Rheological and Viscoelastic Behavior of Dynamically Vulcanized Poly(vinyl chloride)–Epoxidized Natural-Rubber Thermoplastic Elastomers

A. MOUSA, U. S. ISHIAKU, Z. A. MOHD ISHAK

School of Industrial Technology, Universiti Sains Malaysia, 11800 Penang, Malaysia

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ABSTRACT: Dynamically vulcanized poly(vinyl chloride)–epoxidized natural-rubber thermoplastic elastomers (PVC–ENR TPEs) were prepared using a semi-EV vulcanization system. The compounds were melt-mixed, and the rheological behavior was evaluated. The effect of curatives concentration on the rheological behavior using the shear dependence of viscosity and the activation energy for viscous flow was evaluated. Viscoelastic behavior was also investigated with the Monsanto MDR 2000. The parameters studied include the elastic modulus at maximum torque, the loss peak at maximum torque, and their ratio (tan δ). The data obtained were correlated with the material properties, such as hardness and resilience. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2886–2893, 1999

Key words: poly(vinyl chloride); epoxidized natural rubber; activation energy; thermoplastic elastomers; dynamic vulcanization

INTRODUCTION

Epoxidized natural rubber (ENR) is a modified form of natural rubber (NR) in which some of the double bonds in the *cis*-polyisoprene chain have been converted to oxirane groups.[1–3] This produces a new material with improved oil resistance, reduced air permeability, and increased glass transition temperature, etc.[1] The blending of polymers for property enhancement continues to represent a field of intense research activity. Miscibility studies of PVC–ENR blends revealed that the two polymers are miscible.[4–6] Diethylhexyl phthalate (DOP) plasticized PVC–ENR blend has been reported to be a miscible blend with a single T_g.[7–8] Plasticized PVC–ENR blends can be classified as thermoplastic elastomers that look, feel, and perform like vulcanized rubber.[9]

Dynamic vulcanization means the selective curing of the thermosetting rubber component and its fine dispersion in molten thermoplastic resin via intensive mixing or kneading. This process yields a fine dispersion of partially or fully microsize rubber particles in the thermoplastic matrix. Molten polymers are viscoelastic materials, and hence the study of their flow behavior is not without complications. The rheological behavior of thermoplastic and rubber has become the subject of interest due to the growing importance of thermoplastic elastomers. The rheological parameters of the blend control its processibility under operating conditions. These parameters can be measured using a variable torque rheometer, a capillary rheometer, or a moving die rheometer. Several rheological studies on uncrosslinked and crosslinked blends have been carried out.[10–13] According to Coran,[14–15] in plastic–rubber blends such as a polyolefin–EPDM thermoplastic vulcanizate, the shear modulus depends on the viscosity of the rubber phase and on the crystallization

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Correspondence to: A. Mousa.

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Table I Recipe to Produce PVC–ENR TPEs

PVC	70
ENR-50	30
DOP	50 phr PVC
Zinc oxide	3 phr ENR
Stearic acid	1.5 phr ENR
Sulfur	X
MBTS	X
TMTD	$\frac{1}{3}$X

Where X is the amount of sulfur that was varied from 0-1 phr ENR-50.

of the plastic phase. Various factors affecting the die swell, and melt fracture and deformation of the extrudates have been reported.[16] Flot and Smith[10] stated that flow behavior of blends depends on heat history and morphology. The composition dependence and the effect of compounding conditions for the uncrosslinked PVC–ENR blend was reported earlier by Ishiaku et al.[17] as well as the effect of processing variables.[18] The current investigation describes the rheological and viscoelastic behavior of the dynamically vulcanized PVC–ENR thermoplastic elastomers using a Brabender Plasticorder and a Monsanto Moving Die Rheometer 2000 (MDR 2000). The effect of curatives concentration on the rheological and viscoelastic behavior of the TPEs is reported.

