

# Determination of Optimum Blending Conditions for Poly(vinyl Chloride)/Epoxidized Natural Rubber Blends

ZAINAL A. NASIR,\* UMARU S. ISHIAKU, and ZAINAL A. MOHD ISHAK

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

## SYNOPSIS

An attempt to resolve the difficulties normally faced in preparing PVC-dominant PVC/ENR blends with the Brabender plasticorder is discussed. As expected, it was found that the mechanical properties of PVC/ENR blends are greatly influenced by the mixing parameters, which are further reinforced with evidence from both dynamic mechanical analysis (DMA) and morphological studies. Both techniques showed the attainment of compatible 50/50 PVC/ENR blends, the former a single glass transition temperature ( $T_g$ ) and the latter a single-phase system, albeit their inherent properties are dependent on the blending parameters. By utilizing the correlation between mixing temperature and rotor speed derived, good PVC/ENR blends can be easily procured. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

The miscibility of epoxidized polymers with chlorinated polyhydrocarbons is well established.<sup>1-4</sup> Numerous studies, among them Margaritis and Kalfoglou<sup>2</sup> and Varughese and De,<sup>3</sup> showed that PVC/ENR blends exhibit a single glass transition temperature  $T_g$ , which lies between that of PVC and ENR, thus asserting compatibility at molecular level. Since ENR is known to possess characteristics more akin to those of synthetic elastomers<sup>5,6</sup> and PVC/synthetic elastomer blends already enjoy commercial prominence, it is hoped that ENR may soon become a popular polymeric plasticizer.

Earlier work on PVC/ENR blends by Nasir and Ratnam<sup>7,8</sup> indicates the need of using suitable mixing conditions to attain optimum properties. However, for the PVC-dominant blends, using a mixing procedure similar to that used for ENR-dominant blends results in incomplete melting and fusion of the PVC particles, shown by the continuing rise in mixing torques, albeit prolonging the mixing time. Similar observations have also been reported elsewhere.<sup>9,10</sup>

Hence, this paper reports on steps taken to overcome the problems associated with PVC-dominant

blends and also to look into establishing mixing conditions required to achieve optimum blends.

## EXPERIMENTAL

### Materials and Formulations

Epoxidized natural rubber grade "Epoxyrene 50" was supplied by Rubber Research Institute of Malaysia; poly(vinyl chloride) with 65 K value, "Mer-cion HP-65," was obtained from Malayan Electro-Chemical (M) Ltd.; Ba/Cd/Zn-based stabilizer "Ingrastab BC 455s" was supplied by Ciba-Geigy (M) Ltd. Other ingredients: sulfur, ZnO, stearic acid, and accelerators were products of Bayer (M) Ltd. The full recipes are given in Table I.

### Mixing Studies with the Brabender

The Ba/Cd/Zn stabilizer was initially premixed with a Kitmah powder blender at 1000 rpm for 10 min. The mixing studies were conducted with a Brabender Plasticorder Model PL 331 equipped with a mixing cam. The mixing studies can be generally described as follows.

### Preparation of PVC-Dominant Blends

For the PVC-dominant blend (80/20 PVC/ENR), the mixing procedure used previously by Nasir and

\* To whom correspondence should be addressed.

**Table I Recipes of Poly(Vinyl Chloride)/Epoxidized Natural Rubber Blends**

Materials	Blends		
Poly(vinyl chloride) (phr)	20	50	80
Epoxidized natural rubber, ENR50 (phr)	80	50	20
Barium/cadmium/zinc (phr PVC)	4	4	4

Curatives<sup>a</sup> (phr ENR50): Sulfur, 1.5; zinc oxide, 2.0; stearic acid; 1.0; MBTS<sup>b</sup>, 1.5; TMTD,<sup>c</sup> 0.5

<sup>a</sup> Curatives were added before molding of blends.

<sup>b</sup> 2,2-Dibenzothiazole disulfide.

<sup>c</sup> Dithiocarbamate tetramethyltiuram disulfide.

Ratnam<sup>7,8</sup> was modified. Here, PVC was charged into the mixing chamber and then allowed to equilibrate by preheating for 5 min at the desired temperature before starting the rotors. This was subsequently followed by incorporation of the ENR. Blending was then allowed to proceed for 9 min.

#### Effects of Mixing Parameters

For this purpose, three different PVC/ENR blends (80/20, 50/50, and 20/80) were examined. The 50/50 and 20/80 PVC/ENR blends were prepared using the previous procedure,<sup>7,8</sup> in which the ENR was initially charged into the mixing chamber and allowed to equilibrate for 1 min prior to the addition of PVC. In the case of the 80/20 blend, the modified mixing technique described above was utilized. To establish a better understanding between mixing parameters, mixing was carried out with varying temperatures and rotor speeds (120–160°C, 20–60 rpm). Their respective torque–time curves were then recorded.

#### Measurement of Mechanical Properties

For the 80/20 and 50/50 PVC/ENR blends, specimens were prepared by compression moulding at 150°C for 5 min. However, in the case of the 20/80 blend, curative was added on the two-roll mill, which were then compression-molded with  $t_{90}$ , measured using the Monsanto Rheometer Model MR100. Tensile properties were then determined using the Monsanto T10 Tensometer, according to ISO 37: Type III.

Since the use of mechanical properties alone is insufficient to indicate optimum blends, DMA and microscopic techniques were adopted.

