Internal Mixer Studies of Poly(vinyl Chloride) / Epoxidized Natural Rubber Blends

ZAINAL A. NASIR and CHANTERA T. RATNAM, *School of Industrial Technology, University of Science, 11800, Minden, Penang, Malaysia*

Synopsis

Blends of polyvinyl chloride/epoxidized natural rubber (PVC/ENR) blends were studied. Their rheological properties were studied with a Brabrender Plasticorder. It was found that the rheological properties of any PVC/ENR blends are governed by their blending conditions. To ensure homogenous PVC/ENR blends, adequate and suitable blending conditions must be utilized. PVC thermoplastics phases enhances rigidity while ENR rubbery phases imparts flexibility and processability to the blends. With premixing, Ba/Cd/Zn-based PVC stabilizer is effective in stabilizing the PVC/ENR blends. Their properties are further enhanced by the addition of curatives.

INTRODUCTION

Polymer modification by blending two or more different polymers to obtain any desired properties is now a common practice. Among such blends are those which are made up of thermoplastics and elastomers, commonly known as thermoelastomers. Numerous studies[1-6] on different thermoplastics and elastomer systems have been conducted. PVC-based thermoelastomers, mainly with synthetic rubbers, are not uncommon. It is known[1,7,8] that PVC with acrylonitrile rubber blends gives rise to some remarkable properties, which include ease of processing, exceptional ozone and fire resistances, good physical properties, and brilliant colors.

The commercialization of ENR which is advocated[9] to be comparable or superior to synthetic rubbers especially in engineering applications, and the availability of commercial PVC-based thermoelastomers have prompted us to look into similar possibilities with ENR. Our earlier studies[10] have shown that PVC imparts better tensile strengths and chemical resistances while ENR enhances flexibility and tear strength to the blends. We have also found out that only MgO/ZnO/St acid-based stabilizer is effective in stabilizing the PVC phases, whereas common PVC stabilizers fail considerably. Similar observations[7,8] have been reported with PVC/NBR blends. Here, similar studies were carried out; however, the stabilizer was premixed with the PVC before blending. The effects of composition, temperature, and rotor speed on rheological properties are described. The physical and aging properties of the blends are also presented.

TABLE I
Recipes of Poly(vinyl Chloride)/Epoxidized Natural Rubber Blends

Materials	Blends							
Poly(vinyl chloride) (phr)	0	10	20	30	40	50	60	70
Epoxidized natural rubber,								
ENR50 (phr)	100	90	80	70	60	50	40	30
Barium/cadmium/zinc (phr PVC)	4	4	4	4	4	4	4	4
Curatives[a] (phr ENR50) Sulfur, 1.5;								
zinc oxide, 2.0; stearic acid, 1.0; MBTS,[b] 1.5; TMTD,[c] 0.5								

[a] Curatives were added before molding of blends.
[b] 2,2-Dibenzothiazole disulfide.
[c] Dithiocarbamate tetramethyltiuram disulfide.

EXPERIMENTAL

Epoxidized natural rubber, grade "ENR50," was supplied by Rubber Research Institute of Malaysia; poly(vinyl chloride) with a 60 K value, grade "Mercion 60" was purchased from Malayan-Electro Chemical (M) Ltd.; Ba/Cd/Zn, "Irgastab BC 455s," was supplied from Ciba-Geigy (M) Ltd.; other ingredients, viz., sulfur, ZnO, stearic acid, and accelerators, were bought from Bayer (M) Ltd. The full recipes are given in Table I.

PVC and stabilizer were premixed with a Kitmah powder blender at 1000 rpm and 60°C for about 10 min. Blending with the Brabrender was as follows: When the desired temperature was reached, ENR was charged into the mixing chamber and was mixed for 1 min. The PVC compound was then added, and blending was carried on for a further 9 min. A particular blending condition (150°C and 50 rpm) was utilized to study the effect of composition, whereas for effect of temperature and rotor speed, only the 50% PVC blends were chosen. They were blended at 50 rpm, 120–180°C and 20–45 rpm, 150°C, respectively.

To examine the physical properties and aging, curatives were added to the blends on a two-roll mill at about 60°C. The cure times (t_{90}) were determined with a Monsanto rheometer at 150°C which were then used to mold the samples. Samples of different shapes were either cut or molded directly, depending on tests. Physical properties (tensile strength, elongation at break, modulus 100, tear strength) were tested with an Instron universal tester while hardness was tested with a Wallace hardness tester. For aging, samples were aged in an oven at 70°C for 7 days before testing.

