The Effect of Mixing Time on the Rheological, Mechanical, and Morphological Properties of Poly(vinyl chloride)–Epoxidized Natural Rubber Blends

U. S. ISHIAKU, H. ISMAIL, Z. A. MOHD. ISHAK

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

ABSTRACT: The mixing characteristics of 50/50 poly(vinyl chloride)–epoxidized natural rubber (PVC–ENR) blends were studied using a Brabender Plasticorder, and their relationships with the morphological and mechanical properties were examined. In general, it was observed that the mixing time is important in acquiring blends having optimum mechanical properties. Also, through careful appraisal of the respective plastograms and their relationships with dynamic mechanical, morphological, and tensile properties, attainment of optimum mixing conditions can be estimated, which results in optimum blends being prepared. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 75–83, 1999

Key words: poly(vinyl chloride)/epoxidized natural rubber blend (PVC/ENR blend); tensile properties; morphological properties; rheological properties; glass transition temperature (T_g); tan δ

INTRODUCTION

Several studies involving the Brabender Plasticorder have been reported.[1–17] In some cases, the Plasticorder is used simply as an internal mixer to blend polymers or even incorporate fillers into the blends.[2,3,7,11,12] The Plasticorder also enjoys wide application in studies involving the rheological properties of blends with changes in compounding conditions.[1,4,5,14–19] Dynamic curing[1,2] or interchange reactions[16] have also been studied with the Plasticorder.

Attempts have been made to relate Brabender plastograms with blends properties.[5,8,16,17] George et al.[5] in their studies of PVC–NBR blends proposed the existence of optimum temperature for the formation of a particular blend. Nasir and Ratnam[8] found that the rheological properties of PVC–ENR blends are governed by the compounding conditions. However, the behavior patterns to be expected during blending is not yet well elucidated. This is because simple rules for predicting behavior patterns to be expected during compounding are not yet well established.

In an earlier study,[18] the authors reported the determination of optimum properties based on derived composite plots of mixing temperatures and rotor speeds that would yield blends of optimum tensile properties while the mixing time was kept constant. Here, a further attempt to correlate the plastograms obtained as mixing progresses with the mechanical, morphological, and dynamic mechanical properties is presented. The prime objective is to investigate the influence of mixing time and, hence, establish an overall perspective of the influences of compounding conditions. The ultimate aim though is to enable the prediction of optimum blend attainment by making use of the plastogram as an indicator.

EXPERIMENTAL

ENR, grade "Epoxyprene 50" was purchased from Kumpulan Guthrie (M) Ltd. Seremban, Malaysia; suspension grade PVC, "Mercion HP-65" with K value of 65 was supplied by Malayan Electrochemical Industries Sdn. Bhd.; Ba–Cd–Zn-based stabilizer, "Irgastab BC 455S" was obtained from Ciba-Geigy (M) Ltd. The formulations are elaborated in the first report.[18] Here, only the 50 : 50 PVC–ENR was utilized with the purpose of observing the developments taking place as mixing progresses.

However, unlike before, here mixing was performed at intervals of 1 min starting with 1, 2 . . . until 9 min. In all cases, the timing commenced immediately after all the PVC has been charged into the mixing chamber, which takes about 9–10 s while mixing temperature was maintained at 150°C. Two rotor speeds of 20 and 50 rpm were employed to indicate two different levels of deformation rates, that is, low and high, respectively.

Specimens of appropriate thickness were compression-molded at 150°C for 3 min, with 2-min preheating period. Care was taken at this stage to ensure precise timing so as to eliminate any differences that might arise as a result of the samples having different thermal histories. As this could significantly influence the properties being investigated.

Mechanical properties, such as tensile strength, elongation at break, tear strength, and dynamic mechanical properties, were evaluated. Tensile and tear properties were evaluated in accordance with ISO 37, Type III, using the Monsanto tensometer T10 at 250 and 50 mm min^{-1} crosshead speeds, respectively.

For the dynamic mechanical properties, specimens were scanned under the resonant mode at 30 Hz from −100 to 150°C using the Du Pont DMA 923 attached to the thermal analyzer 2000. For the morphological studies, specimens were microtomed to 5–10 μm and then viewed using the light microscope, model Olympus B42-RFCA.