#### Measurement of Dynamic Mechanical Properties

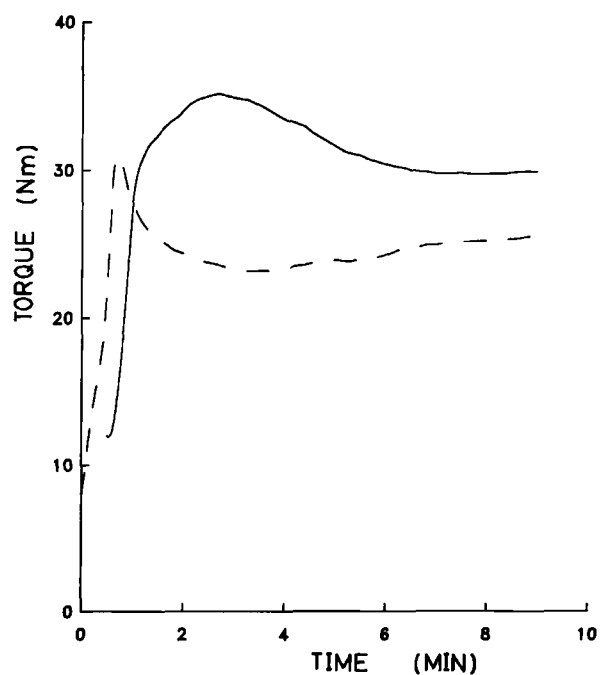
Samples from the Brabender obtained under varying mixing conditions were chosen and then molded into 3-mm-thickness specimens. Dynamic mechanical properties were scanned from –100 to 150°C using the resonant mode, at 30 Hz with the DuPont DMA, Model 983.

#### Morphological Studies

Further, the influences of mixing parameters on the blends' morphologies were investigated using an optical microscope, Model Olympus BH2-KFCA, on selected samples which were microtomed to 5–10  $\mu\text{m}$  at –35°C.

## RESULTS AND DISCUSSION

In earlier studies on PVC/ENR blends,<sup>7,8</sup> there was no effort to use dissimilar mixing procedures with different systems. It was noted that poor properties of PVC-dominant blends were obtained. This was attributed to incomplete melting and fusion of the PVC particles, as observed from the continuing increase in mixing torques. George et al.,<sup>9,10</sup> working with NBR/PVC blends, have reported similar observations.

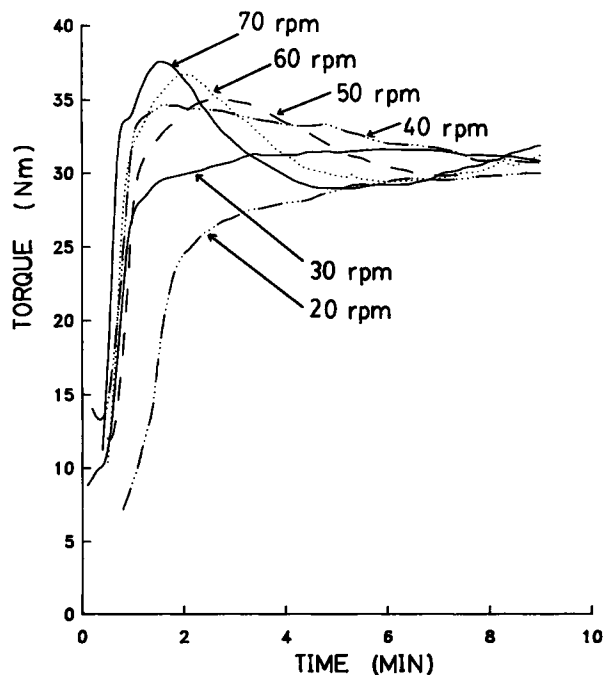


**Figure 1** Plastograms of the modified and unmodified procedures for 80/20 PVC/ENR blend obtained at 150°C and 50 rpm: (—) modified; (---) unmodified.

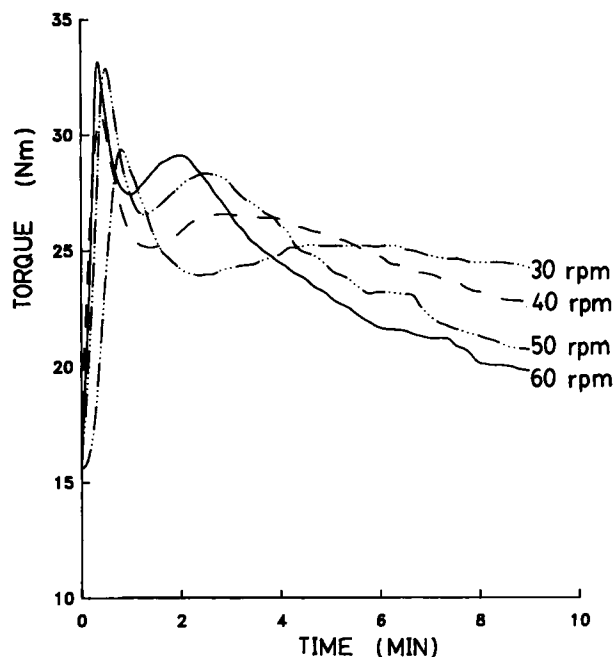
### Brabender Studies

The change of the mixing procedure was intended to overcome the above mentioned problem. Figure 1 shows the plastograms recorded for both the modified and the unmodified procedures. As observed, the presence of the fusion peak, followed by the stabilization zone and the absence of the rising torque, is a clear evidence of a successful blending. Moreover, this is further supported by the improved properties of the blends derived from the modified procedure. Another salient point is that the modified plastogram is a close resemblance to that of PVC alone.<sup>11</sup>

As have been reiterated, attainment of any particular blend is greatly influenced by mixing conditions.<sup>8,9,12</sup> Figure 2 shows the plastograms obtained by varying the rotor speeds for PVC dominant blend. The mixing temperature was fixed at 150°C. The changes occurred clearly illustrates this point. In order to obtain a good blend, rotor speed of 40 or 50 rpm ought to be selected. At 70 rpm, the mixing time of 9 min is unsuitable since excessive degradations have occurred, shown by the rising torque after the stabilization zones are achieved. However, with 20 and 30 rpm rotor speeds, the opposite situation is observed, in which blending is inadequate absence of stabilization zones.

