

Effects of Temperature and Strain Amplitude on Dynamic Mechanical Properties of EPDM Gum and Its Carbon Black Compounds

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SYNOPSIS

The effects of carbon black loadings ϕ , temperature T , and shear frequency ω on dynamic mechanical properties of EPDM gum elastomer and its carbon black compounds were investigated under sinusoidal shear flows. The region of shear flows where the gum elastomer and its carbon black compounds exhibited characteristic plateau in viscoelastic properties were established and found to directly depend on temperature but were inversely proportional to carbon black loading. The gum rubber and its 20% carbon black compound showed rather unusual similar dynamic flow behaviors at 50 and 100°C attributed to the possible presence of crystallinity from the fractional ethylene components in the gum. This fraction could act as nucleation sites for macrogels that required higher temperatures than 50 and 100°C for melting, particularly in the presence of carbon black particles. Dynamic properties were amplified due to carbon black filler. This effect was more pronounced at low frequencies and at 50 and 150°C, respectively. At 100°C, amplifications appeared to have been attenuated by the hydrodynamics of the continuum elastomer matrix. This observation helps the further understanding of the filler-elastomer interactions and the critical role played by temperature, particularly as it affects rubber processors. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Ethylene-propylene-diene terpolymer (EPDM) has emerged as the dominant individual elastomer of choice in several engineering applications in automobile engine seals and mounts, driving belts, ozone resistant side walls for tire builders, and other rubber products requiring chemical and thermal stability without antioxidants. As other new engineering applications of this and other elastomers are being developed, so is the need for accurate and reproducible determination of mechanical properties of gum elastomer and their filled compounds in oscillatory conditions with varying shear frequency and temperature. The interpretations and correlations of these properties with processability and prediction of end use product properties have continued to constitute a challenging task for rubber processors.¹⁻³ One method of addressing elastomer processability

is shown by White⁴ and Nakajima et al.² and involves a wide time scale characterization of EPDM elastomer and interpreted measured viscoelastic data in terms of its molecular structure. As fillers are added to elastomers, however, their viscoelastic properties can no longer be explained in terms of Boltzmann superposition principles. Different techniques must often be devised to characterize the compounds and to predict their processability and ultimate properties.³ This oscillatory mode of measurement has been repeatedly shown to be effective in characterizing plastic resins and gum elastomers and their filled compounds.

When dynamic mechanical properties of filled compounds are accurately determined, a wealth of otherwise inaccessible information about molecular structure and their behavior in shear processing is understood and possibly manipulated in processing for desired product properties.^{2,3} For example the shape, slope, peak, and inflection frequency ω of G' and G'' could be correlated with molecular weight distribution, chain branching,^{2,9-13} and average re-

laxation time.^{2,3} Other derived properties like storage and loss compliance can also be used to estimate molecular behaviors of polymers at time scales different from relaxation time. The incorporation of particulate fillers into the elastomer or blending of two or more elastomers together to make a composite, which undergoes various levels of vulcanization, are sometimes necessary for the desired properties. Applications are commonly found in machineries and automobiles where oscillatory force input creates undesirable mechanical vibrations that are damped or isolated by incorporating materials with a high loss component in their transmission lines. The damping or storage properties of composites are easily reflected in their dynamic mechanical properties under careful measurements.¹² One of several approaches to studying the effects of reinforcing fillers on rubber compounds is to measure increase in moduli with strain amplitude and the possible existence of a filler network usually manifested by yield stress σ_0 , thixotropy, and significant electrical conductivity, among others. Thiele and Cohen¹⁴ used data from creep T jump experimental data for natural and styrene-butadiene rubbers (SBRs) and their vulcanizate compounds to relate activation energy to filler compositions and structure effects. Using SBR rubber at small strains, the values of activation energies were found to range between 13 kcal for the SBR gum elastomer to 30 kcal for its 80 phr N347 (DBPA = 122 cm³/g) carbon black filled compound. When strain level was increased the observed values of activation energy decreased sharply. The obvious variations in the activation energy of the gum and its compounds are thus linked with high surface energies and interactions created by carbon black reticular network formation at sufficient concentrations in the rubber continuum. Due to the known fact of the dependence of activation energy on temperature in a simplified Arrhenius relation, the questions remain as to how strain amplitude and temperature variations affect the dynamic mechanical properties of similar gums and their compounds over a wide range of filler loading. The extensive works of Payne and Whittaker⁵ provide some level of approach to answer this question for vulcanizates. But most fundamentally relevant properties of interest and intrinsic to gum elastomers and their filled compounds are usually lost permanently on vulcanization. In view of the importance of gum elastomers and their unvulcanized compounds as necessary precursors for all known rubber products, we attempt to address this issue using unvulcanized EPDM gum elastomer and carbon black with high surface energy as filler. We

started by first determining the strain amplitude storage modulus for gum and compare these with their corresponding 20, 30, 40, and 50% carbon black filled compounds. These were done at three different temperatures relevant to rubber processing at 50, 100, and 150°C. A narrow window of strain amplitude where both the gum and its filled compound are in harmony with Boltzmann superposition principles is experimentally established. Operating in this window, the effects of temperatures T and oscillating shear frequency ω on their dynamic properties are also compared at the three respective temperatures. Possible explanations of the observed behaviors are examined under discussion.

