

Oil-Resistance Studies of Dynamically Vulcanized Poly(vinyl chloride)/Epoxidized Natural Rubber Thermoplastic Elastomer

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ABSTRACT: Dynamically vulcanized poly(vinyl chloride)/epoxidized natural rubber (PVC/ENR) thermoplastic elastomers (TPEs) were prepared with a Brabender plasticorder coupled with a mixing attachment by melt mixing. The blends were prepared at 150°C at a rotor speed of 50 rpm. Curatives concentration was steadily increased from 0 to 1 phr in order to study the vulcanization effect on the plasticized blend. The effectiveness of the dynamic vulcanization was indicated by the Brabender plastograms. The properties investigated include mass swell, tensile strength, elongation at break, modulus at 100% elongation (M100), tear strength, and hardness. The PVC/ENR samples were exposed to two types of environments, namely, air and oil under otherwise identical conditions. The effect of oil and thermooxidative aging on the mechanical properties were characterized at room temperature and 100°C. It was found that at ambient temperature the samples immersed in oil possessed similar properties to those that were exposed to air. Significant enhancement in mechanical properties were observed for both environments at 100°C. This has been attributed to the increase in crosslink density which was manifested by a steady reduction in percent mass swell with increased sulfur loading. The excellent mechanical behavior of the PVC/ENR TPEs even after immersing the samples in oil at 100°C has provided a good indication of the oil resistance of the materials. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1357–1366, 1998

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

INTRODUCTION

The blending of polymers for property enhancement or for economical purposes has become increasingly important in the last decade.¹ The successful epoxidation of natural rubber has ensured epoxidized natural rubber (ENR-50) its place in the elastomer market.^{2,3} This modified natural rubber has improved oil resistance, reduced air permeability, increased polarity, and glass transi-

tion temperature, etc.^{4–6} Miscibility is an important aspect in polymer blending and blends of ENR with poly(vinyl chloride) (PVC) have been shown to be miscible. Based on previous findings,^{7–11} PVC/ENR blends could be classified as a miscible system characterized by a single glass transition temperature (T_g) located between that of ENR and PVC.^{9–12} Thus, PVC/ENR can be classified as a melt-processible blend.¹³ By virtue of its polarity, ENR 50 has been judged to have an oil resistance similar to that of NBR.¹⁴ Thus, the PVC/ENR blend is expected to perform within the range of the PVC/NBR blend in this respect.

Dynamic vulcanization plays a significant role in thermoplastic elastomer (TPE) technology in

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producing thermoplastic vulcanizates which possess a unique combination of properties. Thus, products that look, feel, and perform like vulcanized rubber can be manufactured. In their previous studies, Ishiaku et al.¹¹ highlighted that in spite of having attractive properties such as being mutually miscible with PVC at all compositions, with synergism in mechanical and dynamic mechanical properties,¹² the uncrosslinked PVC/ENR blend suffered a major drawback in that it exhibits poor thermooxidative stability. Several attempts have been made to improve the aging behavior of the blend, and these include the incorporation of a plasticizer, di-2-diethylhexylphthalate (DOP),¹⁵ and an antioxidant, 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ), and a base such as calcium stearate.¹⁶ Plasticizer addition was found to be particularly effective in curbing degradation.¹⁵

The investigation reported in this article was focused on the oil resistance of the dynamically vulcanized PVC/ENR TPEs. An oil-resistance study is of interest for two main reasons: First, to date, there is no published data on the oil resistance of these materials. It is quite obvious that such data are valuable in predicting the service behavior of the materials. In the case of NBR–polypropylene thermoplastic vulcanizates, for instance, Coran and Patel¹⁷ reported that the vulcanizates exhibited excellent hot-oil resistance. Second, to investigate the role of vulcanization on the oil resistance of the TPEs, the mass swell after immersion of the TPEs in ASTM oil #3 at ambient temperature and 100°C will be used as a measure of oil resistance.

EXPERIMENTAL

Materials

Suspension-grade poly(vinyl chloride) (PVC) in powder form, with a K value of 65 and a degree of polymerization of 920–1060 was supplied by Malayan Electro-Chemical Industry. Epoxidized natural rubber with 50 mol % (ENR-50) epoxidation was obtained from Kumpulan Guthrie. Nitrile rubber (NBR) with 34% acrylonitrile content was purchased from Watas (M) Ltd. Lead stearate was obtained from Komita. Di-2-ethylhexylphthalate (DOP), sulfur, tetramethylthiuramdisulfide (TMTD), 2,2-dithiobisbenzothiazole (MBTS), zinc oxide, and stearic acid were obtained from Bayer (M).