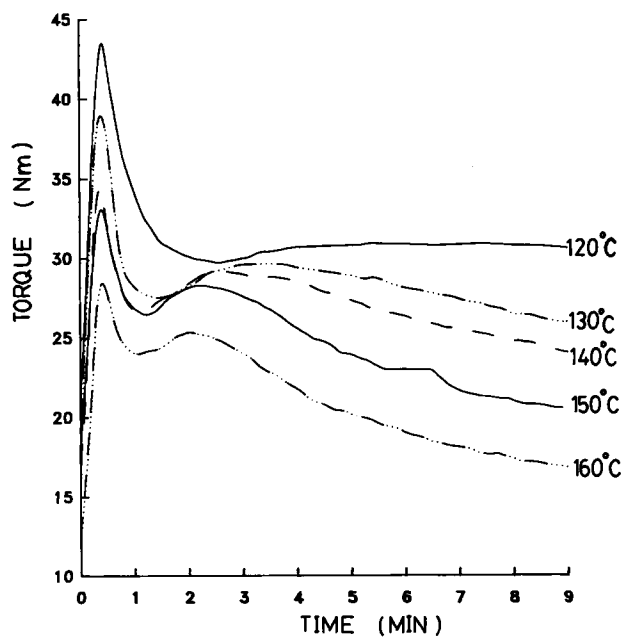


**Figure 2** Effect of changing rotor speed on the plastograms of 80/20 PVC/ENR blends, mixed at 150°C.



**Figure 3** Effect of changing rotor speed on the plastograms of 50/50 PVC/ENR blends, mixed at 150°C.

Similar trends are also noted with 50/50 blend as evident from Figure 3. As before, the mixing temperature was maintained at 150°C throughout. The



**Figure 4** Plastograms of 50/50 PVC/ENR blends obtained between 120 and 160°C at a fixed rotor speed of 50 rpm.

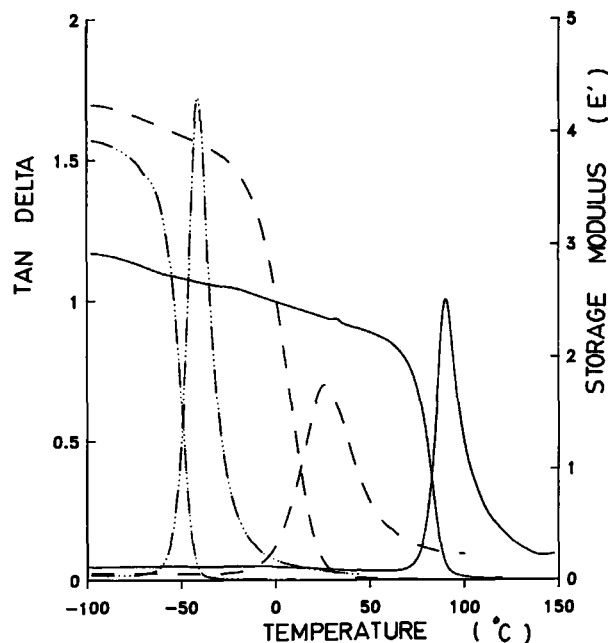
30 rpm speed seems to be the best whereas, at higher rotor speeds, a shorter mixing period could have been employed. In fact, at 50 and 60 rpm, degradation is imminent even after approximately 7 min mixing. The role of mixing temperature is highlighted in Figure 4, although only the 50/50 blend is again referred. It can be concluded that the mixing time of 9 min is best suited only for 130 and 140°C mixing temperatures.

Although the plastograms do show the dependence of mixing parameters in any particular blends, no definite evidence on compatibility is provided. Hence, it is therefore appropriate to look at such fundamental aspect from DMA and morphological studies.

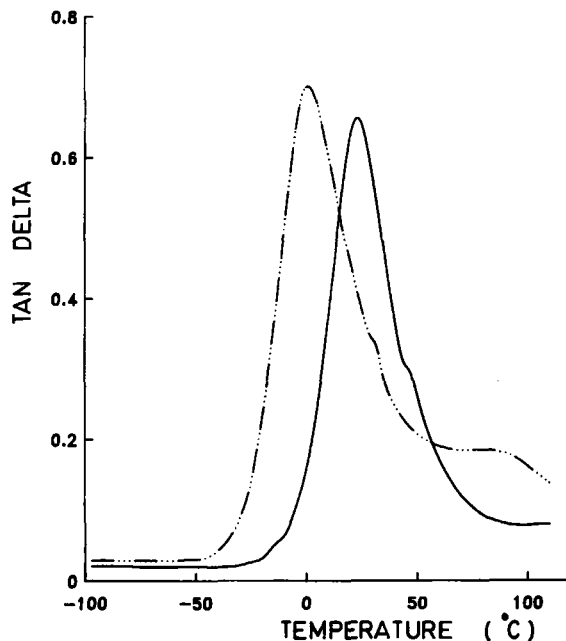
**Dynamic Mechanical Properties**

For this purpose selected cases are highlighted. In Figure 5, the temperature dependence of loss tangent,  $\tan \delta$ , for a particular 50/50 blend is compared with both the homopolymers, PVC and ENR. As evident, a compatible blend with a single  $T_g$  intermediate between those of PVC and ENR is obtained. This is same to those reported earlier.<sup>2,3</sup>

The dynamic mechanical properties of 50/50 blends procured using dissimilar rotor speeds after mixing times of 4 and 9 min are illustrated in Figures

