Effects of Fillers, Maleated Ethylene Propylene Diene Diene Rubber, and Maleated Ethylene Octene Copolymer on Phase Morphology and Oil Resistance in Natural Rubber/Nitrile Rubber Blends

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ABSTRACT: The phase morphology and oil resistance of 20/80 NR/NBR blends filled with different types of fillers and copolymers were investigated. In the case of filler effect, N220, N330, and N660 carbon blacks with different particle sizes were used. Additionally, the blends filled with non-black-reinforcing fillers, that is, precipitated and silane-treated silica, were investigated. To study the compatibilization effect, maleated ethylene propylene diene rubber (EPDM-*g*-MA) and maleated ethylene octene copolymer (EOR-*g*-MA) were added to the blends. The results revealed that the addition of filler, either carbon black or silica, to the blend caused a drastic decrease in NR dispersed phase size. Carbon blacks with different particle sizes did not produce any significant difference in NR dispersed phase size under the optical microscope. Silica-filled blends showed lower resistance to oil than did the carbon black–filled blends. In addition, it was determined that neither EOR-*g*-MA nor EPDM-*g*-MA could act as a compatibilizer for the blend system studied. The oil resistance of the blends with EPDM-*g*-MA is strongly affected by the overall polarity of the blend. In the case of EOR-*g*-MA, the oil resistance of the blends is significantly governed by both overall polarity of the blend and phase morphology. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1156–1162, 2003

Key words: phase behavior; blends; compatibilization; fillers; copolymers

INTRODUCTION

The production of rubber goods having good oil resistance with low cost could be achieved by blending natural rubber (NR) with nitrile rubber (NBR). It is known that NBR is a copolymer of acrylonitrile and butadiene, and possesses outstanding oil resistance. Natural rubber has excellent mechanical properties with relatively poor resistance to oil. However, poor properties of the blends are often obtained, mainly attributed to phase incompatibility, nonuniformity in distribution of filler[1–5] and of curatives.[6,7] Typically, morphological studies have been carried out to determine the compatibility of polymer blends, which significantly affects blend properties. Factors that influence blend morphology include blend composition,[8–11] blending conditions,[12,13] and viscosity ratio.[1,8,14,15] Recently, it was reported that the addition of carbon black to NR/NBR blends could drastically decrease the dispersed phase size.[16]

There were previous attempts to correlate the phase morphology of the unfilled NR/NBR blend, controlled by mixing conditions or viscosity ratio, to oil resistance of the blends.[17,18] It was found that the smaller size of the dispersed phase yields a higher resistance to oil of the blends. Consequently, the objective of the present investigation was to further the work of the previous studies[11,17,18] where the influences of blending conditions and viscosity ratio on blend morphology and oil resistance were reported. The present study focuses on the influence of fillers maleated ethylene propylene diene rubber (EPDM-*g*-MA), and maleated ethylene octene copolymer (EOR-*g*-MA) on changes in phase morphology and oil resistance of NR/NBR blends.

EXPERIMENTAL

Materials

Details of the compounding ingredients and rubber formulas used are given in Table I and Table II, respectively.

Mixing and vulcanization procedures

According to previous work,[17,18] the NR/NBR blend ratio by weight of 20/80 was chosen to ensure the morphology with the NR phase dispersed in the NBR matrix. The blending process was carried out in a Banbury-type internal mixer with a fill factor of 0.6, a

