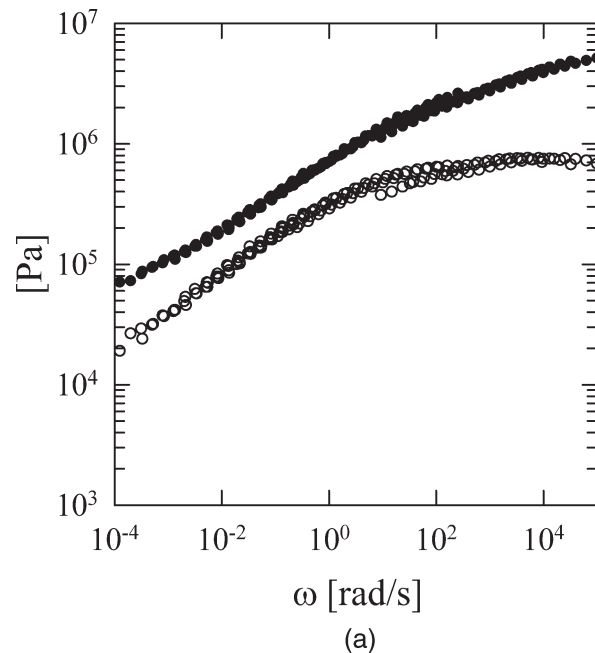

(a)

(b)

Figure 2 Master curves of the storage and loss moduli at a reference temperature of 140°C for (a) 20% DSF and (b) 30% DSF composites. The storage modulus (G') is shown by solid symbols, and the loss modulus (G'') is shown by open symbols.

TABLE I
Dependence of Flow Properties on Filler Content

	E_a [kJ/mol]	G_0 [10^7 Pa]	λ_0 [s]	$f(\Phi)$	n	K [10^5 Pa s^n]
NR	17	3.9	1300	–	0.16	1.3
10% DSF	43	7.1	990	1.5	0.19	1.8
20% DSF	210	26	1100	4.0	0.16	2.8
30% DSF	270	44	1300	4.0	0.19	3.2
10% CB	65	13	960	1.0	0.16	2.3
20% CB	76	46	1000	3.1	0.32	3.2

E_a is the activation energy from time–temperature superposition of the storage and loss moduli. G_0 and λ_0 are the modulus and Maxwell relaxation time from the stress relaxation data. $f(\Phi)$ is the concentration shift factor for the damping function. The power law values n and K are from viscosity measurements at 130°C.

composites. At lower temperatures, these materials would, therefore, provide relatively higher modulus values compared with both NR and the CB composites.

The linear viscoelastic properties of the materials can also be studied by stress relaxation. A sudden displacement (strain) is applied to the sample, and the decrease in the relaxation modulus is measured over time. Figure 3 shows the relaxation modulus for each sample at 120°C after a strain of 0.3% was applied, which was in the linear viscoelastic region. As before, the fillers increase the measured value, with a larger increase observed for CB at a given concentration. These data can be fit to obtain the linear viscoelastic spectrum $\{G_i, \lambda_i\}$, where $G(t) = \sum G_i e^{-t/\lambda_i}$. Although the individual values have no physical meaning and will depend on the fitting procedure, they can be used to compute the modulus $G_0 = \sum G_i$ and a Maxwell relaxation time $\lambda_0 = \sum G_i \lambda_i^2 / \sum G_i \lambda_i$. These values are given in Table I, and as expected, G_0 increases with filler concentration and increases more rapidly with concentration for the CB composites. The λ_0 values do not provide a true measure of the relaxation time as they are influenced by the length of the test (600 s). Longer measurement times would be required to obtain better estimates of λ_0.

