Oil Resistance Controlled by Phase Morphology in Natural Rubber/Nitrile Rubber Blends

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ABSTRACT: Rheological properties, morphology, and oil resistance in natural rubber (NR)/nitrile rubber (NBR) blends were investigated as functions of blending conditions and viscosity ratios of the blends. As for the blending condition effects, Mooney viscosity of the blends depended more strongly on blending time than rotor speed. Size of the NR dispersed phase was approximately independent of rotor speed but decreased with increasing blending time up to 25 min. As blending time further increased, NR dispersed phase size increased. The results of relative tensile strength, which is an indicator for oil resistance, in this study were in agreement with those of the blend morphology, indicating that the oil resistance in 20/80 NR/NBR blend depended strongly on the phase morphology of the blend. The smaller the size of NR dispersed phase was, the higher was the resistance to oil of the blend. However, a decrease in the size of the dispersed phase by the modification of the viscosity ratio via the use of low-molecular-weight rubber (i.e., liquid natural rubber and epoxidized liquid natural rubber) did not result in an improvement in the oil resistance. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 83–89, 2003

Key words: blends; morphology; mixing; viscosity ratio

INTRODUCTION

Each polymer possesses its own advantages and disadvantages in properties. For example, natural rubber (NR) has excellent mechanical properties but relatively poor oil resistance, whereas nitrile rubber (NBR) possesses those properties in an opposite trend. In addition, NR is significantly cheaper than NBR. As a consequence, blending these two rubbers together is one of the best solutions for the achievement of good mechanical properties and oil resistance.

The physical properties of polymer blends are generally controlled by many factors, including the nature of the polymer, blend composition,[1–3] and blend morphology.[4–12] Blend morphology can also be used as an indicator for the determination of blend compatibility. Generally, a smaller phase size of the dispersed phase indicates better blend compatibility of the system, resulting in improved mechanical properties of the blends.[13–19] Speri and Patrick[13] suggested that the relatively high impact resistance of polypropylene (PP)/ethylene–propylene rubber (EPR) blends could be achieved in the blends with small and narrow particle size and particle size distribution, respectively. In a similar system, D'Orazio et al.[14] reported that EPR particle sizes ranging between 0.1 and 1.0 μ with an average diameter of 0.4 μ were more effective for toughening PP than those between 0.1 and 0.5 μ. The effect of average particle size on impact strength was found to be more significant at low temperatures. In chlorinated polyethylene/polyvinyl chloride blends, the addition of epoxidized NR improved blend compatibility and, thus, mechanical properties.[16] Likewise, the tensile properties of linear low-density polyethylene/NR blends have been reported to be improved by the addition of liquid natural rubber (LNR).[17] Oommen et al.[18] revealed that the optimum values of the mechanical properties in NR/poly(methyl methacrylate) blends were obtained at the smallest domain size of NR. Fortelny et al.[19] found that the notched impact strength of PP/ethylene propylene copolymer blends at rubber contents lower than 15% did not depend strongly on the rubber particle size. At higher rubber concentrations, the impact strength decreased with increasing particle size. It is obvious that most of the previous work has dealt mainly with tensile and impact properties. Therefore, in this study, the relationships among blending conditions (i.e., blending time and rotor speed), viscosity ratio, phase size of the dispersed phase, and oil resistance in NR/NBR blends were investigated qualitatively.

EXPERIMENTAL

Materials

NR (STR 5, Thailand) and NBR with acrylonitrile contents of 35% (N230S, JSR, Japan), having Mooney viscosities (ML 1 + 4 at 100°C) of 80 and 57, respectively,

TABLE I
Mooney Viscosity Ratio Used in this Study

Viscosity ratio of NR to NBR	Mooney viscosity ratio of NR to NBR
0.5	28:56
1.0	56:56
2.0	74:37

were used. A peroxide curing system was chosen to minimize the possibility of nonuniform curative distribution in the blends. In this study, dicumyl peroxide (DCP) was used as a curing agent. LNR with a viscosity-average molecular weight (M_v) of 8400 was prepared from NR latex by the use of phenylhydrazine and oxygen peracid in our laboratory. Epoxidized liquid natural rubber (ELNR) with a M_v of 9800 and a percentage epoxidation of 24.5 was prepared from LNR with acid–hydrogen peroxide.