TABLE I
Materials Used in the Study

Chemical name	Grade/supplier
Acrylonitrile butadiene rubber (NBR)	N230S (35% bound acrylonitrile content; ML_{1+4} at 100°C = 56)/ Japan Synthetic Rubber (JSR) Co. Ltd., Japan
Natural rubber (NR)	STR 5, Thailand (ML_{1+4} at 100°C = 72)
Maleic anhydride–*grafted*–ethylene–octene copolymer (EOR-*g*-MA)	In-house preparation; % MA ≈ 0.7
Maleic anhydride–*grafted*–ethylene–propylene diene rubber (EPDM-*g*-MA)	ROYALTUF 490 (% MA ≈ 1)/Uniroyal Company Inc.
Dicumyl peroxide (DCP)	Percumyl D/Chemmin Co. Ltd., Thailand
Carbon black	N660, N330, N220/Thai carbon Product Co. Ltd., Thailand
Precipitated silica	HiSil 255/PPG-Siam Silica Co. Ltd., Thailand
Commercial silane-treated silica	Ciptane 255LD/PPG Industries Inc., Thailand
Hydraulic oil	TELLUS 100/Shell Co., Ltd., Thailand (ASTM oil No.5)

rotor speed of 55 rpm, and circulating water of 40°C. NR was initially masticated to reduce its Mooney viscosity to that of NBR. The NBR and masticated NR were blended in the mixer for 2 min, and filler or compatibilizer to be studied was then charged. After blending for 9 min, dicumyl peroxide was charged, and the mixes were discharged on the cooled two-roll mill at a mixing time of 25 min.

Finally, vulcanization was performed using a compression-molding machine (Wabash Genesis series model G30H). The cure time was 16 min (which gives ~ 94% cure calculated from the half-life of DCP).

Mooney viscosity measurement

A Mooney viscometer (Monsanto model 1500; St. Louis, MO) with a large rotor at a test temperature of 100°C was used to determine the Mooney viscosity (ML_{1+4} at 100°C), according to ASTM D1646-87 and reported in Mooney units. At least five samples were used for each measurement.

Morphological study

The vulcanizate samples were cryogenically microtomed using glass knives. The morphology of thin-sectioned samples was then observed using an optical microscope (Olympus model SC-35). Osmium tetroxide was used to enhance a phase contrast of the thin-sectioned samples.

TABLE II
Compound Formula Used in the Study

Material	Amount (phr)
Rubber	100.0
Carbon black or silica	Varied between 0.0 and 20.0
EOR-*g*-MA or EPDM-*g*-MA	Varied from 0.0 to 7.0
DCP	1.5

Oil resistance measurement

According to previous studies,[17,18] the dumbbell-shape (punched out using Die C; ASTM D412-92) test specimens were immersed in oil at room temperature for 70 h. Thereafter, the specimens were removed from the oil and quickly dipped in acetone and blotted 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 oil resistance, as shown in eq. (1). The relative tensile strength (TS_{rel}), calculated from the ratio of tensile strength after to that before oil immersion, was used to eliminate the mastication effect probably taking place during the blending process. 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 1 kN in accordance with ASTM D638.

$$TS_{rel} = \frac{TS_{after}}{TS_{before}} \qquad (1)$$

where TS_{before} and TS_{after} are tensile strength of specimens before and after oil immersion, respectively.

RESULTS AND DISCUSSION

Effects of fillers

In this section, carbon blacks with different particle sizes were used to study the effect of filler surface area on properties of the blends. Silica with and without silane surface treatment was also used to investigate the filler polarity effect on properties of the blends. Figure 1 shows the relationship between Mooney viscosity and types of filler. It can be seen that in the case of carbon black, N220 carbon black gives the highest Mooney viscosity followed by N330 and N660, respectively, which is undoubtedly attributed to the highest and the lowest surface area of N220 and N660, respec-
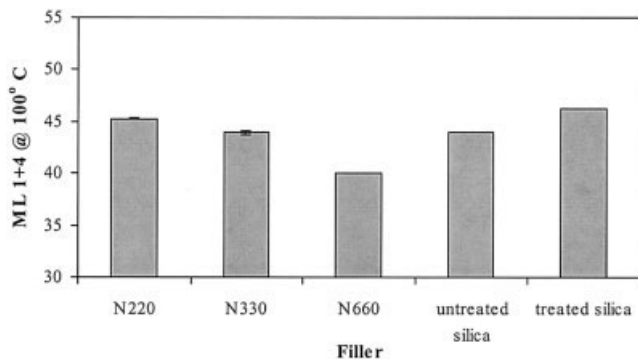
Figure 1 Relationship between Mooney viscosity and types of filler.