MATERIALS AND METHODS

The EPDM gum elastomer used in these studies is a sulfur curable ethylene-propylene-hexadiene terpolymer (Dupont Nordel 1040, spgr 0.670, about 55% ethylene and 5% diene content). The filler used is ISAF N220, a fine grade carbon black with surface area of 122 m²/g and particle size 0.022 μ m (Cabot Corporation).

Dispersive mixing of the gum and carbon black at 20, 30, 40, and 50% carbon black/EPDM were carried out in a Moriyama DS 7.5 dispersion type internal mixer at 100°C. Due to the ethylene content, the mixing batch was first masticated during a preheat period of 10 min and immediately followed by a 15-min mixing with carbon black at 25 rpm. The mixing temperature was monitored and maintained at 100°C by water cooling when necessary. Mixing time and difficulty depended on the level of carbon black introduced and were generally found to increase with carbon black loading. Samples from gum EPDM and its carbon black compounds for the dynamic experiments were compression molded at 100°C into 1.5 mm thickness and 25 mm diameter to fit the parallel geometry of the RMS-800 instrument. The remolded samples were allowed to relax over 7 days. This time helped to minimize and ensure dissipation of any residual stress and strain history associated with the materials sample preparation and molding into shapes suitable for the measuring instrument.

Strain Amplitude Dependence Mechanical Properties

A commercial mechanical spectrometer (model RMS-800, Rheometrics Inc., Piscataway, NJ) was the rotational instrument used for various mea-

measurements of complex flow properties of gum EPDM and its carbon black compounds at 50, 100, and 150°C. This instrument is equipped with a dc servo actuator, a 2000 g-cm capacitive angle transducer feedback attached to the actuator shaft, and a temperature controlled chamber with thermal drift deviation of less than 0.01% °C. The mechanical compliance (angular displacement from actuator shaft zero position) of the feedback transducer was designed and calibrated to be linear with actuator torque in dynamic shear mode, thus eliminating the possibilities of false wave generation in response to very small torque. An alternative 100 g-cm transducer, usually more sensitive for low viscosity polymer solutions but of lower torque range required for high polymers, was found to be unsuitable for measuring these highly filled compounds. The strain amplitude studied covered a range of 10^{-3} – $10^2\%$. The principles of operations of this instrument are based on the torque and normal force generated in response to imposed motion on the sample. In this work, actuator torques were measured by the 2000 g-cm split cylindrical flex pivot string transducer supported by cross fins that allows infinitesimal torsional compliance while maintaining radial stiffness. This arrangement, with stable chamber temperature, enables reproducible dynamic measurements within a frequency range of 10^{-3} to 5×10^2 rad/s with excellent stability. In the strain dependent behavior studies for the gum elastomer and its carbon black compounds, we chose a fixed frequency ω (6 rad/s) and temperature T (100°C) and incrementally varied the applied strain. The establishment of the linear region in these types of studies for highly filled rubber compounds is critical to the usefulness of the experimental data. In its parallel mode we also conducted a frequency sweep for the gum and its carbon black compounds. The magnitude of strain amplitude for the gum elastomer was found from a previous strain sweep to be invariant with dynamic mechanical properties, but we kept it below 10%. Those for the compounds, however, were kept below 1%. This is within the window of strain amplitude where dynamic mechanical properties were found to be invariant with strain amplitude.

RESULTS

Effects of Strain Amplitude and Temperature on Dynamic Mechanical Properties

The elastic shear modulus versus strain amplitude is plotted in Figure 1. A scaling of these properties

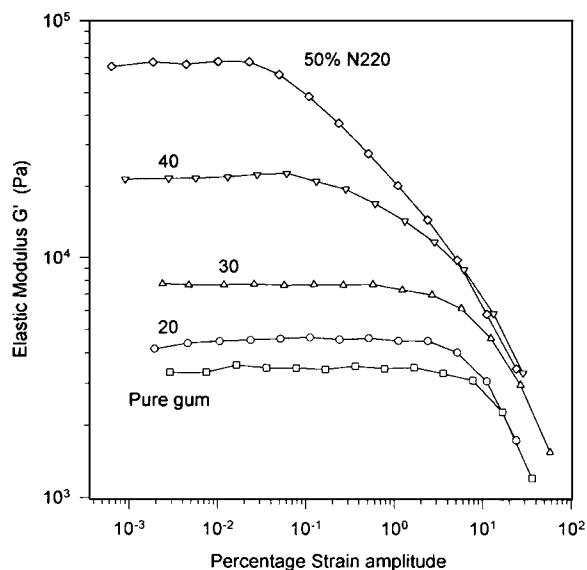


Figure 1 Dependence of dynamic storage modulus on shear strain amplitude.

at very low amplitude for the gum and its carbon black compounds was observed. All the compounds appeared to be strain invariant at very low amplitude. The higher the carbon black content the less invariance the compound exhibits. Thus, while the gum elastomer maintains a plateau covering the widest range of strain amplitudes studied, the 50% compound only exhibited a plateau at amplitude below 10^{-3} . At values of strains below the transition range the gum behaves in accordance with linear viscoelastic theory; but the filled compounds exhibit characteristic nonlinear behavior and dynamic mechanical properties become dependent on strain amplitude.