RESULTS AND DISCUSSION

Numerous studies[5,7,8] on the rheological properties of blends with a Brabrender have been carried out. Here, the effects of composition, blending temperature, and rotor speed on the rheological properties have been studied.

Effects of Composition

The mixing torque–time curves of blends with varying compositions obtained are given in Figure 1. Under similar conditions, as expected, the times to melt and fuse the PVC particles, hence formation of homogenous PVC/ENR
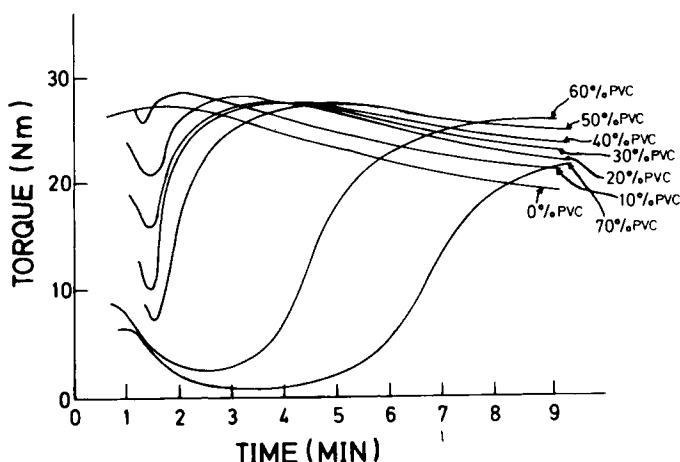
Fig. 1. Mixing torque-time curves at varying compositions of PVC/ENR blends.

blends, change with compositions. For the ENR dominantly blends, viz., 10–40% PVC, homogenous blends are formed after about 5 min of blending. Prolonging the blending to 10 min as has been done results in degradations of both the PVC and the ENR phases, seen from the drops of mixing torques. In PVC dominantly blends, viz., 60–70% PVC, the situations are somewhat different. Melting and fusion of the PVC particles are incomplete, even after 10 min, hence the continuing rise of mixing torques. These observations show the importance of suitable blending conditions to ensure formation of homogenous PVC/ENR blends. Similar observations[10] were also made with the unpremixed PVC/ENR blends. George et al.,[7,11] who studied the PVC/NBR blends also with a Brabrender, have also witnessed a similar trend.

Goodrich and Porter[12] and later Das[13] proposed a method in which torques obtained from a Brabrender can be converted to standard rheological properties with the following equations:

$$\sigma_a = K\tau_a \tag{1}$$

$$\dot{\gamma}_a = K'S \tag{2}$$

$$S = 2\pi/60 \times R \tag{3}$$

where σ_a is the apparent shear stress, τ_a is the apparent mixing torque measured, $\dot{\gamma}_a$ is the apparent shear strain rate, S is the angular rotor speed, R is the rotor speed used, and K and K' are the instrumental constants. The apparent shear viscosity η_a is then given by

$$\eta_a = \sigma_a/\dot{\gamma}_a = K\tau_a/K'S = Q\tau_a/S \tag{4}$$
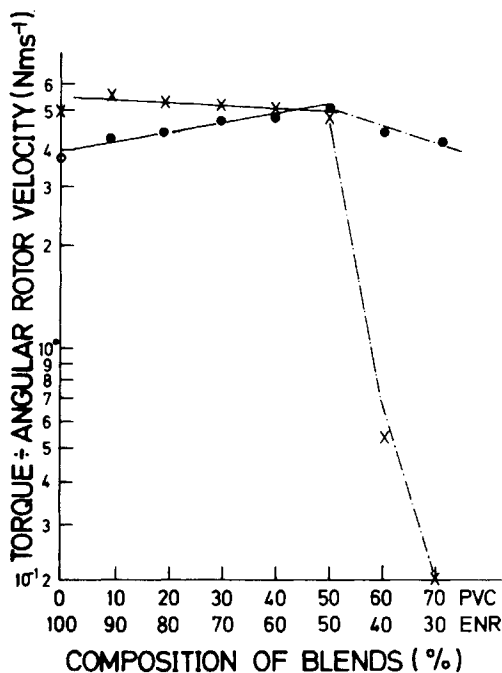
where $Q = K/K'$.

Fig. 2.   Effect of blend's ratio on τ_a/S values: (X) 3 min mixing; (●) 9 min mixing.