Melt Mixing

The preparation of the PVC/ENR blend with a Brabender plasticorder was detailed in an earlier study,¹⁶ while plasticizer incorporation was well elaborated in subsequent reports which dwelled on this subject.^{15,18} The innovation in the current investigation is the incorporation of a semi-EV sulfur vulcanization system into the plasticized PVC/ENR blend. Curative concentration is based on parts per hundred (phr) of ENR-50 that is, ZnO, 3 phr; stearic acid, 1.5 phr; sulfur, X phr; and TMTD, $\frac{1}{3}X$ phr.

PVC was initially premixed with the lead stabilizer in a Jankel IKA Labotchnik Model RE 162/P mixer 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). Mixing was carried out at 150°C and a rotor speed of 50 rpm.¹⁶ The ENR was charged into the mixing chamber to equilibrate, followed by PVC and other related additives. Mixing was allowed to proceed for 8 min, after which the curatives were added to the compound.¹⁹ Mixing was then continued until a constant torque was obtained. The compound was removed from the mixer and sheeted on a cold two-roll mill. It was passed once through the nip to produce an approximately 1-mm-thick sheet. The sheet was cut into strips and again subjected to Brabender mixing at 150°C for 3 min, after which it was again sheeted out prior to compression molding.

Molding

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

Characterization and Testing

Oil Resistance

The test was conducted according to ASTM D 471. The test specimens were immersed in ASTM #3 oil (which is similar to IRM 903) at room temperature and 100°C for 70 h. The test specimens were then removed from the oil, wiped with tissue paper to remove excess oil from the surface, and weighed. The percentage mass swell was then calculated as follows:

$$\text{Change in mass} = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

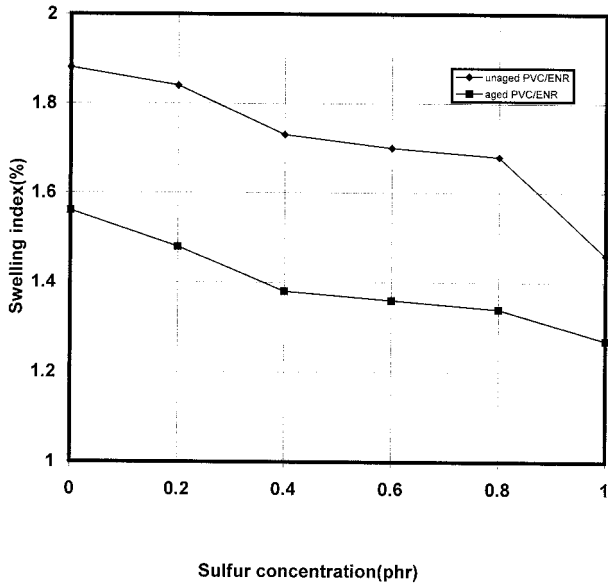


Figure 1 Effect of sulfur loading on swelling index of aged and unaged PVC/ENR TPEs.

where W_1 and W_2 are the weights of the samples before and after immersion, respectively. For the purpose of comparison, samples were also placed in an air oven and aged at 100°C for 70 h.

Swelling Index

Specimens in the form of circular discs of diameter 40 mm were immersed in toluene for 12 h and the swollen sample was determined and the swelling index was calculated as follows:

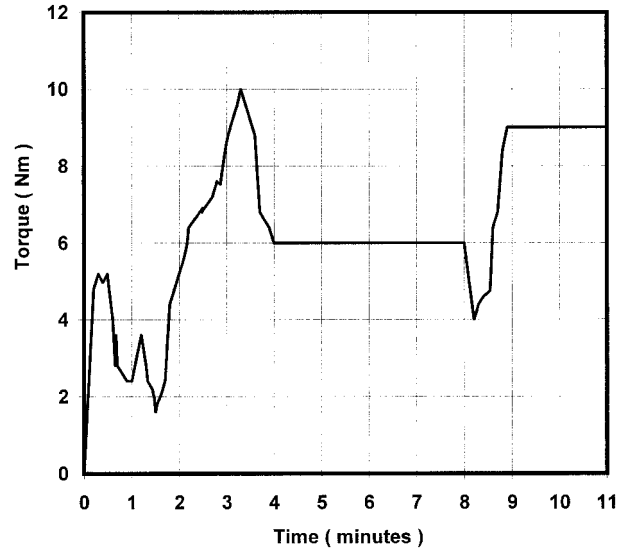


Figure 3 Torque–time curve of PVC/ENR TPEs at 1 phr sulfur loading.