In Figure 2(a–c) the plots of storage modulus $G'(\omega)$ versus shear frequency ω (rad/s) for the elastomer and its compounds at 50, 100, and 150°C, respectively, are shown. In Figure 3(a–c) similar plots are shown for the loss modulus. Figure 4 illustrates the behavior of dynamic shear viscosity $\eta^*(\omega)$ with shear frequency ω (rad/s).

DISCUSSION

Fundamental Dynamic Mechanical Properties

On the sudden imposition of finite shear strain $\gamma(t) = \gamma_0 \sin \omega t$ as functions of time on a viscoelastic material, the response is a stress that lags behind by an angle defined by⁷

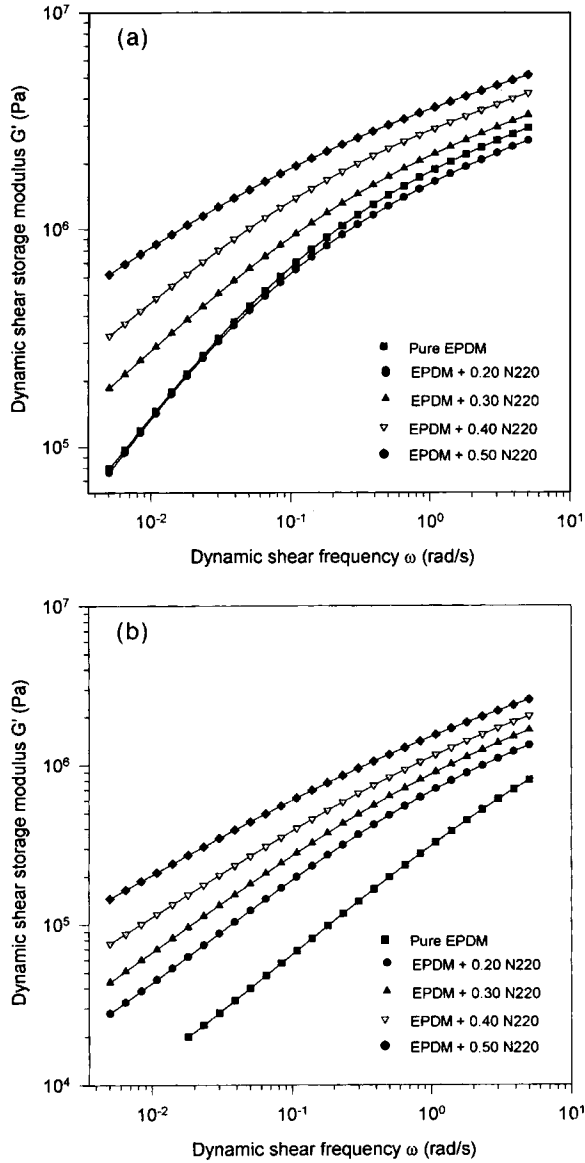


Figure 2 Observed variations of storage modulus $G(T, \varphi, \omega)$ of gum and EPDM/N220 compounds with temperature T , filler compositions φ , and shear frequency ω . (a) 50°C, (b) 100°C, (c) 150°C.

$$\begin{aligned}
 \sigma(t) &= \sigma_o \sin(\omega t + \delta) \\
 &= \sigma_o \sin \omega t \cos \delta + \sigma_o \cos \omega t \sin \delta \\
 &= \sigma_o [\cos \delta \sin(\omega t) + \sin \delta \cos(\omega t)] \quad (1) \\
 &= \gamma_o [G'(\omega) \sin(\omega t) + G''(\omega) \cos(\omega t)].
 \end{aligned}$$

A similar expression could also be written using components of viscosity $\eta'(\omega)$ and $\eta''(\omega)$ for the coefficients. In that case we have the complex viscosity $\eta^*(\omega)$ given as

$$\eta^*(\omega) = \eta'(\omega) + i\eta''(\omega). \quad (2)$$

Effects of Frequency and Temperature on Dynamic Mechanical Properties

Observation reveals a close similarity in flow behaviors of the gum and its 20% filled compound, particularly at low frequencies below 0.1 rad/s or less. That this could not be attributed to material slippage is confirmed in the distinct behaviors of the other compounds at the same low frequency. In addition, as frequency increased to higher values, where slippage should be more apparent, differences in flow properties become more manifested. At 100°C, the pure gum is lower in magnitude than the 20% compound, but at 150°C both the gum and its 20% compound appeared to manifest similarity in materials flow properties. Also revealed in the plots is the temperature effects on the dynamic rheological properties of the gum rubber and its 20% carbon black compound. The storage modulus $G'(\omega, \varphi)$ appears identical at 50 and 150°C, particularly at lower shear frequencies. At 100°C the gum exhibits a distinct magnitude of flow properties from that of the 20% compound over the frequency range of our investigations. At 50°C, it would appear that there is a strong filler/elastomer adhesion; but at 20% carbon black, this adhesion is not enough to significantly affect the flow properties. In addition, the EPDM used in these studies has about 55% ethylene content. At this ethylene level, the crystalline fraction of the gum could nucleate macrogels that re-