Mixing and vulcanization procedures

We chose a NR/NBR blend ratio by weight of 20/80 to ensure the morphology with NR dispersed in NBR matrix. The masticated NR with a Mooney viscosity of 56 and raw NBR were blended in a Banbury internal mixer with a fill factor of 0.6 at a circulating water temperature of 40°C. Mixing times of 15, 20, 25, 30, and 40 min and rotor speeds of 40, 45, 55, and 60 rpm were used. The mix was then sheeted on the cooled two-roll mill and finally, compression-molded into 2 mm thick sheets. A cure time of 16 min was used (which gave about 94% cure calculated from the half-life of DCP).

For the study of the viscosity ratio effect, three viscosity ratios of NR to NBR were used for preparing the blends (0.5, 1.0, and 2.0), as illustrated in Table 1. To prepare the blend with viscosity ratio of 1.0, NR was masticated from the Mooney viscosity of 74 to 56 (i.e., equivalent to NBR Mooney viscosity). For the viscosity ratio of 0.5, the masticated NR with a Mooney viscosity of 56 was further masticated with 5-phr LNR to yield a Mooney viscosity of 28. Likewise, for the viscosity ratio of 2.0, the NBR was masticated with 5-phr ELNR to give a Mooney viscosity of 37. The blending process was carried out in a Banbury-type internal mixer with a fill factor of 0.6, a circulating water temperature of 40°C, and a rotor speed of 55 rpm for 25 min. The mixes were then sheeted on a cooled two-roll mill and, finally, compression-molded into 2 mm thick sheets.

Rheological measurement

Rheological properties of the compounds were measured with a Mooney viscometer. The values of Mooney viscosity (ML 1 + 4 @100°C) were determined according to ASTM D 1646 87 and reported in Mooney units.

Morphological study

The vulcanizate samples were cryogenically microtomed with glass knives. The morphology of thin-sectioned samples was then observed with an optical microscope that was connected to an image analyzer.

Oil resistance measurement

The dumbbell-shaped (punched out with Die C, ASTM D 412 92) test specimens were immersed in oil (Grena DX, Bangjak Petroleum, Co. Ltd., Thailand) at room temperature for 70 h. Thereafter, we removed the specimens from the oil and quickly dipped them in acetone and blotted them lightly with filter paper to eliminate the excess oil on the specimen surfaces. Changes in the tensile strength of specimens after oil immersion were used to determine the oil resistance. In this study, the relative tensile strength, which was calculated from the ratio of tensile strength of specimens after oil immersion to that before oil immersion, was used to eliminate the mastication effect that took place during blending process, which might have affected the oil resistance.

Tensile properties were measured with an Instron 4301 tensile tester with a crosshead speed of 500 mm/min and a full-scale load cell of 100 kg in accordance with ASTM D 638.

RESULTS AND DISCUSSION

Influence of rotor speed

Figure 1 shows that the Mooney viscosity did not change significantly with increasing rotor speed, indicating a low degree of mastication effect. In theory, an increase in rotor speed and, thus, shear rate should increase shear stress, promoting mechanical mastica-
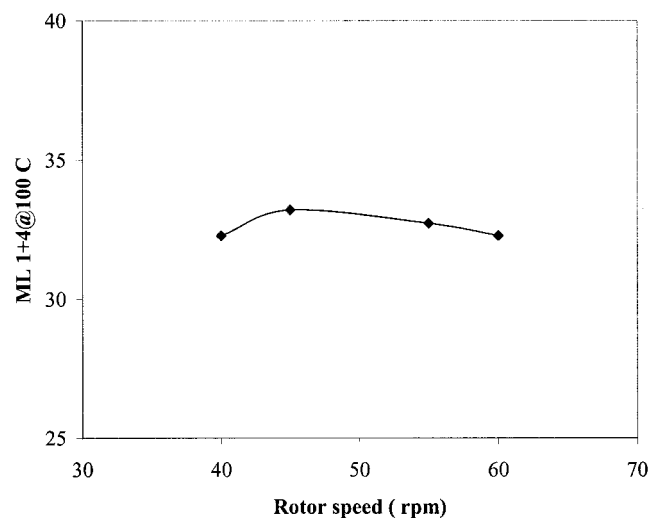

