

Study of Rheological Behavior and Miscibility of Epoxidized Natural Rubber Modified Neoprene

Hsien-Tang Chiu, Peir-An Tsai, and Tzu-Chi Cheng

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The Mooney viscosity, curing rates, vulcanization behavior, and the relationship between molecular motion of epoxidized natural rubber (ENR) and neoprene (CR) blends at different blending ratios have been studied. The experimental results of ENR/CR blends show that the Mooney viscosity decreased gradually. Plasticization was most pronounced at an ENR/CR ratio of 75/25 and is thus the easiest to process. Owing to the ring opening of the epoxy group of ENR, the rate of crosslink formation is much faster than that of CR at higher temperature. The vulcanized rate increased with increasing ENR content. The results indicated that 175 °C and 5 min were the optimum processing conditions for ENR/CR blends. The DMA spectra showed a single damping peak for the ENR/CR blends, which suggests that ENR and CR are miscible. As seen in the Arrhenius plot of frequency against T_g , the activation energy increased with increasing ENR contents. This suggests the existence of interpenetration of these two rubber molecular networks.

Keywords activation energy, damping peak, epoxidized natural rubber, Mooney viscosity, neoprene

1. Introduction

The blending of two types of rubber can improve the mechanical properties of the rubber, achieve better processibility, and reduce production costs. For example, blending with neoprene (CR) can reduce the flammability and improve the solvent resistance (Ref 1). When blended with ethylene-propylene-diene terpolymer (EPDM) or chlorosulfonated polyethylene; hypalon (CSM), ozone resistance is improved (Ref 2). Blending with natural rubber (NR) can improve the processibility of synthetic rubber. Blending with styrene-butadiene rubber (SBR) can reduce the cost. The primary consideration behind any rubber blend is the miscibility between ingredients, the vulcanization, and the basic physical properties.

Epoxidized natural rubber (ENR) is a recently developed rubber, obtained by epoxidizing natural rubber with peracetic acid (Ref 3, 4). Both ENR and NR have strain-crystalline structure, but ENR is more antioxidizing than NR. In addition, ENR has good features, such as oil resistance, low gas permeability, and high damping. The Mooney viscosity (ML_{1+4} , 100 °C) of NR is between 50 and 90, and that of ENR is between 70 and 100. This higher initial viscosity makes the processing of ENR more difficult than that of NR (Ref 5). Furthermore, during the vulcanization of ENR, the epoxy ring will be opened by sulfonic acid to form polysulfur crosslinks, causing aging to occur. Therefore, the vulcanization of ENR is not suitable through conventional means; instead, an effective vulcanization (EV), or semi-EV, is suggested (Ref 6).

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CR is one of the earliest synthetic rubbers; it was developed by Du Pont in 1931 (Ref 7). The Mooney viscosity (ML_{1+4} , 100 °C) of CR is between 34 and 130, depending on the specification. Vulcanized CR has excellent oil resistance, thermal stability, self-extinguishability, and ozone resistance (Ref 8). Therefore, CR remains an important material.

The miscibility of blending compounds can be examined by means of dynamic mechanical analysis (DMA). If these compounds are immiscible, two damping characteristic peaks will appear. If they are partially miscible, then these two peaks will partially overlap. When they are miscible, only one peak will be observed (Ref 9). Results of blending ENR with NR as shown by differential scanning calorimetry (DSC) and DMA reveal that they are immiscible (Ref 10). When ENR/Hyplon blends are studied (Ref 11), although they can form self-crosslinks, DMA results still indicate that they are only partially miscible. On the other hand, the DMA results of ENR/PVC have only one peak, thus they are miscible (Ref 12).

In this work, ENR and CR were blended together at various ratios to study the effect of blending ratio on processibility, plasticization, curing rate, and vulcanization. Through a series of investigations, the interaction between rubber molecular chains can be understood, and the knowledge base for choosing the optimum composition and the processing conditions can be increased. In addition, the miscibility of ENR/CR using DMA is studied herein, and interactions between molecules with respect to activation energy are analyzed at different frequencies.

2. Experimental

2.1 Blending

Mastication of ENR (ENR-50, Malaysian Rubber Producers' Research Association), CR (ES-2-16K, Du Pont), vulcanizing agent, accelerator, and other related ingredients was carried out in a pressurized kneader (SYD-5, Star-King Enterprise Co., Taiwan) for 17 min under a rotation rate of 77 rpm. Each sample's composition is listed in Table 1. The addition se-

Table 1 Composition of ENR/CR blends

Ingredient (phr)	EC1	EC2	EC3	EC4	EC5
ENR	100	75	50	25	0
CR	0	25	50	75	100
HAF	25	25	25	25	25
Stearic acid	0.66	0.66	0.66	0.66	0.66
CaCO ₃	0.63	0.63	0.63	0.63	0.63
DM	0.7	0.7	0.7	0.7	0.7
M	0.2	0.2	0.2	0.2	0.2
NA-22	0	0.5	0.5	0.5	0.5
PBN	0	1	1	1	1
MgO	0	4	4	4	4
ZnO	5	5	5	5	5
S ₈	2.5	2.5	2.5	2.5	2.5

phr, part per hundred parts of rubber; ENR, epoxidized natural rubber; CR, neoprene; HAF, carbon black (N330); CaCO₃, calcium carbonate; DM, 2-benzothiazole disulfide; M, 2-mercaptobenzothiazole; NA-22, ethylene thiourea (ETU); PBN, phenyl-naphthylamine; MgO, magnesium oxide; ZnO, zinc oxide; S₈, sulfur

quence of these ingredients is given in Table 2. The blended rubber was removed and cooled at room temperature for 30 min and then mixed using a two-roll mixer. During mixing, the gap between rollers was narrowed from 20 to 8 mm and the movement of the narrowing was repeated 20-30 times for a rolling step. Green rubber was prepared.