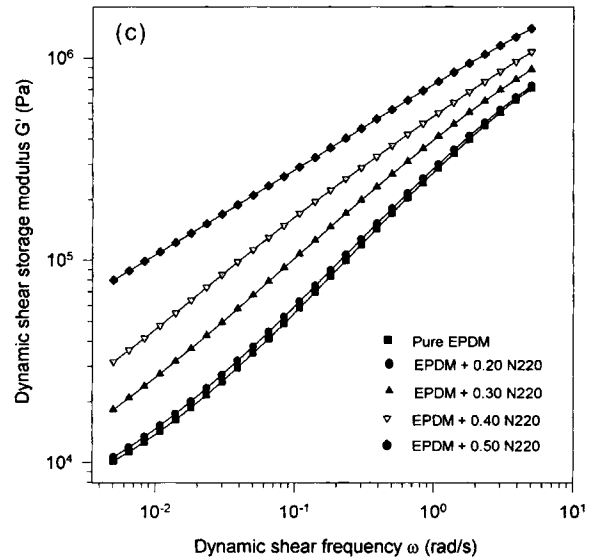


Figure 2 (Continued)

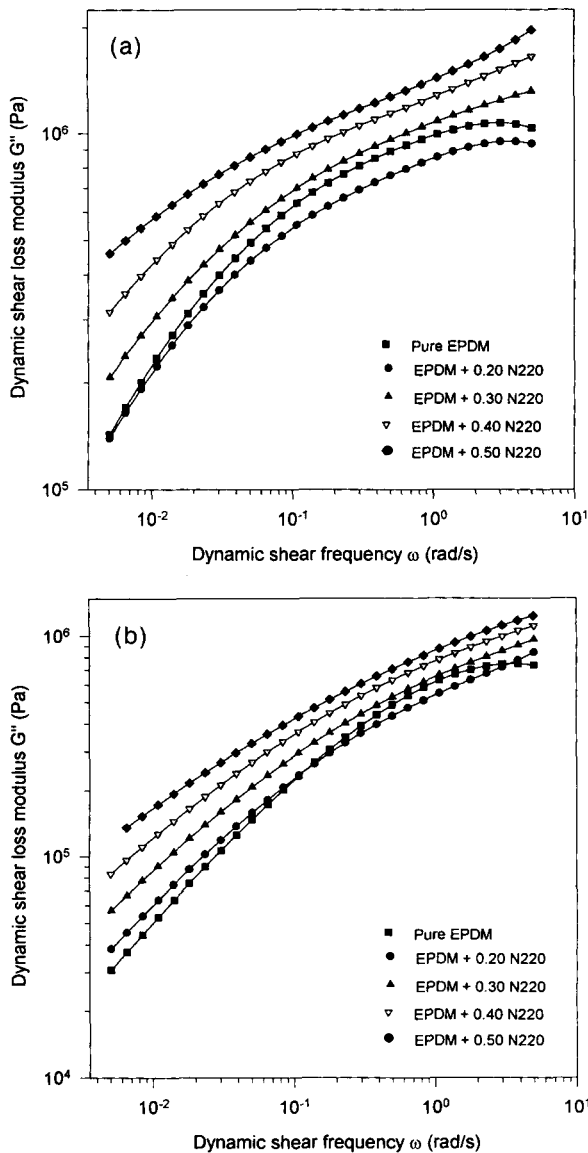


Figure 3 Observed variations of loss modulus $G''(T, \varphi, \omega)$ of gum and EPDM/N220 compounds with temperature T , filler compositions φ , and shear frequency ω . (a) 50°C, (b) 100°C, (c) 150°C.

quired higher temperature to melt and soften to allow greater filler–elastomer wetting. At higher carbon black loadings, we noticed higher moduli as shown in plots of Figure 2(b); and in addition, we noticed that as frequency increased, the gum elastomer manifested higher loss modulus than the 20% compound. This perhaps indicates the possibilities that carbon black at this level and temperature may be acting as a lubricant due to the presence of large particle agglomerates. There is an additional possibility that at 50°C, filler–elastomer interaction is minimal resulting in an even smaller wetted particle

surface. In the latter case, particulate filler agglomerates would slide past each other in shear flow yielding to lower viscosity and moduli. This phenomenon was not observed in the 20% compounds at 100 and 150°C where higher temperature appeared to enhance filler surface contact, wetting, and adhesion. The dynamic shear viscosity $\eta^*(\omega)$ data is shown in Figure 4 for 50, 100, and 150°C, respectively. The viscosities of the compounds are generally in the order of $\eta^*(\omega, \varphi, 50) > \eta^*(\omega, \varphi, 100) > \eta^*(\omega, \varphi, 150)$. At all temperatures and for all compounds investigated, the viscosities increased as shear frequency ω decreased corresponding to the infinite steady shear viscosity manifested in earlier investigations.^{9,10}

In Figure 4 we have plotted the complex viscosity $\eta^*(\omega)$ for the gum and its compounds against dynamic shear frequency at the same temperatures. The dynamic complex viscosity $\eta^*(\omega)$ for the compounds at 150°C exhibit some differences at lower frequencies. As frequency increased to higher values the dynamic viscosities showed some tendency to asymptotically converge to a correspondingly steady shear single power law behavior.^{9,10} We also observed similarity in magnitude and flow pattern of the gum and its 20% compound over the entire dynamic shear frequencies studied. The effect of temperature on the flow viscosity behavior of gum elastomers is best summarized as shown in the plots of Figure 5 where $\eta^*(\omega, 50) > \eta^*(\omega, 100) > \eta^*(\omega, 150)$.