tively. Generally, the degree of rubber–filler interaction as determined by bound rubber content increases with increasing surface area. Small-particle blacks, therefore, yield high Mooney viscosity values. The silane-treated silica unexpectedly yields a higher Mooney viscosity than that of the untreated silica, which might result from the chemical crosslink (i.e., sulfur linkage generated from sulfur in the silane coupling agent at the silica surfaces) between rubber and silica taking place during mixing.

Optical micrographs of the blends as a function of filler type given in Figure 2 show that, compared to the unfilled blend, the filled blends containing 20 phr of either carbon black or silica possess very fine phase morphology. This result is probably a consequence of the increase in bulk shear viscosity as the filler was added, yielding the increase in shear stress available for disrupting the NR dispersed phase. In addition, it was previously reported that carbon black located at the interphase could act as a compatibilizer in blends.[16] However, the size of the NR dispersed phase in filled blends is not discernible from the optical micrographs and therefore the relationship between blend morphology and oil resistance could not be established.

The tensile strengths of blends filled with different types of filler are shown in Figure 3. It seems that the tensile strengths of blends are low as a result of the peroxide cure used in the study. The main reason for choosing the peroxide cure was to avoid the uneven distribution of curatives in each phase of the blends. From Figure 3, it appears that the N220 black gives the highest tensile strength, followed by N330 and N660, respectively. The explanation is based on the reinforcing effect provided by the smallest particle size and thus the largest surface area of N220. Surprisingly, the silane treatment of silica does not significantly improve the tensile strength of the compounds. After oil immersion, the tensile strength of all compounds [denoted as $TS_{(oil)}$] decreases and the magnitude of reduction in tensile strength is significantly more obvi-

ous in the case of N220 and silica-filled blends. The relative tensile strength as an indicator for oil resistance (shown in Fig. 4) reveals that N330 carbon black yields the highest relative tensile strength and thus the greatest oil resistance.

To explain the result of oil resistance, there are two main factors responsible for the result of oil resistance in filled blends, crosslink density and phase morphology. The crosslink density could, in theory, play a strong role in oil resistance (i.e., the higher the crosslink density, the higher the oil resistance). It is possible that silica reduces the cure efficiency and therefore the silica-filled compound would have the lower crosslink density, resulting in the lower oil resistance than that of the black-filled compounds, as shown in Figure 4. For the investigation of phase morphology effect on oil resistance, it is unfortunate that the phase size in the filled compounds studied is so fine that it could not be characterized under the optical microscope used in the present study. In other words, in the present study, it was not possible to establish the relationship between phase morphology and oil resistance in blends filled with various types and sizes of fillers.

Effects of EOR-_g_-MA and EPDM-_g_-MA

Blends of highly incompatible elastomers could sometimes be improved by the addition of small amounts of compatibilizer. Generally, the function of a compatibilizer added to the blends is the reduction of interfacial tension between the dispersed phase and the matrix and thus a reduction in the phase size of the blends. In the present study, EOR-_g_-MA and EPDM-_g_-MA, which were previously reported for their function as compatibilizers in many blend systems between polar and nonpolar polymers,[19] were mixed into the blends. A reduction in NR dispersed phase size and an improvement in oil resistance were initially expected because of the compatibilizing effect.