2.2 Measurement of Mooney Viscosity (ML_{1+4} , 100 °C)

The measurement was carried out using a Mooney scorch tester (HI-8725, Hungta Co., Taiwan). Two pieces of greens, of 1.5" (3.81 cm) in diameter, were placed above and beneath a 1.5" disk. According to ASTM D1646, the Mooney viscosity was measured at 100 °C, preheated for 1 min, and tested for 4 min, at a rotational speed of 2 rpm, which gave an average shear rate of 1.6 s⁻¹.

2.3 Determination of Scorch Time

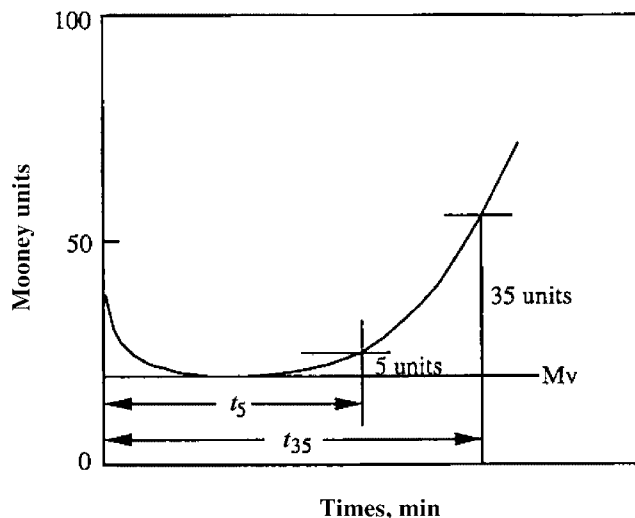
The specimens and the tester are the same as those mentioned in the previous section. The measurement was carried out at 100, 125, and 150 °C. The scorch time t_5 and the cure index Δt at each temperature were then determined from the Mooney viscosity curve, similar to Fig. 1, where t_5 and t_{35} are the times when the Mooney viscosity equals the minimum viscosity (Mv) plus 5 and 35 units, respectively, and Δt is their difference.

2.4 Curing Behavior During Vulcanization

The curing behavior during vulcanization was observed using a rheometer (MDR-2000, Monsanto Co., USA). A curing curve similar to Fig. 2 was obtained by placing 4-5 g of the mixed ingredients in the disk and measuring the torque for 40 min at different temperatures: 165, 175, and 185 °C. In this figure, the following quantities can be obtained: the minimum torque M_L , the equilibrium torque M_{HF} , the precuring time t_{s2} , and the optimum cure time t_{c90} .

2.5 Vulcanization

The hot press was heated to 175 °C, and the mold was placed in the press for a short time. Green rubber was put into the mold, which was then closed and pressurized to 150 kg/cm² (14.7 MPa). For 2 mm thick specimens, 125 g of green rubber was placed in a mold measuring 250 × 250 mm and heated at

**Fig. 1** Typical Mooney scorch and viscosity curve**Table 2** Banbury mixing time of ENR/CR blends

Addition sequence	Elapsed time, min	Holding time, min
Sequence a		
ENR-50	0-5	5
Filler (ZnO, CaCO ₃ , stearic acid, etc.)	5-6	1
HAF	6-9	3
DM, M, S ₈	9-10	1
Blending	10-17	7
Total	17	17
Sequence b		
ENR-50/CR	0-5	5
Filler (MgO, CaCO ₃ , stearic acid, PBN, etc.)	5-6	1
HAF	6-9	3
DM, M, S ₈ , NA-22	9-10	1
Blending	10-17	7
Total	17	17
Sequence c		
CR	0-5	5
Filler (MgO, CaCO ₃ , stearic acid, PBN, etc.)	5-6	1
HAF	6-9	3
DM, M, S ₈ , NA-22	9-10	1
Blending	10-17	7
Total	17	17

175 °C for 5 min. For 12.5 mm thick specimens, 680 g of green rubber was placed in the mold and heated for 12 min.

2.6 Dynamical Mechanical Analysis

Dynamic mechanical analysis was carried out using a dynamic mechanical tester (Qualimeter 3031, Gabo, Germany). The dimensions of the specimens are 2 × 10 × 6 mm. Frequencies used in the measurement were 1, 10, and 100 Hz. Scanning was done at temperatures from -70 to 70 °C at a rate of 2 °C/min.

2.7 Activation Energy

Arrhenius plots were plotted according to the data from the DMA measurement. The activation energy was determined from the slope of the straight line.