In Figure 6 is plotted the loss tangent $G''(\omega)/G'(\omega)$ with shear frequency ω . At 50°C, the loss factor for the gum and its compounds decreased with shear

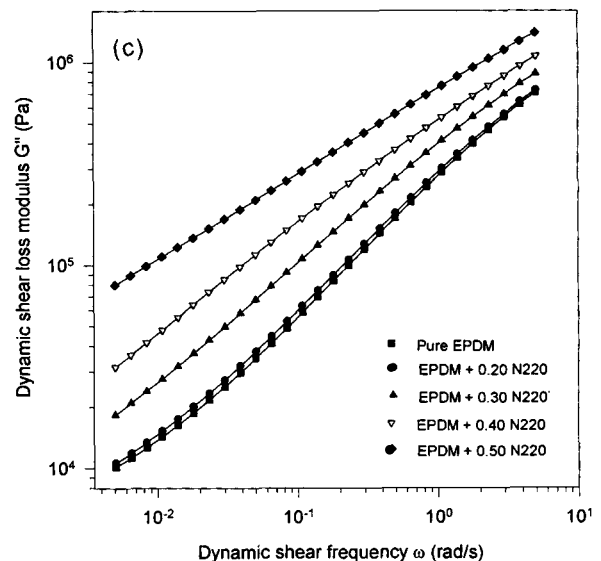


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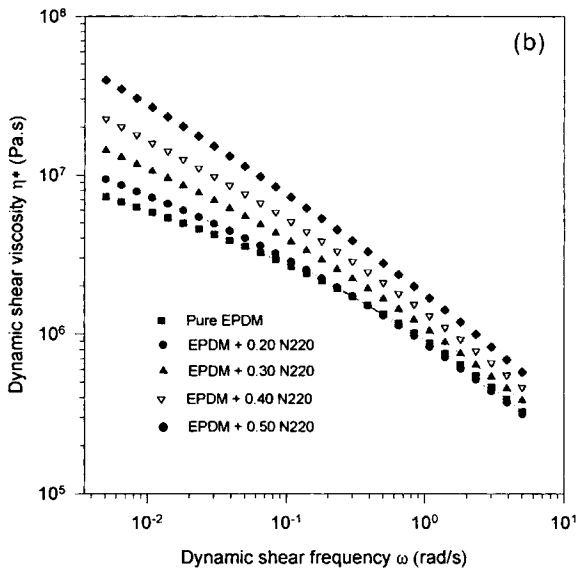
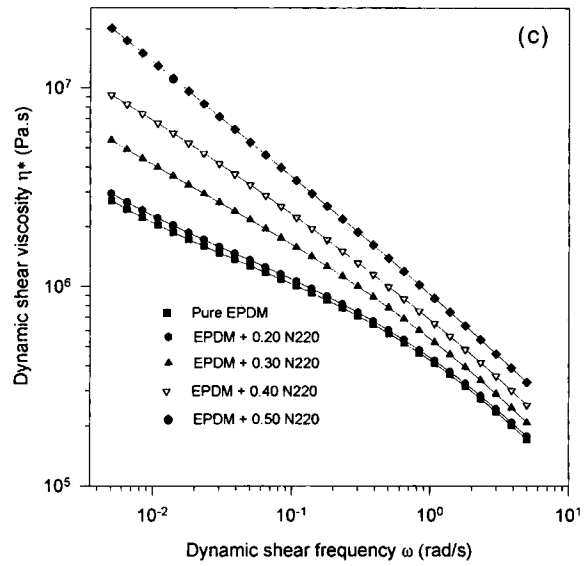
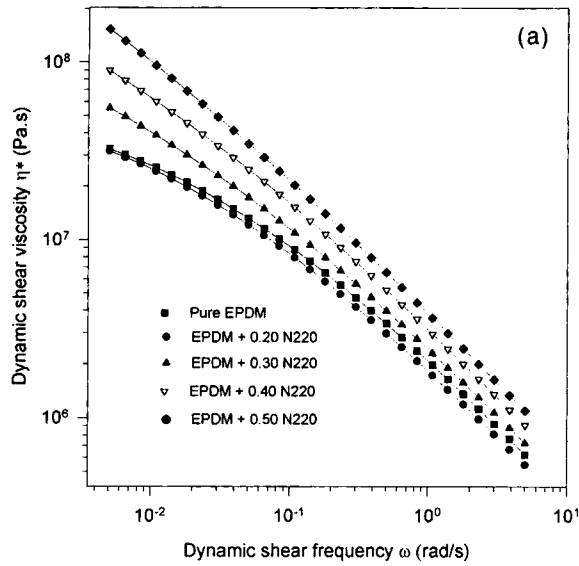


Figure 4 (Continued)

perature only the 50% compound remains fairly constant over the frequency covered in the studies.