Figure 5 shows the unexpected morphological result of NR/NBR blends as a function of EOR-_g_-MA concentration. It was found that the NR dispersed phase size increases by increasing the amount of EOR-_g_-MA, which is believed to be attributed to the migration of EOR-_g_-MA to the NR phase, leading to the increase in viscosity of the NR dispersed phase. To support the proposed explanation, the measurement of mixing torque of both pure components and their blends, before and after the addition of EOR-_g_-MA, was carried out. The results obtained are shown in Table III. It is clear that the addition of EOR-_g_-MA significantly increases the mixing torque of the pure NR system (i.e., ~ 28%), but slightly reduces that of the pure NBR system (i.e., ~ 9%). In the 20/80 NR/NBR blend, the mixing torque appears to increase by about 17%, indicating that EOR-_g_-MA should migrate mainly to the
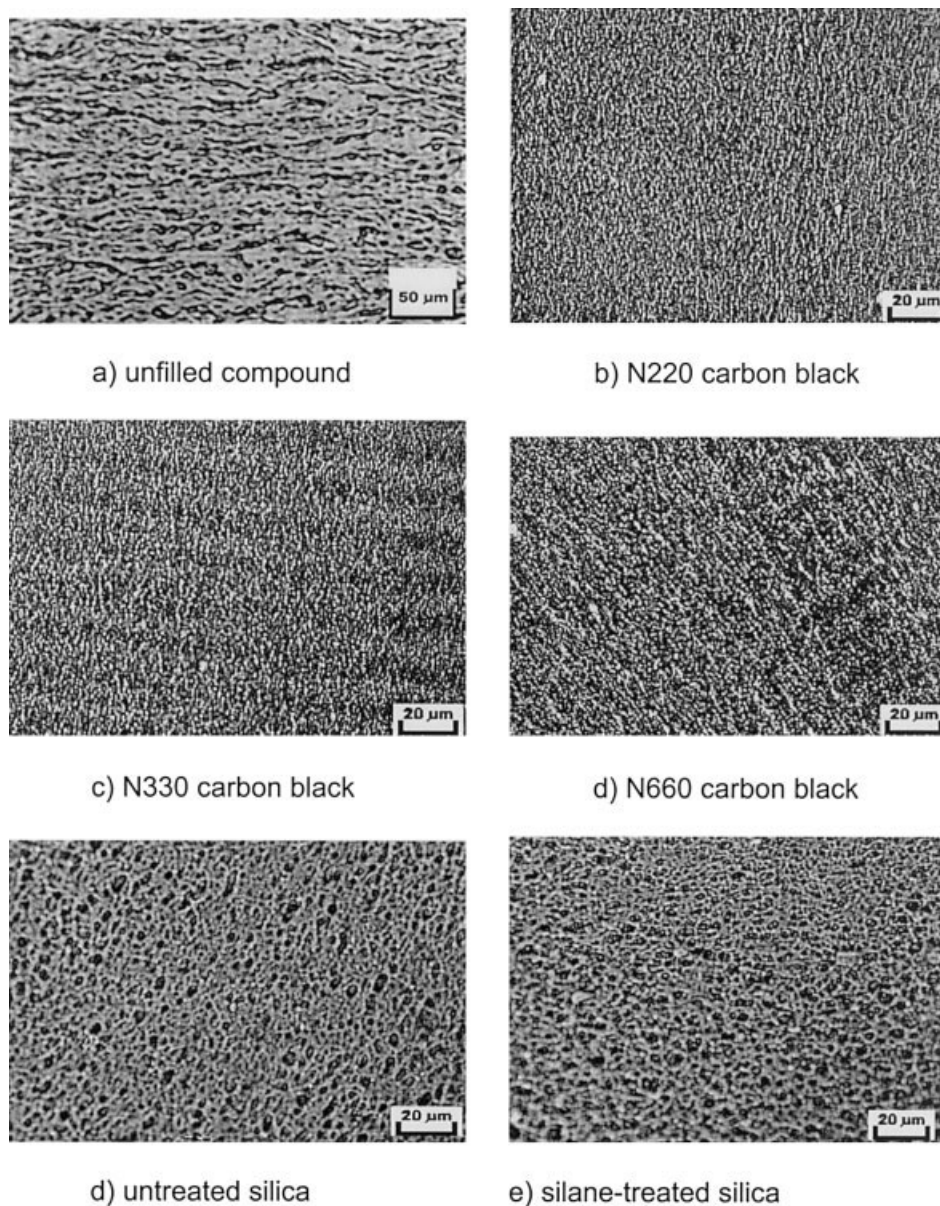
Figure 2 Optical micrographs of NR/NBR blend with various types of filler: (a) unfilled compound; (b) N220; (c) N330; (d) N660; (e) untreated silica; (f) silane-treated silica.
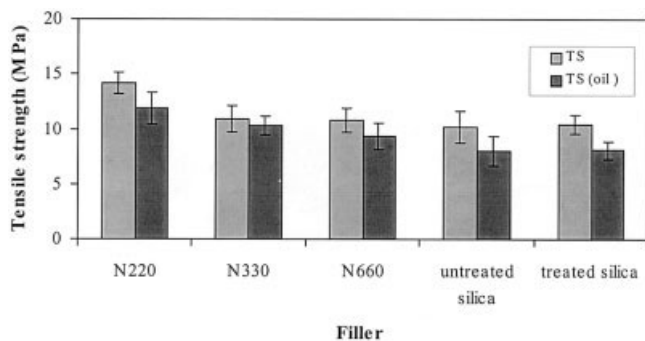

