

A Study on Morphology and Physical Properties of Natural–Acrylic Rubber Blends

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Received 7 March 2001; accepted 21 December 2001

ABSTRACT: Morphology and physical properties of natural–acrylic rubber blends were investigated as a function of blend compositions and mixing methods. In the first method, the masticated natural rubber was cross-blended with the acrylic rubber for 15 min, followed by a sequential addition of vulcanizing chemicals (ZnO, stearic acid, MBT, sodium stearate, and sulfur), and the mixing was terminated within 15 min. In the second method, the masticated natural rubber was premixed with its relevant vulcanizing chemicals (excepting the sulfur) for 7 min, followed by blending it with the acrylic rubber and sodium stearate for 20 min. Finally, the sulfur was added and the mixing was continued for further 3 min before termination. The resulting blends were vulcanized to their optimum cure time in a compression mold. The rubber sheet was cut into a dumbbell-shaped specimen, and tensile properties were determined at a cross-head speed of 500 mm/min. The morphology of the blends was examined with scanning electron microscopy (SEM). The SEM specimen was prepared by cryo-fracturing, fol-

lowed by staining with OsO₄. It was found that all of the rubber blends were immiscible, as shown by there being two separated phases in the SEM micrographs. The result was in a good agreement with that from a thermal analysis (using a differential scanning calorimeter), which showed two glass transition temperatures. Morphology of the rubber blends changed from a cocontinuous morphology to a dispersed particle morphology as the natural rubber content was increased from 20% to 80% by weight. Increasing the natural rubber content enhanced tensile properties of the rubber blends at the expense of their oil and heat resistance. Most of these properties being examined seemed to be unaffected by the mixing method, with the exception of the retention of tensile strain after aging. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1532–1539, 2002

Key words: natural rubber; acrylic rubber; blend; miscibility; vulcanization; electron microscopy

INTRODUCTION

Vulcanization is an important step in rubber processing, leading to a final rubber product. It also plays an important role in preparing and processing rubber blend, in which relevant vulcanizing chemicals such as curing agents, accelerators, activators, and fillers may not be evenly distributed throughout the rubber blend but might preferentially migrate into one phase. For example, sulfur, as a common curing agent, was claimed to be well soluble in the more polar rubber¹ and in some rubbers containing diene or styrene groups. Many accelerators also have a greater affinity in polar rubbers.² As a result, large differences in the cross-linking density of the different phases may be obtained on vulcanization. Furthermore, concentration of cross-links at the interface may be different from that in the rubber bulk. If the vulcanizing chemicals are soluble in both rubbers, particular compo-

nents may be more abundant at the interface than in the rubber bulk because of migration of these chemicals, occurring in proximity to this region. Cross-link distribution in rubber blends may be improved by selecting a suitable curing system³ and/or by modifying the mixing condition. For example, it has been claimed² that by separately adding relevant vulcanizing chemicals to each of the individual rubbers before blending the rubber compounds (phase blending), the distribution was better.² Unfortunately, there have been few reports concerning the effect of mixing conditions on the morphology and physical properties of rubber blends. In this work, natural–acrylic rubber blends were considered. The aim is to examine the morphology and physical properties of the natural–acrylic rubber blends as functions of both compositions and mixing procedures.

EXPERIMENTAL

Materials

Acrylic rubber (AR-71, Mooney viscosity ML [1+4] 100°C-55) was supplied by the Zeon Advanced Polymix Co., Ltd., Thailand. The natural rubber (STR 5L grade rubber) and curing agents (sulfur, sodium stear-

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TABLE I
Blending Formulations

Materials	Content (phr)						
	1	2	3	4	5	6	7
Natural Rubber	—	20.0	40.0	50.0	60.0	80.0	100
Acrylic Rubber	100	80.0	60.0	50.0	40.0	20.0	—
Sulfur	0.75	1.5	1.5	1.5	1.5	1.5	0.75
Sodium Stearate	7.5	7.5	7.5	7.5	7.5	7.5	—
MBT	—	1.5	1.5	1.5	1.5	1.5	1.5
Zinc Oxide	—	5.0	5.0	5.0	5.0	5.0	5.0
Stearic Acid	—	1.0	1.0	1.0	1.0	1.0	1.0

ate, 2-mercaptobenzothiazole [MBT], zinc oxide, and stearic acid) were supplied by the Hi-Tech Elastomers Co., Ltd., Thailand.

Blending

The basic formulations for rubber blends and two control compounds (natural rubber and acrylic rubber) are given in Table I. The blends were prepared by either of the two methods described as follows: in method A, the natural rubber (NR) was first masticated in a two-roll mill for 15 min, followed by blending with the acrylic rubber (AR) for 15 min. After that, zinc oxide, stearic acid, MBT, sodium stearate, and sulfur were added subsequently to the rubber blend, and mixing was terminated after 15 min. In method B, all vulcanizing chemicals relevant to the NR (ZnO, MBT, and stearic acid, except sulfur, which might cause prevulcanization) were sequentially added to the masticated natural rubber. The mixing was performed within 7 min. Later, the acrylic rubber was added and was then mixed with sodium stearate. The mixing continued for 20 min more. Finally, sulfur was added to the rubber mixture and the mixing was continued for 3 min before termination.