Dynamic Properties Under Small Strain Amplitude

The high modulus observable in the plots of viscoelastic properties against strain amplitude as shown in Figure 1 occurred at small strain amplitudes. As the strain amplitude increased we observed a gradual but steady decrease in these properties. At the highest strain imposed the properties level again ap-

Figure 4 Observed variations of dynamic shear viscosity $\eta^*(T, \varphi, \omega)$ of gum and EPDM/N220 compounds with temperature T , filler compositions φ , and shear frequency ω . (a) 50°C, (b) 100°C, (c) 150°C.

frequency ω to a point at 5 rad/s. As the temperature increased to 100°C, there was a reduction in the rate of decrease of this property with frequency ω and a clear distinction between pure gum and the 20% carbon black filled compound established. Furthermore they do not converge at a point. As the temperature increased further to 150°C, the loss characteristics of the gum and its compounds dramatically changed. The gum and its 20% compound developed a peak loss at about 1 rad/s after it decreased again to a point at 10 rad/s. At this tem-

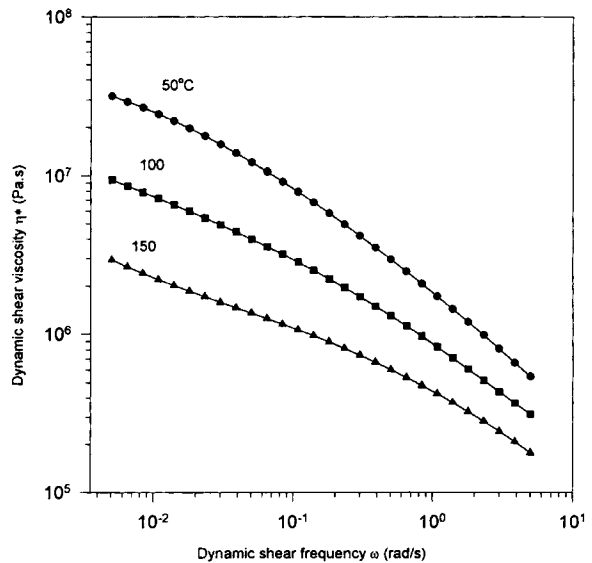


Figure 5 Effects of temperature on the dynamic viscosity behavior of gum EPDM.

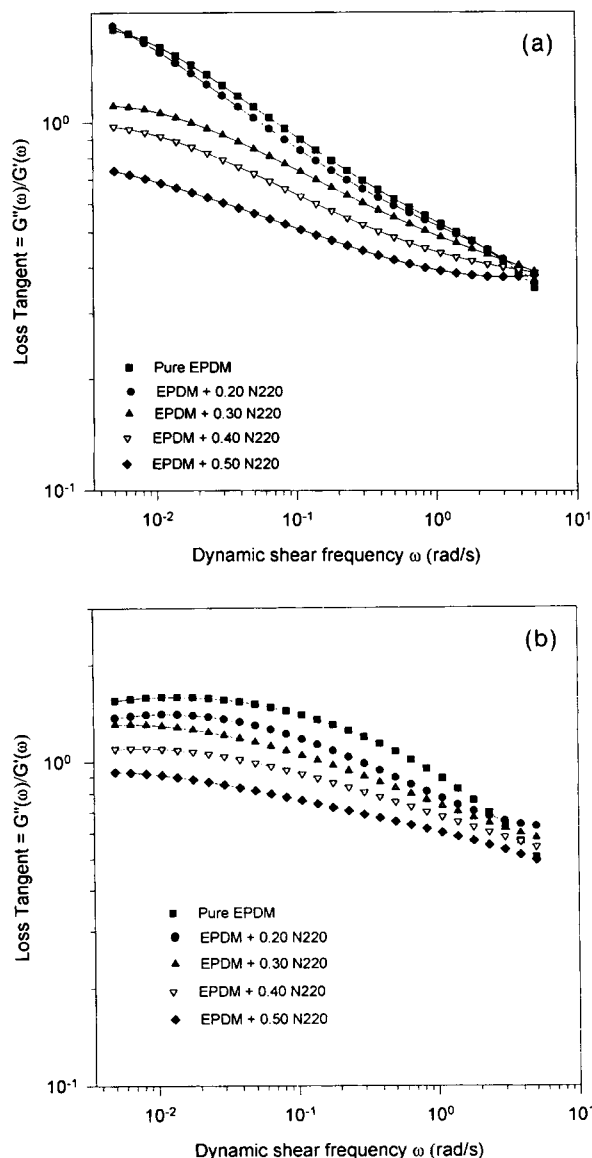


Figure 6 Dependence of loss factor $\tan \delta (T, \varphi, \omega) = G''(T, \varphi, \omega)/G'(T, \varphi, \omega)$ of gum and EPDM/N220 compounds with temperature T , filler compositions φ , and shear frequency ω . (a) 50°C, (b) 100°C, (c) 150°C.