Figure 3 Relationship between tensile strength (before and after oil immersion) and types of filler.
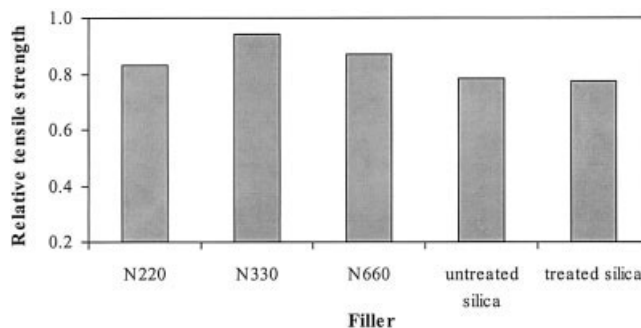

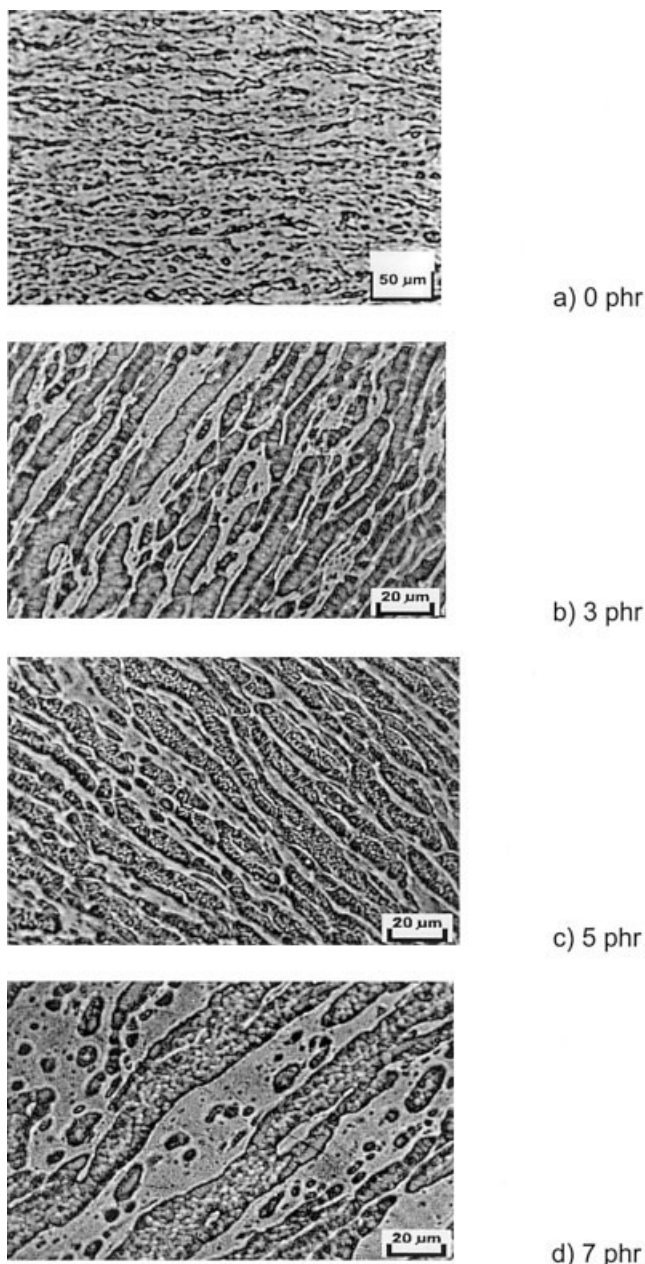**Figure 4** Relationship between relative tensile strength and types of filler.

