Relationships Among Blending Conditions, Size of Dispersed Phase, and Oil Resistance in Natural Rubber and Nitrile Rubber Blends

CHAKRIT SIRISINHA,[1,2] SAUVAROP BAULEK-LIMCHAROEN,[1] JARUNEE THUNYARITTIKORN[1]

[1] Department of Chemistry, Mahidol University, Rama 6 Road, Bangkok 10400, Thailand

[2] The Polymer Technology Research and Development Center, Institute of Science and Technology for Research and Development, Salaya Campus, Nakorn Pathom 73170, Thailand

ABSTRACT: The rheological properties, morphology, and oil resistance in natural rubber and nitrile-butadiene rubber (NR/NBR) blends are investigated as functions of the blending conditions. It is found that the Mooney viscosity of the blends depends more strongly on the blending time than the rotor speed. The size of the NR dispersed phase is approximately independent of the rotor speed, but it decreases with increasing blending time up to 25 min. With a further increase in the blending time the NR dispersed phase size decreases. The results for the relative tensile strength, which is an indicator of oil resistance, are in agreement with those of the blend morphology, indicating that the oil resistance in a 20/80 NR/NBR blend strongly depends on the phase morphology of the blend. The smaller the size of NR dispersed phase, the higher the blend resistance to oil. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1232–1237, 2001

Key words: rubber blend; morphology; oil resistance; relative tensile strength; mixing conditions; Mooney viscosity

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 and nitrile rubber (NBR) has the opposite. As a consequence, blending these two rubber together is one of the best solutions to achieving good mechanical properties and oil resistance.

The physical properties of polymer blends are generally controlled by many factors including the nature of the polymer, the blend composition,[1–3] and the blend morphology.[4–12] It is also known that the blend morphology can be used as an indicator for determining the blend compatibility. Generally, the smaller phase size of the dispersed phase indicates the 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/epoxidized natural rubber (PP/ENR) blends could be achieved in the blends with small and narrow particle size and particle size distribution, respectively. In a similar system D'Orazio and coworkers[14] reported that the EPR particle sizes ranging between 0.1 and 1.0 μm with an average diameter of 0.4 μm were more effective for toughening PP than those between 0.1 and 0.5 μm. The effect of

the average particle size on the impact strength was found to be more significant at low temperature. In chlorinated polyethylene/polyvinyl carbonate (CPE/PVC) blends the addition of ENR could improve the blend compatibility and thus the mechanical properties.[16] Likewise, the tensile properties of linear low-density PE/NR blends were reportedly improved by the addition of liquid natural rubber.[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-diene monomer blends at rubber contents lower than 15% did not strongly depend on the rubber particle size. At higher rubber concentrations the impact strength decreases with increasing particle size. It is obvious that most of the previous work mainly dealt with tensile and impact properties. Therefore, in the present study the relationships among the blending conditions (i.e., blending time and rotor speed), the phase size of the dispersed phase, and the oil resistance in NR/NBR blends are investigated qualitatively.

EXPERIMENTAL

Materials

The NR (STR 5) and NBR with acrylonitrile content of 35% (N230S, JSR) that were used had Mooney viscosities (ML1+4 at 100°C) of 80 and 57, respectively. In the present study, dicumyl peroxide (DCP) was used as a curing agent. The peroxide curing system was chosen to minimize the possibility of nonuniform curative distribution in the blends.

Mixing Procedure

The NR/NBR blend ratio of 20/80 (w/w) was chosen to ensure the morphology with a NR dispersed phase in the NBR matrix. Before blending the NR was masticated to reduce the Mooney viscosity from 80 to 56 using a Banbury-type internal mixer with a fill factor of 0.6, circulating water at 40°C, and a rotor speed of 55 rpm for 15 min. Thereafter, the masticated NR and raw NBR were blended in the internal mixer with mixing times of 15, 20, 25, 30, and 40 min and rotor speeds of 40, 45, 55, and 60 rpm. DCP was charged to a mixer at a mixing time of 11 min

after blending. The mix was then sheeted on a cooled two-roll mill and finally compression molded into 2-mm thickness sheets. The cure time used was 16 min, which gave about 94% cure calculated from the half-life of DCP.