Stress relaxation data can also be used to study a material's nonlinear flow properties by applying larger strains. Up to about 1% strain, the relaxation modulus remains the same as shown in Figure 3 for all of the materials. However, at higher strains the relaxation modulus decreases with increasing applied strain, as shown in Figure 4 for 10% DSF. Although the magnitude of the relaxation modulus decreases, the curves remain parallel for all strains. This shows that time–strain separability applies, and that the modulus can be written as $G(t, \gamma) =$
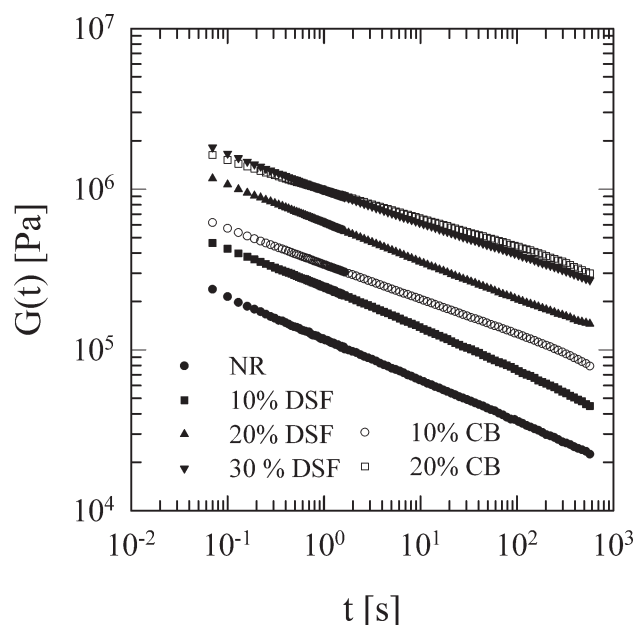

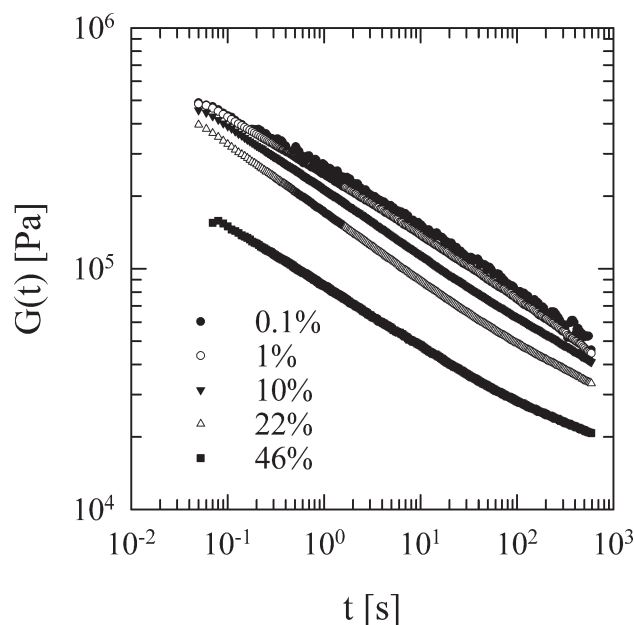**Figure 3** Relaxation modulus at 120°C and a strain of 0.3%.

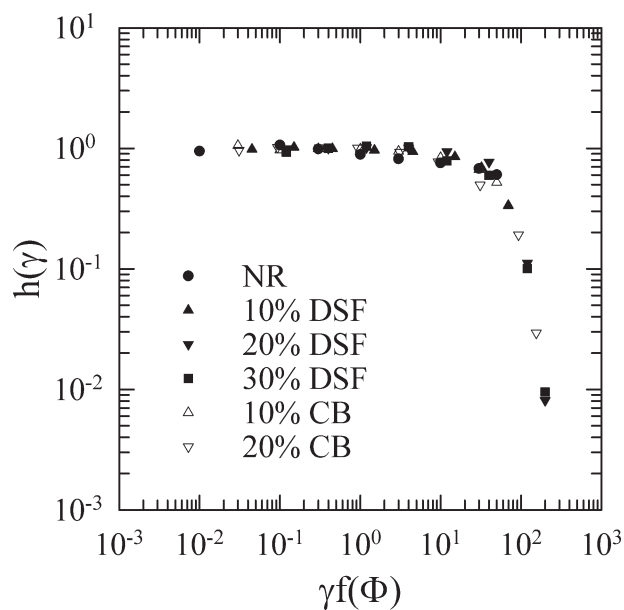**Figure 4** Relaxation modulus at 120°C for the 10% DSF composite at different strains.