RESULTS AND DISCUSSION

Mixing Time

The plastograms obtained for the 50 : 50 blend obtained for 20 and 50 rpm while mixing was carried out for 9 min are illustrated in Figure 1.

Figure 1   Brabender plastograms of the 50 : 50 PVC–ENR blend mixed at 150°C with different rotor speeds.

The contrasting differences are clearly evident. For instance, the plastogram for the 20 rpm exhibits lower initial peak and a broader minimum combined with a delay in the inception of fusion. Secondly, the plastogram continues to rise until the 9-min period expires. In short, the rates of the melting and fusion are profoundly impeded due to inadequate shearing and heating actions. Consequently, more than 9-min mixing is required to attain the fusion peak similar to that of the 50 rpm.

In contrast, the 50 rpm plastogram is observed to rise sharply to the loading peak on charging PVC into the mixing chamber containing ENR. This initial peak is due to the initial resistance from the PVC particles. With heating, shearing, and mixing with ENR, the torque quickly drops to a minimum in the compression zone. Fusion is indicated by the fusion peak, and mixing being eventually completed is indicated by a lowering of torque and the subsequent attainment of the plateau or stability regimes. Further mixing beyond this point leads to a drop in mixing torque, which signals degradation. This plastogram approximates the mixing process, as outlined by several workers,[4,19] including by Luben[20] and Brown.[21] This implies that under the prevailing conditions, a transition from multiphase to single phase might have occurred with the exact characteris-

Figure 2 Plastograms of the 50 : 50 PVC–ENR blend showing the effect of mixing time at a constant rotor speed of 50 rpm at a mixing temperature of 150°C.

tics being governed by the respective mixing times at the various stages. For example, the product obtained with 1-min mixing is expected to be heterogeneous, in which PVC and ENR exist in separate phases. While at 7 min, the material should be in a homogeneous phase, with the PVC no longer existing as discrete entities, but fused and well blended with the ENR. The miscibility of PVC and ENR solid state has been established by the confirmation of hydrogen bonding from Fourier transform infrared (FTIR) studies and synergism in mechanical and dynamic mechanical properties.[22,23] Evaluation of the morphological, mechanical, and dynamic mechanical properties reveals the detailed characteristics.

The plastograms obtained at various time intervals for the 50 : 50 blend mixed at 150°C and 50 rpm are shown in Figure 2. The inception points of the plastograms have been shifted so as to show the various stages of the mixing process. By simple superposition at these origins, it is easily seen that, trend wise, they are components of the 9-min plastogram shown in Figure 1. Similar plastograms were also recorded for the various stages of the 20-rpm plastogram (Fig. 3).

Morphological Development

As mentioned earlier, the differences in shear and thermal deformation rates at 20 and 50 rpm is

expected to yield blends of different properties. In this respect, these two different deformation rates are considered separately.

At 20 rpm, the loading peak corresponds to 1 min of mixing (Fig. 3). The corresponding micrograph [Fig. 4(a)] at this stage shows the powder grains (100–150 μm diameter) mostly intact, suspended in the ENR matrix. With 2-min mixing (Fig. 3), the plastogram is halfway through the compression zone. Here, a good number of the powder grains have been broken to yield primary particles [Fig. 4(b)]. With 3-min mixing, which corresponds to the minimum after the loading peak, most of the powder grains have disappeared, and the primary particles predominate, although some powder grains are still visible, as illustrated in [Fig. 4(c)]. With 4-min mixing, the plastogram is still within the minimum zone. Here, all the powder grains have been broken up, and the mixture consists mainly of primary particles, held together by the ENR matrix [Fig. 4(d)]. Beyond this point, the torque gradually rises, as shearing and increase in temperature lead to melting and, thus, an increase in viscosity. The phases gradually become finer, as shown in Figure 4(e) and (f). However, evidences of multiphases are still visible even with 9-min mixing, as shown in

Figure 3 Plastograms of the 50 : 50 PVC–ENR blend showing the effect of mixing time at a constant rotor speed of 20 rpm and a mixing temperature of 150°C.

Figure 4   Photomicrographs of the 50 : 50 PVC–ENR blend mixed at 150°C and 20 rpm: (a) 1, (b) 2, (c) 3, (d) 4, (e) 7, and (f) 9 min.