Determination of cross-linking characteristic

Optimum cure time (time to reach 90% of the maximum torque by a curometer) of the compounded

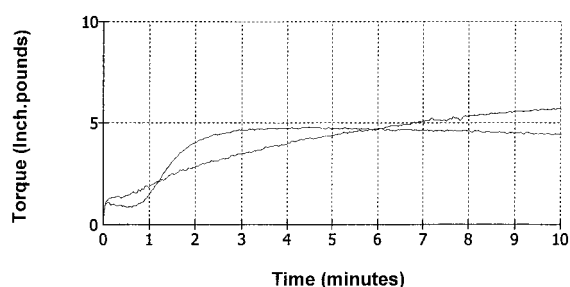


Figure 1 Curing traces of natural rubber (NR) and acrylic rubber (AR) obtaining from an oscillating disk rheometer (ODR).

NR/AR blend (at a curing temperature of 170°C) was predetermined by using an Oscillating Disk Rheometer (ODR) (Rheo TECH MD+ from TECH PRO INC., Ohio) in accordance with ASTM D2084. A biconical disk was oscillated through the rotational amplitude of 1 degree with a standard frequency of 100 cpm (1.7 Hz).

Vulcanization

The compounded rubber blends were vulcanized to their optimum cure time in a compression mold (2 mm thick), at the curing temperature of 170°C and under the molding pressure of 20 MPa.

Scanning electron microscopy

Morphological properties of the rubber blends were assessed by scanning electron microscopy (SEM) technique. The sample was cut into a small piece and then fractured in its glassy state (using liquid nitrogen). The fracture surface was stained with an osmium tetroxide (OsO_4) aqueous solution (2%, v/v). The

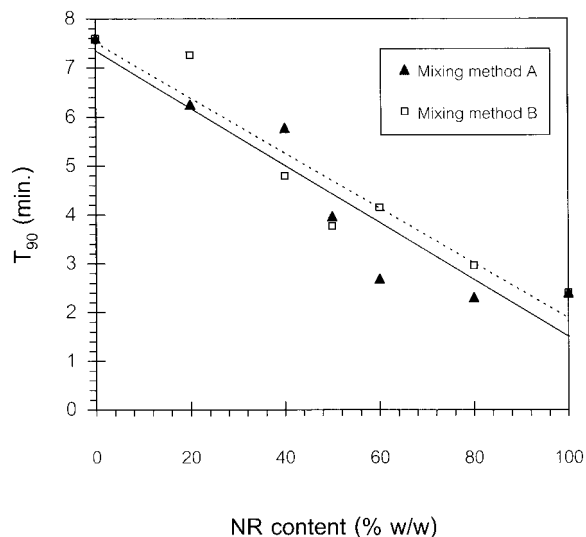


Figure 2 Relationships between natural rubber content and optimum cure time of the natural-acrylic rubber blends.

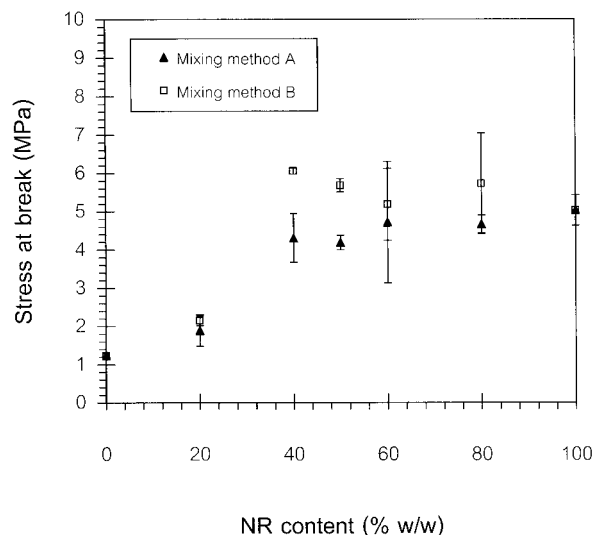


Figure 3 Tensile stress of the natural-acrylic rubber blends as a function of natural rubber content and mixing method.

specimen was then coated with carbon before SEM analysis, using a vacuum coating unit (JEOL JEE-400, Tokyo, Japan). Finally, the specimen was analyzed by using a JEOL (JSM-5800LV) scanning electron microscope at an accelerating voltage of 15 kV. A back-scattering electron detector was used to provide an electron micrograph with a compositional contrast.