$$\text{Swelling index} = \frac{\text{swollen mass}}{\text{original mass}} \quad (2)$$

Tensile Tests

Tensile tests were carried out according to ASTM D412 on a Monsanto tensometer T10. Dumbbell specimens of 2 mm thick were cut from the molded sheets with a Wallace die cutter (S/6/1/4). A crosshead speed of 50 cm/min was used and the tests were performed at $25 \pm 3^\circ\text{C}$. Three speci-

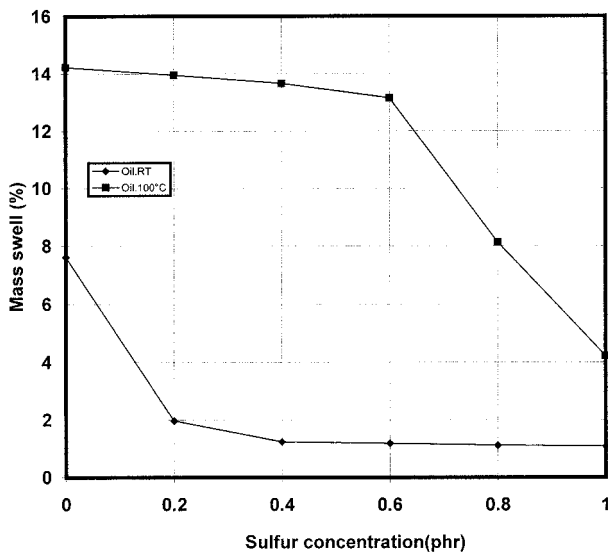


Figure 2 Effect of sulfur loading on mass swell of PVC/ENR TPEs at various exposure conditions.

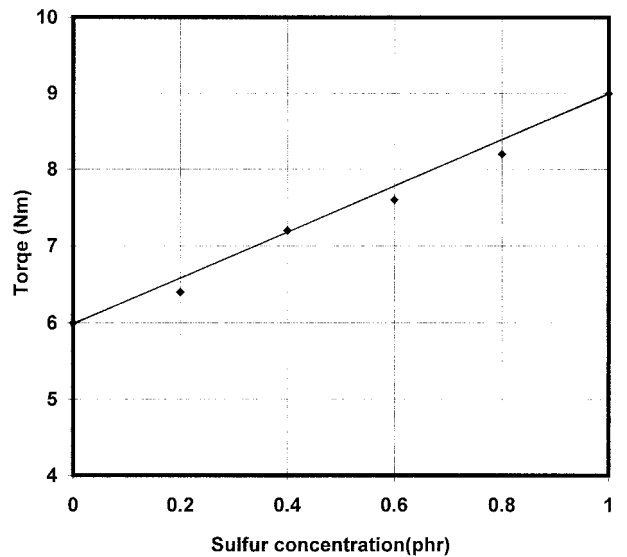


Figure 4 Effect of sulfur loading on the torque of PVC/ENR TPEs at the end of mixing time (i.e., 11th min).

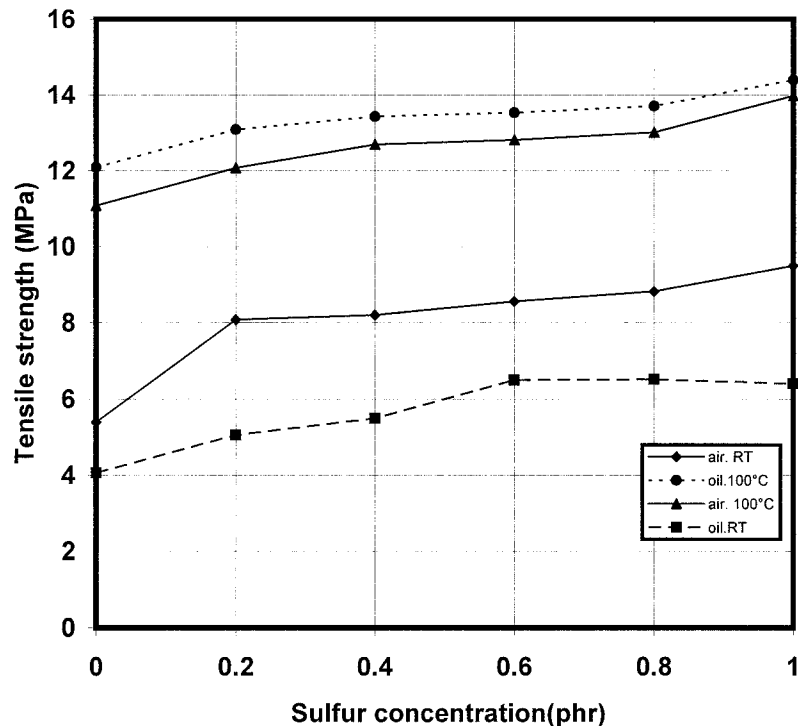


Figure 5 Effect of sulfur loading on tensile strength of PVC/ENR TPEs under various exposure conditions.

mens were used and the average was calculated in each case.

