

# Phase Separation Structure in the Polymer Blend of Fluorocarbon Elastomer and Hydrogenated Nitrile Rubber

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**ABSTRACT:** Hydrogenated nitrile rubber (HNBR) and a ternary copolymer of vinylidene fluoride, tetrafluoropropylene, and perfluoromethyl vinyl ether (FKM) were blended and vulcanized rubbers that have the excellent low temperature characteristics and oil resistance were successfully obtained. The results of dynamic mechanical analysis demonstrated the great improvement of low temperature characteristics for one of the polymer blend materials (FKM/HNBR = 30/70). Subsequently, the structures of the polymer blends were analyzed by using atomic force microscopy (AFM) and transmission electron microscopy (TEM). The results of AFM and TEM showed that the polymer blend materials have phase-separated structures with

the sea-island morphology. The sea regions were HNBR and the island regions were FKM for the samples containing less than 50% of FKM. On the other hand, the sea region was FKM for the sample containing 70% of FKM. Even in the stretched polymer blend, no gap or crazing was observed at the interface of FKM and HNBR. Therefore, some kind of strong bonding was presumed to exist between the two types of phases. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 149–156, 2005

**Key words:** phase separation; blends; vulcanization; elastomers

## INTRODUCTION

Several special performances including thermal resistance, chemical resistance, and the low temperature characteristic are sometimes required for elastomeric materials. Recently, they have come to be used in more severe conditions and, accordingly, higher performances are desired. Their use in cold districts is especially increasing. Even in low-temperature environments, conservation of elasticity is essential for elastomeric materials. Otherwise, they cannot play their role.

Rubber elasticity at low temperature is closely related to the glass-transition temperature of the material. The glass-transition temperature can be measured as a peak in the  $\tan \delta$  temperature chart of the dynamic mechanical analysis. The elastomeric materials with lower glass-transition temperatures tend to have more excellent low-temperature characteristics. Hydrogenated nitrile rubber (HNBR) is one such materials that has a relatively low glass-transition temperature.<sup>1</sup> On the other hand, improvement of other performances is also required for HNBR.

Development of new elastomers that satisfy the multiple requirements is difficult. However, there are some cases in which the required performances can be satisfied by mixing different polymer materials into polymer alloys or polymer blends. Polymer blending is one reforming techniques for the development of new materials.<sup>2</sup> By combining various polymers with different characteristics, new blend materials that have more suitable characteristics can be developed. The authors tried blending fluorocarbon elastomer and HNBR and successfully obtained vulcanized rubber that has excellent low-temperature characteristics and oil resistance. Subsequently, the structure of this polymer blend was analyzed using atomic force microscopy (AFM)<sup>3</sup> and transmission electron microscopy (TEM).<sup>4</sup>

In this paper the interesting physical properties of the polymer blend are reported. The compatibility and the interfacial state between HNBR and the fluorocarbon elastomer are discussed.

## EXPERIMENTAL

### Materials

The ternary copolymer of vinylidene fluoride, tetrafluoropropylene, and perfluoromethyl vinyl ether (FKM, item code, Dai-El LT-302) was supplied by Daikin Industries, Ltd., Osaka, Japan. HNBR (item code,

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TABLE I  
The Compositions and Blend Designations

Sample	1	2	3	4	5
FKM <sup>a</sup>	100	70	50	30	
HNBR <sup>a</sup>		30	50	70	100
PO <sup>b</sup>	2	2	2	2	2
TAIC <sup>b</sup>	4	4	4	4	4

<sup>a</sup> The polymer blend ratio was calculated by the volume ratio.

<sup>b</sup> Organic peroxide and coagent were compounded with 100 parts of the rubber mixture.

Zetpol 4310; ACN, 19 wt%; iodine value, 5) was supplied by Nippon Zeon, Co. Ltd., Tokyo, Japan. Organic peroxide, 2,5-dimethyl-2,5-di(*t*-butyl peroxy) hexane (PO) was provided from NOF Co. Ltd., Tokyo Japan. Co-agent, triallyl isocyanurate (TAIC) was provided from Nippon Kasei Chemical Co. Ltd., Tokyo, Japan. Other chemicals above were procured from indigenous sources and were used as such.