Figure 4(f). This could be attributed to the fact that fusion has not been completed. The slow fusion process due to the low shear and thermal deformation rates makes it possible to obtain a clear picture of the early stages of the fusion process.

Figure 5 Photomicrographs of the 50 : 50 PVC–ENR blend mixed at 150°C and 50 rpm: (a) 1, (b) 2, (c) 3, and (d) 4 min.

The photomicrograph obtained with 1 min of mixing at 50 rpm is illustrated in Figure 5(a). This corresponds to the minimum in the torque curve after 1 min of mixing (Fig. 2). Here, the powder grains have been broken, and the mixture consists mainly of primary particles suspended in ENR matrix. This is identical to the situation obtained with 4-min mixing at 20 rpm [Fig. 4(d)].

Two minutes of mixing [Fig. 5(b)] corresponds to the area of the plastogram where the torque is beginning to rise (Fig. 2). As the temperature increases due to shear heating, the primary particles begin to melt, and, thus, increasing the torque. Maximum torque is attained with 3 min of mixing, which corresponds to the fusion peak or gel point. Here, most of the primary particles are fused together, although they are still distinguishable, as illustrated in Figure 5(c).

With 4-min mixing, the torque has fallen from the peak to the extent that the peak is now well defined (i.e., the highest point is halfway from the minimum after the loading peak) (Fig. 2). The micrograph at this stage [Fig. 5(d)] shows that all traces of multiphases have disappeared, and a homogeneous single phase is evident. Further mixing beyond this point does not yield any visible changes in morphology.

Mechanical Properties

In polymer blend studies, mechanical properties are very important parameters of characterization. For this purpose, tensile strength, the percentage of elongation at break, and the tear strength are referred to in Figures 6, 7, and 8, respectively. It is obvious in all cases that the mechanical properties of blends obtained at 20 rpm are generally inferior to those obtained at 50 rpm. In fact, blends of measurable properties are obtainable only after 5 min of mixing at 20 rpm.

Figure 6 The effect of mixing time on tensile strength at different rotor speeds for 50 : 50 PVC–ENR blend at 150°C.

That the properties continue to rise beyond the 9-min mixing time indicate that blends of optimum tensile properties and tear strength are yet to be realized. This implies that at 150°C, much longer mixing times are required if mixing is to be carried out at 20 rpm.

At a 50 rpm rotor speed, blends of better mechanical properties are obtained. The tensile properties and tear strength increase sharply until they attain peaks with 4 to 5 min of mixing. This corresponds to the zone where plasticization is just completing (Figs. 1 and 2). This implies that optimum properties actually correspond to the end of the fusion peak, that is, before stabilization. At the stabilization region, that is, at a mixing time range of 5–7 min, the properties are actually high and stable. Because of the need to stabilize the melt, blending is normally extended to this region.[20] This means that blending should be terminated anywhere between 4–6 min in order to optimize blend properties. Beyond 7 min of blending, the mechanical properties are observed to decrease. This is in accordance with the fall in torque at this region, which implies that degradation has already set in.

Dynamic Mechanical Properties

The presence of a single tan δ peak in dynamic mechanical analysis (DMA) results is an indication of a homogeneous single phase or good dispersion.[20,21,24] For PVC–ENR blends, numerous findings of a single T_g have been reported,[18,23,25–28] which yield favorable mechanical properties.

Some of the tan δ plots obtained for the 20-rpm rotor speed at the various stages of mixing are illustrated in Figure 9. With 1 min of mixing, the two peaks due to PVC and ENR are quite obvious. These peaks disappear gradually as mixing progresses, and the tendency is towards forming a single peak, which is not really achieved until mixing terminates at 9 min. This is indicated by the fact that the right arm of the peak is not properly formed and still looks different from the left arm. To further support this contention, the tan δ peaks obtained with 9 min of mixing at 20 and 50 rpm were compared. While the 50-rpm curve has leveled off after the peak has been attained (Fig. 10), the 20-rpm curve still shows signs of inhomogeneity, and this accounts for the differences of the two curves (Fig. 9). This observation is in agreement with that based on the photomicrographs [Fig. 4(f)].

Figure 7 The effect of mixing time on the percentage of elongation at break at different rotor speeds for the 50 : 50 PVC–ENR blend at 150°C.