Tear Tests

Tear tests were carried out according to the ISO 34 Type III using the crescent-shape specimens. A Monsanto tensometer T10 was used at a cross-head speed of 50 cm/min. Five specimens were used and the average value was calculated.

Hardness Test

ASTM Shore A was used to measure hardness in International Rubber Hardness Degrees (IRHD) according to ISO 48 (1979).

Morphological Studies

Studies on the morphology of PVC/ENR TPEs fracture surfaces were carried out using a Leica Cambridge S-360 Model scanning electron microscope (SEM). The fracture ends of the specimens were mounted on an aluminum stub and sputter-coated with a thin layer of gold to avoid electrostatic charging during examination.

RESULTS AND DISCUSSION

Swelling Index

Figure 1 shows the relationship between the sulfur loading and the swelling index of PVC/ENR TPEs. It can be seen that the swelling index decreases continuously with increasing sulfur concentration. This provides a good indication of the increase in the crosslink density. As the crosslink density increases within the ENR phase, it can be expected that the vulcanizates will become stiffer and less penetrable by the solvent. The decrease in the swelling index at all sulfur concentrations for the aged TPE is evidence of further crosslink formation during aging, which has been attributed to postcuring.

Mass Swell

Figure 2 shows the effect of sulfur loading on the mass swell of PVC/ENR TPEs at room temperature and 100°C. A sharp decrease in the mass swell with the addition of sulfur is initially shown, but the rate of decrease lessens at higher concentrations of sulfur. Some ideas on the swelling behavior of the TPEs can perhaps be obtained from

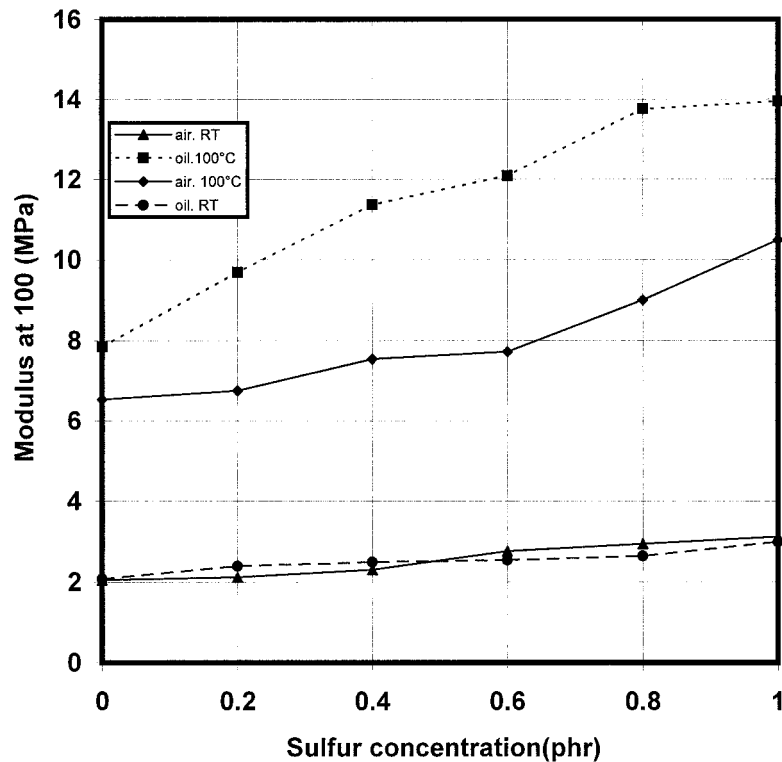


Figure 6 Effect of sulfur loading on the modulus at 100% elongation (M100) of PVC/ENR TPEs under various exposure conditions.

the Flory–Huggins equation which correlates osmotic pressure and the degree of crosslinking²⁰:

$$\frac{\pi}{C} = \frac{RT}{M_2} + \frac{RTd_1}{M_1d_2^2} \left[\frac{1}{2} - \mu \right] C \quad (3)$$

where π is the osmotic pressure; C , the concentration; R , the gas constant; T , the absolute temperature; M_1 , the molecular weights of the polymer; M_2 , the molecular weights of the solvent; D_1 , the density of the solvent; D_2 , the density of the polymer; and μ , the reciprocal constant.