Figure 5 Damping functions for the strain and concentration dependence of the relaxation modulus at 120°C.

$G_0(t)h(\gamma)$, where $h(\gamma)$ is the damping function. $G_0(t)$ is the time-dependent value of $G(t)$ for small-strain experiments, whereas $h(\gamma)$ measures the downward shift as a function of strain. The damping function can then be used to compare the strain dependence of the materials outside the linear viscoelastic region. It has further been shown[13] that a concentration shift factor can be applied to the damping function to superimpose the curves for filled systems. The damping function is shown in Figure 5 for all of the composites studied, and the concentration shift factors $f(\Phi)$ are given in Table I. The damping function is by definition unity at low strains for each material, and in this case, the concentration shift factor has been determined by adjusting the strain for each sample so the curves overlay at high strains relative to the unfilled NR. The large values of $f(\Phi)$ for the DSF samples show that the filler network in these samples is more easily disrupted, leading to a decrease in the damping function at lower strains.

The processing characteristics of the filled rubber were studied by measuring the viscosity at high shear rates in a capillary rheometer. The corrected viscosity as a function of shear rate at 130°C is shown in Figure 6(a) for the same materials that were considered in Figure 1. A small increase is seen in the viscosity for the filled systems, but the effect here is much smaller than for the linear viscoelastic properties. This suggests that at high shear rates the filler network is disrupted by the flow, and the filler can no longer enhance the rubber's properties. The curves in Figure 6 are fits to the power law model, $\eta(\dot{\gamma}) = K\dot{\gamma}^{1-n}$, where K is the consistency index (equivalent to the viscosity at $\dot{\gamma} = 1 \text{ s}^{-1}$), and

n is the power law index, which is a measure of how rapidly the viscosity decreases with shear rate. Table I shows that other than the sample with the highest CB loading, all of the composites had similar shear rate dependence. The consistency index values show that the maximum variation across samples is a factor of 2.5 at high shear rates, when compared with a factor of 20 in the linear viscoelastic regime. Figure 6(b) shows the viscosity for the 30% DSF sample at three different temperatures. The temperature dependence of the viscosity is still clear at high
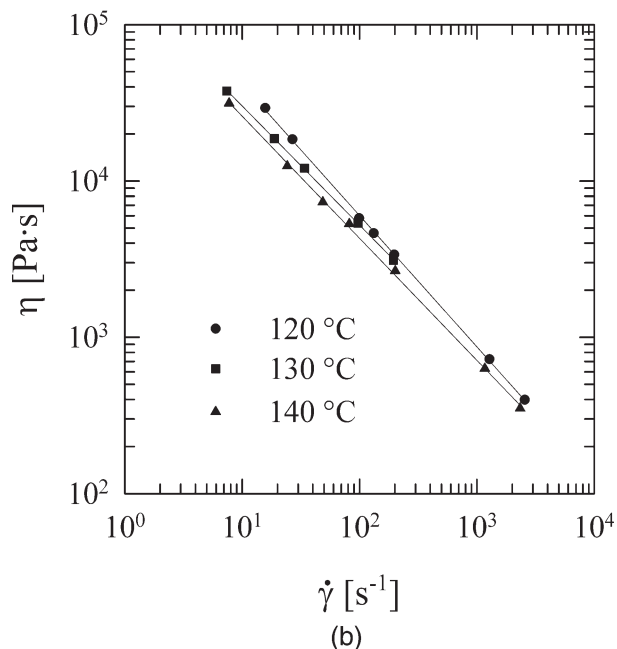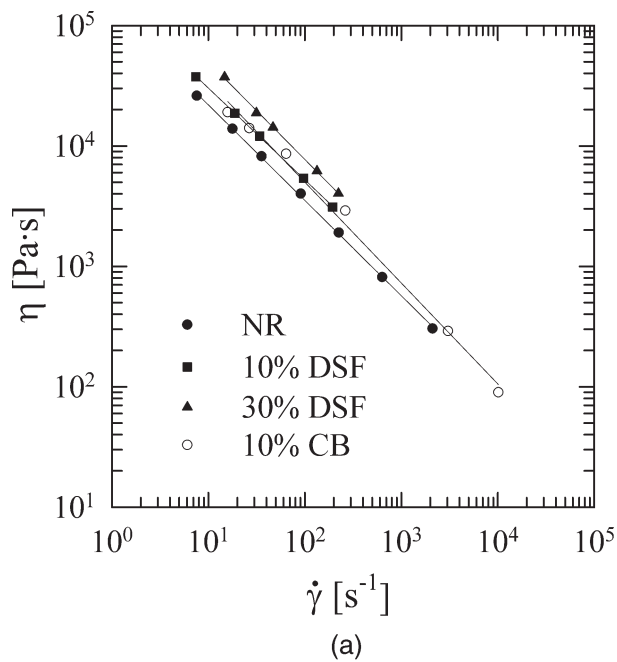