### Preparation of the samples

The compositions and blend designations used in this study are listed in Table I. FKM was mixed with HNBR in the following blend ratio: 100/0, 70/30, 50/50, 30/70, and 0/100 (v/v) using a laboratory water-cooled two-roll mill (8 × 18 inch, Imanaka Mechanical Industry Co. Ltd.) at 40°C for 10 min at a roll speed of 20 rpm. In the same manner 100 parts of the rubber mixture, 2 parts of the PO curing agent, and 4 parts of the TAIC were compounded by the laboratory water-cooled two-roll mill at 40°C for 20 min at a roll speed of 20 rpm. In order to avoid perturbation of the internal structure, no filled water was added. The samples were then molded in a metal mold (sheet shape: 190 × 150 × 2 mm) in a two-plate hydraulic press (Tokai Yuki Jitugyo, Ltd.) at 170°C for 20 min at pressure of 7 MPa. Cure time at 170°C was determined by a Curelastometer Type V (Nichigou Shouji Co. Ltd.).

### Measurements

#### Dynamic mechanical analysis

Dynamic mechanical thermal properties of the samples (25 × 3 × 2 mm) were evaluated using a DMTA, DVE-V4 FT Rheo Spectra (UBM Co. Ltd.). The experiments were carried out at a frequency of 11 Hz. The data were taken from -100 to 150°C at heating rate of 3°C/min and a double strain amplitude of 4 μm peak-to-peak displacement. The loss modulus ( $E''$ ) and the loss tangent ( $\tan \delta$ ) were measured for all samples under identical conditions.

#### Mechanical tests

Dumbbell-type specimens for the mechanical tests were punched out from the molded sheets using ASTM Die-C. The mechanical tests were carried out per the ASTM D412-99 method in a Shopper-type examination machine at a crosshead speed of 500 mm/min at 25°C. The average value of three tests for each sample was reported.

#### Oil resistance test

The oil resistance tests were carried out per the ASTM D471-79 method at 170°C for 70 h in IRM903 oil. The changes in volume and hardness after immersion and subsequent drying were evaluated. The average value of three tests for each sample was reported.

#### Atomic force microscopy

The AFM analysis was performed with a scanning probe microscope system (SPI3800, Seiko Instruments, Inc.) operated under ambient conditions. In this work, analysis was always conducted in the dynamic force mode that vibrates the cantilever slightly below its resonance frequency and scans the surface so as to keep the amplitude of the vibration. Cantilevers, each with a length of 250 μm, a Si tip, and a spring constant of 20 N/m, were used for the measurements. The height and phase images were recorded.

The surface layer of each sample was quickly sectioned off using a clean razor blade (the razor blade had been cleaned with methyl alcohol before use) at room temperature and the cross section was observed. Additionally, each sample (original dimension, 50 × 2 × 2 mm) was extended from 50 to 75 mm and then fixed with epoxy adhesive on a sample plate of AFM. Subsequently, a cross section of the stretched sample

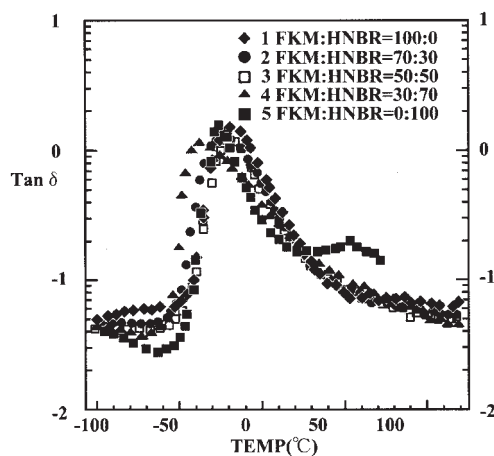


Figure 1 Temperature dependence of  $\tan \delta$ .