Since eq. (4) shows that τ_a/S is directly proportional to the apparent shear viscosity, therefore, τ_a/S can be used to represent the apparent shear viscosity. Figure 2 shows the effect of composition on τ_a/S, taking τ_a after 3 and 9 min. After 3 min, blends with less than 50% PVC must have undergone slight changes; some of the PVC particles have started to melt and fuse. However, for the 60 and 70% PVC blends, the PVC particles obviously have not undergone any changes; hence, they fail to mix with the ENR phases. This explains the sudden drop of the τ_a/S values. A different situation is observed after 9 min blending. Here, all PVC particles have undergone almost complete fusions, consequently, forming homogenous blends, especially those of the ENR-dominant blends. However, in the PVC dominant blends, some of the PVC particles are still unfused, hence explaining the slight drops of τ_a/S.

It is clear that to obtain homogenous PVC/ENR blends of any compositions, suitable blending conditions must be utilized. The blending conditions which were used here are only suitable for 40–60% blends. For rubber-dominant blends, it might cause degradations to the PVC phases, albeit the initial homogenous blends obtained. For example, the 30% PVC blends if blended at 150°C and 50 rpm, it must be blended for about 4 min only, not 10 min as used here. For the PVC-dominant blends, the blending conditions are still inadequate. Another interesting feature which is noted is the plasticization effect of ENR, especially in rubber-dominant blends. Here increasing the ENR, decreases the τ_a/S values. It is known[7,8] that the plasticization action of the rubber component in the blend normally can impart flexibility, extensibility, and ease of processing.
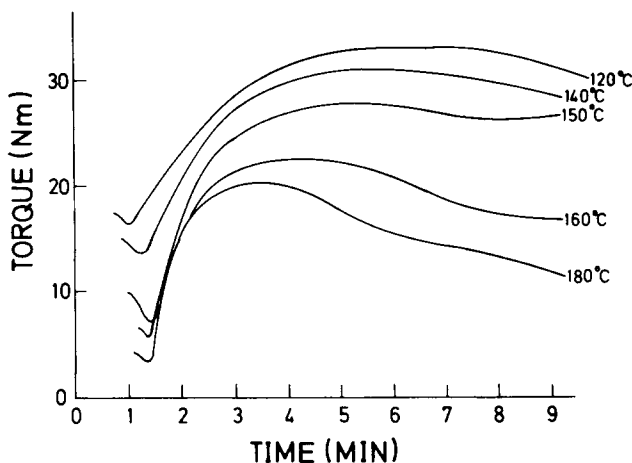
Fig. 3. Mixing torque-time curves of 50% PVC/ENR blends mixed at different temperatures.

Effect of Blending Temperatures

The mixing torque–time curves which were obtained at varying temperatures are shown in Figure 3. As expected, the mixing torque decreases with rising temperature. The times for the 50% PVC blends to attain the homogenous states are dependent on the temperatures. It is evident that 10 min of blending is probably too long for the 160–180°C, because it might have caused degradations to occur, seen from the drops in mixing torques.

An Arrhenius type of relationship can be obtained by plotting $\log \tau_a/S$ vs. $1/T$, again taking torques after 3 and 9 min. (Fig. 4). For the data corresponding to 3 min of mixing, a linear relationship was obtained. This is not surprising since minimum changes must have occurred, especially at lower temperatures. However, after 9 min of mixing, a dual relationship was obtained, which can be due to a morphological transition from multiphase structures to a single compatible phase structure of PVC and ENR. Widmayer and Meyer[14] have proposed a concept of critical temperature (T_{cr}), which is a temperature above which a homogenous blend is obtained. For the 50% PVC blend, the T_{cr} is at 150°C. Therefore, to ensure a homogenous PVC/ENR blend, blending must be carried out at temperatures above the critical temperatures. It must be reiterated that other factors such as composition, rotor speed, and time must also be considered.