Rheological Measurement

The rheological properties of the compounds were measured using a Mooney viscometer (Monsanto 1500) with a large rotor at a test temperature of 100°C. The Mooney viscosity (ML1+4 at 100°C) values were determined according to ASTM D1646-87 and reported in Mooney units. At least five samples for each formula were used for a measurement.

Morphological Study

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

Oil Resistance Measurement

Dumbbell-shaped (punched out using die C, ASTM D412-92) test specimens were immersed in oil (Tellus 100, Shell Co. Ltd.) at room temperature for 70 h. Thereafter, the specimens were removed from the oil, quickly dipped in acetone, and blotted lightly with filter paper to eliminate the excess oil on the specimen surfaces. The changes in the tensile strength of the specimens after oil immersion were used to determine the oil resistance. In this study the relative tensile strength, which is calculated from the ratio of the tensile strength of the specimens after oil immersion to that before oil immersion, was used to eliminate the mastication effect caused by varying mixing times and rotor speeds.

The tensile properties were measured using 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 D638.

RESULTS AND DISCUSSION

Influence of Rotor Speed

Figure 1 shows that the Mooney viscosity does not change significantly with increasing rotor speed, indicating a low effect for the degree of mastica-
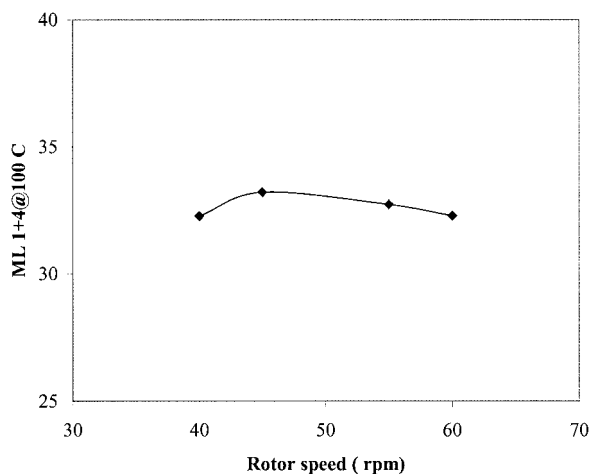
Figure 1 The relationship between the Mooney viscosity and the rotor speed.

tion. In theory, an increase in the rotor speed and thus the shear rate should increase the shear stress, promoting mastication. By contrast, an increase in rotor speed leads to a rise in the bulk temperature due to shear heating, which causes a decrease in the shear viscosity. A decrease in the shear stress therefore results and it decreases the efficiency of the mechanical mastication. In other words, from the result obtained, it is possible that an increase in the bulk temperature as a function of rotor speed might cancel out the mastication effect.