**TABLE II**  
**Values and Temperatures of Loss Modulus ( $E''$ ) and Loss Tangent ( $\tan \delta$ ) at the Maximum Peaks**

Sample	1	2	3	4	5
$E''$ value (dyn/cm <sup>2</sup> )	$3.7 \times 10^9$	$3.4 \times 10^9$	$2.8 \times 10^9$	$2.9 \times 10^9$	$2.4 \times 10^9$
Peak temperature of $E''$ (°C)	-34.2	-39.7	-35	-48.4	-36.6
$\tan \delta$ value	1.48	1.26	1.24	1.11	1.56
Peak temperature of $\tan \delta$ (°C)	-19.3	-22.5	-18.2	-37.3	-26.8

(by 50%) was also observed. Most specimens were examined by AFM within 24 h of sectioning.

#### Transmission electron microscopy

The TEM observation was performed using a transmission electron microscope (JEOL JEM 100U) operated at 80 kV. A thin section of the sample was prepared with a cryoultramicrotome and then observed without staining.

## RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of  $\tan \delta$ . Each sample showed a single peak in  $\tan \delta$ . The curves for pure FKM and pure HNBR don't appear to be very different. However, their blend materials showed noticeable departure from the curves of the pure polymers. Especially, the peak of  $\tan \delta$  for sample No. 4 (FKM/HNBR = 30/70) was 10°C lower than that for the unblended HNBR. The peak temperatures and values of  $\tan \delta$  and  $E''$  are listed in Table II, which again indicates that the dynamical mechanical properties of the blended samples were not the same as that between the dynamical mechanical properties of the raw materials. The peak temperatures of  $\tan \delta$  and  $E''$  for sample No. 4 were lower than for the other samples.  $E''$  of sample No. 2 also shifted to the lower temperature side compared to the raw materials, although the degree of shift was not as much as that of sample No. 4. In general, when two polymers are mixed, the polymer blend often shows the intermedi-

ate characteristics of the constituents. When the ratio of either constituent increases, the characteristics of the major one generally tend to become dominant. Interestingly, however, the general tendency did not apply to the case shown in Figure 1 and Table II.

Table III shows the results of mechanical and oil resistance tests. Most mechanical properties, hardness ( $H_S$ ), tensile strength ( $T_B$ ), and elongation ( $E_B$ ), hardness change ( $\Delta H$ ), and volume change ( $\Delta V$ ) showed values almost linearly related to the polymer blend ratio. As for the tensile stress ( $M_{100}$ ), the polymer blend materials were stronger than the raw materials. The data in Table III suggest that samples 2 and 4 have reasonable oil resistance and mechanical properties along with excellent low-temperature characteristics and, accordingly, these blend materials are very interesting from the industrial viewpoint.

It is very important to investigate why the above-mentioned physical properties have emerged. Therefore, the internal structures of the samples were examined.

In general, when immiscible polymers are mixed, multiple peaks will appear in the temperature  $\tan \delta$  chart, as long as the peak position of each constituent is not closely located.<sup>5</sup> Because the  $\tan \delta$  chart (Figure 1) showed the single peak for each blend material, the constituent polymers were expected to be mutually compatible and to form a uniform phase. However, phase separation structures were observed by morphological observation.

Figure 2 shows the phase images of samples 1–5 by AFM. The images for pure FKM and pure HNBR