proach constant values that depend on the carbon black loading. A measure of strain amplitude effects on the gum and its filled compounds are usually quantified by the difference $G'_0 - G'_\infty$ or $\Delta G'$ that reflects the difference between the magnitude of property at the lowest and highest strain amplitudes designated. The quantity represents the degree of particle network rupture due to strain imposed.^{5,6} The magnitude of this parameter has been measured for some vulcanizates and has been shown to depend on filler dispersion in the polymer matrix.^{1,11} A plot of $\Delta G'_i = G'_i - G'_{i+1}$ versus double strain amplitude

$= 2 \times \text{strain amplitude/length of sample}$, reveals an intrinsic characteristic slope of each compound that provides a graphical comparative rate of particle network breakdown. Mukhopadhyah and Tripathy,¹³ in their work with silica/EVA compounds, also shows that particles generally manifest this reinforcement characteristic at critical or threshold filler loading. The high values at small strain amplitude suggest the existence of well-developed structures consisting of interconnecting carbon black networks of particulate aggregates.⁵ This structure has also been associated with yield stress, thixotropy,^{9,10} and high electrical conductivity.⁷ This result is similar to earlier data of Thiele and Cohen¹⁴ from their studies of the role of filler properties in creep deformation of filled elastomers. In their results they found that creep activation energy in gum and vulcanizate SBR rubber compounds, were proportional to carbon black loadings, the type of blacks used, and the level of strain applied. This led them to suggest two mechanisms governing low strain deformations of gum and filled rubber compounds. The first mechanism was associated with the gum and the second with the carbon black filler. The contributions of the gum elastomer to deformation at moderate carbon black loading and high strain is not as pronounced as those from the carbon black filler that decreases under these conditions. The reticular network structure created by carbon black, due to their very close proximity, is extended over the whole rubber continuum and is associated on an extended scale with surface energies and interactions such as Van der Waal forces among particles. At

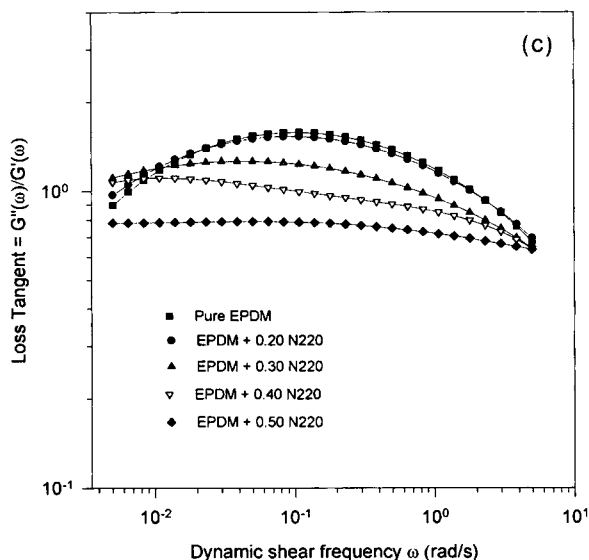


Figure 6 (Continued)

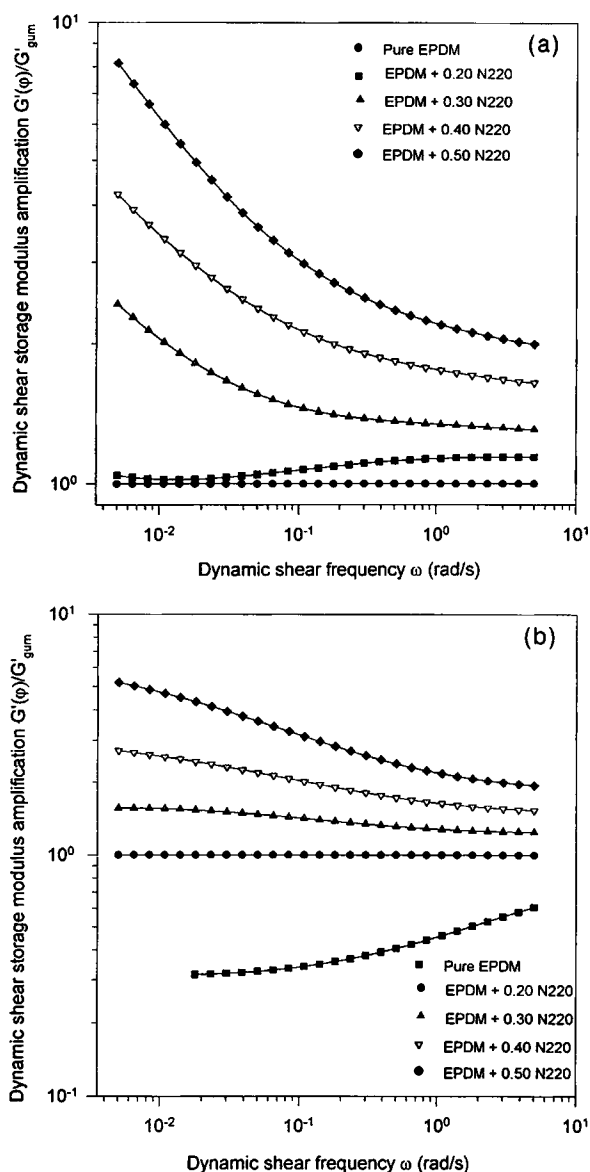


Figure 7 Viscoelastic property amplification effects of carbon black fillers in EPDM elastomer for 20 and 50% compounds. (a) 50°C, (b) 100°C, (c) 150°C.