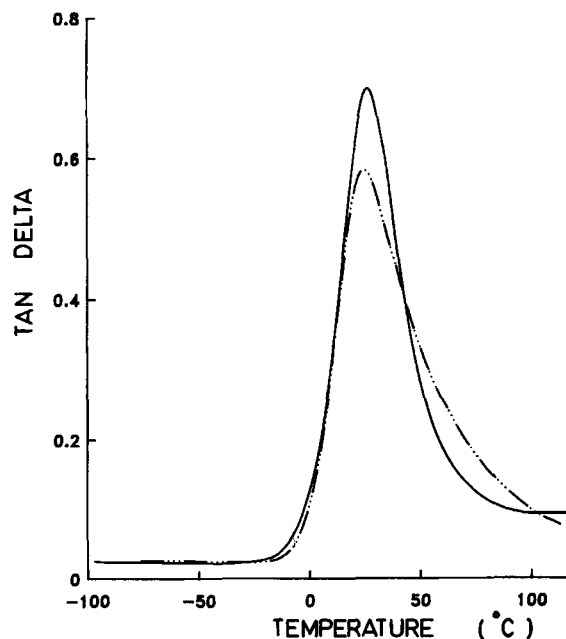


**Figure 5** Dynamic mechanical properties of 50/50 PVC/ENR blend, PVC and ENR homopolymers: (· · · ·) ENR; (---) PVC/ENR; (—) PVC.

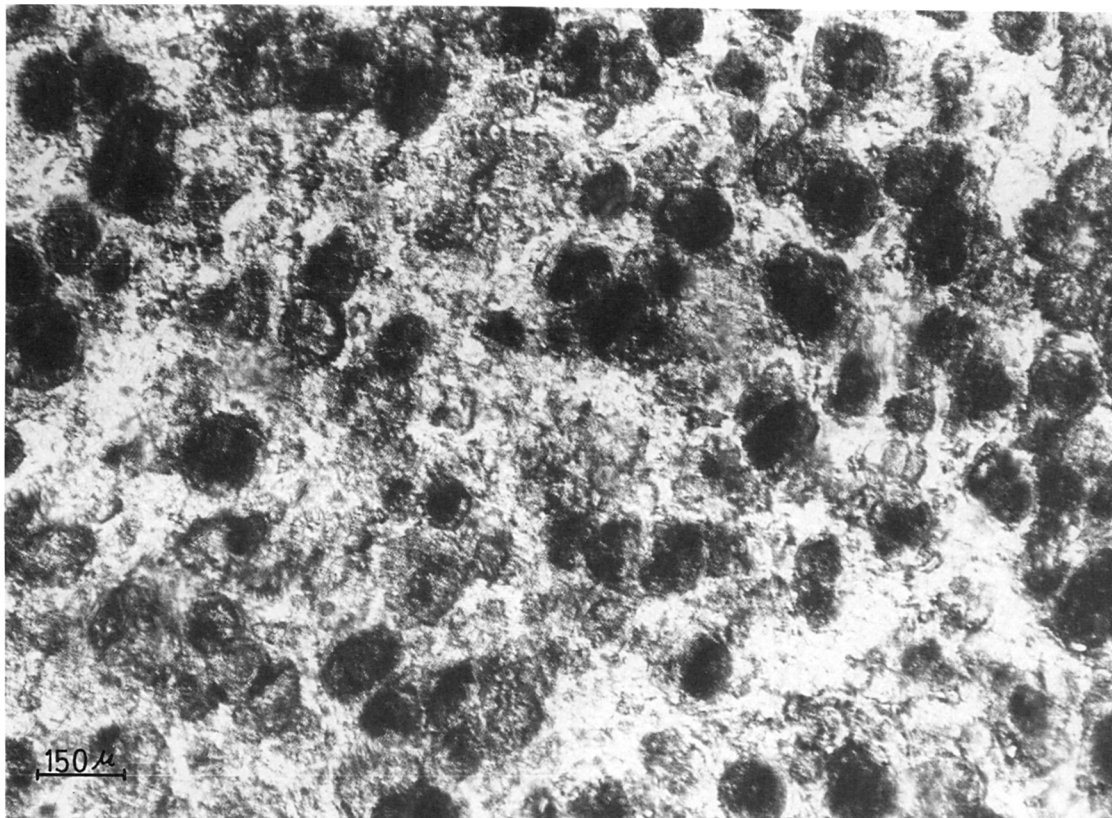
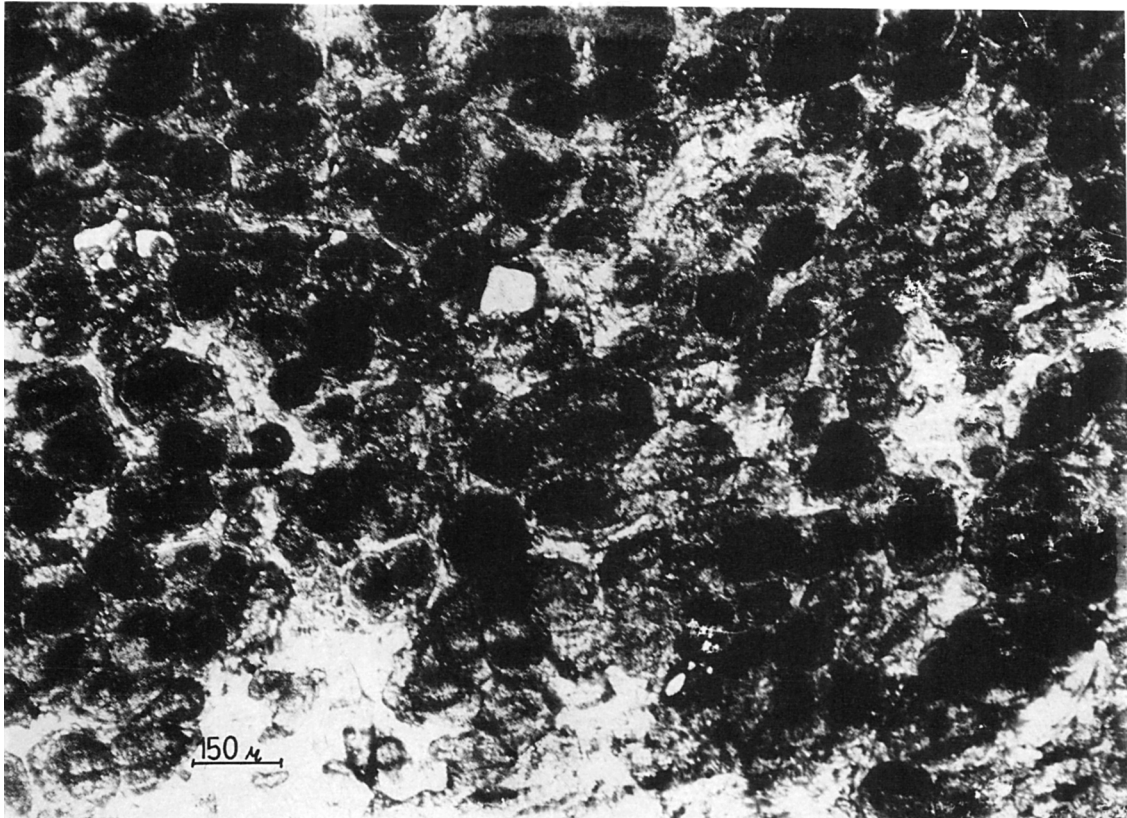