Figure 5 Optical micrographs of NR/NBR blends with various contents of EOR-*g*-MA: (a) 0 phr; (b) 3 phr; (c) 5 phr; (d) 7 phr.

NR phase and increase the viscosity of the NR dispersed phase. In other words, the viscosity ratio (i.e., ratio of dispersed phase to matrix viscosities) of the blend is increased by the addition of EOR-*g*-MA. It is known that the higher the viscosity ratio, the larger the phase size of the dispersed phase.[20]

Micrographs of NR/NBR blends as a function of EPDM-*g*-MA content are shown in Figure 6. It appears that the size of the NR dispersed phase also slightly increases as EPDM-*g*-MA is added to the blends. Similar to EOR-*g*-MA, EPDM-*g*-MA increases the viscosity of the NR dispersed phase, but with lower magnitude, as shown in Table III. Therefore, only a slight increase in phase size is obtained when EPDM-*g*-MA is added to the blend. From the morphological result obtained, it is evident that neither EPDM-*g*-MA nor EOR-*g*-MA could provide the compatibilizing effect to the blends of NR/NBR studied. The possible explanation for the migration of EOR-*g*-MA and EPDM-*g*-MA to the NR phase is proposed based on the degree of MA grafting as low as 1%. Thus, both EOR-*g*-MA and EPDM-*g*-MA are mainly nonpolar, and therefore tend to migrate to the NR phase, which is a nonpolar phase in blends.

Figure 7 shows that the relative tensile strength appears to increase with increasing concentration of EPDM-*g*-MA. One might expect that the result could be explained by an increase in overall polarity of the blend provided by the maleic anhydride (MA) functional group grafted on EPDM main chains.

In the case of EOR-*g*-MA, as the concentration of EOR-*g*-MA is increased to 5 phr, the relative tensile strength increases, as shown in Figure 7. A similar explanation of the EPDM-*g*-MA result based on the high overall polarity of the blends provided by the MA functional group could be applied to the EOR-*g*-MA result. Notably, at concentrations above 5 phr, the relative tensile strength drops sharply, and, simultaneously, the phase size obviously increases (see Fig. 5). Thus, at this concentration, it seems that the effect of overall polarity of the blends is overridden by the morphological effect. Previous studies[17,18] established that the smaller the dispersed phase size, the higher the oil resistance.