The results for the compound morphology are shown in Figure 2(a–d). It is evident that the NR dispersed phase appears to be in elongated structure rather than a droplet structure, which could be attributed to insufficient shear stress for disrupting the elongated dispersed phase into the droplet structure. The viscosity during blending of the NR dispersed phase might be too high and/or that of the NBR matrix might be too low. However, at a rotor speed as fast as 60 rpm, the NR dispersed phase appears to be less elongated because of the pseudoplasticity of the blends. It is known that elastomers are highly pseudoplastic and their viscosity is therefore reduced as the shear rate is increased. The lower matrix viscosity during blending at higher rotor speeds promotes the dropletlike formation through the strain recovery of the elongated structure.
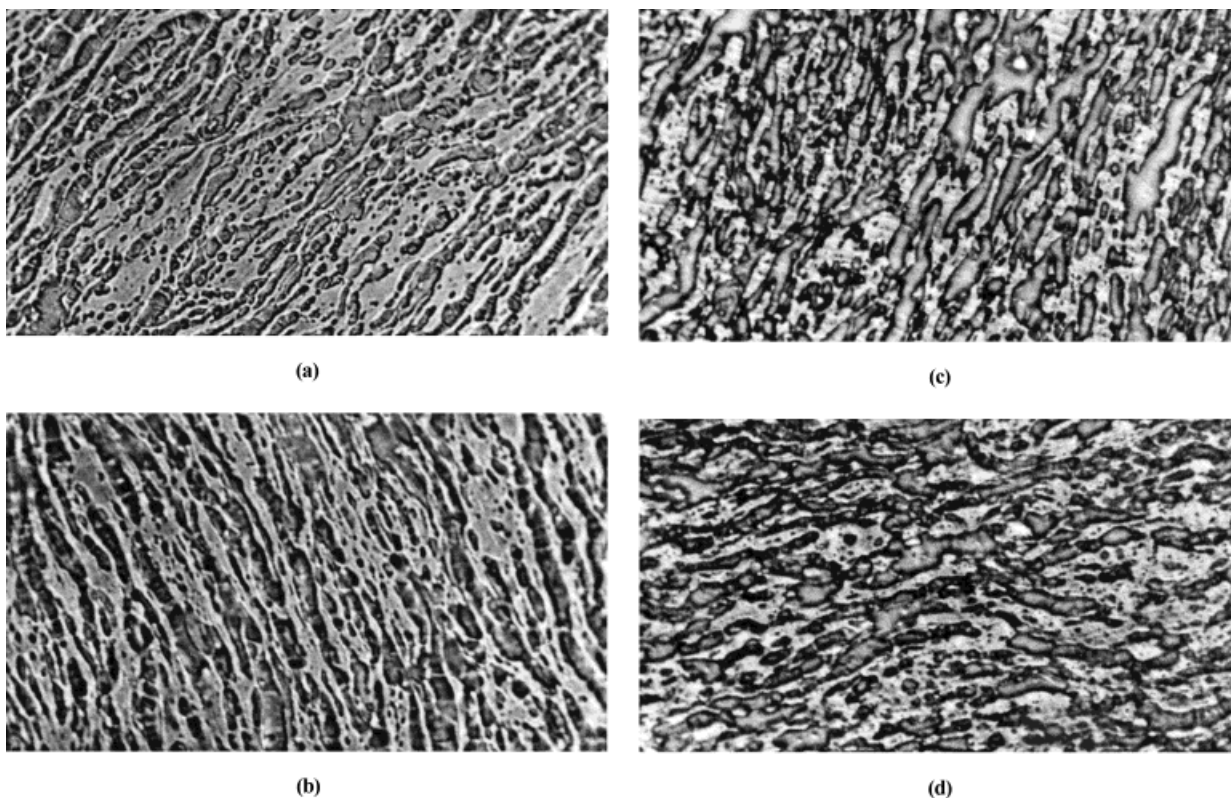

Figure 2 Micrographs (original magnification ×200) of blends prepared with rotor speeds of (a) 40, (b) 45, (c) 55, and (d) 60 rpm.

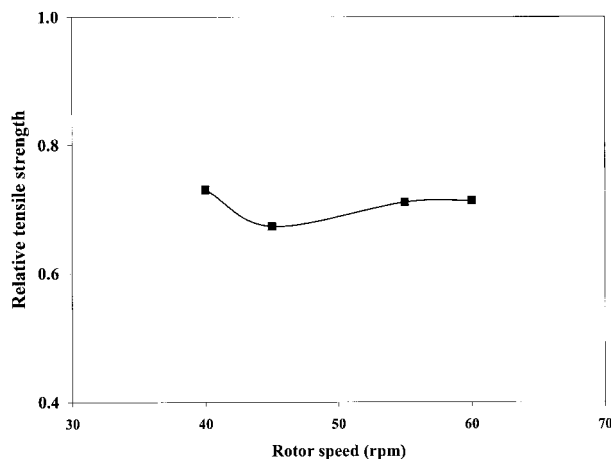**Figure 3** The relationship between the relative tensile strength and the rotor speed.

Figure 4 The relationship between the Mooney viscosity and the blending time.