(a)

(b)

Figure 6 Corrected viscosity measurements from the capillary rheometer: (a) the effect of composition at 130°C and (b) the effect of temperature for the 30% DSF composite.

shear rates, although it is not as strong as for materials in the linear viscoelastic region. The K value at 140°C was 1.8 times higher than the value at 120°C for the capillary measurements, whereas the difference was a factor of 2.4 for the elastic modulus.

Viscosity measurements were also obtained at low shear rates in the parallel plate geometry (Fig. 7). Each shear rate was applied to the sample until the viscosity approached a constant value. No evidence of slip was apparent for the shear rates shown here, although at higher rates the large deformation caused the samples to twist and separate from the plates. There was very little difference in the viscosities for the DSF samples compared with the NR, but the viscosity of the 10% CB sample was about twice as high. The n values obtained from these measurements were higher (0.27–0.31) than those given in Table I for the capillary rheometer measurements. Extrapolating these results to 1 s^{-1} to compare with the K values of Table I gave results that were lower by from 10% (10% CB) to 70% (30% DSF).

The diameter of the material exiting the rheometer was measured, and it is shown as the die swell in Figure 8 as a function of shear rate for each material at 130°C. The die swell is the ratio of the diameter of the material to the diameter of the die. No significant difference was observed for the 10 or 20% DSF compared with the NR, and the die swell for the 30% DSF material was slightly lower. The extent of die swell is related to normal stress differences in the material.[14] A filler would be expected to increase the normal stress differences, so the lack of die swell further indicates that the DSF has only a limited
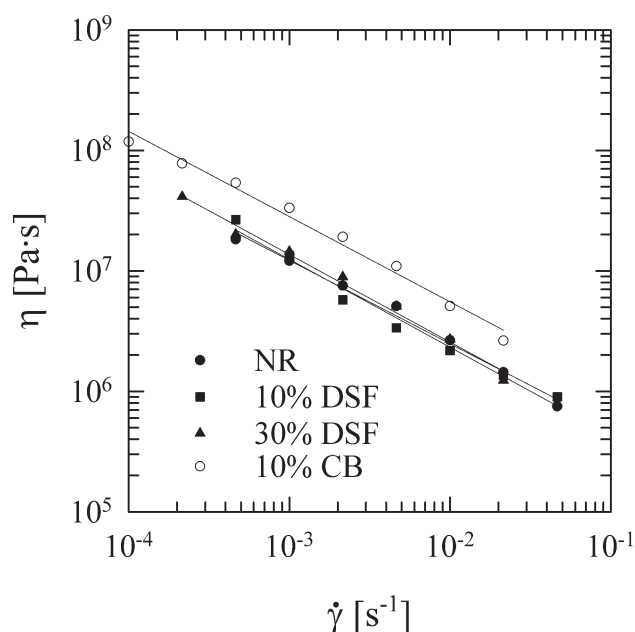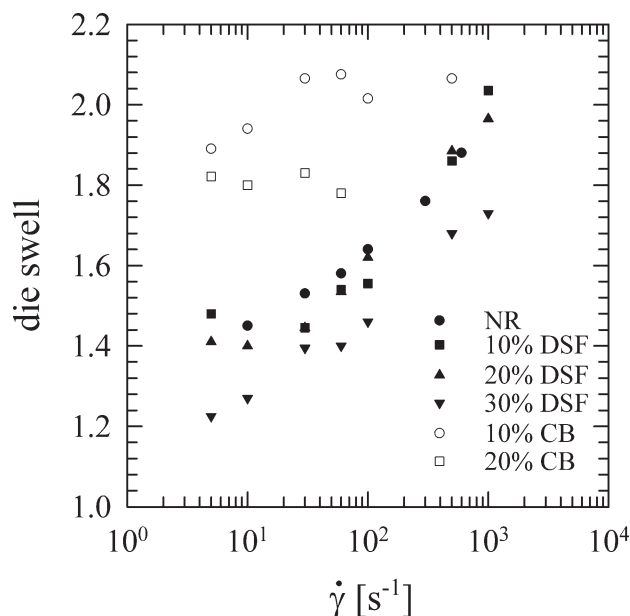