Thermal analysis

Thermal characteristics of the rubber blends were analyzed by using a differential scanning calorimeter (DSC; NETZSCH DSC200, Selb-Bayern, Germany). Approximately 25 g of the sample was used and the

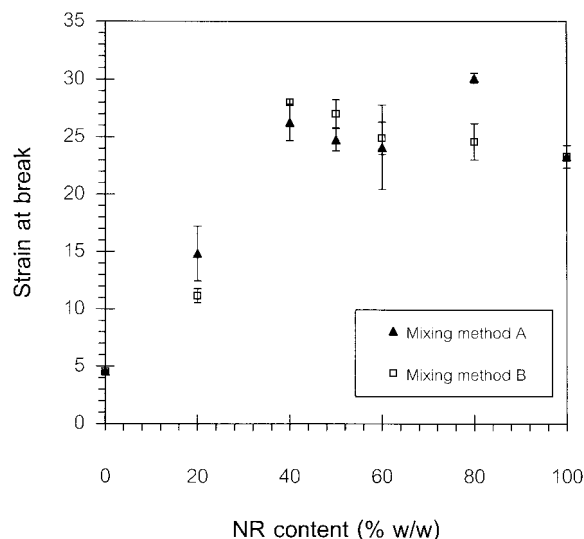


Figure 4 Strain at break of the natural-acrylic rubber blends as a function of natural rubber content and mixing method.

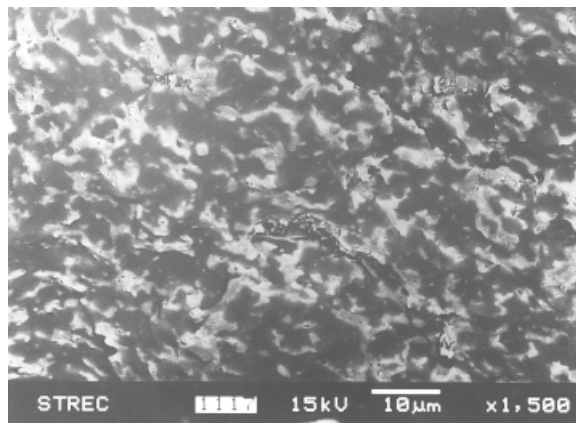


Figure 5 Scanning electron micrograph of a natural-acrylic rubber blend (20% by weight of natural rubber, mixing method A).

experiment was performed at a heating rate of 10°C/min. under the environment of nitrogen gas.

Tensile test

The cured rubber sheet was punched into a dumbbell-shaped specimen in accordance with an ASTM D412. The tensile properties were determined using a SHIMADZU (AGS500-D) universal testing machine at a cross-head speed of 500 mm/min at room temperature. At least five specimens were tested for each blend, and the averaged values were reported.

Determination of heat resistance

To compare the influence of elevated temperature on physical properties of various rubber blends, an aging test was performed in accordance with a standard method (ASTM D573). The compression-molded specimens was cut in to a dumbbell shape and then placed

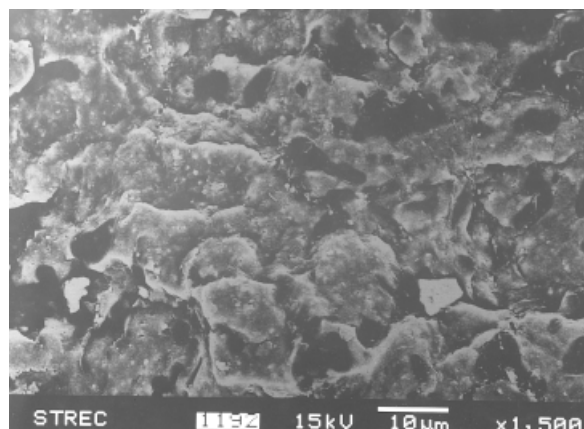


Figure 6 Scanning electron micrograph of a natural-acrylic rubber blend (50% by weight of natural rubber, mixing method A).

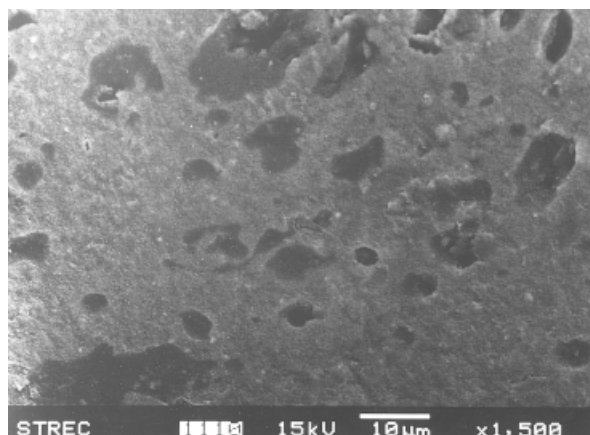


Figure 7 Scanning electron micrograph of a natural-acrylic rubber blend (80% by weight of natural rubber, mixing method A).

(suspended) in a preheated air-circulating oven at 140°C for 24 h. After that, elongation of the aged specimens was determined by the tensile test. Five specimens were tested for each rubber sample, and the average values were reported.