Effect of Rotor Speed

Figure 5 depicts the mixing torque–time curves of 50% PVC blends, blended at 150°C, 10 min but at varying rotor speeds. Unlike the earlier effects, here the trends are not so distinctive. However, the times to attain homogenous states are as expected, with 20 rpm the slowest and 95 rpm the fastest. The plots of $\log \tau_a/S$ vs. $\log S$, analogous to $\log \tau_a$ against $\dot{\gamma}_a$ are shown in Figure 6. Similarly, mixing torques after 3 and 9 min were chosen. As seen, PVC/ENR
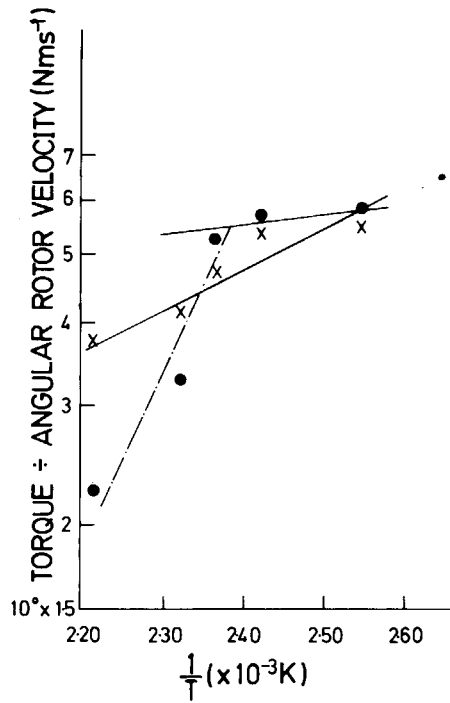
Fig. 4.   Arrhenius type plots of τ_a/S vs. $1/T$ of 50% PVC/ENR blends: (X) 3 min mixing; (●) 9 min mixing.
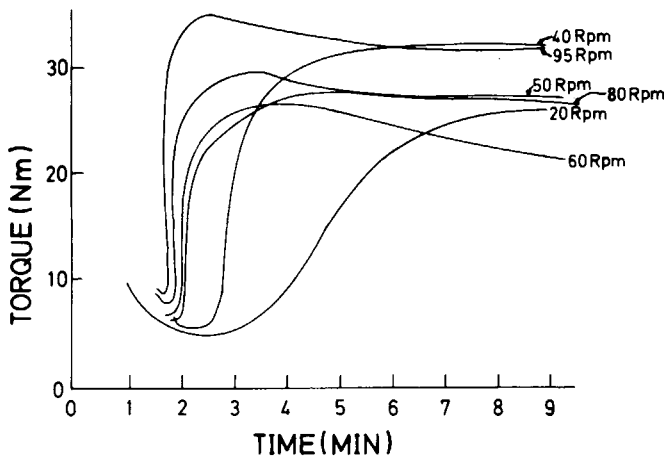

Fig. 5.   Mixing torque-time curves of 50% PVC/ENR blends mixed at varying rotor speeds.

blends after 3 min behave more like a Bingham body in which the behavior is being controlled by the rubber component; hence it requires a limit yield stress to initiate a flow.[15] This can be attributed to incomplete fusion of the PVC particles; hence, homogenous blends were unattainable. With 9 min of mixing, the τ_a/S increases and then decreases with further increase of S. This pseudoplastics behavior observed can be attributed to the complete fusion of the PVC particles; hence a homogenous blend is formed.
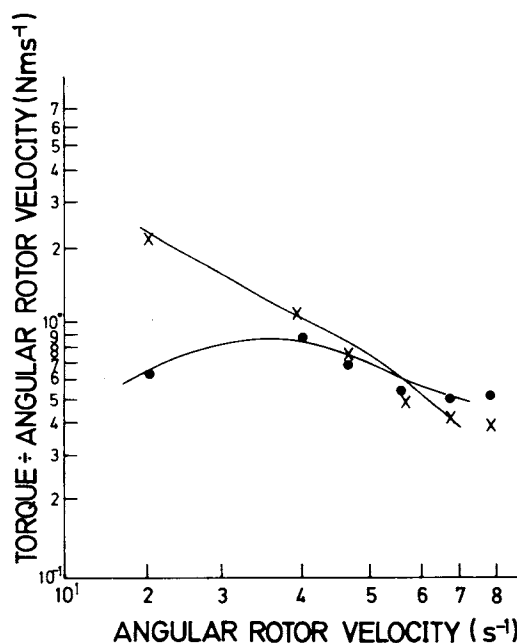
Fig. 6. τ_a/S values as a function of angular rotor speed: (X) 3 min mixing; (●) 9 min mixing.

Physical and Aging Properties

The effect of composition and blending temperature on physical properties of PVC/ENR blends are given in Tables II and III, respectively. Evidently, the properties (tensile strength, aging resistance) increase with PVC content. However, only blends with PVC content up to 50% are shown. The conditions used enable a complete fusion of PVC particles and a formation of homogenous blends, as discussed earlier. This explains why improved blend properties were observed. Similar observations were reported by others.[1-6] Sebastio and Birley,[16] working on a commercial thermoelastomer, have concluded that the enhancement of physical properties is mainly attributed to the hard domains of the thermoplastics phases of the blends.

