

Studies on NBR/PVC Blends

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Synopsis

Studies conducted on butadiene-acrylonitrile copolymer (NBR)/poly(vinyl chloride) (PVC) blends at different temperatures indicate that an optimum temperature exists for the formation of a particular blend. The mechanical properties of the blends confirm this observation. PVC stabilizer based on magnesium oxide, zinc oxide, and stearic acid was found to be very useful in NBR/PVC blends.

INTRODUCTION

Blending of polymers for property improvement or for economic advantage has gained considerable importance in the field of polymer science in the last decade. Miscibility of the constituent polymers is often a necessity for forming successful blends. One of the commercially important and miscible polymer blends is that of NBR and PVC.¹⁻³ NBR acts as a permanent plasticizer for PVC in applications like wire and cable insulation, food containers, pond liners used for oil containment, etc. On the other hand, PVC improves ozone, thermal aging, and chemical resistance of NBR in applications like feed hose covers, gaskets, conveyor belt covers, printing roll covers, etc. PVC also vastly improves abrasion resistance, tear resistance, and tensile properties. It also adds gloss and improves finish of the extruded stock and imparts flame-retardant character. NBR/PVC blends can be conveniently milled, extruded, and compression-molded using traditional processing equipments for natural and synthetic rubbers.⁴ One difficulty in forming successful blends of NBR and PVC is the lack of suitable stabilizers for PVC which do not affect NBR. Although the barium stearate/cadmium stearate combination, the commonly used PVC stabilizer in NBR/PVC blends,⁴ does not seem to produce any obvious deterioration in the physical properties, it does produce a yellowish tint which limits the color flexibility of the blends.⁵ Recently it was shown that magnesium oxide and zinc oxide combination along with stearic acid could efficiently stabilize plasticized PVC.⁶ These conventional ingredients in rubber compounding do not produce any color. Hence magnesium oxide and zinc oxide along with stearic acid were tried as the stabilizer for PVC in this study on NBR/PVC blends. A Brabender Plasticorder has been used extensively for assessing the fusion characteristics and mechanical and thermal stability and processing characteristics of polymers.⁷⁻¹⁰ Such an investigation has been carried out on NBR/PVC blends using a Plasticorder. The results of this evaluation are checked with the mechanical properties of the blends.

EXPERIMENTAL

Materials

Polymers. NBR (medium nitrile, Mooney viscosity (ML 1 + 4, 100°C)—40.9) and PVC (powder, suspension polymer, K value—65).

Stabilizer. Magnesium oxide (light magnesia, rubber grade), zinc oxide (white seal, rubber grade), and stearic acid (rubber grade).

Curatives. Sulfur, benzothiazyl disulfide (MBTS), tetramethylthiuram disulfide (TMTD), zinc oxide, and stearic acid (all rubber grade).

Studies on a Brabender Plasticorder

The study was conducted on a Brabender Plasticorder Model PL 3S (rotor speed 30 rpm, sensitivity 0–5000 mg). A total weight of 34 g was selected as the sample weight for each run on the Plasticorder after carefully observing the torque curves for different sample weights.¹¹ Six combinations of blends were made by taking PVC 10, 20, 30, 40, 50, and 60% of the total weight. 4.0 parts per hundred PVC (phr) MgO, 4.0 phr zinc oxide and 3.0 phr stearic acid were taken together with PVC as stabilizer.⁶ The rest of the weight constituted NBR and its curatives—1.5 phr sulfur with accelerators (1.5 phr MBTS and 0.5 phr TMTD) and activators (2.0 phr ZnO and 1.0 phr stearic acid). The recipe for the blend containing 20% PVC is shown in Table I as an example. For all the test runs on the Plasticorder, NBR was added initially, after the mixer attained the required temperature. After giving 1 min time for the rubber to heat up and homogenise in the mixer, PVC with its stabilizer was added. The polymers were blended for 5.5 min and then the curatives were added. Once the mass broke down to crumbs it was removed. The study was repeated for the six combinations of blends at different temperatures.

Evaluation of Mechanical Properties

For measuring the mechanical properties, the blend containing 20% PVC was made at 135, 145, and 155°C and the blend containing 50% PVC at 145, 155, and 165°C. These blends were prepared in the Brabender Plasti-

TABLE I
Recipe for the Blend with 20% PVC

I. PVC and Stabilizer	
PVC	6.80 g (20% of total weight)
MgO	0.27 g (4.0 phr PVC)
ZnO	0.27 g (4.0 phr PVC)
Stearic acid	0.20 g (3.0 phr PVC)
II. NBR and Curatives	
NBR	24.85 g
S	0.37 g (1.5 phr NBR)
Activator	
ZnO	0.50 g (2.0 phr NBR)
Stearic acid	0.25 g (1.0 phr NBR)
Accelerators	
MBTS	0.37 g (1.5 phr NBR)
TMTD	0.12 g (0.5 phr NBR)
	34.00 g

order using the same recipe as that used for Brabender studies. However, a blending time of 10 min was employed,¹² and the curatives in each case were added later in a two-roll laboratory mixing mill at about 50°C since it could not be added in the Plasticorder at this temperature because of the very high torque involved. The cure times of the various compounds were determined at 150°C in a Monsanto Rheometer Model R100. Test samples for evaluating the physical properties were vulcanized up to the respective cure times at 150°C. The tensile properties were determined in a Zwick Universal Testing Machine as per ASTM D 412 (1968). A Shore-A type durometer was used for determining the hardness of the vulcanizates as per ASTM 224D (1968).