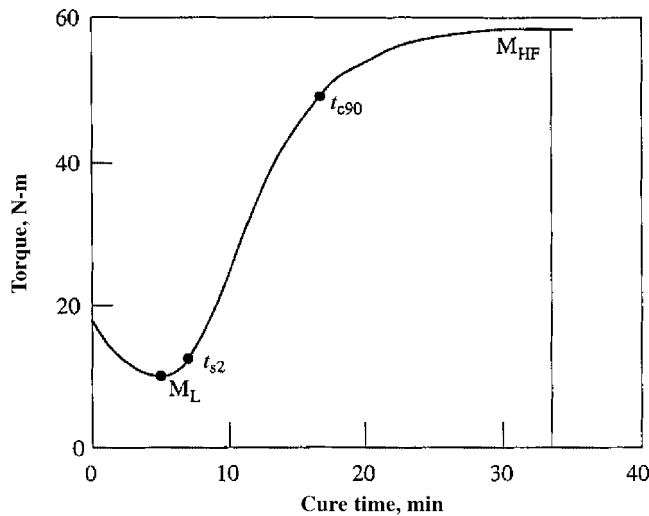


Fig. 2 Typical Monsanto curing curve

3. Results and Discussion

3.1 Plasticization

The processing of rubber compounds is performed under constant temperature and pressure. Thus, the processibility of rubber can be described using the initial fluidity, the intermediate vulcanization rate, and the final vulcanization. Factors affecting the fluidity include the type of the rubber and the composition. The fluidity of the rubber can be attributed to the plasticization. As suggested by Einhorn (Ref 13), one index for evaluating the initial fluidity is the Banbury processibility index, which is ML_{1+4} at 100 °C. This effectively evaluates the initial plasticization of the rubber after mastication in a Banbury masticator.

From the curve in Fig. 3, the Mooney viscosity (ML_{1+4} , 100 °C) of ENR is 72 (Mooney units) while that of CR is 93 (Mooney units), indicating that the initial fluidity of CR is lower than that of ENR. The stiff molecular chains of CR were lubricated by the blending of ENR. Viscosity decreased with ENR content. At an ENR/CR blending ratio of 75/25, the viscosity was the lowest, the fluidity was the highest, and the effect of ENR on the plasticization of CR was the most pronounced. The improvement in CR processibility due to the blending of ENR is well illustrated in Fig. 4. This is similar to the lowering of T_g of polymeric materials due to the addition of plasticizer (Ref 14).

3.2 Curing Rate

Due to the elevated temperature, crosslinks begin to occur. The initial rate of crosslink formation can affect the properties of the product. This can be evaluated by means of the Mooney scorch time.

From the Mooney scorch curve shown in Fig. 5, the scorch time t_5 and the cure index Δt of ENR are 4.7 and 0.97 min, respectively, and those of CR are 18.75 and 3.08 min, respectively. As can be seen, the pre-curing time of ENR is shorter than that of CR and is thus more prone to crosslinking. When heated during vulcanization, the epoxy group of ENR can be activated and opened by sulfonic acid, thus facilitating the formation of crosslinks. On the other hand, CR can be vulcanized in the presence of ZnO, and the resulting $ZnCl_2$ can be absorbed by MgO, hence lengthening the t_5 of CR (Ref 15) and

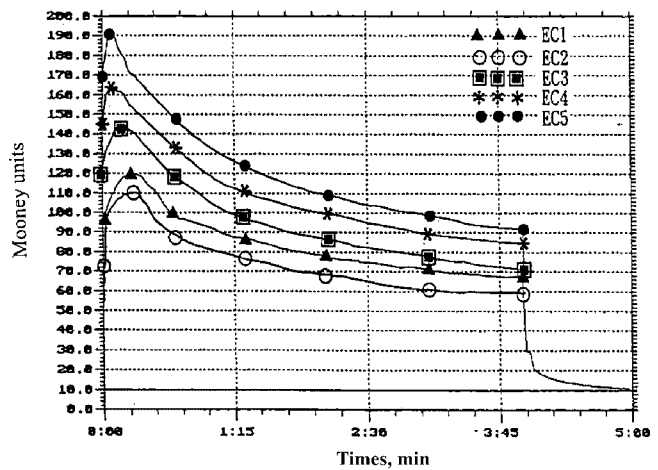


Fig. 3 Mooney viscosity curves of ENR/CR blends at 100 °C

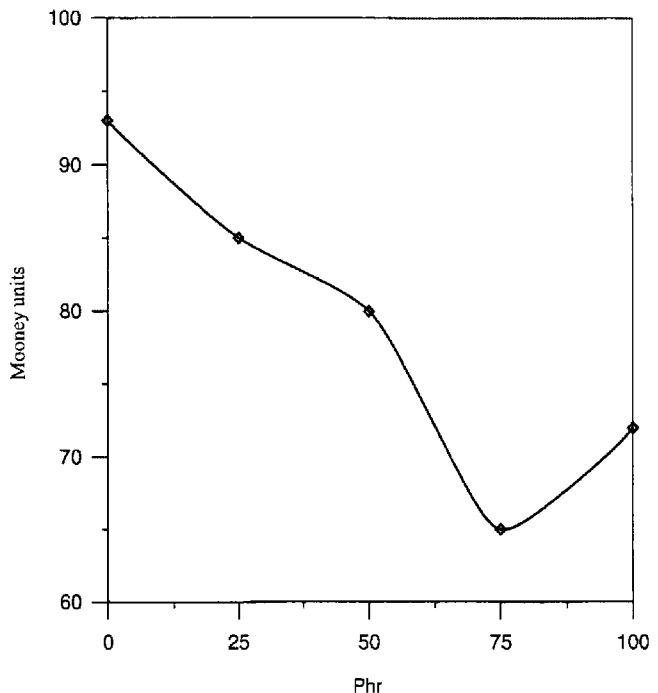


Fig. 4 Effect of ENR content on Mooney viscosity of ENR/CR blends

decreasing the curing rate. In addition, as seen in Fig. 5, the curing rate of ENR/CR blends increases with the ENR content.