Figure 8 The effect of mixing time on tear strength at different rotor speeds for the 50 : 50 PVC–ENR blend at 150°C.

The tan δ peaks obtained at the various stages of mixing at 50-rpm rotor speed are illustrated in Figure 10. With 1 min of mixing, the influence of

Figure 9 Tan δ dependence of mixing time for the 50 : 50 PVC–ENR blend at 20 rpm and 150°C.

Figure 10 Tan δ dependence of mixing time for the 50 : 50 PVC–ENR blend at 50 rpm and 150°C.

the PVC peak is still obvious. This decreases through 2 and 3 min of mixing until it disappears completely with 4 min of mixing. The tan δ peak obtained with 4 min of mixing shows a single peak representing a homogeneous blend. Comparison of the peak here with those obtained at 7 and 9 min show that it is similar to those obtained with longer mixing times. This indicates the absence of any observable morphological changes after 4 min of mixing, in agreement with the observations from microscopy.

Mixing Characteristics

So far, all evidence indicates that close relationships exist between mixing characteristics (rheology), morphology, and mechanical and dynamic mechanical properties. At 50 rpm, mechanical properties exhibit maximum values at about 4–6 min, which coincide with the observations of the fusion peak from torque curves, a single tan δ peak from DMA, and a single phase from morphology. In short, at 50 rpm, all the various stages of PVC fusion[4,18,19,20] have been realized. An overall picture of PVC–ENR fusion characteristics can be outlined to summarize the observations. In order to highlight some salient points, which might not be indicated by the plastograms,

it is better to convert the plastograms to the standard and more familiar rheological plot using the method proposed by Das[29] and also used by Nasir and Ratnam.[8] The plot of torque divided by the angular rotor speed, which is synonymous to viscosity against time, is illustrated in Figure 11.

Marked differences in mixing characteristics between the 20 and 50 rpm emerged. At the lower deformation rate, that is, at a rotor speed of 20 rpm, only two zones are observed, corresponding to the loading and fusion zone, which is still incomplete, as shown by the gradual rise in viscosity. Another important feature is the difficulty in mixing at 20 rpm, shown by the much higher viscosity; and, subsequently, higher energy is expended, even though mixing is not as effective as that at 50 rpm. The energy expended is indicated by the area under the curve.[13,20,30]

However, at the higher deformation rate (50 rpm), a complete mixing process is attained with the following three distinct zones: zone 1, a heterogeneous mixture of unfused PVC particles with ENR (loading peak); zone 2, a multiphase mixture with fusion and mixing (fusion zone); and zone 3, a homogeneous phase in which fusion or gelation has occurred and individual phases cannot be identified (stabilization zone). Beyond zone 3, samples show imminent signs of degradation.

Figure 11 Apparent viscosity–time curves for 50 : 50 PVC–ENR blend at different rotor speeds and 150°C.

Table I   Dependence of Optimum Mixing Times on Temperature and Rotor Speed Determined from the Respective Plastograms[18]

| Mixing Conditions | | Optimum Mixing Time (min) |
Temperature (°C)	Rotor Speed (rpm)	
(1) 120	50	[a]
130	50	9
140	50	7–9
150	50	4–6
160	50	3.5–6
(2) 150	20	[a]
150	30	9
150	40	7–9
150	50	4–6
150	60	3.5–6

[a] Beyond a 9-min period.

Estimation of Optimum Mixing Conditions

Suppose an optimum 50 : 50 PVC–ENR blend is desired using the Brabender Plasticorder, the combined influences of all the compounding conditions, such as rotor speed, mixing temperature, and mixing time, can be deduced from the Brabender plastograms. The blending time should be fixed somewhere after the fusion peak, while allowing for homogenization just before degradation sets in. Based on an earlier report, which considered the combined effects of rotor speed and temperature,[18] it is evident that at higher deformation rates or temperature, shorter mixing times are required to obtain blends of optimum properties. This is shown by the presence of the various peaks and plateaus, which appear earlier with an increase in rotor speed or temperature.[20] Suitable mixing times based on the criteria established above were estimated from the previous report.[18] The compounding conditions so estimated for the 50 : 50 blend are given in Table I. The overall implication of considering the time element in addition to the effects of rotor speed and/or temperature is that it is possible to predict optimum blend attainment by using the plastogram as an indicator.