Additionally, the phase size of NR does not strongly depend on the rotor speed used for blending, which could be explained by an increase in the bulk temperature due to shear heating generated as a function of the rotor speed, resulting in a decrease in shear stress available for disrupting the dispersed phase. The insensitivity of the phase size to a change in rotor speed was reported previously by Favis[20] in a blend system of polycarbonate/PP.

Figure 3 and Table I illustrate the relationship between the relative tensile strength (used for determining oil resistance) and rotor speed. It is clear that the relative tensile strength does not change significantly with increasing rotor speed. Obviously, the results of the morphology and relative tensile strength are in good agreement, which leads to a preliminary conclusion that the oil resistance of NR/NBR compounds is controlled by the size of the NR dispersed phase. Nonetheless, further investigation of the dependence of the oil resistance on the blending time needs to be carried out before the final conclusion can be drawn.

Influence of Blending Time

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

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

Figure 6 and Table II reveal the relationship between the relative tensile strength and blending time. It is clear that the relative tensile strength increases with increasing blending time up to 25 min and then decreases with further increasing blending time. The results of the morphology and relative tensile strength are in good agreement, similar to the rotor speed mentioned previously.

From all results obtained, it can be concluded that the phase morphology of the blends played an important role in the oil resistance as a function of the relative tensile strength. The smaller

Table I Relative Tensile Strength of 20/80 NR/NBR Blends as Function of Rotor Speed

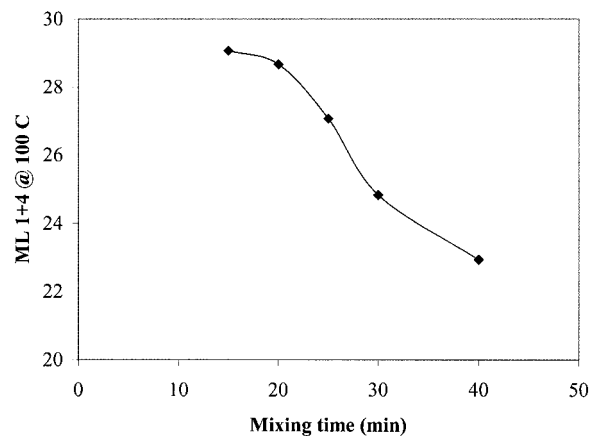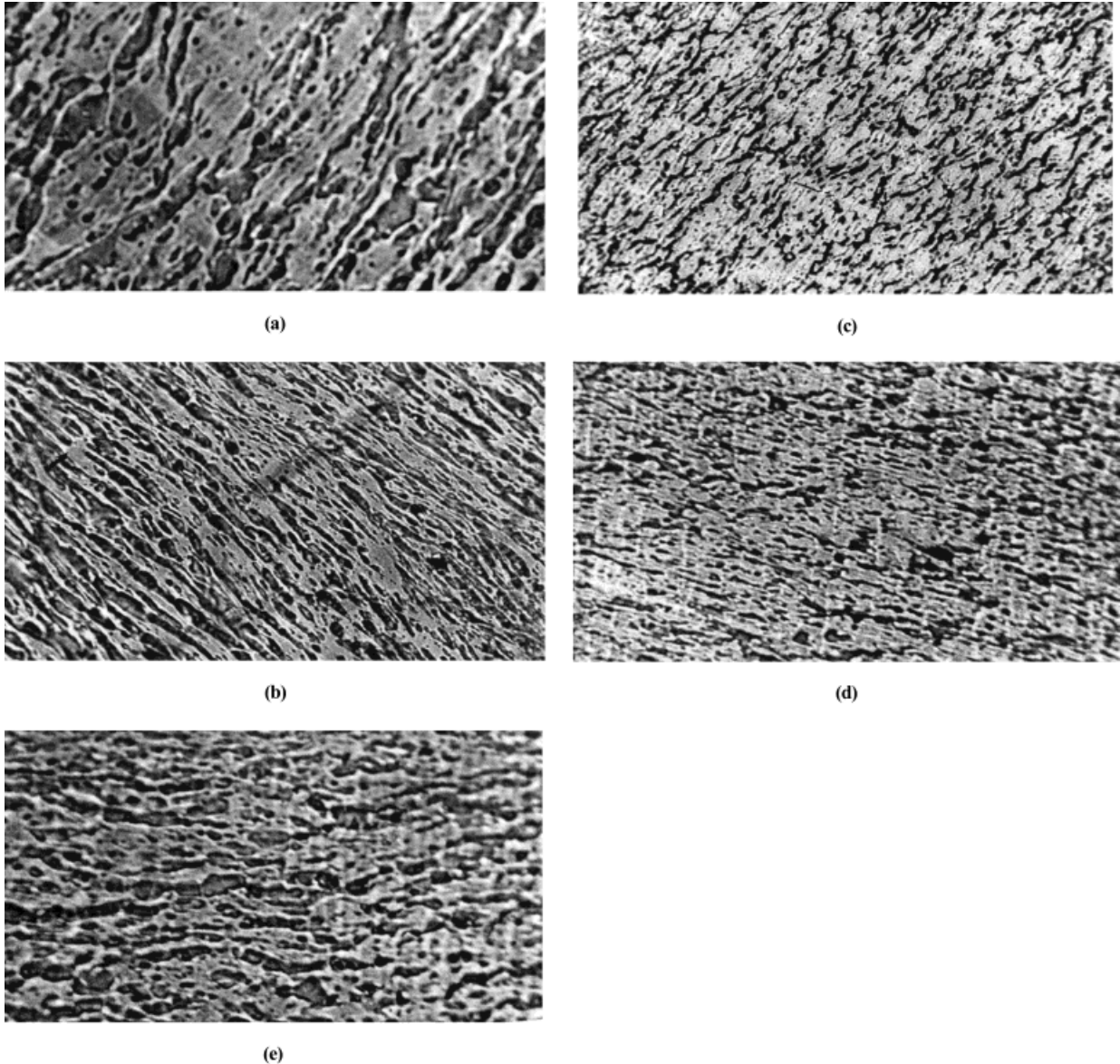| Rotor Speed (rpm)	Relative Tensile Strength
40	0.73
45	0.67
55	0.71
60	0.71