According to the above equation, swelling will not occur until the osmotic pressure of the solvent (i.e., ASTM #3 oil used in the present study) is stronger than the intermolecular bonding of the molecules in the PVC/ENR blend. As the number of crosslinks increases, the molecular weight will decrease, due to the increased crosslink density. This will reduce the osmotic pressure. Thus, the diffusion of the solvent into the blend will result in less swelling. Another aspect which should be taken into consideration is the cohesive energy density (CED), which is defined as the energy required to separate all the molecules in a given

material from each other.²¹ The CED becomes stronger as the intermolecular forces increased due to crosslinking while the solvating power of the solvent remains constant. Therefore, the crosslinked PVC/ENR blend will become more resistant to the solvent attack (in this case, oil), thus leading to a reduction in mass swell as shown in Figure 2. At 100°C, the rate of decrease of the mass swell with increasing sulfur concentration is initially low but decreases sharply at higher concentration (i.e., 0.8 and 1 phr of sulfur). The reduction in the mass swell with increasing sulfur loading is in agreement with a previous work reported by Coran and Patel.¹⁷ The mass swell results of the vulcanized ENR-based TPEs is within the range of other specialty rubbers such as chlorinated rubber and NBR.¹⁴

Brabender Plastograms

A typical trace from the Brabender torque rheometer or plastogram is presented in Figure 3. Melt mixing is essentially completed with 8 min of mixing,^{10,15} at which point the curatives were added. The torque drops immediately due to the lubrication

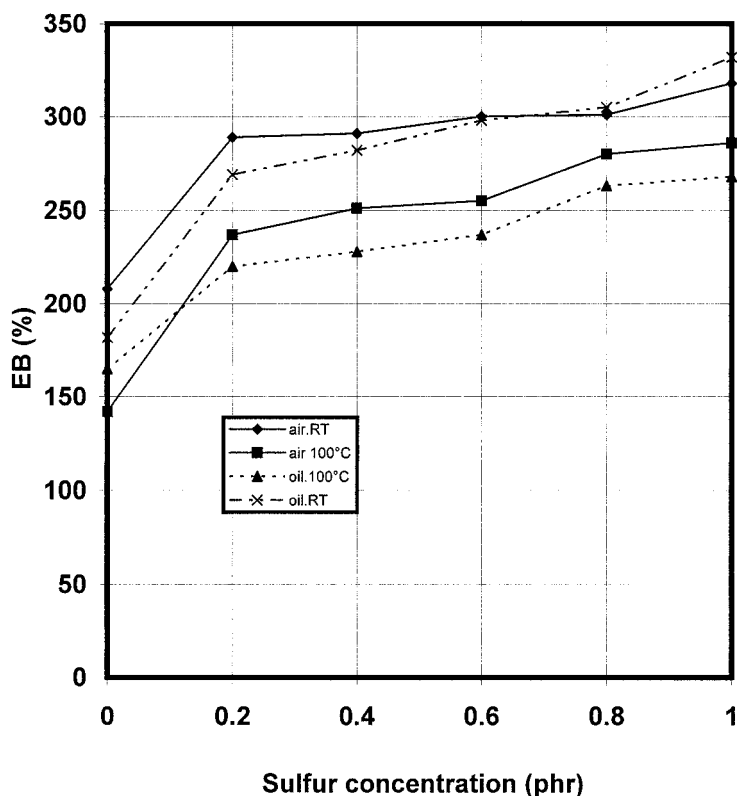


Figure 7 Effect of sulfur loading on EB of PVC/ENR TPEs under various exposure conditions.

tion effect of the curatives. The torque then rises immediately as crosslinking commences and mixing is continued at a reduced speed until a constant torque value is attained. The torque values at the stable end (11 min) were plotted at various sulfur concentrations (Fig. 4). It is shown that the stable values of the torque at the end of mixing increase continuously with increase in curative concentration. This also provides evidence of an increase in the crosslink formation with increasing concentration of the curatives. It can thus be inferred from the above observations that dynamic vulcanization has been essentially effected.