low strains it appears these networks remained relatively intact and unbroken because of interparticle cohesive energy. As strain level increases due to applied stress, the network is subjected to progressive disruption. As strain level increases still further, the presence of the particles in the gum matrix and their contributions to flow properties becomes less noticeable on a macroscopic flow scale. This probably corresponds to the transition region observed in Figure 1. The effects of fillers on the dynamic properties of rubber/carbon black compounds is seen here to be strongly strain dependent. Property am-

plification effects are attributed partly to the molecules proximal to inextensible filler particles. In addition, the consideration of possible hydrodynamic effects of rubber occlusion by filler particles appears to account for much of the rheological behaviors of filled rubber compounds at small strains.

Dynamic Property Amplification

The relationship between the moduli values at near zero strain G_0 and at infinite strain G_∞ was given by Payne and Whittaker^{5,6,15} as

$$G_\infty = G_{\text{pure gum}} k f(c, \varphi) \quad (3)$$

where K , c , and φ are the particle-polymer matrix interaction constant, the particle shape factor, and filler volume concentration, respectively. Equation (3) suggests a strong hydrodynamic effect of particles embedded into polymer matrix and particle-polymer interactions.^{16,17} The unsuccessful early accounts for these were based on an Einstein model for very dilute suspensions^{18,19} but were soon corrected by Guth⁷ and Guth and Gold²⁰ who added a square of concentration term to account for the hydrodynamic effect that gives rise to dynamic property enhancement as

$$G'(\phi)/G'_0 = 1 + K_1(f\varphi) + K_2(f\varphi)^2 + \dots \quad (4)$$

The amplifications measure the effects of carbon black loadings on the dynamic rheological properties of gum rubber and are displayed in forms of plots of $G'(\phi)/G'_0$ versus frequency ω in Figure 7. The effects of loading is shown to be more pronounced at lower than at higher frequencies. While the amplification for 20 and 30% compounds are moderate, those for 40 and 50% compounds show significant high values at low frequencies. The effects of temperature appeared to be more dramatic especially when one observes their behaviors at 50 and 150°C. At 50°C, the viscosity of each compound except that of the 20% compound, decreased asymptotically from an infinite value to a constant value that remained invariant with shear frequency. At 150°C, it appeared at low frequency, viscosity assumed a plateau from where it decreased with shear frequency, and, again, it leveled up to a constant value. This behavior is consistent with and comparable to observed steady shear viscosity data and behavior for filled compounds at low shear rates.^{9,10}

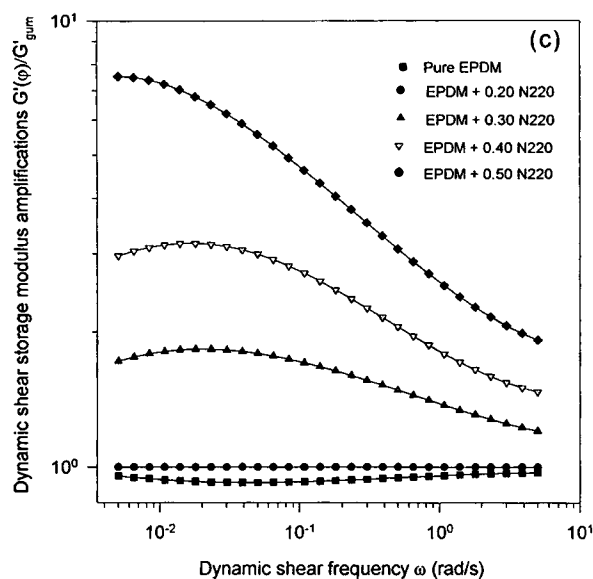


Figure 7 (Continued from the previous page)

CONCLUSION

Processability and product properties of most rubber products could be evaluated by using appropriate dynamic shear tests on the gum elastomer over a wide range of filler compositions, temperatures, and shear frequencies. These tests on the gum elastomer and its filled compounds offer significant insight and understanding on the mechanisms of filler/rubber behavior at the microstructural level and serves as a precursor to characterizing the vulcanized compounds. Mechanical properties of gum EPDM/carbon black compounds were evaluated in dynamic mode over several carbon black compositions and temperatures. Strain amplitude measurement revealed a very narrow window where linear viscoelastic proposition could be used. This window decreased with carbon black composition and tended to increase with temperature. The shapes and magnitudes of initial and final dynamic mechanical properties were used to explain the magnitude of change in the carbon black network structure in these compounds. In this work, we found that the viscosities of the 20% carbon black compound was

not much higher than the viscosity of the gum elastomer. The storage modulus of the gum and its 20% carbon black compound at 50 and 150°C were similar but different at 100°C. These observations indicate the dependence of processability on temperature.

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