**Figure 6** The effect of rotor speeds on the temperature dependence of  $\tan \delta$  of 50/50 PVC/ENR blends after 4 min mixing at 150°C: (· · · ·) 20 rpm; (—) 50 rpm.

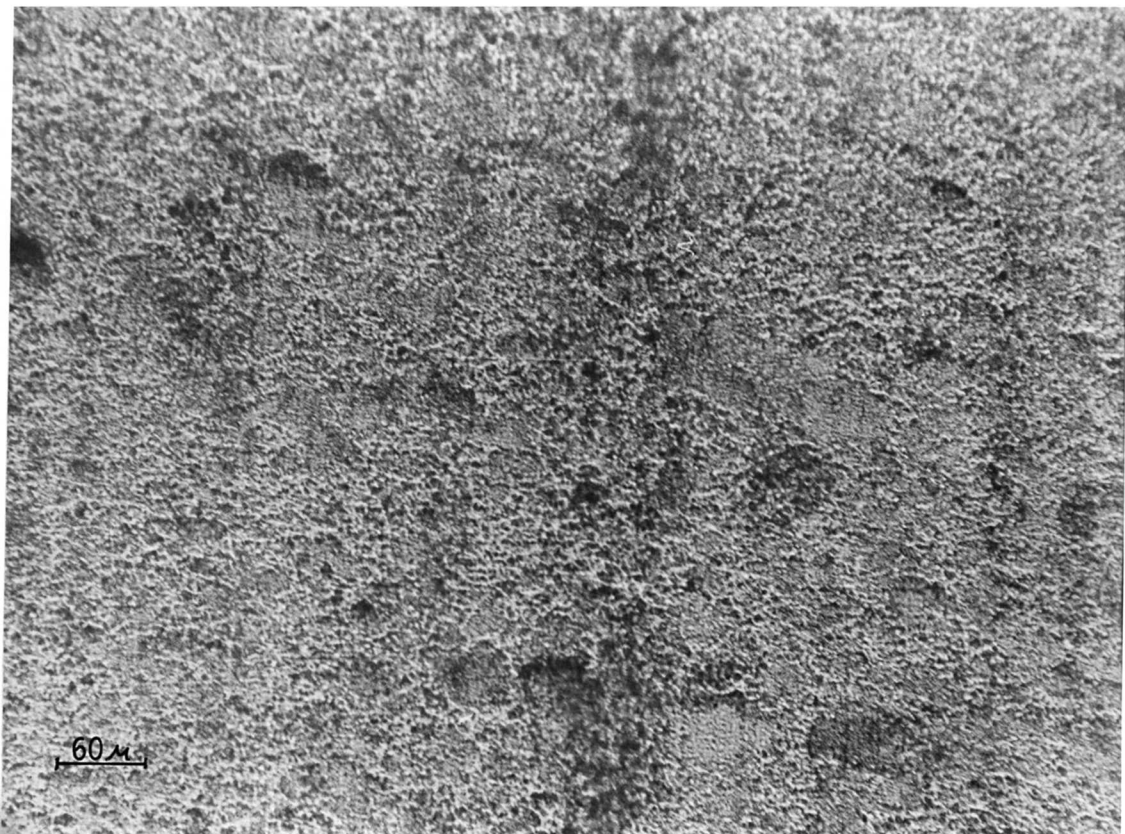
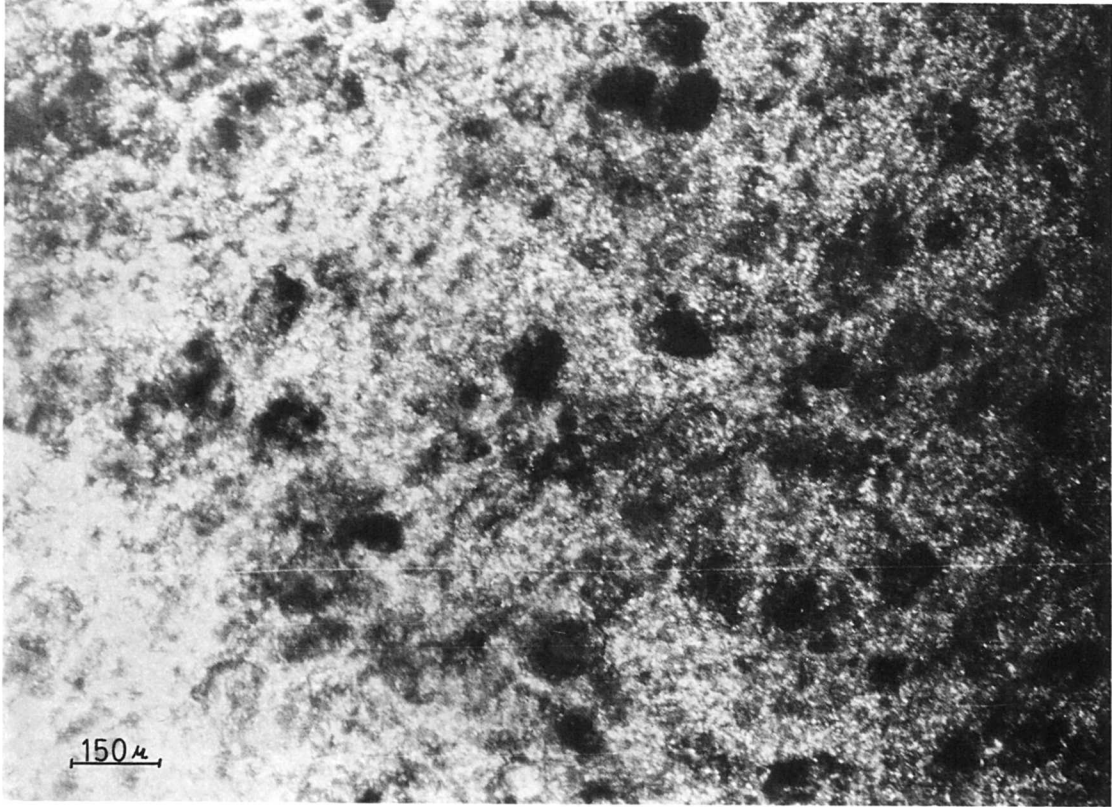
6 and 7, respectively. When mixing was stopped after 4 min, only that at 50 rpm rotor speed results in compatible blends, while, at 20 rpm, traces of in-