EXPERIMENTAL

Materials

Suspension PVC in powder form, with a K-value of 65 and a degree of polymerization of 920–1,060 was supplied by Malayan Electro Chemical Industry Sdn Bhd, Penang, Malaysia. ENR with 50 mol % epoxidation (ENR-50) was obtained from Kumpulan Guthrie Bhd Seremban, Malaysia. Lead stearate, $Pb(St)_2$, was obtained from Komita Sdn Bhd, Malaysia. DOP, sulfur, tetramethylthiuram disulfide (TMTD), 2,2-dithiobis benzothiazole (MBTS), zinc oxide, and stearic acid were obtained from Bayer (M) Sdn Bhd, Malaysia.

Formulations

A semiefficient sulfur vulcanization system (semi-EV) was incorporated into the plasticized PVC–ENR blend. In the present work the formulation is shown in Table I.

Melt Mixing

PVC was initially premixed with 3-phr lead stabilizer in a Janke and Kunke IKA Labotechnik Model RE 162/P at 300 rpm for 10 min at 30°C. Melt mixing was performed using a Brabender Plasticorder Model PLE 331 coupled with a mixer–measuring head (W 50H) at 150°C and a 50-rpm rotor speed.[17] The ENR-50 was charged into the mixing chamber to equilibrate, followed by PVC, zinc oxide, and stearic acid. After sufficient melt mixing of the PVC, the accelerators, TMTD and MBTS, were added. Mixing was allowed to proceed for 8 min after which sulfur was incorporated. Curing then occurred and was indicated by an increase in mixing torque with increased sulfur concentration. Mixing was then continued at a reduced speed of 30 rpm until a constant torque was obtained, as reported in our previous work.[19,20] The compound was removed from the mixer and sheeted on a cold two-roll mill. It was passed once through the nip to produce approximately a 1-mm thick sheet. The sheets were cut into strips and again subjected to Brabender mixing at 150°C and 50 rpm for 2 min after which it was again sheeted out prior to compression moulding.[14,19] Melt rheological properties of the blends were evaluated using a Brabender plasticorder at mixing speeds of 30, 40, 50, and 60 rpm and mixing temperatures of 130, 140, 150, and 160°C.

Molding

Sheets of 2-mm thickness were molded with a KAO Tieh compression molding machine with a force of 10 MPa at 150°C for 15 min.

Characterization and Testing

Resilience

The resilience test was carried out using a Dunlop Pendulum according to BS 903, Part A8, and the rebound resilience was calculated as follows:

$$\text{Resilience } (R) = \frac{1 - \cos(\text{angle of rebound})}{1 - \cos(\text{angle of fall})} \qquad (1)$$

The energy not recovered is hystersis and appears as heat. Hysteresis = 100 − resilience.

Hardness Test

The Wallace Dead load hardness tester was used to measure the hardness in an international rubber hardness degree (IRHD) according to ISO 48 (1979).

Swelling Index

Specimens in the form of 2-mm-thick circular discs of 40 mm in diameter were immersed in toluene for 12 h, and the diameters of the swollen samples were measured. The swelling index was calculated as follows:

$$\text{Swelling index} = \frac{\text{Swollen mass}}{\text{Original mass}} \tag{2}$$

Viscoelastic Parameters

The viscoelastic test was carried out according to ASTM D2084. A 2-mm-thick test specimen of the vulcanizates was inserted into the cure meter test cavity of Monsanto MDR2000. The test temperature was set at 150°C for 45 min. The dies were closed, and the disk was oscillated at a frequency of 1.7 Hz and an applied strain of 0.5°–1°. The test was completed after the predetermined time had elapsed where an equilibrium torque value was recorded. Viscoelastic parameters such as elastic modulus, E', loss modulus E'', and tan δ were recorded automatically.

RESULTS AND DISCUSSION

Rheological data obtained from the Brabender Plasticorder had been reported earlier based on the equation of the non-Newtonian flow behavior.[21–22] The relationship obtained from the Brabender Plasticorder can be stated as

$$M = CS^a \tag{3}$$

where M is torque, S is rpm, and C and a are constants. The above equation resembles the power law equation,[21–22] which is given as

$$\tau = K(\gamma)^n \tag{4}$$

where τ is shear stress; K, constant; γ, shear rate; and n, melt flow index.

Based on the above two equations it can be inferred that the torque recorded on the Brabender Plasticorder is an indirect indication of the shear stress, while the rotor speed (rpm) is an indirect indication of shear rate. Thus, the viscosity that is given as the ratio of shear stress to shear rate in the case of the Brabender Plasticorder can be obtained from the ratio of torque to rpm.