Figure 1　Relationship between Mooney viscosity and rotor speed.
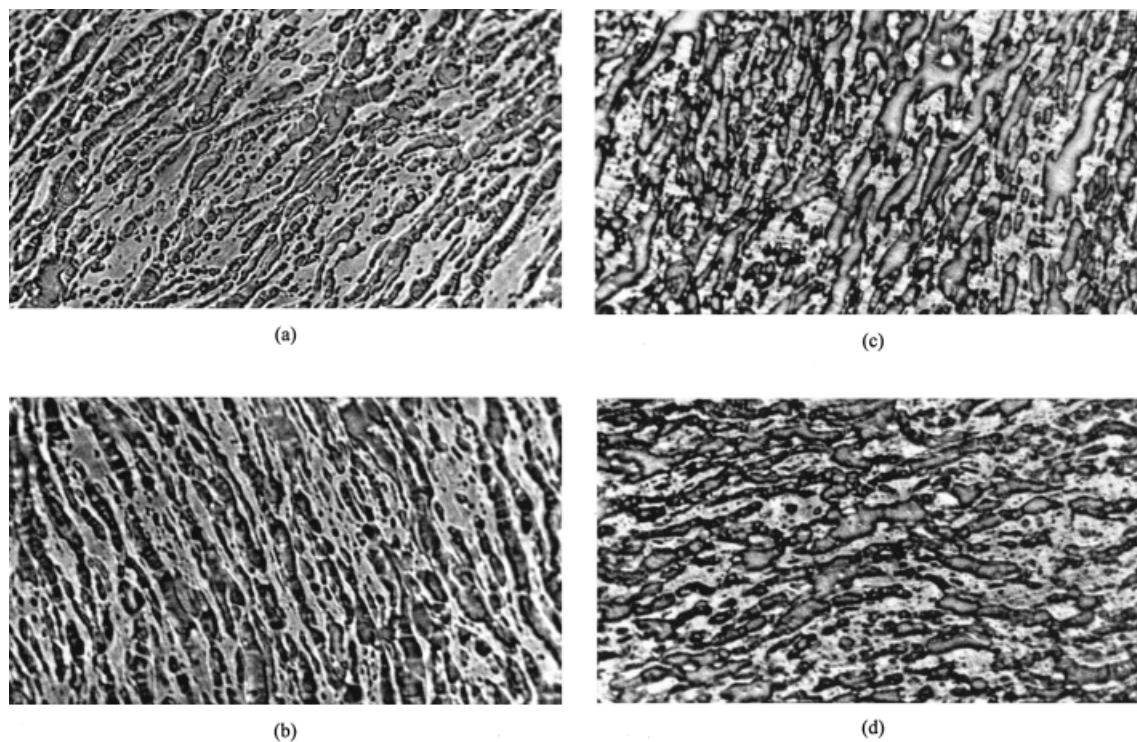
Figure 2 Micrographs of blends prepared from various rotor speeds ($\times$ 200): (a) 40, (b) 45, (c) 55, and (d) 60 rpm.

tion. By contrast, an increase in rotor speed led to a rise in bulk temperature, due to shear heating, which caused a decrease in shear viscosity. A decrease in shear stress therefore occurred, which decreased the efficiency of mechanical mastication. In other words, from the results obtained, it is possible that an increase in bulk temperature as a function of rotor speed might have canceled out the mastication effect.