Determination of oil resistance

Comparative ability of various rubber compounds to withstand the effect of oil was evaluated in accordance with a standard method (ASTM D471). In a typical experiment, three specimens having a rectangular shape (2 cm × 4 cm × 0.2 cm) were immersed in a suitable test tube containing 150 mL of a commercial

gasoline engine oil (SAE 20W-50, API SJ/CF from the Petroleum Authority of Thailand, Rayong, Thailand). The test tube was then placed in a heated oil bath (70°C). After performing the immersion test for 7 days, the test specimens were transferred to a cool and clean portion of the test liquid, dipped in acetone, gently cleaned with a tissue paper, and finally weighed. Percentage change in mass of the tested specimens was calculated using following equation:

$$\Delta M, \% = (M_2 - M_1) / M_1 \times 100$$

where ΔM = change in mass (%), M_1 = initial mass of specimen in air (g), and M_2 = mass of specimen in air after immersion (g).

RESULTS AND DISCUSSION

Figure 1 compares the curing traces of natural rubber and acrylic rubber at 170°C. It can be seen that the natural rubber reached the optimum cure time within 2.4 min. The acrylic rubber, however, showed a gradual increase of the torque with time. This agrees with the literature⁴ claiming that the curing of acrylic rubber with a sulfur-based system is scorchy and relatively slow. Such a compound usually requires a post-cure in a hot air environment to develop a low compression set.⁵

Figure 2 compares the optimum cure time (T_{90}) of various rubber blends. It can be seen that the higher the NR content, the smaller the optimum cure time, regardless of the mixing methods. The optimum cure

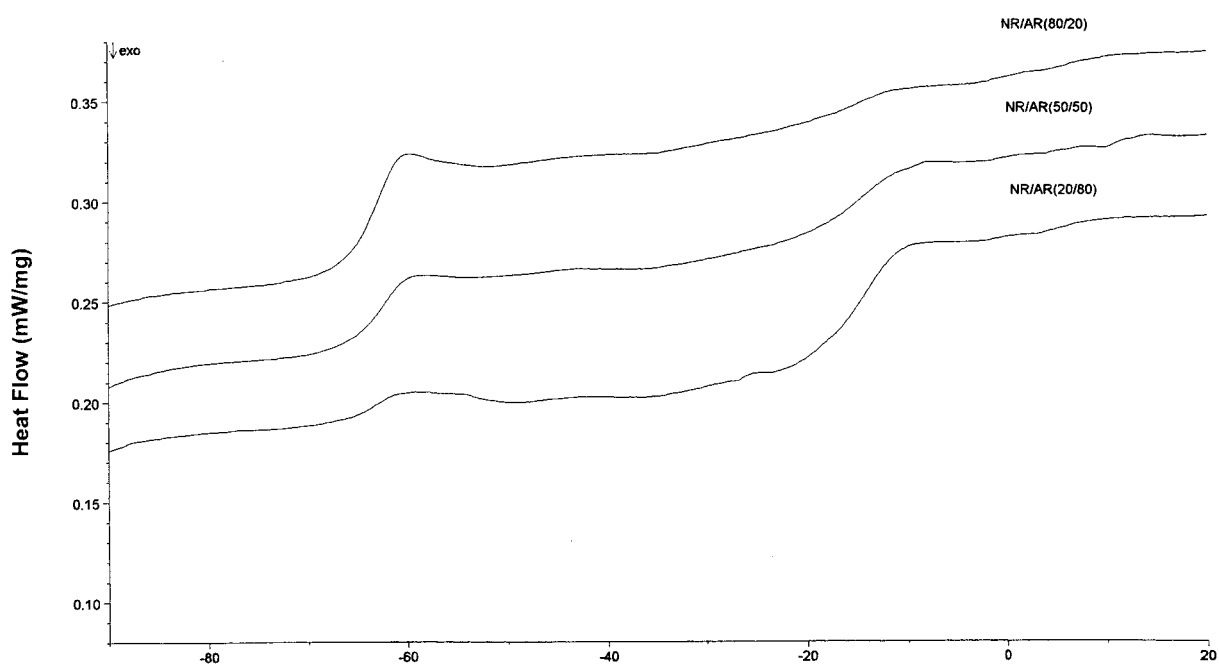


Figure 8 Overlaid differential scanning calorimeter thermograms of the natural-acrylic rubber blends, at various compositions.