Effect of Dynamic Vulcanization

Mechanical Properties at Ambient Temperature

The effect of sulfur loading on the tensile properties of the PVC/ENR TPEs is presented in Figures 5–7. In Figure 5, it can be seen that there is a moderate increase in tensile properties with increasing sulfur concentration. This could be attributed to the progressive increase in crosslink density. As indicated by the swelling index data

and the Brabender torque rheometer, the crosslink density increases with increasing sulfur loading. Thus, the number of the individual macromolecular chains increases, albeit they become shorter. Shorter chains, being stiffer and more numerous, require a higher applied stress to cause rupture. ENR, like NR, is capable of undergoing strain-induced crystallization. Thus, the tensile strength is governed by the degree of crystallization attained as the break point is approached.²² The increase in tensile strength with increase in sulfur loading can be related to the ability of ENR to crystallize when stretched due to the orientation of the intermolecular chains. The formation of crystals will increase the number of intermolecular network chains per unit volume in the direction of the extension. Thus, the crystallized sample becomes firmer and this could also account for the enhancement in the tensile strength. This trend is similar to the earlier observation reported by Coran and Patel²³ for EPDM/PP TPVs.

The same explanation could also be used to account for the effect of sulfur concentration on the modulus at 100% extension (M100) shown in Fig-

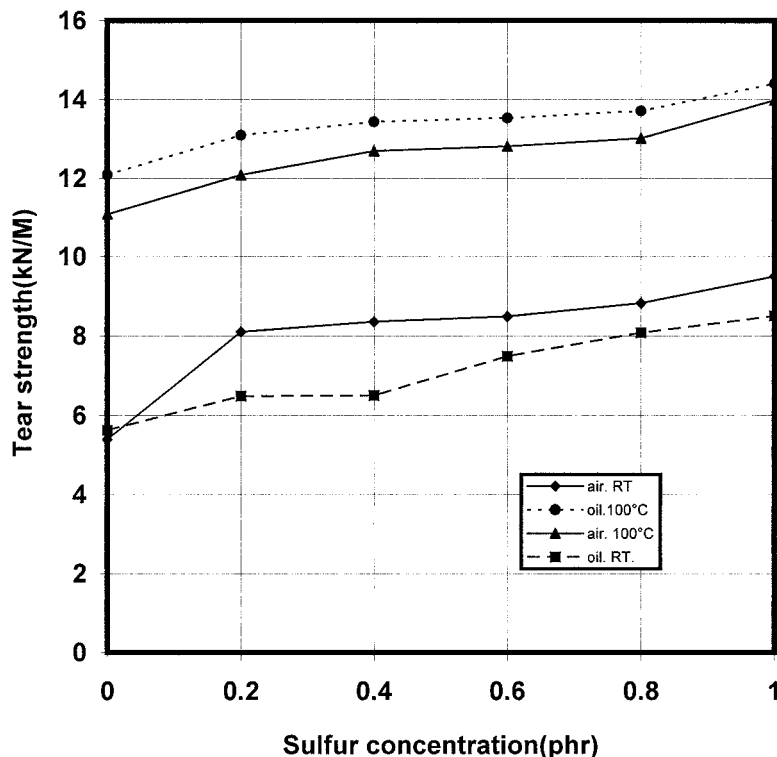


Figure 8 Effect of sulfur loading on tear strength of PVC/ENR TPEs under various exposure conditions.

ure 6. The incorporation of sulfur has to a certain extent increased the M100 of the PVC/ENR TPEs. Since M100 is directly proportional to the number of crosslinks formed,²⁴ the data presented provide a suitable means for assessing the crosslink density. This notion is strongly supported by the decrease in the swelling index presented in Figure 1.

The percent elongation at break (EB) initially increases sharply with 0.2 phr loading of sulfur followed by a gradual increase with subsequent addition (Fig. 7). This trend is expected since the EB is known to increase with increase in the crosslink density for lightly vulcanized rubber.²⁵ The continuous increase in EB with increase in crosslink density indicates that crosslink formation in the ENR phase of the blend has not yet peaked off. This again suggests that the ENR in the blend is lightly crosslinked.

Tear strength also increases with the increase in sulfur loading as shown in Figure 8. Tear strength is a toughness-related property which is known to increase with increase in the crosslink density for lightly crosslinked elastomers.²⁵

Hardness

The continuous increase in hardness with increasing sulfur concentration shown in Figure 9 is also

expected since hardness is known to be strongly related to the crosslink density. The increase could be attributed to the shorter and therefore more rigid network chains as the level of crosslinking increases.

Oil Resistance and Mechanical Properties

The introduction of crosslinks in the plasticized blend as discussed above has also conferred tremendous changes in the oil resistance of the TPEs as elaborated below.