The results of blend morphology are shown in Figure 2(a–d). It was evident that the phase size of NR did not change significantly with increasing rotor speed, which could be explained by an increase in
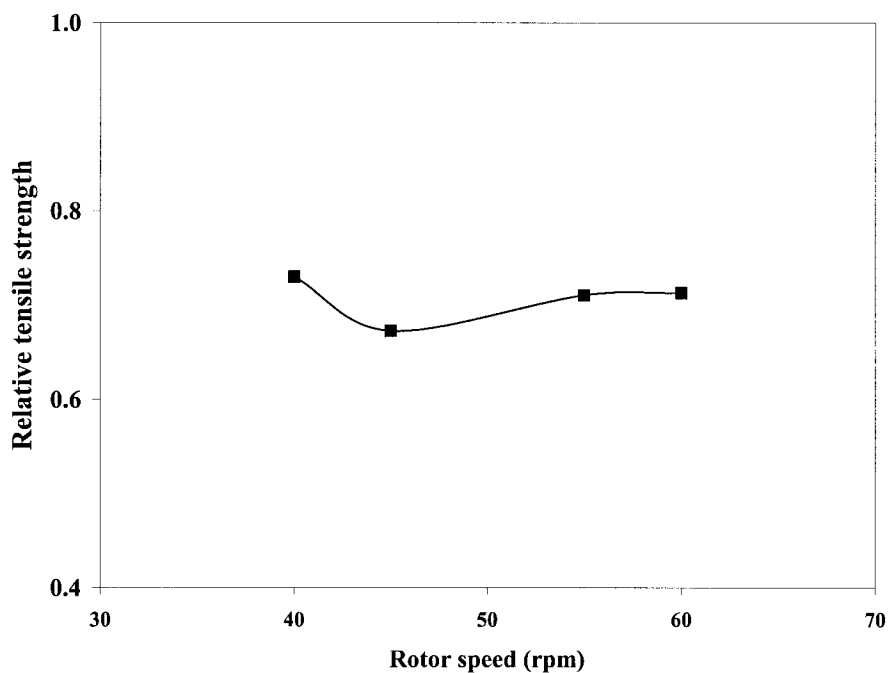

Figure 3 Relationship between relative tensile strength and rotor speed.
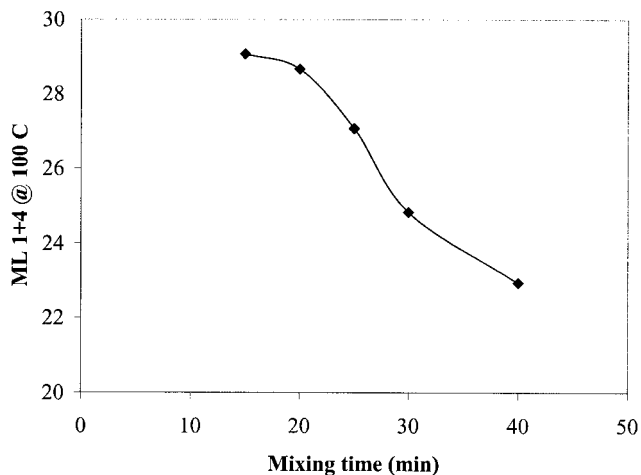
Figure 4 Relationship between Mooney viscosity and blending time.

bulk temperature due to shear heating generated as a function of rotor speed. The temperature rise led to a decrease in the shear stress taking place for disrupting the dispersed phase. The insensitivity of phase size to a change in rotor speed has been reported previously by Favis[20] in a blend system of polycarbonate and PP.