The effect of ENR content on the scorch time t_5 is observed in Fig. 6. During thermal compression, the vulcanization of rubber is affected by the thermal history; hence t_5 can affect directly the fluidity and thus the homogeneity of the product. The scorch time t_5 should be slightly longer than the accumulated maximum thermal history. Figure 6 shows that t_5 decreases with increasing ENR content, and hence, the curing rate of the blended rubber increases. With increasing temperature, the required energy of crosslink formation is gradually reached, and hence, t_5 is shortened. The effect of ENR content on the cure index is shown in Fig. 7. Because the activation of the epoxy group accelerates the rate of crosslink formation, the curing rate is hence increased with ENR content. This trend is most pronounced at 100 °C.

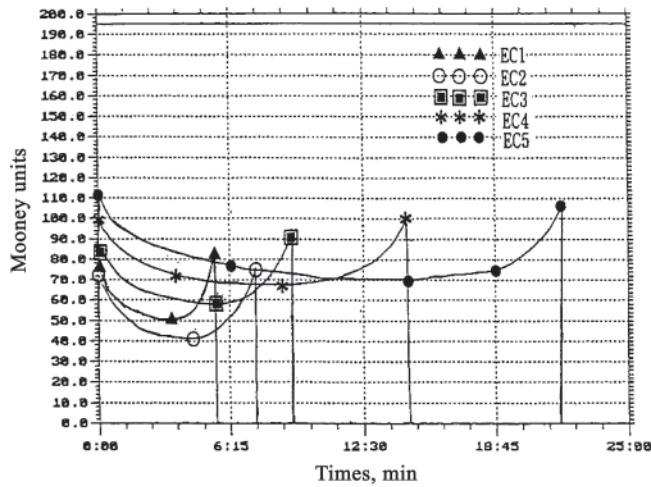


Fig. 5 Mooney scorch curves of ENR/CR blends at 125 °C

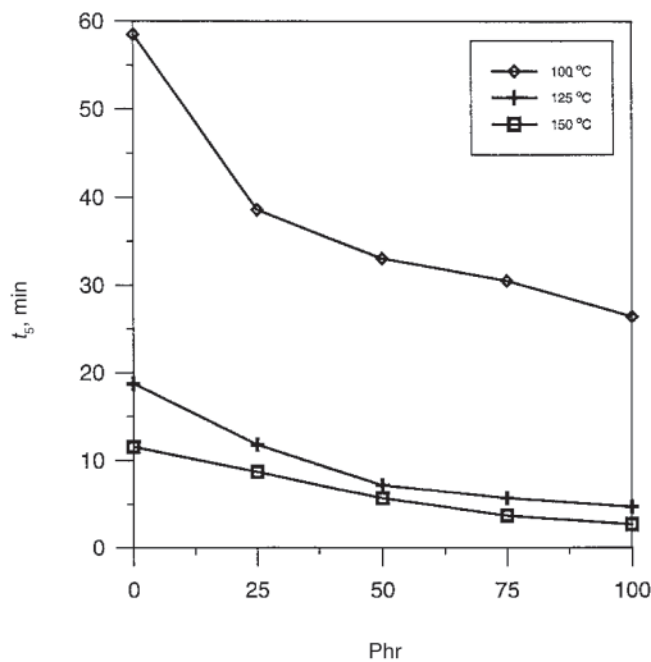


Fig. 6 Effect of the ENR content on Mooney scorch time at different temperature

3.3 Vulcanization of ENR/CR Blends

The rheological curve of vulcanization exhibits three types of behavior: (a) curve ascends without reaching the equilibrium point; (b) curve reaches the equilibrium torque; (c) curve descends after it reaches the maximum torque (“reversion phenomenon”). When this rheological curve reaches the equilibrium point without the reversion phenomenon, the processing condition is the optimum, and the temperature is the optimum processing temperature.

The rheographs of ENR/CR at 165, 175, and 185 °C are shown in Fig. 8, 9, and 10, indicating that the torque increases with cure time. This is due to the formation of crosslinks. Because of the ring-opening of the epoxy group of ENR, the rate of crosslink formation is much faster than that of CR. At the same temperature, with the introduction of ENR, crosslinks of CR are increased. In addition, crosslinks are also formed