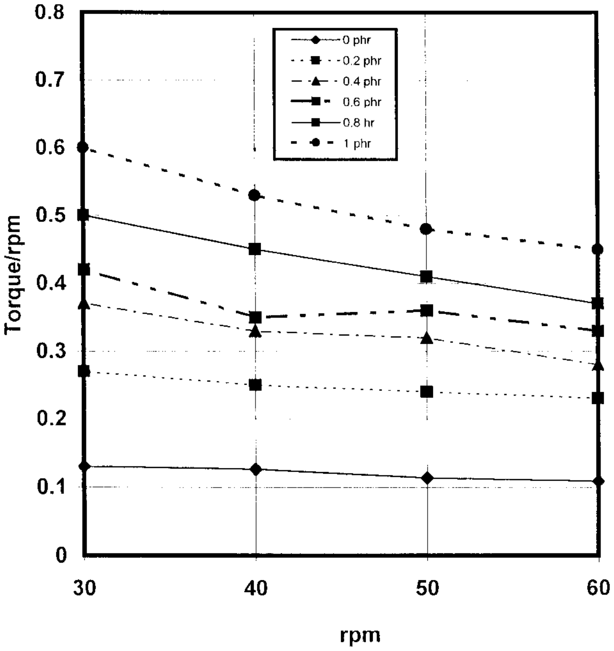

Figure 1 The effect of apparent shear rate on the viscosity of PVC–ENR TPEs at various amounts of sulfur concentration.

Rheological Behavior

Power Law Index

Figure 1 shows the effect of shear rate on the apparent viscosity of the PVC–ENR blend at various amounts of sulfur loading. It is obvious that viscosity increases with an increase in sulfur loading. This trend is in agreement with previous findings on an uncured PVC–ENR blend[17] and PVC–NBR thermoplastic elastomers.[23] The higher viscosity of the cured PVC–ENR blends could be related to the effect of crosslinking and the intermolecular network formation that is known to inhibit melt flow. In other words, the crosslinked samples will not be deformed easily by the mechanical work induced by the internal mixer. This observation suggests that the formation of the crosslinks has enhanced the frictional resistance of the samples against deformation. The melt flow behavior of the samples can be described by a power law index as shown above. Figure 2 shows the relationship between shear stress and shear rate of the PVC–ENR TPEs at various sulfur

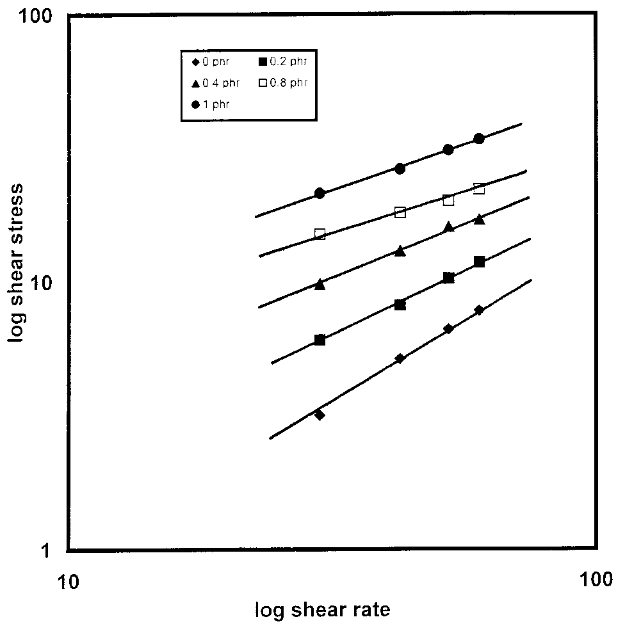

Figure 2 The effect of apparent shear rate on the torque of PVC–ENR TPEs at various amounts of sulfur concentration.