Figure 3 represents the relationship between relative tensile strength (used for determining oil resistance) and rotor speed. It is clear that the relative tensile strength did not change significantly with increasing rotor speed. Obviously, the results of blend morphology and relative tensile strength were in good agreement, which led to a preliminary conclusion that the oil resistance of NR/NBR compounds was controlled by size of the NR dispersed phase. Nonetheless, further investigation of the dependence of oil
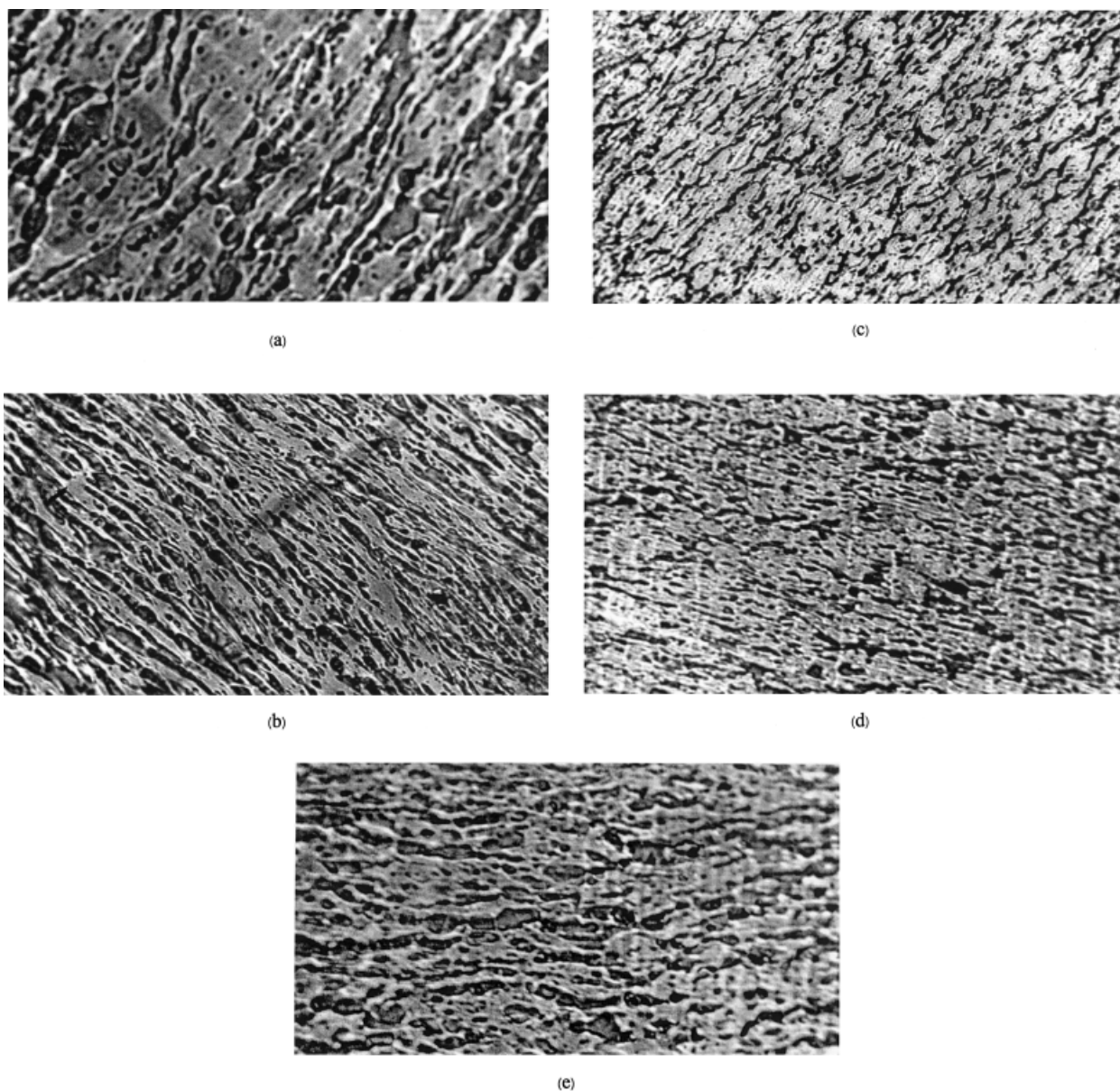

Figure 5 Micrographs of blends prepared from various blending times ($\times$ 400): (a) 15, (b) 20, (c) 25, (d) 30, and (e) 40 mins.
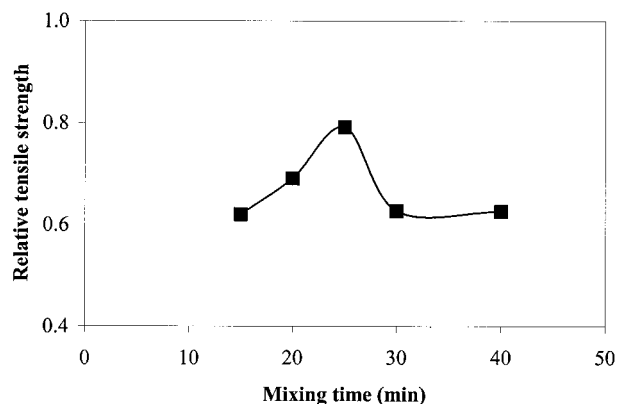
Figure 6 Relationship between relative tensile strength and blending time

resistance on blending time needed to be carried out before the final conclusion could be drawn.

Influence of blending time

Unlike the rotor speed, blending time appeared to strongly affect Mooney viscosity, as shown in Figure 4. The longer the blending time was, the lower was the Mooney viscosity. Certainly, the mastication effect was responsible for the decrease in compound viscosity.