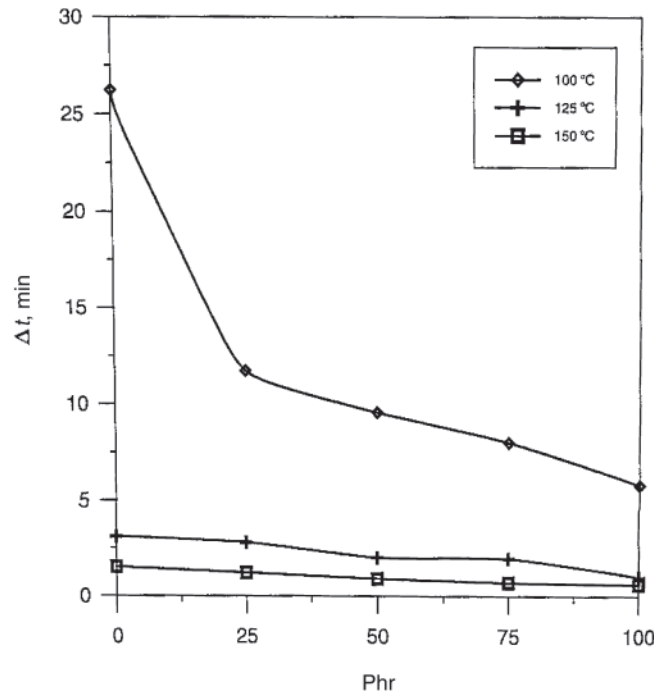


Fig. 7 Cure index of ENR/CR blends at different temperature

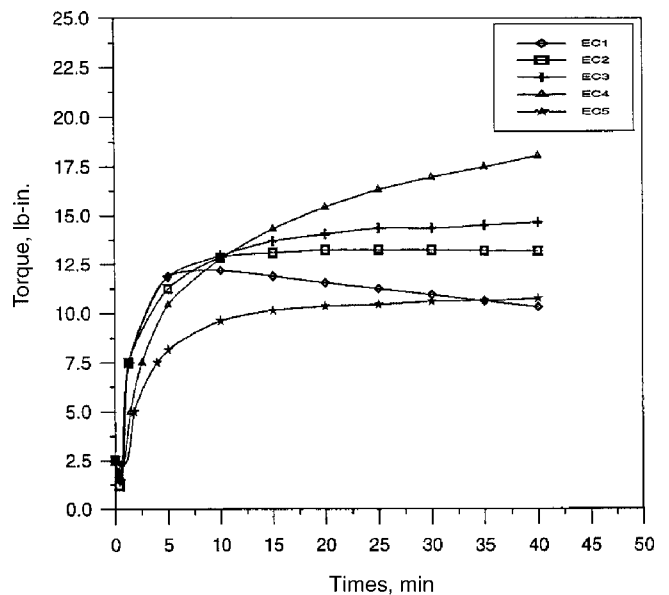


Fig. 8 Rheographs of ENR/CR blends at 165 °C

between ENR and CR. Therefore, the crosslink density of the blended rubber is increased. It was reported in the literature that ENR/Hypon has a maximum torque for a blend ratio of 50/50 (Ref 16). Blending of ENR/NR shows similar behavior (Ref 17). As for ENR/CR blending, the torque increased with ENR content and reached the maximum value at a blending ratio of 75/25.

According to Fig. 8-10, the optimum processing conditions for the blending of ENR/CR is 175 °C and 5 min. At 165 °C, it is difficult for the curves of these compositions to reach steady state. On the other hand, at 185 °C, the rheographs are dominated by a descending trend, which is attributed to aging.