TABLE II
Effect of PVC Content on Tensile Strength, Tear Strength,
and Aged Tensile Strength of PVC/ENR

PVC content (%)	Tensile strength (MPa)	Tear strength (MPa)	Tensile strength after 70°C, 76 h (MPa)
10	6.1	10.2	4.5
20	6.0	10.2	4.5
30	7.3	12.7	6.5
40	10.5	22.3	10.5
50	15.9	60.0	16.3

TABLE III
Effect of Blending on Physical Properties of 50% PVC/ENR Blends[a]

Physical properties	120°C	150°C	170°C	180°C
Tensile strength (MPa)	14.0	15.9 (14.9)	20.7	18.5
Elongation at break (%)	300	470 (300)	200	350
Modulus 100	11.6	13.6 (10.4)	17.8	12.8
Tensile strength after 70°C, 76 h (MPa)	15.9	17.6 (9.5)	23.0	9.5
Hardness (IRHD)	86.5	87.0 (−)	99.0	97.0

[a] Values in brackets are for unvulcanized 50% PVC blends.

Table III shows the effect of blending temperatures on physical and aging properties of 50% PVC blends. It shows that 170°C gives the maximum properties, instead of 150°C, which was earlier observed with rheological properties. This is as expected since 170°C is closer than 150°C to the melting point of PVC. The addition of curatives further enhances the properties of 50% PVC blends. The physical properties of the unvulcanized 50% PVC blends are shown in brackets. This improvement can be attributed to a dynamic crosslinking as suggested by Coran and Patel.[3,4]

Finally, another salient point which is worth mentioning here, is the effectiveness of Ba/Cd/Zn PVC-based stabilizer when it is premixed with PVC prior to the blending. By premixing, its tendency to migrate to the ENR phases is greatly hampered, which hence enhances its stabilizing action towards the PVC phases. This shows that PVC stabilizers can be used with PVC-based blends provided that premixing is performed.

CONCLUSIONS

From the studies, evidence of compatibility between PVC and ENR is clearly shown. However, the extent of mixing of any blend depends on the blending temperature, rotor speed, and time. For example, to obtain an homogenous 50% PVC blend, it requires conditions of at least 150°C, 50 rpm, and 6 min of blending. With premixing, Ba/Cd/Zn-based PVC stabilizer was found to be an effective stabilizer for the PVC/ENR blends. It is the PVC which contributes to rigidity while the ENR imparts flexibility and processability to the blends. Addition of curatives further enhances the properties of blends.

References

1. W. S. Penn, *PVC Technology*, 3rd ed., Applied Science, London, 1971.
2. D. J. Elliot, *Nat. Rubber Technol., Part 3*, **12**, 53 (1981).
3. A. Y. Coran and R. Patel, *Rubber Chem. Technol.*, **54**, 91 (1981).
4. A. Y. Coran and R. Patel, *Rubber Chem. Technol.*, **54**, 892 (1981).
5. V. L. Folt and R. W. Smith, *Rubber Chem. Technol.*, **46**, 1193 (1973).
6. D. S. Campbell, D. E. Elliot, and M. A. Wheelans, *Nat. Rubber Technol., Part 2*, **9**, 21 (1978).

7. K. E. George, R. Joseph, and D. J. Francis, *J. Appl. Polym. Sci.*, **32**, 2867 (1986).

8. G. A. Zakrzenski, *Polymer*, **14**, 348 (1973).

9. I. R. Gelling, *Nat. Rubber Technol., Part 7*, **16**, 1 (1985).

10. R. Chantera Thevy and M. Nasir, *Developments in the Plastics and Rubber Product Industries*, 1987, CAPS Enterprise, Kuala Lumpur.

11. K. E. George, R. Joseph, and D. J. Francis, *Plast. Rubber Process Appl.*, **5**, 179 (1985).

12. J. F. Goodrich and R. S. Porter, *Polym. Eng. Sci.*, **7**, 45 (1967).

13. C. K. Das, *Int. J. Polym. Mater.*, **11**, 211 (1986).

14. J. M. Widmayer and G. C. Meyer, *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 1659 (1981).

15. J. A. Brydson, *Flow Behaviour of Polymer Melts*, George Godwind, London, 1987.

16. V. C. Sebastio and A. W. Birley, *Br. Polym. J.*, **32**, 2867 (1986).