The morphology of the blends prepared from various blending times is shown in Figure 5(a–e). It was obvious that size of the NR dispersed phase decreased with increasing blending time up to 25 min [Fig. 5(e)]. Then, the size of the dispersed phase increased again. The decrease in dispersed phase size was attributed to the increase in total shear strain applied to the compounds. At a given shear rate, the longer blending time gave a larger total shear strain and, thus, a smaller dispersed phase size. The increase in phase size of the dispersed phase with the blending time longer than 25 min might have been the result of the sufficiently long time available for the collision of the unstabilized dispersed phase leading to phase coalescence.[21,22]

Figure 6 reveals the relationship between relative tensile strength and blending time. It was clear that the relative tensile strength increased with increasing blending time up to 25 min and then decreased with further increasing blending time. The results of morphology and relative tensile strength were in good agreement, similar to the case of rotor speed mentioned previously.

From all of the results, it could be concluded that the phase morphology of the blends played a strong role in oil resistance as a function of relative tensile strength. The smaller the dispersed phase size was, the higher was the relative tensile strength, and, thus, the higher the oil resistance was. As shown in Figure 7, the proposed

explanation is as follows: compared to NR, NBR possesses excellent resistance to hydrocarbon liquids. Thus, when the blends were immersed in oil, the NR dispersed phase swelled markedly, leading to low resistance to failure of the blends. In the case of the small dispersed phase size of NR, the large surface area of the small dispersed phase of NR was surrounded by the NBR phase, possessing high resistance to oil. Thus, oil swelling occurring mainly within small NR phase was stopped by the surrounding NBR, resulting in a high value of relative tensile strength. By contrast, a large degree of swelling in a large NR dispersed phase was stopped ineffectively by NBR due to a small surface area of the NR dispersed phase surrounded by NBR. This led to low resistance to failure and, thus, low relative tensile strength.

Influence of viscosity ratio

Figure 8(a–c) reveals the morphology of the blends with different viscosity ratios. At a high viscosity ratio of 2.0 (i.e., the viscosity of the dispersed NR was higher than those of the NBR matrix), the NR phase size was remarkably larger than that at the low viscosity ratios of 0.5 and 1.0, respectively. This was evidence that high shear stress caused by the high shear viscosity of the NBR matrix in the blends with viscosity ratios of 0.5 and 1.0 could transfer to the NR dispersed phase and then promoted the disruption of the dispersed phase.

However, Figure 9 shows the unexpected results of relative tensile strength. It appeared that the blend with a viscosity ratio of 2.0, possessing a relatively large NR dispersed phase, showed higher relative tensile strength than that with a viscosity ratio of 0.5. In other words, the blend with a smaller NR dispersed phase resulted in lower oil resistance, which was contrary to the proposed model and to the results obtained earlier. This unexpected result could be explained by the dilution effect. Because the blend with a viscosity ratio of 0.5 was prepared by the addition of 5-phr LNR possessing poor oil resistance to the blend, the blend contained a relatively large amount of the phase with poor resistance to oil (i.e., NR phase). This could have led to a significant decrease in the oil resistance of the blend with a viscosity of 0.5,
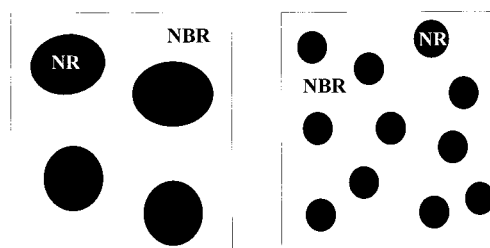

Figure 7 Proposed model of blends with different dispersed phase: (a) large and (b) small sizes.