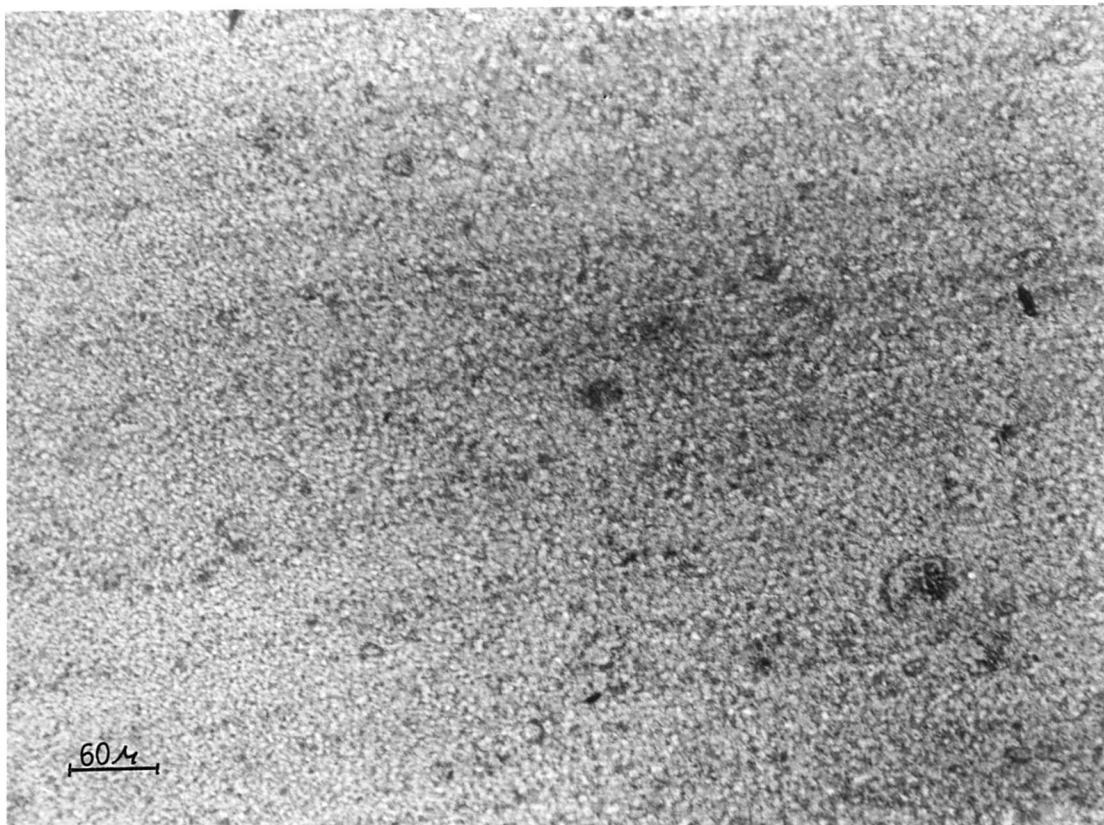
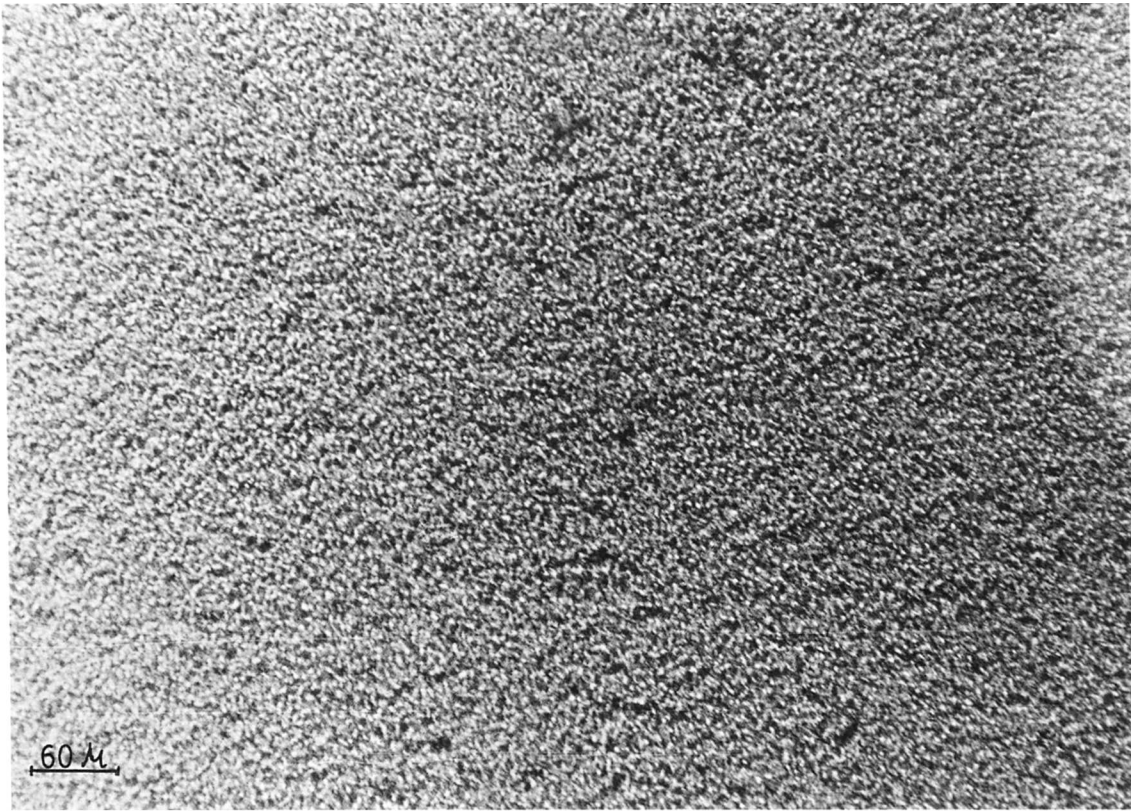
**Figure 7** The effect of rotor speeds on the temperature dependence of  $\tan \delta$  of 50/50 PVC/ENR blends after 9 min mixing at 150°C: (· · · ·) 20 rpm; (—) 50 rpm.