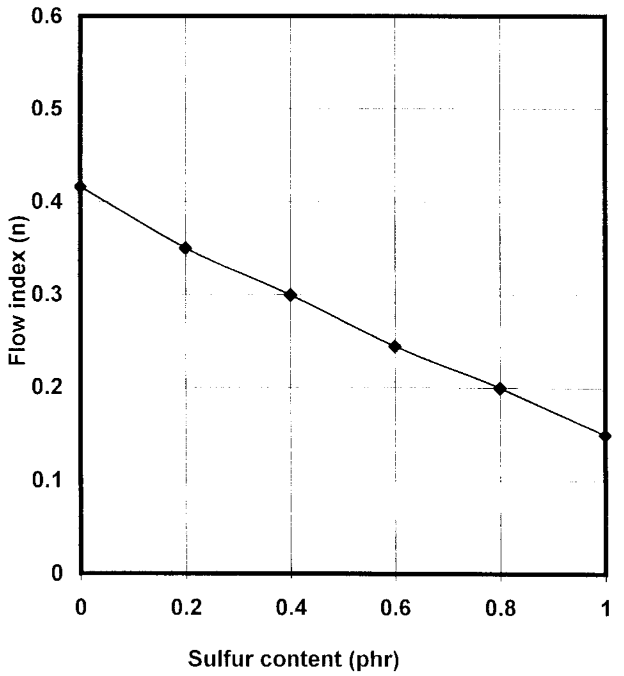

Figure 3 The effect of sulfur concentration on the melt flow index (n) of PVC–ENR TPEs.

loadings. In all cases the shear stresses increased linearly with shear rates, although the rate of increase in shear stress is affected by the curative concentration. This might be related to the enhanced frictional resistance introduced by the crosslink formation. The slope of these straight lines could be used to estimate the value of the melt flow index (n). The variation of n with sulfur concentration is presented in Figure 3. The values of n decrease with increasing sulfur loading. Again, this might be due to the formation of more intermolecular network structure at higher sulfur concentrations. These crosslinks will obviously increase the rigidity of the polymer chain and consequently prevent the chains from slipping. Thus, the ability of the samples to resist flow increases with sulfur content. The values of n dictate the pseudoplastic nature of the PVC–ENR blends since $n < 1$ and show that the apparent viscosity decreases as shear rate increases.

Flow Activation Energy

The temperature dependence of the viscosity can be expressed in term of an Arrhenius equation as[23]

$$\eta = Ae^{Ea/RT} \tag{5}$$

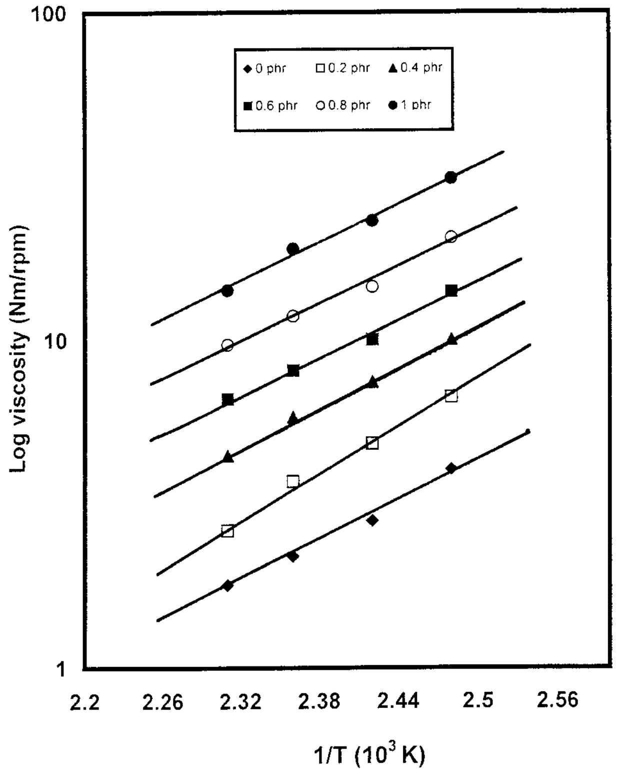

Figure 4 The variation of viscosity with temperature for PVC–ENR TPEs at various amounts of sulfur concentration.

where η is viscosity; A, constant; Ea, activation energy; T, temperature in K; and R, the gas constant.