despite the relatively small size of the NR dispersed phase. On the other hand, the blend with a viscosity ratio of 2.0 was prepared by plasticizing NBR with ELNR. As a result, the blend with viscosity ratio of 2.0 contained a relatively large amount of the phase with high resistance to oil, leading to an increase in the oil resistance of the blend, although the NR phase size in this blend was relatively large. Clearly, from the results obtained, it could be concluded that although the addition of LNR for controlling the viscosity ratio could reduce the NR phase size, it reduces the oil resistance of the blends.
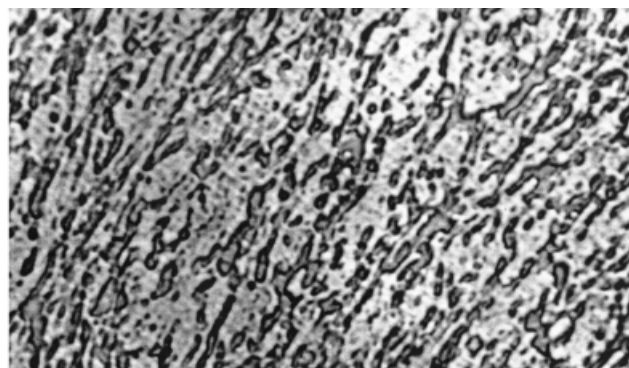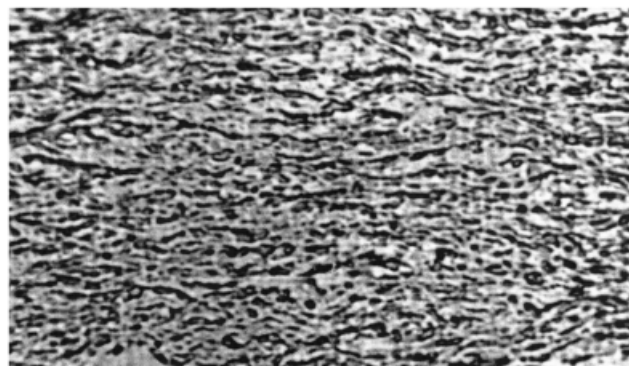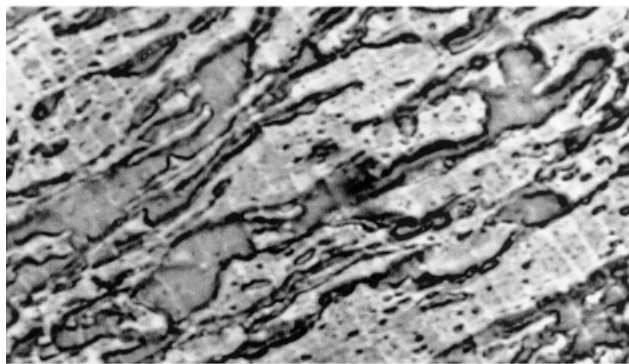
Figure 8 Micrographs of the blends prepared with different NR/NBR viscosity ratios ($\times$ 200): (a) 0.5, (b) 1.0, and (c) 2.0.
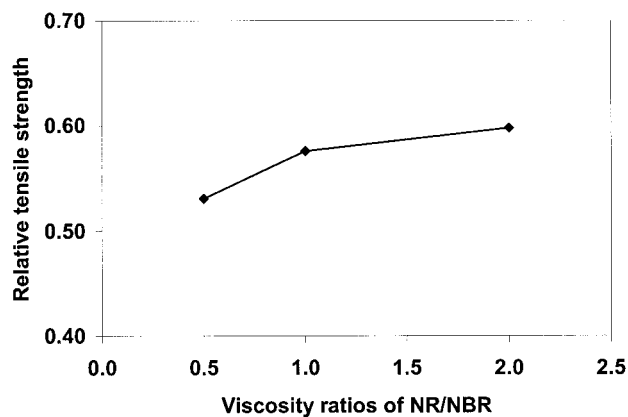

Figure 9 Relationship between viscosity ratio and relative tensile strength.

CONCLUSIONS

The relationship between phase morphology, blending conditions (i.e., rotor speed and blending time), and oil resistance in 20/80 NR/NBR blends was investigated. The Mooney viscosity of the blends depended more strongly on blending time than on rotor speed. The size of the NR dispersed phase was approximately independent of rotor speed but decreased with increasing blending time up to 25 min before it increased again with a further increase in blending time. Results of relative tensile strength, which is an indicator for oil resistance, in this study were in agreement with those of the blend morphology, indicating that the oil resistance in 20/80 NR/NBR blend depended significantly on the phase morphology of the blend. The smaller the size of NR dispersed phase was, the higher was the resistance to oil of the blend.

The viscosity ratio significantly affected the phase morphology of the blends; that is, the low viscosity ratio gave the small phase size of the blend. However, the small phase size of NR obtained by the use of LNR to modify the viscosity ratio did not result in an enhancement of oil resistance, which might be attributed to the dilution effect.

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