**Figure 8** The photomicrographs (130 $\times$  magnification) illustrating the morphological changes occurring with mixing time in the 50/50 blend obtained at 20 rpm and 150 $^{\circ}$ C: (a) 1 min; (b) 2 min; (c) 3 min; (d) 4 min.



**Figure 8** (continued from the previous page)



**Figure 9** Photomicrographs (320× magnification) showing close resemblance in morphologies between those at 20 rpm after 7 min and at 50 rpm after 2 min mixing: (a) 20 rpm/7 min.; (b) 50 rpm/2 min.

compatibility are still present, shown by the small peak, which can be attributed to traces of the PVC phases. However, after 9 min, both rotor speeds give rise to compatible blends but slightly different  $\tan \delta$  values or dynamic properties.

### Morphological Properties

The photomicrographs in Figures 8 and 9 show the morphological development occurring in 50/50 PVC/ENR blends, consequences of different mixing conditions. As is evident from Figure 8, the transformation from the multiphase or heterogenous system to the one-phase system at 20 rpm is not fully achieved after 4 min mixing. At this stage, traces of PVC particles are still noted from the photomicrograph. Further, in Figure 9, the similarity between the morphologies procured at 20 rpm/7 min and 50 rpm/2 min is clearly illustrated, which further supports the above observation. These examples combined with observations noted earlier on from Brabender and DMA studies exemplify clearly the importance of mixing parameters in any PVC/ENR blending endeavors.

The above discussion clearly illustrates the importance of mixing parameters in ensuring a good blend, and also the need to establish some kind of control or preferences, be it mixing temperature or rotor speed or mixing time in any mixing endeavor.

### Correlations between Mixing Parameters

Here an attempt to achieve the above objective is presented. To start with, only the ultimate tensile properties are used as indicators of optimum blends.

Tables II and III are sets of ultimate tensile strength for 80/20 and 20/80 PVC/ENR blends,

**Table II Ultimate Tensile Strength (MPa) of PVC-Dominant Blends (80/20) Prepared with Varying Mixing Temperatures and Rotor Speeds**

Rotor Speed (rpm)	Mixing Temperature (°C)				
	120	130	140	150	160
20	—	—	—	20.4 <sup>a</sup>	16.2
30	14.0	14.3	23.1	24.9 <sup>a</sup>	20.2
40	18.8	19.8	25.4 <sup>a</sup>	25.3	15.5
50	23.4	24.4 <sup>a</sup>	20.8	21.2	—
60	22.4	23.6 <sup>a</sup>	—	22.2	11.0

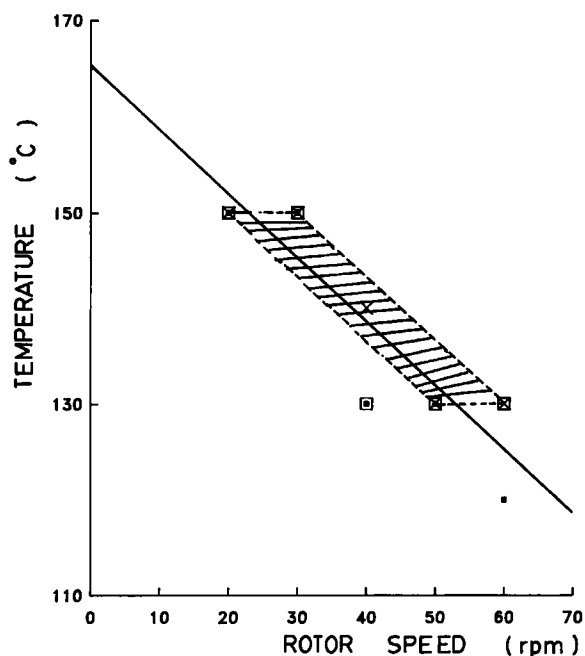
<sup>a</sup> Optimum; maximum tensile strength at respective rotor speeds.