RESULTS AND DISCUSSION

Figure 1 shows the Brabender torque curves of the NBR/PVC blend containing 20% PVC and that of NBR alone at 155°C. The curve for the blend may be explained as follows. NBR is charged into the mixing chamber in the region A to B, and hence the torque rises. Once the addition of NBR is over, the rubber homogenizes and the torque begins to decrease at B mainly due to degradation in the rubber, especially mechanical. At C, PVC is added. As the PVC melts, the torque rises again up to D and thereafter remains almost steady up to E. It may be observed that the tendency for degradation in the blend is not so obvious as before, and this might be due to the protection offered by the PVC phase. Curatives are added at E. The torque decreases to a minimum value F due to the lubricant action of these additives. Once crosslinking starts, the torque rises again. At G, the curing is completed and the material breaks down, which accounts for the sudden decrease in torque up to H. The torque curve for NBR alone shows that the decrease in torque due to degradation continues from the point B up to the point E. However, the rate of decrease in torque falls off from B to E due to the decrease in shear as a result of the degradation. Table II shows the torque at the points B, C, D, E, and G of the blends containing different

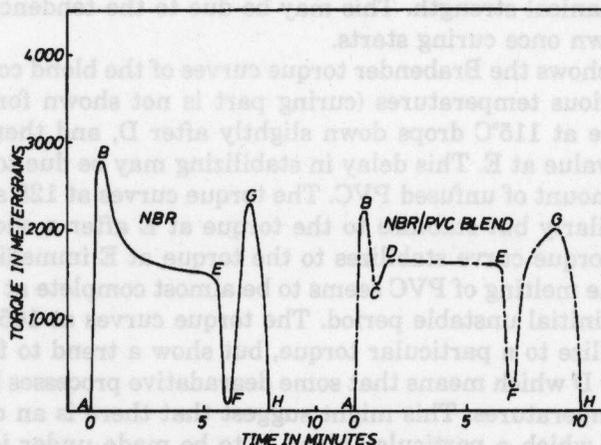


Fig. 1. Brabender torque curves of NBR and NBR/PVC blend containing 20% PVC at 155°C: (A, B) addition of rubber; (C) addition of PVC; (E) addition of curatives.

TABLE II
 Brabender Torque Values of the Blends at 155°C^a

Blend composition % of PVC	Torques at various points (metergrams)				
	B	C	D	E	G
10%	2500	1500	1800	1550	2000
20%	2200	1400	1650	1600	2000
30%	1900	1100	1750	1750	2200
40%	1600	800	1750	1850	2200
50%	1200	500	1700	1950	2300
60%	1100	300	1400	1850	2200

^a Reference, Figure 1.

percentages of PVC at 155°C. In the case of the blend containing 10% PVC there is some decrease in torque from D to E. This shows that this amount of PVC is not enough to protect the rubber phase under the conditions existing in the mixer. The 20% PVC blend shows only a slight decrease in torque from D to E. For the blends containing 30, 40, and 50% PVC, the torque rises again after the point D, and then stabilizes to the torque value at E, which suggests that the melting of PVC is not complete at point D, but continues in the mixing time. In the case of the blend containing 60% PVC, the torque continues to rise till the end of the mixing time, indicating insufficient mixing time and/or mixing temperature. The torque observed at point E increases with the percentage of PVC as expected, and this torque may be assumed to reflect the mechanical strength of blends. However, the 60% blend shows a lesser torque at E than that of the 50% blend. Clearly, the PVC has not melted properly to show the full torque. The torque shown by the blends after curing (torque at G) seems to be only a rough measure of the mechanical strength. This may be due to the tendency of the mass to break down once curing starts.