The effect of blending ratio on the optimum cure time t_{c90} is

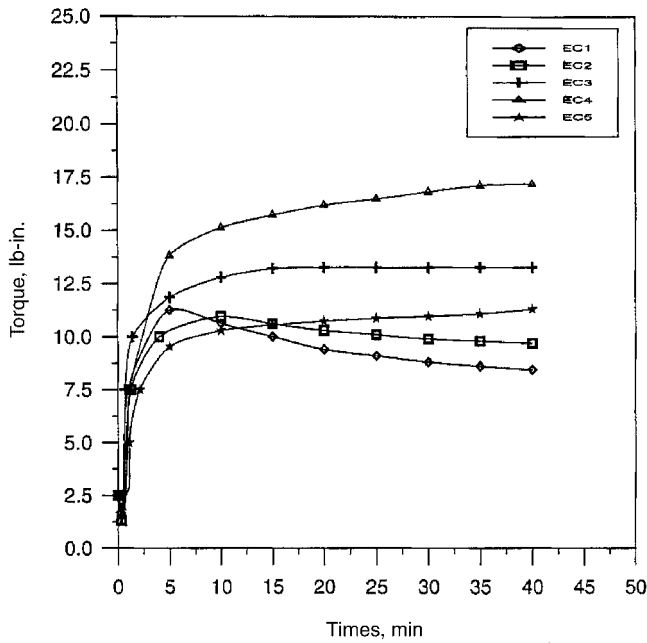


Fig. 9 Rheographs of ENR/CR blends at 175 °C

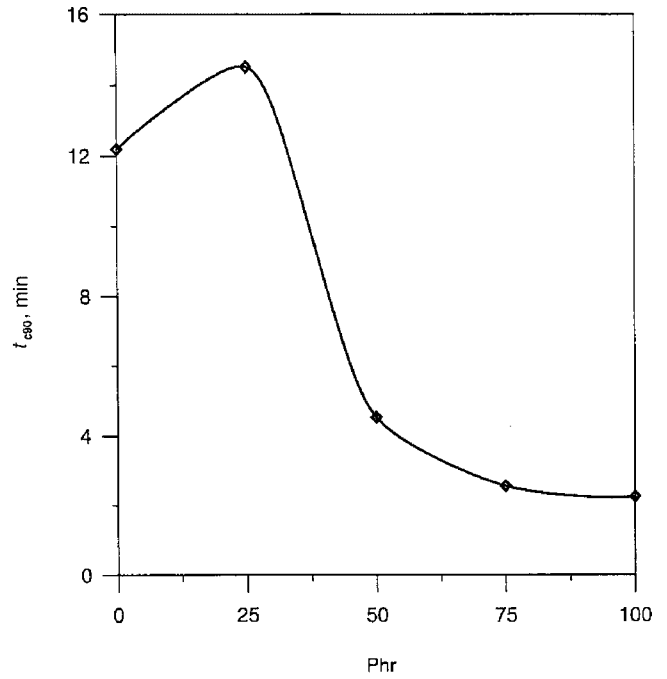


Fig. 11 Effect of ENR content on t_{c90} of ENR/CR blends at 175 °C

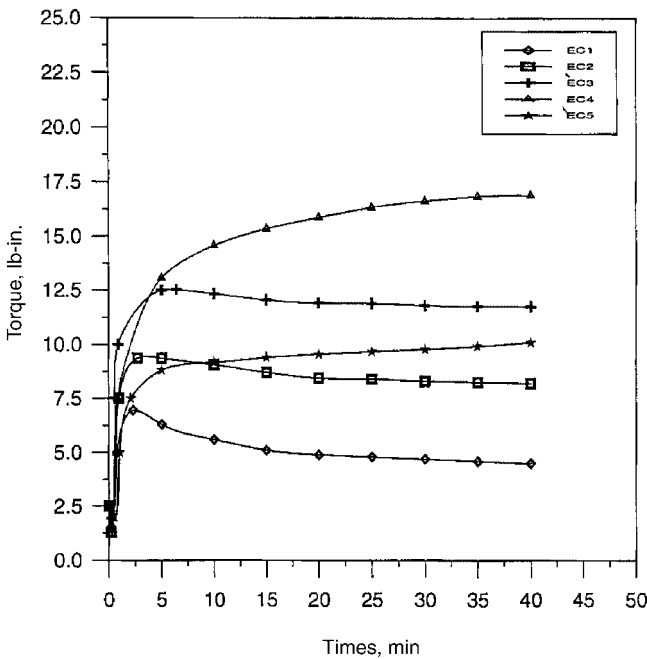
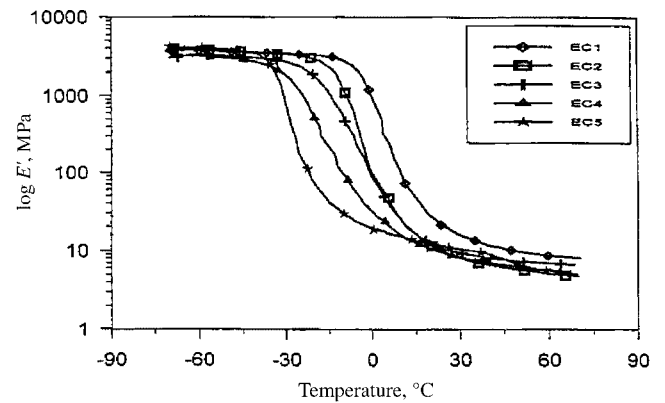


Fig. 10 Rheographs of ENR/CR blends at 185 °C

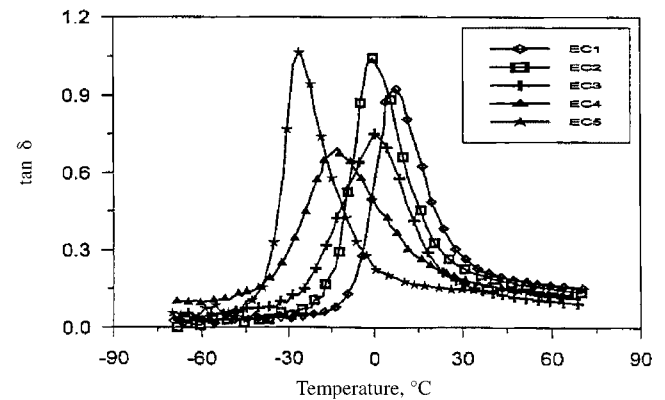
shown in Fig. 11. As can be seen, pure ENR has a shorter t_{c90} than CR, and t_{c90} is related to the curing rate and the equilibrium torque. Experimental results show that t_{c90} decreased with the ENR content and reached the maximum at an ENR/CR ratio of 25/75.

3.4 DMA and Miscibility

The loss factor, $\tan \delta$, is most sensitive to the motion of the molecular chain. The temperature corresponding to the peak of $\tan \delta$ is the T_g of the material (Ref 18). Figure 12 shows the temperature spectra of storage modulus E' and $\tan \delta$ of ENR/CR blends at 1 Hz. As can be seen, ENR and CR have similar



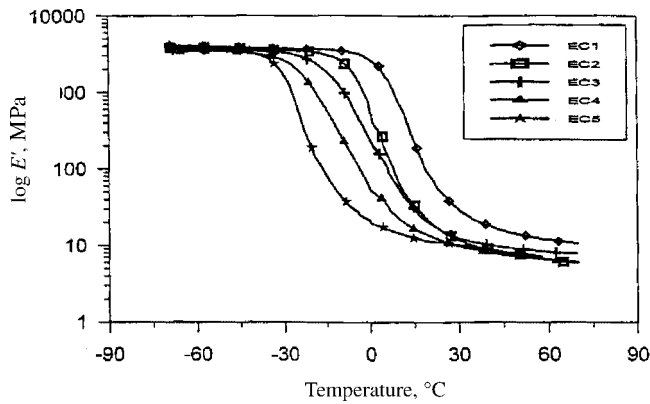
(a)