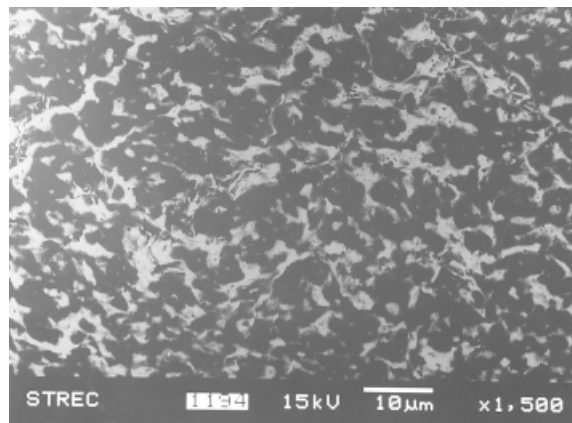


Figure 9 Scanning electron micrograph of a natural-acrylic rubber blend (20% by weight of natural rubber, mixing method B).

time did not change significantly with the mixing method, taking into account the small and fluctuated variations. Figure 3 shows the tensile stress at break of the rubber blends as a function of NR content. The stress tended to increase with NR content before reaching a plateau. In most cases, the effect of blending method on tensile stress was not obvious. However, for some rubber blends containing 40% and 50% NR, the effect of blending methods was noticeable.

The tensile stress of the blend using mixing method B was slightly higher than that of the blend using mixing method A. It might be possible that the former method created a more appropriate initial location of accelerators compared with the latter. This would lead to a better cross-linking characteristic in the natural rubber phase. In terms of tensile strain at a break (Fig. 4), the values initially increased with NR content and then reached a plateau. The effect of the mixing method on the tensile strain of a rubber blend can be negligible.

Figures 5–7 show the SEM photographs of various blends undergoing mixing method A. At 20% NR content, the blend shows a typical cocontinuous morphology. In this image, the dark phase represents the acrylic rubber and the bright phase corresponds to the stained natural rubber. As the NR content increased to 50%, continuity of the acrylic rubber broke down (Fig. 6). Finally, at the highest NR content (80%), a dispersed particle morphology having the NR as a matrix was observed (Fig. 7). By considering DSC thermograms of these rubber blends (Fig. 8), it can be seen that there are two endothermic baseline shifts at the temperatures corresponding to the glass transition of natural rubber (-64°C) and acrylic rubber (-18°C). These results confirm that the above rubber blends are immiscible.

Similarly, the rubber blends undergoing mixing method B are immiscible, regardless of their composition (Figs. 9–11). At the lowest NR content (20% by

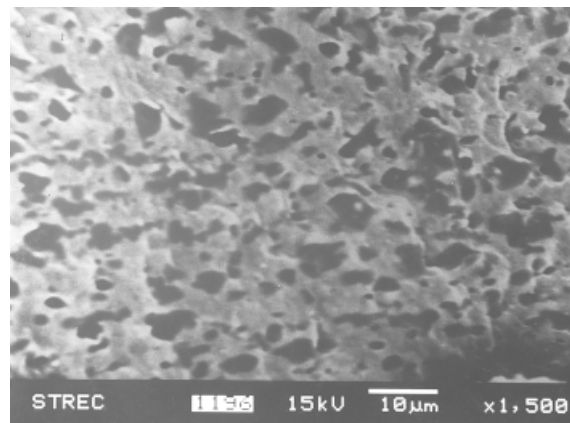


Figure 10 Scanning electron micrograph of a natural-acrylic rubber blend (50% by weight of natural rubber, mixing method B).

weight), both rubber phases are continuous (cocontinuous morphology). As the NR content was increased to 50% (by weight), dispersed particle morphology showing a discrete acrylic rubber phase within the natural rubber matrix was noted. This is the result of the increase in NR content; the greater the NR weight fraction, the greater chance the NR will be a matrix. At 80% (by weight) NR content, the dispersed size decreased and appeared to be in a fiber-like morphology (Fig. 11).

Figure 12 compares the oil resistance property of various rubber blends. After the oil immersion test, percentage mass change of the blends almost linearly decreased with the acrylic rubber content. This is because of the fact that the acrylic rubber, containing ester groups in their molecules, has a greater polarity than the natural rubber. Therefore, the former swelled less than the latter in the engine oil. The effect of mixing method on percentage mass change was not significant.

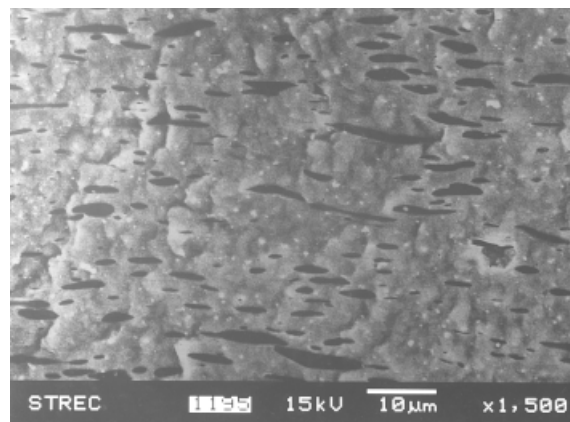


Figure 11 Scanning electron micrograph of a natural-acrylic rubber blend (80% by weight of natural rubber, mixing method B).