Figure 2 shows the Brabender torque curves of the blend containing 20% PVC at various temperatures (curing part is not shown for clarity). The torque curve at 115°C drops down slightly after D, and then stabilizes to the torque value at E. This delay in stabilizing may be due to the presence of a good amount of unfused PVC. The torque curves at 125 and 135°C also behave similarly but stabilize to the torque at E after a shorter time. At 145°C, the torque curve stabilizes to the torque at E immediately after D. At 155°C, the melting of PVC seems to be almost complete at D itself, since there is no initial unstable period. The torque curves at 165 and at 175°C do not stabilize to a particular torque, but show a trend to fall off continuously after D which means that some degradative processes become active at these temperatures. This might suggest that there is an optimum temperature at which a particular blend is to be made under identical rotor speed and blending time. A comparison of the torque values at E of the 20% blend at various temperatures (Table III) shows that when the temperature goes up from 115 to 125°C, the torque goes down by 150 metergrams. Since the PVC might not be fully melted at this temperature even at the point E, this difference in torque might have occurred predominantly

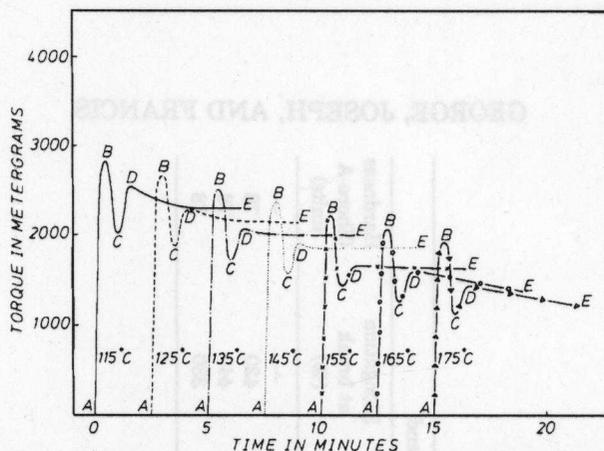


Fig. 2. Brabender torque curves of NBR/PVC blend containing 20% PVC at different temperatures (curing part not shown): (A, B) addition of rubber, (C) addition of PVC. Times marked in the abscissa refers only to the curve at 115°C. For the others, zero starts from the point marked A. The scale, however, is the same.

from two factors: an overall tendency for the viscosity to come down due to the rise in temperature and the tendency of the PVC phase to enhance the viscosity by melting more of that phase. From 125 to 135°C and from 135 to 145°C the difference in torque remains the same, indicating that these two factors continue to exert almost the same influence. Between 145 and 155°C the difference in torque rises to 250 metergrams, which might suggest that the effect of more PVC melting is almost negligible in this case. Since some degradative processes might be under operation at higher temperatures as observed earlier, 145°C might be the best temperature for making 20% blends. Table III also shows the torque at the point E of the 50% blend at various temperatures. Again, comparison of the torques indicates that 155°C might be the minimum temperature at which this blend fully homogenizes and hence this may be the optimum temperature for making 50% blend.

Table IV gives the scorch time, cure time, tensile strength, elongation at break, and hardness of the 20 and 50% PVC blends made at different

TABLE III
Brabender Torque Values of 20% PVC and 50% PVC Blends at Different Temperatures*

Temp (°C)	Torque at the point E of 20% PVC blend (metergrams)	Torque at the point E of 50% PVC blend (metergrams)
115	2300	2050
125	2150	2250
135	2000	2200
145	1850	2100
155	1600	1950
165	1400	1625
175	1225	1450

* Reference, Figures 1 and 2.

TABLE IV
Cure Characteristics and Mechanical Properties of Blends Made at Different Temperatures

Temp (°C)	20% PVC blend					50% PVC blend				
	Scorch time (min)	Cure time (min)	Tensile strength (N/mm ²)	Elongation at break (%)	Hardness (Shore-A units)	Scorch time (min)	Cure time (min)	Tensile strength (N/mm ²)	Elongation at break (%)	Hardness (Shore-A units)
135	6.5	14	5.3	425	53	—	—	—	—	—
145	7.5	14	6.1	490	52	9.0	14.5	14.2	420	78
155	7.0	14.5	5.5	470	51	9.5	14.5	15.2	440	78
165	—	—	—	—	—	9.0	15.0	14.8	380	78

temperatures. The 20% blend made at 145°C and the 50% blend made at 155°C show the maximum scorch safety in agreement with the Brabender evaluation. The tensile strengths observed for the blends is much higher than that observed for NBR alone (1.81 N/mm²). For the 20% blend, maximum tensile strength is observed for the blend taken at 145°C and for the 50% blend maximum is observed for the blend taken at 155°C, again in agreement with the observation made on the Brabender Plasticorder. The elongation at break of the blends is higher than that of NBR alone (285%). But this property seems to fall off after a particular percentage of PVC since the 50% blend shows a lower value than the 20% blend. In this case also the highest value is observed for the blend made at 145°C for the 20% blend and for the blend made at 155°C for the 50% blend. The hardness of the blends increases with the percentage of PVC, as expected. Although the change in hardness of a blend made at different temperatures is small, the 20% PVC blend made at 135°C shows a higher hardness than that made at 145°C, which might indicate inferior homogeneity. Further, the blend made at 155°C shows a lesser value, which indicates that some degradations have occurred.

CONCLUSION

The study shows that the stabilizer system MgO and ZnO with stearic acid is very effective in NBR/PVC blends. Further, an optimum temperature exists for the formation of a particular NBR/PVC blend and this temperature can be determined using a Brabender Plasticorder.

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