As the ratio of torque to rpm can be used to represent the apparent viscosity of the blend, E_a can be evaluated from the graph of log torque/rpm against the reciprocal absolute temperature $1/T$, as shown in Figure 4. The apparent viscosity of the PVC–ENR TPEs was calculated from torque values at a shear rate of 50 rpm for mixing temperatures ranging from 130 to 160°C. It is shown that the viscosity of both uncured and cured samples decreased as mixing temperature increases. This can be attributed to the increase in the kinetic energy of the blend components arising from thermal energy transferred from the mixer wall and the friction between the samples and the mixer rotors. Thus, intermolecular bonds that hold the samples together will not be strong enough to prevent the blend components from flowing. As expected, the viscosity of the cured blends increases as the sulfur content increases. This may because the effect of crosslinking, which is known to increase the viscosity of polymer melts.[5] Moreover, the viscosity depends on the strength of the intermolecular structure of the blend components. Based on this observation it can be inferred that the introduction of crosslinks via dynamic vulcanization has hindered the flow of the vulcanized PVC–ENR TPEs. The temperature dependence of the viscosity of PVC–ENR TPEs might be evaluated by the flow activation energy using Arrhenius eq. (5). The flow activation energy, which is shown in Figure 5, was calculated from the slopes of the straight lines in Figure 4 using linear regression analysis. Up to 0.6-phr sulfur loading there is a gradual increase in activation energy. However, a more dramatic increase was observed once the sulfur loading exceeded 0.6 phr. This might be related to the formation of intermolecular network structures, which increase with increased sulfur loading. This claim is supported by the variation of the swelling index with sulfur loading, shown in Figure 6. A decrease in swelling index is a direct function of increase in crosslink density.[20] This is consistent with an earlier report by Mathew et al.[23] on PVC–NBR thermoplastic elastomers.

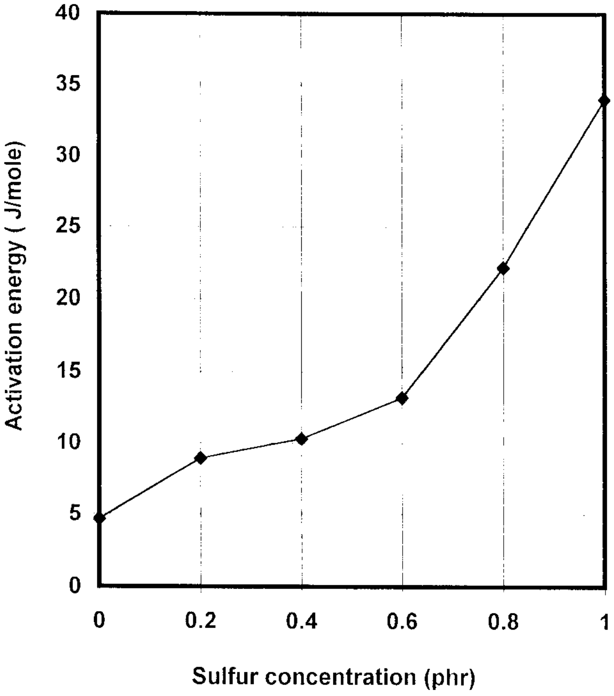

Figure 5 The effect of sulfur concentration on the flow activation energy of PVC–ENR TPEs.

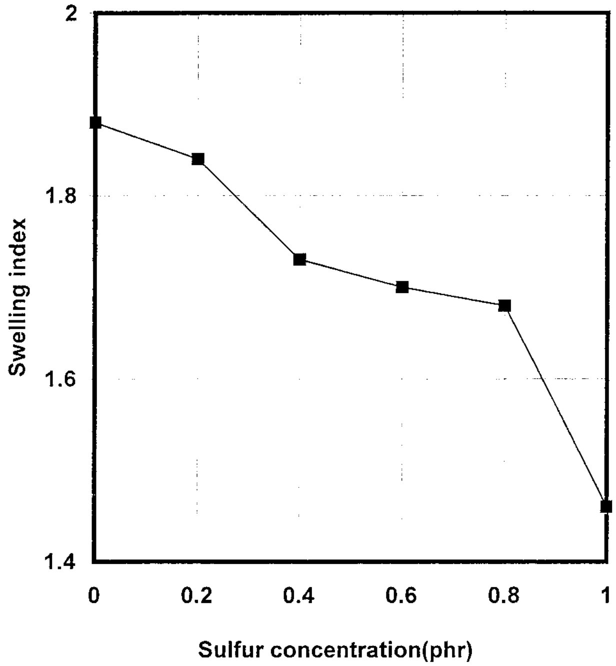

Figure 6 The effect of sulfur loading on the swelling index of PVC–ENR TPEs.