The proposed explanation[17,18] is as follows (see Fig. 8): compared to NR, NBR possesses excellent resis-

TABLE III
Effects of EOR-*g*-MA and EPDM-*g*-MA on Mixing Torque of Pure Components and Their Blends

Compound	Torque of uncompatibilized rubber (Nm)	EOR-*g*-MA (7 phr)		EPDM-*g*-MA (7 phr)	
		Torque (Nm)	ΔTorque[a] (%)	Torque (Nm)	ΔTorque[a] (%)
NR	9.2	11.7	+27.7	9.7	+5.4
NBR	21.0	19.2	−8.6	20.8	−0.9
NR/NBR (20/80)	13.0	15.2	+17.0	13.8	+6.0

[a] %Δtorque = (torque of compatibilized Rubber) − (torque of uncompatibilized rubber)/(torque of uncompatibilized rubber) × 100 .
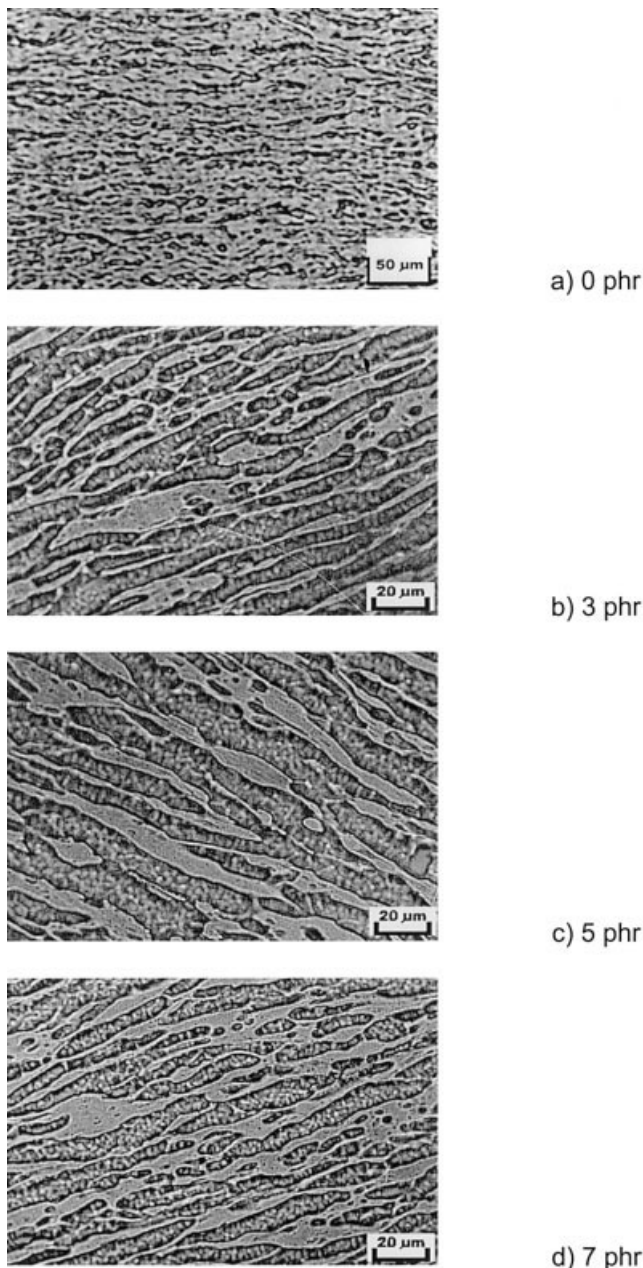
Figure 6 Optical micrographs of NR/NBR blends with various contents of EPDM-*g*-MA: (a) 0 phr; (b) 3 phr; (c) 5 phr; (d) 7 phr.