Tensile Strength

Figure 5 also illustrates the effect of different exposure conditions on the tensile strength of PVC/ENR TPEs. It shows that at room temperature the tensile strength of the blend samples immersed in oil is not so different from those exposed to air. This indicates that there is no significant change in the microstructure of the materials. This similarity in the behavior of the blend (uncrosslinked and crosslinked) in air and in oil is an indication of good oil resistance at ambient conditions. The oil resistance of specialty rubbers originate mainly from their polarity, whereby the

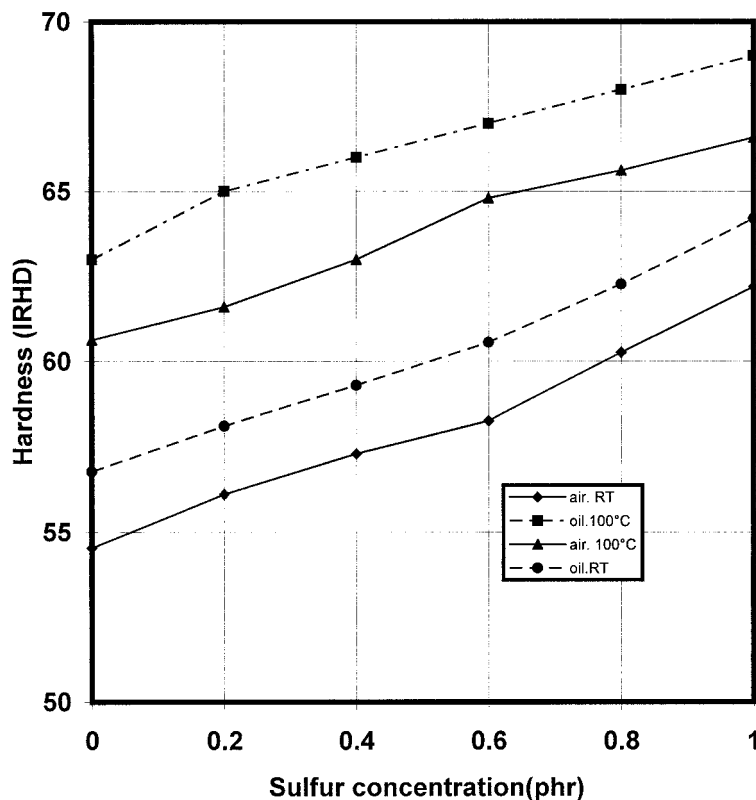


Figure 9 Effect of sulfur loading on hardness of PVC/ENR TPEs under various exposure conditions.

oil resistance is expected to increase with increase in polarity. ENR-50 is a polar rubber due to the presence of the oxirane group and it has been proven to show oil resistance similar to medium-grade NBR.⁴ The oil resistance of plasticized PVC/ENR blends is within the same range as that of plasticized PVC/NBR as demonstrated by Mousa.²⁶

As the immersion temperature is increased to 100°C, a significant increase in tensile strength was observed. In comparison, samples exposed to oil show superior tensile strength to those exposed to air for the same duration. The good correlation between the two tests implies that the exposure of the blends at higher temperature results in the formation of more crosslink network, which eventually enhanced the tensile properties. The ability to sustain the tensile strength upon exposure at 100°C for 168 h is an indication of the good oil resistance of PVC/ENR TPEs, that is, comparable to the mid-performance specialty rubbers.¹⁴ In addition, the tremendous increase in tensile strength can be attributed to postcuring. For example, the tensile strength increased from about 4 MPa for the unvulcanized blend at room temper-

ature to almost 16 MPa for the 1 phr sulfur blend after exposure to oil at 100°C for 168 h. This reveals that dynamic vulcanization has conferred excellent oil resistance to the blend. In other words, this observation demonstrated that the dynamically vulcanized PVC/ENR TPE is capable of withstanding exposure to oil at 100°C for a reasonable period of time. Also, this exposure is synonymous to an accelerated aging test and the observed synergism in tensile strength signals good service life at ambient conditions. Further tests will still be required for prolonged exposure at high temperatures. The increased tensile strength correlates well with the increased crosslink density predicted by the swelling index and modulus at 100 elongation as a consequence of postcuring.