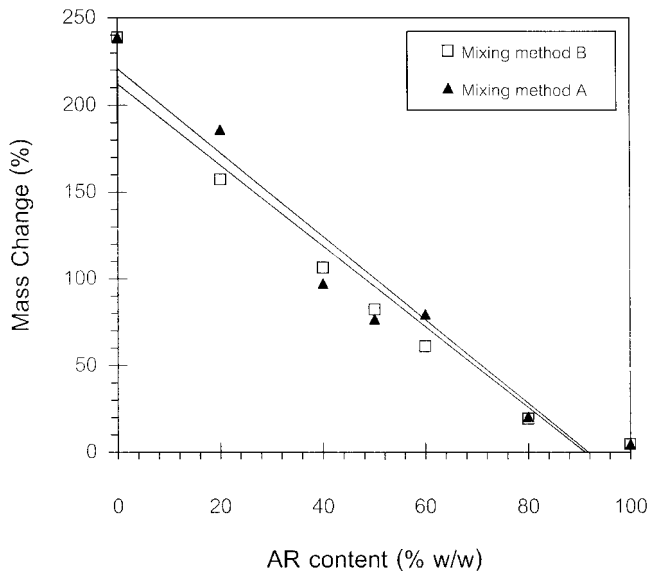


Figure 12 Change in mass of the rubber blends after an oil resistance test.

Table II shows the retention of tensile strain of rubbers and rubber blends after performing the aging test at 140°C. The natural rubber shows the lowest value, as expected. This was probably because of an oxidative degradation of the natural rubber at an elevated temperature in the presence of oxygen. In contrast, tensile strain of the acrylic rubber did not decrease but slightly increased after performing the aging test for 24 h. In addition, it was also noted that an ultimate tensile force of the acrylic rubber increased from approximately 15.7 to 24.0 N after the aging. In this regard, it seems that the acrylic rubber had experienced postcuring in the oven at 140°C for 24 h, leading to the greater tensile properties. Further performing the aging test for 40 h showed that the acrylic rubber still retained the initial tensile strain, indicating its excellent heat resistance. Postcuring of the rubber blends was not conducted in this work, taking into account that the natural rubber phase can degrade on

further heating. It is believed that curing of the rubber blend to an optimum cure time (T_{90}) is sufficient to optimize its mechanical strength and oil and heat resistance.

For the rubber blends, retention of tensile strain tended to decrease with the natural rubber content. The change, however, did not seem to occur in a linear fashion. In this case, the effect of mixing method on the retention of strain was significant. For example, the retention value of the rubber blends containing 50% natural rubber and experiencing mixing method A was 50.2%, whereas that of the rubber blend experiencing mixing method B was 80.7%. It is worth noting that the initial tensile strains of both rubber blends were very close and, thus, that the difference should be mainly attributed to the different tensile strain between the two rubber blends after aging. The rubber blends experiencing blending method B showed a higher tensile strain after aging. This was accompanied with our observation noting that the specimen possesses two layers. The outer skin was dark brown and initially broke down during the tensile test. After that, the inner core, being tacky and lighter in color, elongated up to approximately 550 mm (initial gage length was 25 mm). This behavior was also reflected in its tensile force-displacement trace (Fig. 13), showing two distinct characteristics. The initial yield point corresponded to a rupture of the outer skin, and the long displacement was related to a high tensile strain of the inner core. It is apparent that the inner core was only slightly aged. By further aging this rubber blend to 40 h, the retention of the tensile strain rapidly drops (Table II) and the characteristics (double layer and high elongation) disappeared. In the case of an analogue rubber blend (same composition but experiencing mixing method A), this phenomenon was also noted but was less intense, probably because of different curing characteristics between the two blends.

Finally, by performing an energy-dispersive X-ray spectroscopy (EDX) analysis of a carbon-coated immiscible rubber blend at a higher magnification

TABLE II
Retention of Tensile Strain of Various Rubbers After an Aging Test at 140°C

Sample	Mixing method	Aging time (hrs.)	Initial strain	Strain after aging test	Retention of strain (%)
Natural rubber (NR)	—	24	23.3	6.2	26.6
Blend (20% NR)	A	24	14.8	10.2	68.7
Blend (50% NR)	A	24	24.7	12.4	50.2
Blend (80% NR)	A	24	30.1	4.5	14.9
Blend (20% NR)	B	24	12.4	11.9	96.4
Blend (50% NR)	B	24	27.0	21.8	80.7
Blend (80% NR)	B	24	24.6	6.5	26.4
Blend (20% NR)	B	40	12.4	7.5	60.7
Blend (50% NR)	B	40	27.0	4.2	15.5
Acrylic rubber	—	24	4.6	5.4	100.0
Acrylic rubber	—	40	4.6	4.4	96.0