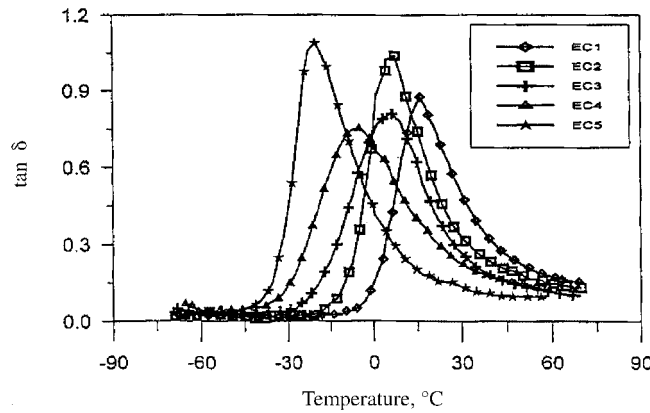
(b)

Fig. 12 Dynamic mechanical properties of ENR/CR blends at 1 Hz: (a) $\log E'$ versus temperature; (b) $\tan \delta$ versus temperature

E' at lower temperature. At higher temperature, E' increases with increasing ENR content. In addition, there is only one damping peak (T_g) for each blend, and T_g increases (the damping peak shifts toward higher temperature) with increasing



(a)



(b)

Fig. 13 Dynamic mechanical properties of ENR/CR blends at 10 Hz: (a) $\log E'$ versus temperature; (b) $\tan \delta$ versus temperature

ENR content. Similar trends were observed for the results at 10 and 100 Hz, as shown in Fig. 13 and 14.

Figure 12(b) shows that the height of damping peak increases with increasing ENR content and reaches a maximum at an ENR/CR blending ratio of 75/25. This indicates that ENR has higher damping than CR. By blending with ENR, it is possible to improve the damping performance of CR. Similarly, the same trend is also observed in Fig. 13(b) and 14(b).

As shown in Fig. 15, T_g increases with increasing ENR content. Interactions between molecules increase with increasing ENR content. Due to the entangling of networks of both ENR and CR, coordinated motion occurs, and thus a single damping peak is observed. In other words, ENR and CR are miscible.

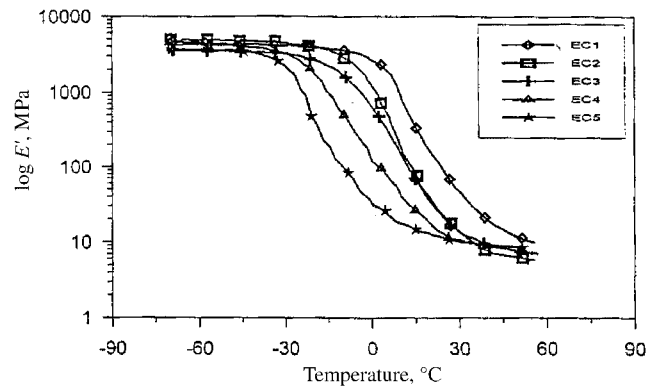
3.5 Activation Energy

The motion of polymer molecular chain is a thermal-activation process. Below T_g , the main chain molecules are frozen. The mobility increases with rising temperature, and the required activation energy decreases accordingly. Therefore, for rigid or higher- T_g materials, the activation energy is higher. According to the Arrhenius equation, the activation energy and the frequency have the following correlation:

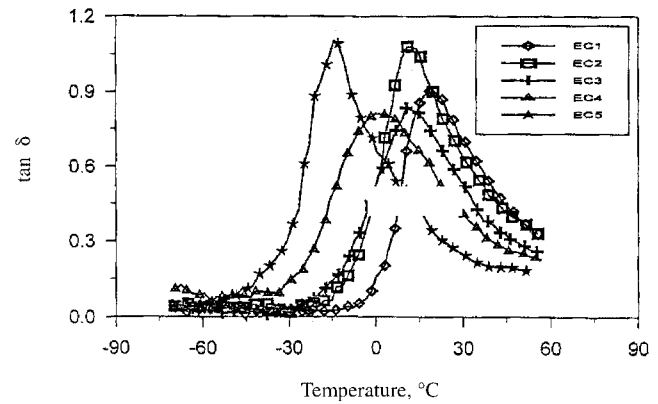
$$f = A \exp(-E_a/RT) \quad (\text{Eq 1})$$

or

$$\ln f = \ln A - E_a/RT \quad (\text{Eq 2})$$



(a)



(b)

Fig. 14 Dynamic mechanical properties of ENR/CR blends at 100 Hz: (a) $\log E'$ versus temperature; (b) $\tan \delta$ versus temperature