CONCLUSIONS

1. The properties of 50 : 50 PVC–ENR blends are strongly dependent on all the com-

pounding variables, namely, rotor speed (shear rate), temperature, and mixing time.

2. Evidence relating the plastogram with the corresponding mechanical, dynamic, mechanical, and morphological properties clearly illustrate the important role of mixing. Correlation of a structure–property relationship with mixing time and the plastogram can facilitate the prediction of optimum blend attainment by using the plastogram as an indicator.

3. The attainment of optimum PVC–ENR blends is not limited to any particular set of conditions but obtainable by using appropriate mixing conditions, which yields a plastogram with a distinct fusion peak. Thus, it is possible to fix mixing parameters for optimum blend production through a careful study of the plastograms.

REFERENCES

1. Coran, A. Y.; Patel, R. Rubber Chem Technol 1980, 53, 141.
2. Coran, A. Y.; Patel, R. Rubber Chem Technol 1980, 53, 781.
3. Coran, A. Y.; Patel, R. Rubber Chem Technol 1981, 54, 893.
4. Kosior, E. I.; Stachurski, Z. H. Br Polym J 1986, 18, 94.
5. George, K. E.; Joseph, R.; Francis, D. J. J Appl Polym Sci 1986, 32, 2867.
6. Zizko, J. J.; Barlow, J. W.; Paul, D. R. Polymer 1981, 22, 918.
7. Thomas, S. Int J Polym Mater 1987, 12, 1.
8. Nasir, Z. A.; Ratnam, C. T. J Appl Polym Sci 1989, 38, 1219.
9. Varughese, K. T.; Nando, G. B.; De, P. P. J Mater Sci 1988, 23, 3894.
10. Chen, T. Y. B. Tech Thesis Universiti Sains Malaysia, 1988.
11. Nasir, M.; Poh, B. T.; Ng, P. S. Eur Polym J 1989, 25, 267.
12. Akhtar, S.; Kuriakose, B.; De, P. P.; De, S. K. Plast Rubber Process Appl 1987, 7, 11.
13. Blyler, L. L., Jr.; Daane, J. H. Polym Eng Sci 1967, 7, 178.
14. Schreiber, H. P.; Kapuseinski, K. Polym Eng Sci 1981, 21, 433.
15. Folt, V. L.; Smith, R. W. Rubber Chem Technol 1973, 46, 1193.
16. Mondragon, I. J Appl Polym Sci 1986, 32, 6191.
17. McGill, W. J.; Wittstock, T. Plast Rubber Process Appl 1987, 7, 185.
18. Nasir, Z. A.; Ishiaku, U. S.; Mohd Ishak, Z. A. J Appl Polym Sci 1994, 47, 951.
19. Hofmann, G. H. Polymer Science and Technology, Vol. 20, Polymer Alloys III; Klempner, D.; Frisch, K. C., Eds.; Plenum Press: New York, 1983.
20. Luben, H. E. Presented at Seminar on Flow and Cure of Polymers, Measurement and Control, RAPRA Technol Ltd, 1990.
21. Brown, R. J. Plast Compound 1991, 14, 63.
22. Ishiaku, U. S.; Nasir, M.; Mohd Ishak, Z. A. J Vinyl Technol 1994, 16, 226.
23. Ishiaku, U. S.; Nasir, M.; Mohd Ishak, Z. A. J Vinyl Technol 1994, 16, 219.
24. Wetton, R. E.; de Blok, R.; Corish, P. J. Int Polym Sci Technol 1991, 18, 63.
25. Gelling, I. R.; Matherell, C. Technical Update, Malaysian Rubber Bureau, Hertford, UK, 1990.
26. Varughese, K. T.; De, P. P.; Sanyal, S. K.; De, S. K. J Appl Polym Sci 1989, 37, 2537.
27. Margaritis, A. G.; Kallitsis, J. K.; Kalfoglou, N. K. Polymer 1987, 28, 2122.
28. Varughese, K. T.; De, P. P.; Nando, G. B.; De, S. K. J Vinyl Technol 1987, 9, 161.
29. Das, C. K. Int J Polym Mater 1986, 11, 211.
30. Utraki, L. A. Polymer Alloys and Blends; Hanser Publishers: Munich, 1990.