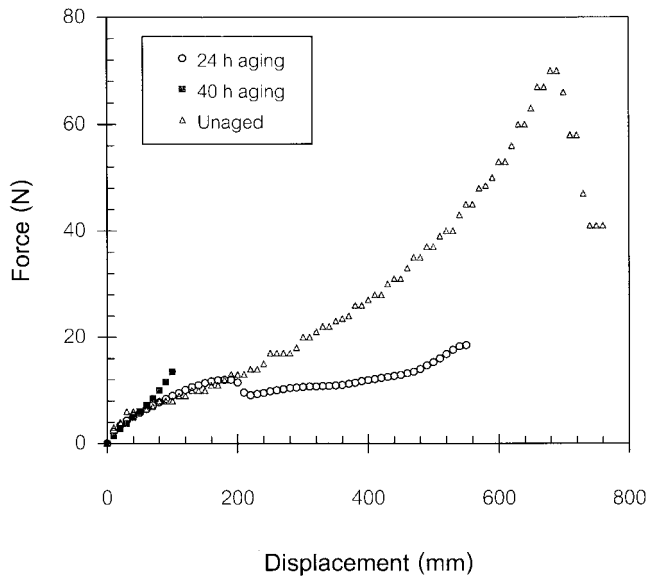


Figure 13 Tensile force-displacement traces of the rubber blends containing 50% natural rubber (mixing method B), before and after the aging test.

(3500 \times), an interesting result regarding sulfur distribution can be observed. Figure 14 shows a typical EDX spectrum of a rubber blend containing 20% NR (method A). The X-ray peak at 2.308 keV, corresponding to the $K\alpha$ -line of sulfur, can be noted. The osmium ($M\alpha$) peak at 1.91 keV, corresponding to a complex

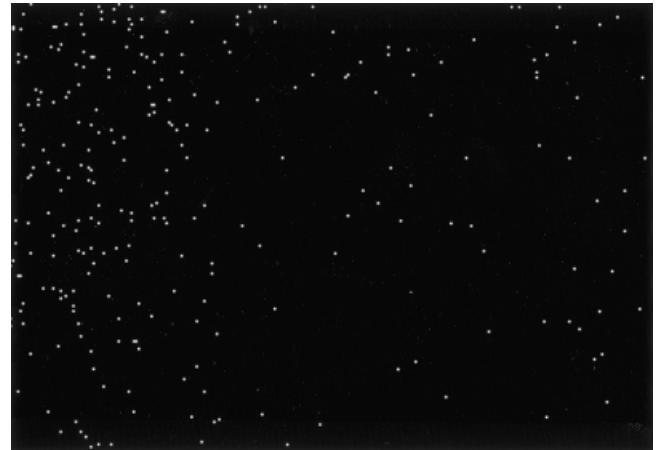


Figure 15 Elemental map of sulfur, produced by accepting only the signal from the appropriate region of the X-ray spectrum.

formed between the staining agent and the natural rubber, was also obvious. The Na peak (1.04 keV, $K\alpha$) attributed to sodium stearate (curing agent for acrylic rubber) and the Cl peak (2.622, $K\alpha$; from the chlorine cure site monomer in the acrylic rubber molecules and sodium chloride by-product) can also be observed. By performing dot-mapping analysis of the surface, using the selected energy (sulfur $K\alpha$, 2.308 keV), it was found that sulfur distribution was not uniform across the sample surface (Fig. 15). In addition, the Os X-ray