Figure 5   Micrographs (original magnification ×400) of blends prepared with blending times of (a) 15, (b) 20, (c) 25, (d) 30, and (e) 40 min.

the dispersed phase size, the higher the relative tensile strength and thus the higher the oil resistance. 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 was markedly swollen, leading to low resistance to failure of the blends. In the case of a small dispersed phase size for the NR, the large surface area of the small dispersed phase of the NR was surrounded by the NBR phase, which possessed high resistance to oil. Thus, oil swelling mainly occurred within a small phase size of NR
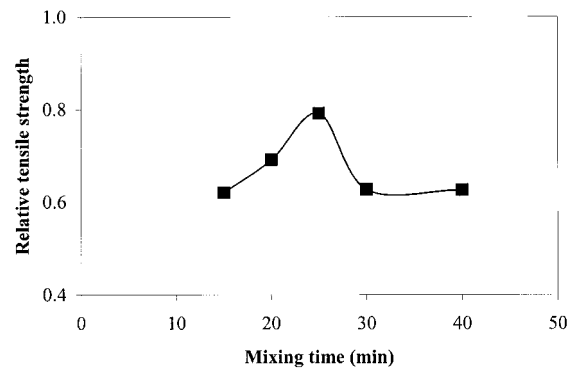

Figure 6   The relationship between the relative tensile strength and the blending time.

Table II   Relative Tensile Strength of 20/80 NR/NBR Blends as Function of Mixing Time

Mixing Time (min)	Relative Tensile Strength
15	0.62
20	0.69
25	0.79
30	0.62
40	0.62

that was stopped by the surrounding NBR, resulting in a high value of the relative tensile strength. By contrast, a large degree of swelling in a large NR dispersed phase would be ineffectively stopped by NBR because of the small surface area of the NR dispersed phase surrounded by NBR. This would lead to low resistance to failure and thus low relative tensile strength.

CONCLUSIONS

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

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