Viscoelastic Parameters

Figure 7 illustrates the influence of sulfur content on the viscoelastic behavior, i.e., elastic and viscous components and the tan δ of PVC–ENR at 150°C and maximum torque (MH) as derived from the MDR 2000. A gradual increase in the elastic modulus (E') with increase in sulfur dosage was observed. This could be due to the formation of intermolecular networks, i.e., increased crosslink density. The damping behavior is a very sensitive indicator of crosslinking.[24] The loss modulus (E'') of all the tested specimens illustrates the general phenomena always found: Damping decreases with an increased degree of crosslinking for lightly crosslinked rubbers. This is in agreement with an earlier observation by Nielsen.[24] An interesting correlation between the swelling index and the damping behavior is shown in Figure 8: At 150°C, the swelling index is approximately a linear function of the damping. From this correlation it is obvious that in addition to the swelling index, damping could also be used to evaluate the degree of crosslinking. Another important parameter that is frequently used to characterize viscoelastic behavior of polymeric materials is tan δ, a measure of the ratio of the dissipated energy as heat to the maximum energy stored in the material during one cycle of oscillation.[24] Thus, it can be expected that tan δ is also very sensitive to curatives variation. As illustrated in Figure 7, tan δ decreases to a minimum value at maximum sulfur dosage. This again could be attributed to the microstructural changes that have occurred through the crosslink formation via dynamic vulcanization. The continuous increase in the storage modulus (E') which is accompanied by a continuous reduction in the loss modulus (E'') with increase in sulfur concentration is thus responsible for the observed trend in tan δ.

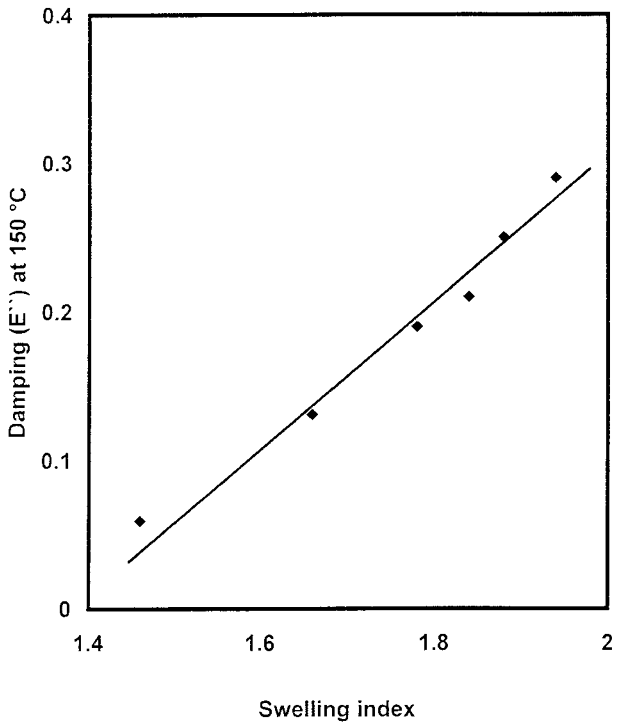

Figure 8 The relationship between swelling index and damping (E'') for PVC–ENR TPEs.