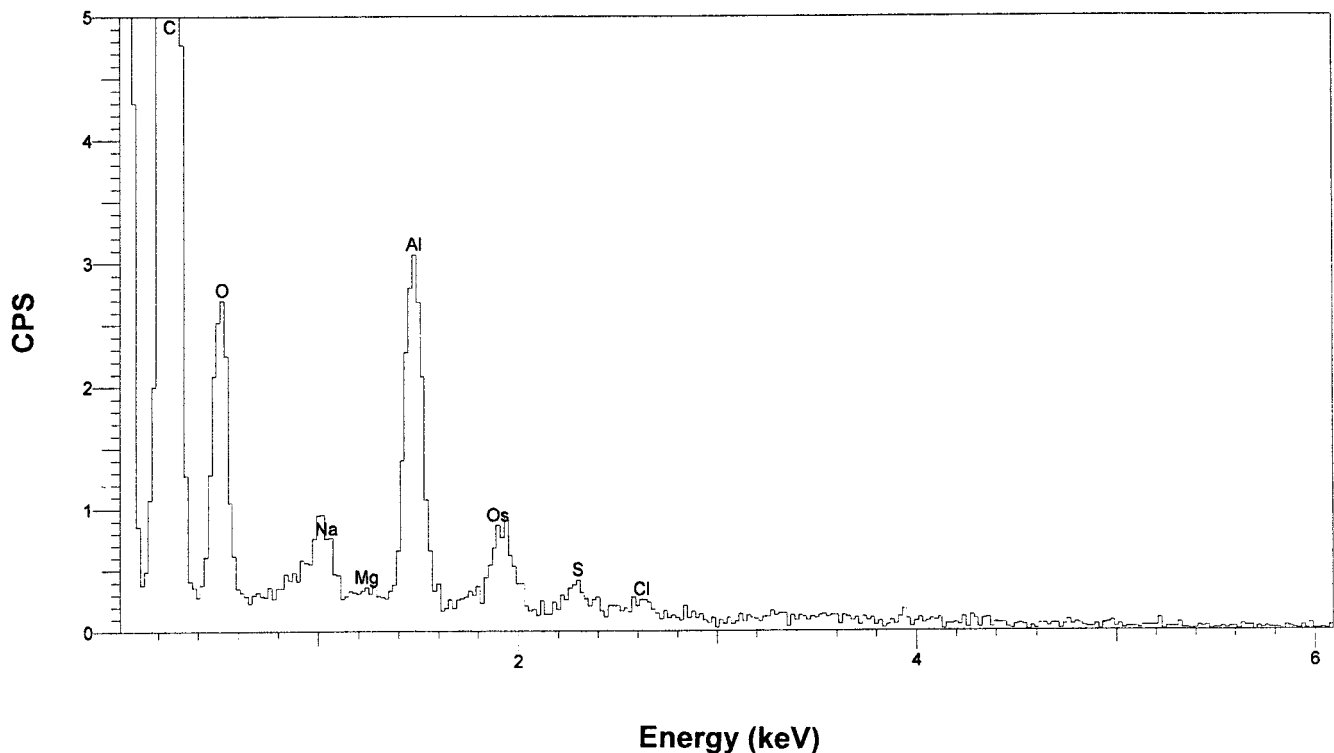


Figure 14 Energy-dispersive X-ray spectroscopy (EDX) spectrum of a natural-acrylic rubber blend (20% by weight of natural rubber, mixing method A).

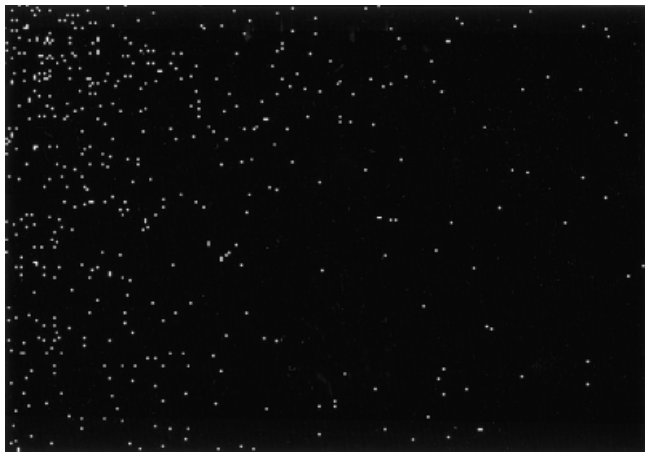


Figure 16 Elemental map of osmium.

(1.91 keV) was mapped, and a similar distribution profile was observed (Fig. 16). This result suggests that the sulfur preferentially migrated into the natural rubber, taking into account the fact that the osmium tetroxide only reacted with the double bonds in the natural rubber molecules. Additional work has been conducted to investigate the distribution of sulfur and other additives (accelerator, activator, carbon black) as a function of blending variables. It is expected that, if the distribution is properly controlled, the properties of the rubber blend will be optimized.

CONCLUSIONS

The natural-acrylic rubber blends were immiscible regardless of their compositions. Cocontinuous mor-

phology was observed in the blend containing 20% NR content. At 80% NR content, the blends showed a dispersed morphology having the NR as a matrix. Tensile properties of the vulcanized rubber blends initially increased with natural rubber content before reaching a plateau. On the other hand, oil and heat resistance of the rubber blend increased with the acrylic rubber content. Most of the properties (morphology, tensile properties, and oil resistance) of the rubber blends were rarely affected by the change in mixing method except in the retention of tensile strain.

We are sincerely grateful to the National Metal and Materials Technology Center (MTEC) for providing a financial support for this study (grant MT-B-43-POL-20-146-G). We would also like to thank the Advanced Zeon Polymix Co. Ltd. for the supply of Acrylic rubber (AR-71) used in this work. Special thanks go to S. Laorattana from the Hitech Elastomer Co. Ltd. for providing the materials (curing agents and natural rubber) and for assistance in accessing the oscillating disk rheometer.

References

1. Gardiner, J. B. *Rubber Chem. Technol* 1968, 41, 1312.
2. Datta, S. *Polymer Blends*. Paul, D. R.; Bucknall, C. B., Eds. Wiley: New York, 2000; Vol. 2, chap. 34.
3. Lewan, M. V. Cross-link density distribution in NR/NBR blends. PhD Thesis, Loughborough University, 1996
4. Bhowmick, A. K.; Stephens, H. L., Eds. *Handbook of Elastomers*, Marcel Dekker: New York, 1988; p. 635.
5. Stammer, P. H. *Progress in Rubber and Plastics Technology*, 1987, 3, No. 1.