Figure 8 Die swell as a function of shear rate at 130°C.

effect on the material properties at these high shear rates. In contrast, both CB materials exhibited increased die swell relative to the NR sample, indicating that CB still provides some reinforcement effect at high shear rates. These results are consistent with those obtained from strain recovery experiments on cofilled samples,[9] which found that samples with high-CB content were more elastic.

CONCLUSIONS

DSF was incorporated at different levels into NR elastomers. Measurements of the linear viscoelastic properties of the composites showed an increase in the storage and loss modulus values with increased filler content. The maximum observed value was 20 times higher than in the unreinforced rubber, which is not as large an increase as has been previously observed for the reinforcement of SB rubbers with soy products. The results were compared with rubbers reinforced with CB, and at filler weight concentrations of 10 and 20%, the CB provided greater reinforcement. In high strain stress relaxation experiments, the modulus values for DSF-reinforced composites decreased at lower strains than for the CB-reinforced samples. The viscosity of the composites was also measured at high shear rates in a capillary rheometer. All filled systems had higher viscosities than the NR, but the effect was much smaller than for the linear viscoelastic properties. Measurements of the die swell showed no increase for the DSF-filled composites, whereas the CB materials had higher die swell than the unreinforced rubber. Differences in the reinforcement effect of DSF compared with the SB rubber system will be investigated to

Figure 7 Viscosity measurements from the parallel-plate geometry at 130°C.

guide our further efforts to develop effective composite systems based on renewable fillers.

References

1. Nair, K. G.; Dufresne A. Biomacromolecules 2003, 4, 666.
2. Imanah, J. E.; Okieimen, F. E. J Appl Polym Sci 2003, 90, 3718.
3. Akinlabi, A. K.; Okieimen, F. E.; Okwu, U. N.; Oladoja, N. A. J Appl Polym Sci 2007, 104, 2830.
4. Jong, L. J Polym Sci B 2005, 43, 3503.
5. Jong, L. Composites A 2005, 36, 675.
6. Jong, L. J Polym Environ 2005, 4, 329.
7. Jong, L. J Appl Polym Sci 2005, 98, 353.
8. Jong, L. Composites A 2006, 37, 438.
9. Jong, L. J Appl Polym Sci 2007, 106, 3444.
10. Heinrich, G.; Kluppel, M. Adv Polym Sci 2002, 160, 1.
11. Gandhi, K.; Salovey, R. Polym Eng Sci 1988, 28, 877.
12. Ferry, J. D. Viscoelastic Properties of Polymers; Wiley: New York, 1980.
13. Mongruel, A.; Cartault, M. J Rheol 2006, 50, 115.
14. Bird, R. B.; Armstrong, R. A.; Hassager, O. Dynamics of Polymeric Liquids; Wiley: New York, 1987.