Elongation at Break

Figure 7 presents the variation of the elongation at break (EB) of PVC/ENR with different exposure conditions. Again, the EB of the samples exposed to air at room temperature is more or less the same as that for the sample immersed in oil at room temperature. On the other hand, at

100°C, the EB decreased for all sulfur concentrations. This can be due to the formation of new crosslinks which will shorten the network chains. Thus, the sample cannot be stretched to higher ranges. It is obvious, however, that the EB increases with increase in sulfur concentration to the extent that with 1 phr of sulfur the EB is well above 200%, which is within acceptable range for a TPE of this nature.

Tear Strength

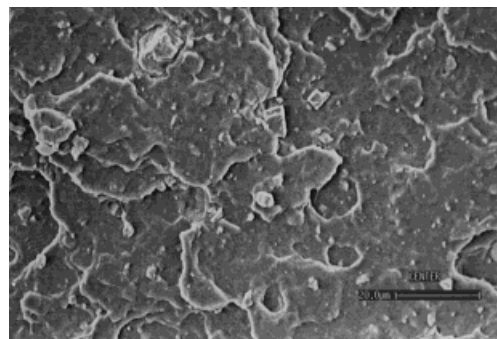
Figure 8 shows the relationship between tear strength and the exposure condition at different concentrations of sulfur. In all cases, there is a gradual increase in tear strength with sulfur loading. As expected, the tear strength of the samples exposed to air and those immersed in oil at room temperature were quite close to each other. This indicates the good oil resistance of the crosslinked PVC/ENR TPEs. The same figure shows that the tear strength has increased significantly when the temperature is increased to 100°C. The superior retention of the tear strength in oil at 100°C compared to air at 100°C is again an indication of good oil resistance. This can be due to the formation of more crosslinks which impart better resistance against tearing forces. Thus, a higher applied load is required to fail the samples.

Hardness

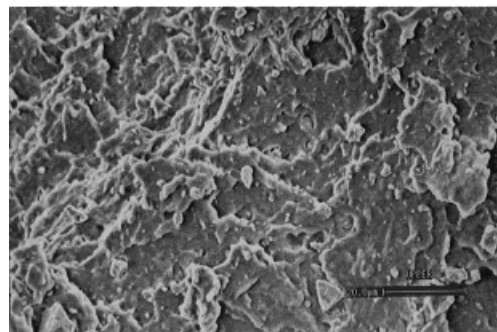
Figure 9 shows the effect of exposure conditions on the hardness of PVC/ENR TPEs. The closeness of the hardness values for the samples in both media at room temperature and 100°C, respectively, is an indication of good oil resistance. It can be seen also that the hardness of the samples at 100°C is higher than that at room temperature. This again may be related to the formation of new crosslinks which increase the crosslink density and, consequently, increase the rigidity of the vulcanizates. In addition, the increase in hardness is closely related to the increase in (M100) presented in Figure 6. This observation is in agreement with an earlier investigation observed by Ishiaku et al.²⁷

Morphological Studies

Figure 10(a) shows the SEM micrograph of the fracture surface for the aged uncrosslinked PVC/ENR sample. The rather smooth fracture plane provides a good indication that the samples fractured in a more brittle manner as compared to



(a)



(b)

Figure 10 SEM micrographs of fractured samples of PVC/ENR TPEs: (a) uncrosslinked, aged; (b) crosslinked, aged.

that of the crosslinked counterpart shown in Figure 10(b). This failure behavior can be related to the absence of a three-dimensional crosslinked network. On the contrary, Figure 10(b) (crosslinked samples) shows that extensive matrix tearing still persists even after the sample has been subjected to thermooxidative aging. The presence of a crosslink network has enabled the samples to be stretched to a greater extent as compared to the uncrosslinked samples. This explains the superior mechanical properties displayed by the dynamically vulcanized PVC/ENR TPEs discussed earlier.

CONCLUSIONS

It can be seen that the oil resistance of the PVC/ENR TPEs has been improved dramatically with the addition of curatives, which leads to the formation of crosslinks. The increase in crosslink density is evident from the swelling index study and Brabender plastograms. The excellent retention of the tensile properties upon exposure to oil

at higher temperature, that is, 100°C, clearly indicates that dynamically vulcanized PVC/ENR TPEs possess good oil resistance. The enhancement in tensile strength, modulus (M100), and tear strength of the samples immersed in oil and exposed to air at 100°C has been attributed to the postcuring effect which produced more crosslinks. The production of these crosslinks has resulted in the hardening and embrittlement of the samples, which, consequently, leads to a reduction of the EB. Thus, it can be concluded that a significant enhancement in mechanical properties coupled with excellent oil resistance has been conferred on the dynamically vulcanized PVC/ENR TPEs.

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