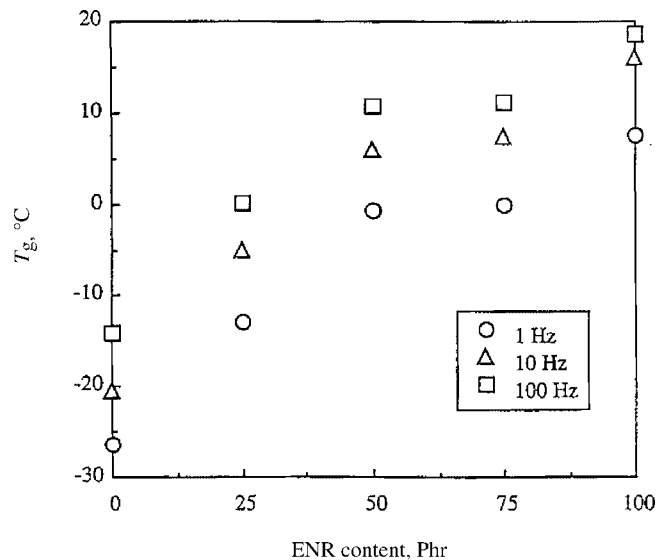


Fig. 15 Effect of ENR content on T_g

where f is the frequency, E_a is the activation energy, R is the gas constant, T is temperature (in K), and A is a constant or the frequency factor. The Arrhenius plots of frequency versus T_g of five such blends are shown in Fig. 16. The effect of ENR content on the activation energy is shown in Fig. 17, which shows that the activation energy increases with the increasing ENR content. This indicates that, with increasing ENR content,

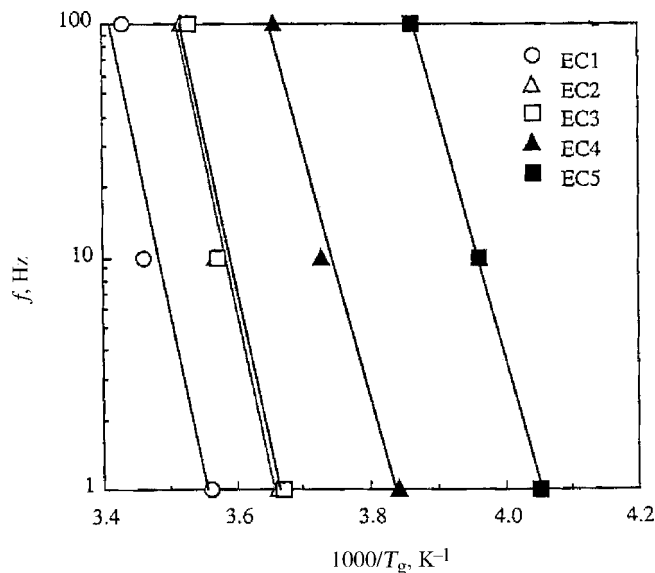


Fig. 16 Arrhenius plot of frequency versus T_g of ENR/CR blends

the required activation energy for molecular motion increases, thus shifting the T_g toward higher temperature. The increase in activation energy is caused by the restriction of the CR network by the ENR network. This suggests interpenetration of these two rubber molecular networks.

4. Conclusions

In this work, the Mooney viscosity, scorch curve, curing curve, and dynamic mechanical properties of ENR/CR blends have been measured. From these measurement results, the following conclusions can be drawn:

- The initial fluidity increased with the ENR content, and reached the maximum at an ENR/CR ratio of 75/25.
- With the ring-opening reaction of the epoxy group of ENR, the curing rate increased with the ENR content. The scorch time became shorter with the increase in temperature. The curing rate also increased with increasing temperature.
- The t_{c90} of ENR/CR blends decreased with the ENR content and reached its maximum at an ENR/CR ratio of 25/75.
- In ENR/CR blends, the networks interacted. The DMA spectra of these blends had only one damping peak, suggesting miscibility of ENR and CR. With increasing ENR content, the T_g also increased.
- The height of the damping peak increases with increasing ENR content and reaches a maximum at an ENR content of 75 phr (parts per hundred parts of rubber). This indicates that ENR has higher damping than CR. By blending with ENR, it is possible to improve the damping performance of CR.
- The activation energy increased with increasing ENR content. This indicates that, with increasing ENR content, the required activation energy for molecular motion increases, thus shifting the T_g toward higher temperature.

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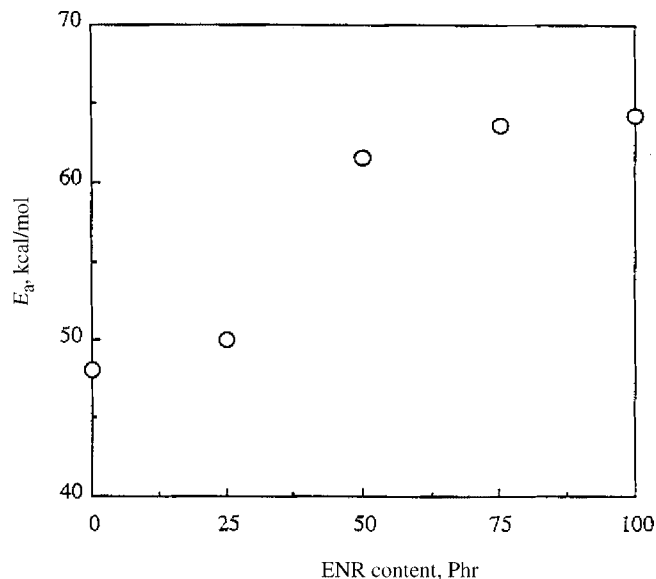


Fig. 17 Effect of ENR content on the activation energy of ENR/CR blends

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