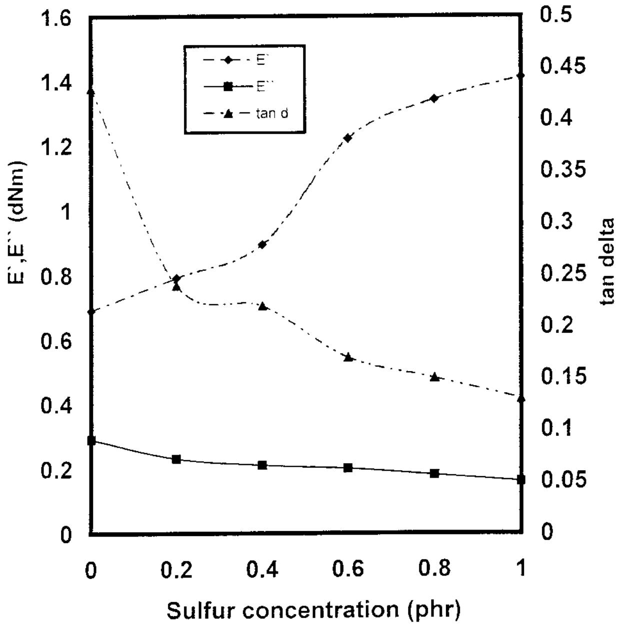

Figure 7 The effect of sulfur loading on E', E'', and tan δ of PVC–ENR TPEs at maximum torque.

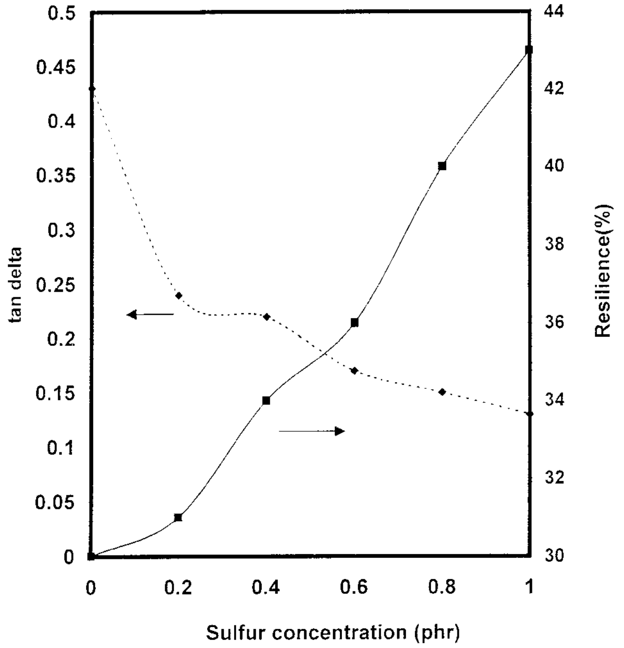

Figure 9 The variation of tan δ at maximum torque and resilience with sulfur loading of PVC–ENR TPEs.

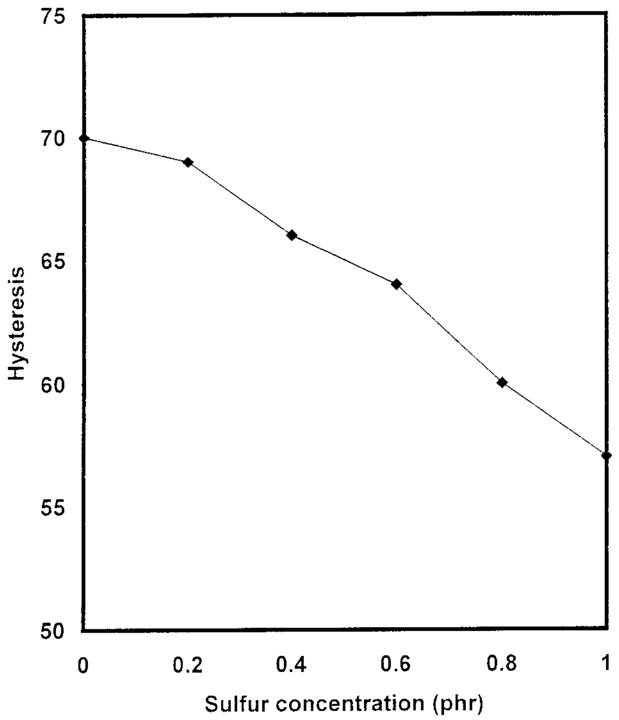

Figure 10 The variation of hysteresis with sulfur loading of PVC–ENR TPEs.