**Table III Ultimate Tensile Strength (MPa) of ENR-Dominant Blends (20/80) at Varying Mixing Temperatures and Rotor Speeds**

Rotor Speed (rpm)	Mixing Temperature (°C)				
	120	130	140	150	160
20	—	—	—	10.4 <sup>a</sup>	8.9
30	7.8	8.6	10.0	12.8 <sup>a</sup>	10.6
40	13.7	13.9 <sup>a</sup>	12.3	13.4	11.8
50	15.5	15.7 <sup>a</sup>	14.5	13.8	11.2
60	13.2	15.4 <sup>a</sup>	15.0	12.7	9.5

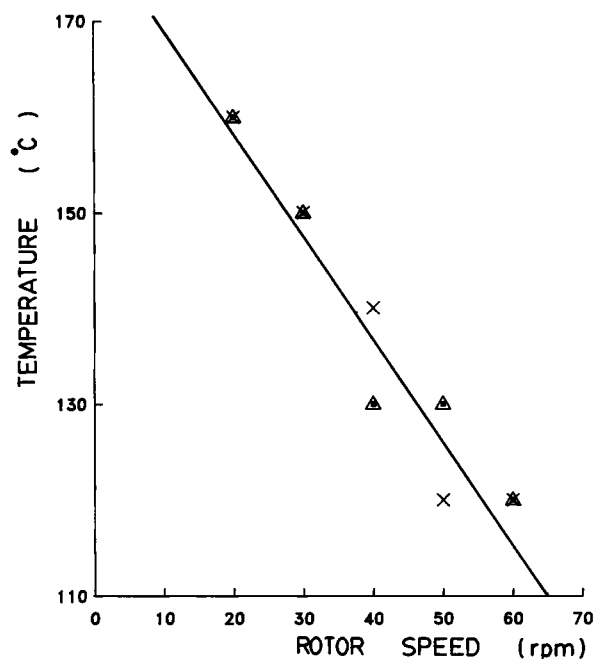
<sup>a</sup> Optimum; maximum tensile strength at respective rotor speeds.

respectively, obtained by varying either the mixing temperatures or the rotor speeds. It is interesting to note that a definite pattern exists between both mixing parameters. For 80/20 blend, optimum properties are attainable by mixing either at high rotor speed and low temperature or vice versa. However, for the 20/80 blend, optimum conditions are rather restricted to high temperature and low rotor speed only. The wider choice in ensuring optimum PVC dominant than the ENR dominant blends can be attributed to the latter poorer flow properties. As



**Figure 10** Composite plot of mixing temperature versus rotor speed with ultimate tensile strength as indicator: (□) 80/20; (■) 50/50; (×) 20/80.





**Figure 11** Composite plot of mixing temperature versus rotor speed for maximum elongation at break (■) 80/20; (△) 50/50; (×) 20/80.

expected, the same trend is also observed with elongation at break.

This situation can be easily summarized by composite plots, given in Figures 10 and 11. In general, an inverse relationship between the mixing temperatures and rotor speeds is obtained, with correlation factors of 0.934 and 0.948, respectively. Moreover, when each blend is considered separately, correlation factors of 0.949, 0.943, and 0.943 are attained for 80/20, 50/50, and 20/80 blends, respectively (Fig. 10). The high correlation for the PVC-dominant blend further explains its wider choice in optimum mixing conditions.

Also, all points seem to be confined within a certain region, shown by the shaded area, which clearly demarcate the boundary conditions to be selected in order to procure a good blend. This is in fact useful in assisting or guiding any mixing to be done. For example, to obtain 80/20 PVC/ENR blend having a good tensile strength, one can either use high temperature, say 150°C, and low rotor speed or higher rotor speeds at a lower temperature.

## CONCLUSIONS

1. Improved PVC dominant blends can be prepared using the Brabender plasticorder by using the modified mixing procedure.
2. Compatible PVC/ENR blends are obtainable by using appropriate mixing conditions, evident from both DMA and morphological techniques.
3. From the composite plots between mixing parameters, any good PVC/ENR blend can easily be prepared, although, due to its poor flow properties, the choice for ENR-dominant blend is rather selective.

The authors would like to take this opportunity to thank Universiti Sains Malaysia and the Malaysian Government for providing the financial assistance and to anyone who has in one way or another helped in ensuring the completion of this manuscript.

## REFERENCES

1. A. G. Margaritis, J. K. Kallistis, and N. K. Kalfoglou, *Polymer*, **28**, 2122 (1987).
2. A. G. Margaritis and N. K. Kalfoglou, *Eur. Polym. J.*, **24**(11), 1043 (1988).
3. K. T. Varughese and P. P. De, *J. Appl. Polym. Sci.*, **37**, 2537 (1989).
4. A. G. Margaritis and N. K. Kalfoglou, *Polymer*, **28**, 497 (1987).
5. I. R. Gelling, *Rubber Chem. Technol.*, **58**, 86 (1985).
6. I. R. Gelling, in *Proc. Int. Rubber Technol. Conf., RRIM*, Penang, Malaysia, 1988.
7. C. T. Ratnam and M. Nasir, in *Developments in the Plastics and Rubber Product Industries*, J. C. Rajoo, Ed., CAPS Enterprise, Malaysia, 1987, p. 403.
8. Z. A. Nasir and C. T. Ratnam, *J. Appl. Polym. Sci.*, **38**, 1219 (1989).
9. K. E. George, R. Joseph, and D. J. Francis, *Plast. Rubber Process. Appl.*, **5**, 179 (1985).
10. K. E. George, R. Joseph, and D. J. Francis, *J. Appl. Polym. Sci.*, **32**, 2867 (1986).
11. H. E. Luben, *Flow and Cure of Polymers Measurement and Control*, Rapra Technology, Shawbury, U.K., 1990.
12. L. E. Utracki, *Polymer Alloys and Blends*, Hanser, New York, 1989.

Received February 26, 1991

Accepted April 6, 1992