tance to hydrocarbon liquids. Thus, when the NR/NBR blends are immersed in oil, the NR dispersed phase swells substantially, leading to low resistance to failure of the blends. In the case of a small dispersed-phase size of NR, the large surface area of the small dispersed phase of NR is surrounded by the NBR phase, possessing high resistance to oil. Thus, oil swelling occurring mainly within the small phase size of NR will be stopped effectively by the surrounding NBR, resulting in a high value of relative tensile strength (or high oil resistance). By contrast, a large degree of swelling in a large NR dispersed phase
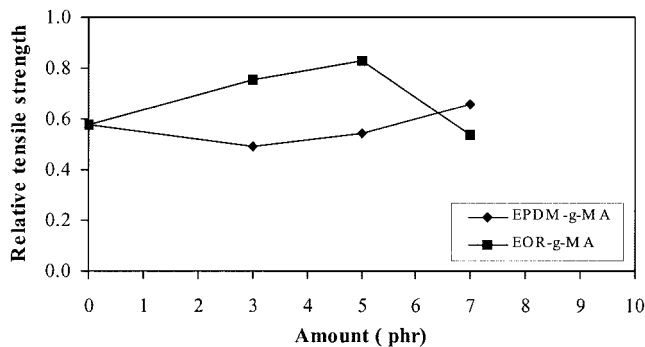

Figure 7 Relationship between relative tensile strength and concentration of compatibilizers.

could not be stopped effectively by the NBR matrix because of the small surface area of the NR dispersed phase surrounded by the NBR phase. This leads to low resistance to failure, and thus low relative tensile strength.

In addition, compared to EOR-*g*-MA, EPDM-*g*-MA gives lower relative tensile strength, particularly at low concentrations. There are two possible factors responsible for the result, blend overall polarity and blend morphology. The former effect was investigated by comparing the MA content in EPDM-*g*-MA and EOR-*g*-MA. It appears that the MA content in EPDM-*g*-MA is not significantly different from that in EOR-*g*-MA (i.e., 1.0 versus 0.7% in EPDM-*g*-MA and EOR-*g*-MA, respectively), which is not in agreement with the result of relative tensile strength. Therefore, only the phase morphology should be responsible for the result. It can be seen from Figures 5 and 6 that at concentrations up to 5 phr, the phase size of the blend with EOR-*g*-MA is smaller than that of the EPDM-*g*-MA, resulting in higher relative tensile strength. By contrast, at the concentration of 7 phr, the phase size of the blend with EOR-*g*-MA becomes much larger than that of EPDM-*g*-MA, resulting in a significantly lower relative tensile strength and thus oil resistance, as shown in Figure 7.

CONCLUSIONS

The phase morphology and oil resistance of 20/80 NR/NBR blends filled with various types and sizes of
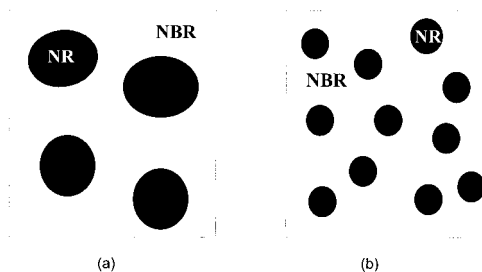

Figure 8 Proposed model of the blends with different sizes of the NR dispersed phase: (a) large phase size; (b) small phase size.

fillers as well as with EOR-*g*-MA and EPDM-*g*-MA were investigated. The following conclusions could be drawn:

1. Compared to N220 and N660 blacks, N330 black gives the highest relative tensile strength (and thus the highest oil resistance). Silica-filled compounds give lower oil resistance than the black-filled compounds.
2. The relationship between oil resistance and blend morphology affected by filler addition could not be established because the phase size could not be determined under the magnification power of the optical microscope.
3. The NR dispersed phase size increases with increasing EOR-*g*-MA or EPDM-*g*-MA concentration. The magnitude of increase is more significant in the blends with EOR-*g*-MA, which is believed to be attributed to the increase in viscosity of the NR phase. In other words, neither EPDM-*g*-MA nor EOR-*g*-MA is effective in compatibilizing the NR/NBR blend system studied.
4. The relative tensile strength of the blends with EPDM-*g*-MA is strongly affected by the overall polarity of blends. In the case of EOR-*g*-MA, the relative tensile strength of the blends is strongly affected by both the overall polarity and the phase morphology in the blends, depending on EOR-*g*-MA concentration.

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