Resilience

Good resilience is vital for elastomers to reduce heat buildup. Correlation between material properties such as resilience and hardness with the MDR 2000 parameters has been claimed by DiMauro.[25] Figure 9 shows an inverse relationship between the effect of sulfur concentration on both the percentage resilience and the tan δ of PVC–ENR TPEs. This is most likely due to the action of the curatives that results in network formation. As explained previously, the increase in crosslink density with increased sulfur dosages increases the elastic modulus while at the same time reducing the loss modulus. This implies that the molecular retractability of the network upon deformation had been increased; that is, the elastic behavior of PVC–ENR becomes more pronounced. This is in agreement with data presented in Figure 7. A similar trend has also been reported by Coran[26] for the general effects of vulcanization on the resilience properties of the vulcanizate structure.

Hysteresis

Hysteresis is an important aspect in studying the service performance of elastomers. It is a measure of energy loss when elastomeric materials are subjected to dynamic deformation. The energy loss that causes heat buildup and subsequently chain scission will eventually reduce the mechanical properties. Figure 10 shows the influence of sulfur concentration on hysteresis for the PVC–ENR TPEs. The trend is similar to that of tan δ—that is, the extent of heat loss or damping has been reduced. Thus there is a less hysteretic compound with increased rebound resilience and reduced heat buildup. From this observation it can be inferred that the sample with the higher sulfur content is less sensitive toward changes in dynamic deformation. In a related study Mousa et al.[27] have observed that the fatigue life of PVC–ENR TPEs increased with increasing sulfur concentration. The increase in crosslink density is believed to be responsible for increasing the resistance of the materials against dynamic stress.

Hardness

Curemeter elastic modulus (E') generally correlates with hardness of the vulcanized samples.[25] Figure 11 shows the correlation between maximum torque (E') and hardness of PVC–ENR TPEs. As the sulfur dosage increases, both hard-

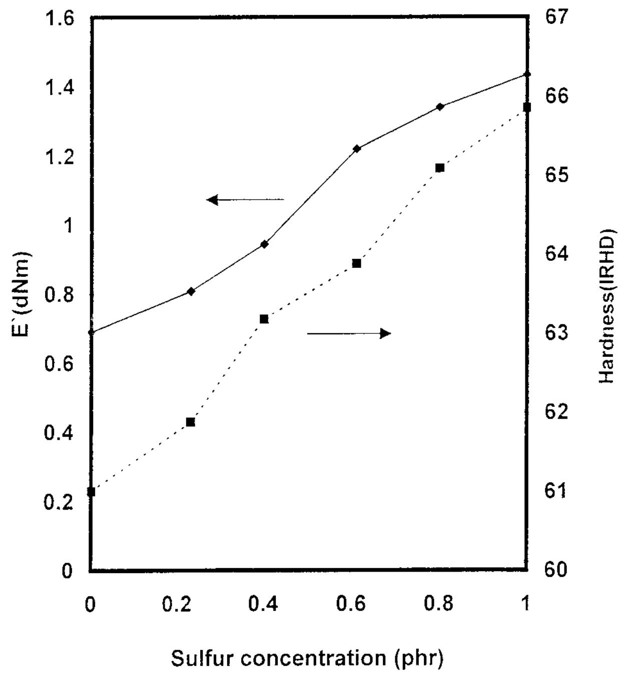

Figure 11 The variation of E' at maximum torque and hardness with sulfur loading of PVC–ENR TPEs.

ness and E' increases, thus indicating increased rigidity of the samples.

CONCLUSION

Melt rheology of PVC–ENR TPEs was evaluated using an internal mixer Brabender Plasticorder. The behavior of the blends can be represented by a power law index, and the melt flow index was calculated from the slope of log-apparent shear stress against log-apparent shear rates lines. It was found to be affected by the curative dosages. The temperature dependence of viscosity of the PVC–ENR TPEs was evaluated using an Arrhenius equation. It was found that the increase in mixing temperature has decreased the viscosity of both the crosslinked samples and the uncrosslinked samples. The estimated flow activation energy seems to be influenced by the microstructural changes produced by the crosslink formation. Investigations on the viscoelastic behavior using MDR 2000 revealed that the crosslink formation via dynamic vulcanization had significant influence on the elastic modulus (E'), loss modulus (E''), and tan δ of PVC–ENR TPEs. The derived parameters could be correlated to the physical properties of the materials, such as hardness and resilience.

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