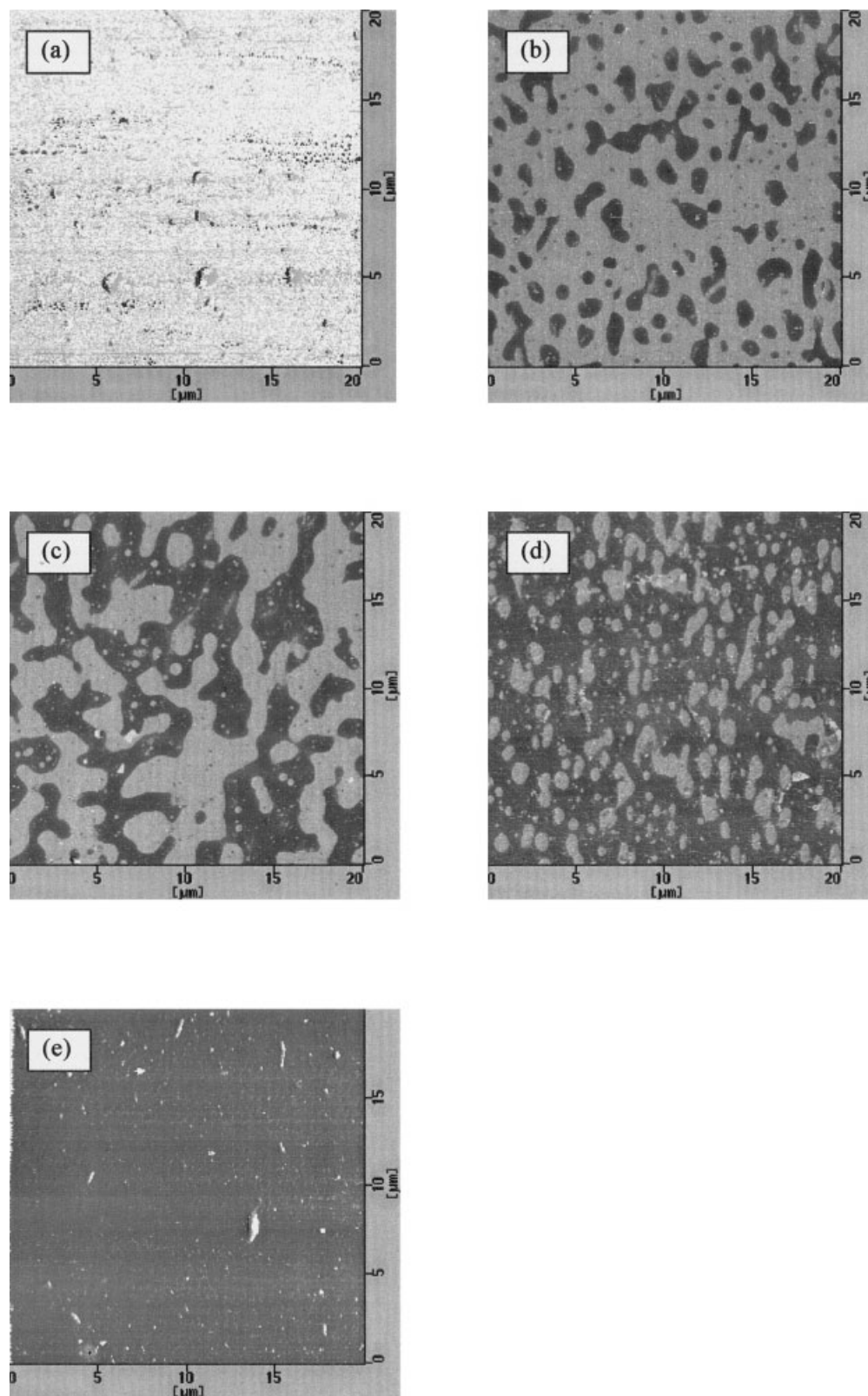
**TABLE III**  
**Mechanical Properties and Oil Resistance Data**

Sample	1	2	3	4	5
Mechanical properties					
$H_S$ (shore A) <sup>a</sup>	52	52	50	53	43
$T_B$ (MPa) <sup>a</sup>	5.8	5.0	4.5	3.6	1.4
$E_B$ (%) <sup>a</sup>	280	240	220	190	200
$M_{100}$ (MPa) <sup>a</sup>	1.1	1.3	1.3	1.3	0.8
Oil resistance					
$\Delta H$ (shore A) <sup>b</sup>	-1	-5	-4	-10	-12
$\Delta V$ (%) <sup>c</sup>	+2	+17	+28	+37	+59

<sup>a</sup>  $H_S$ , hardness;  $T_B$ , tensile strength;  $E_B$ , elongation;  $M_{100}$ , 100% tensile stress.

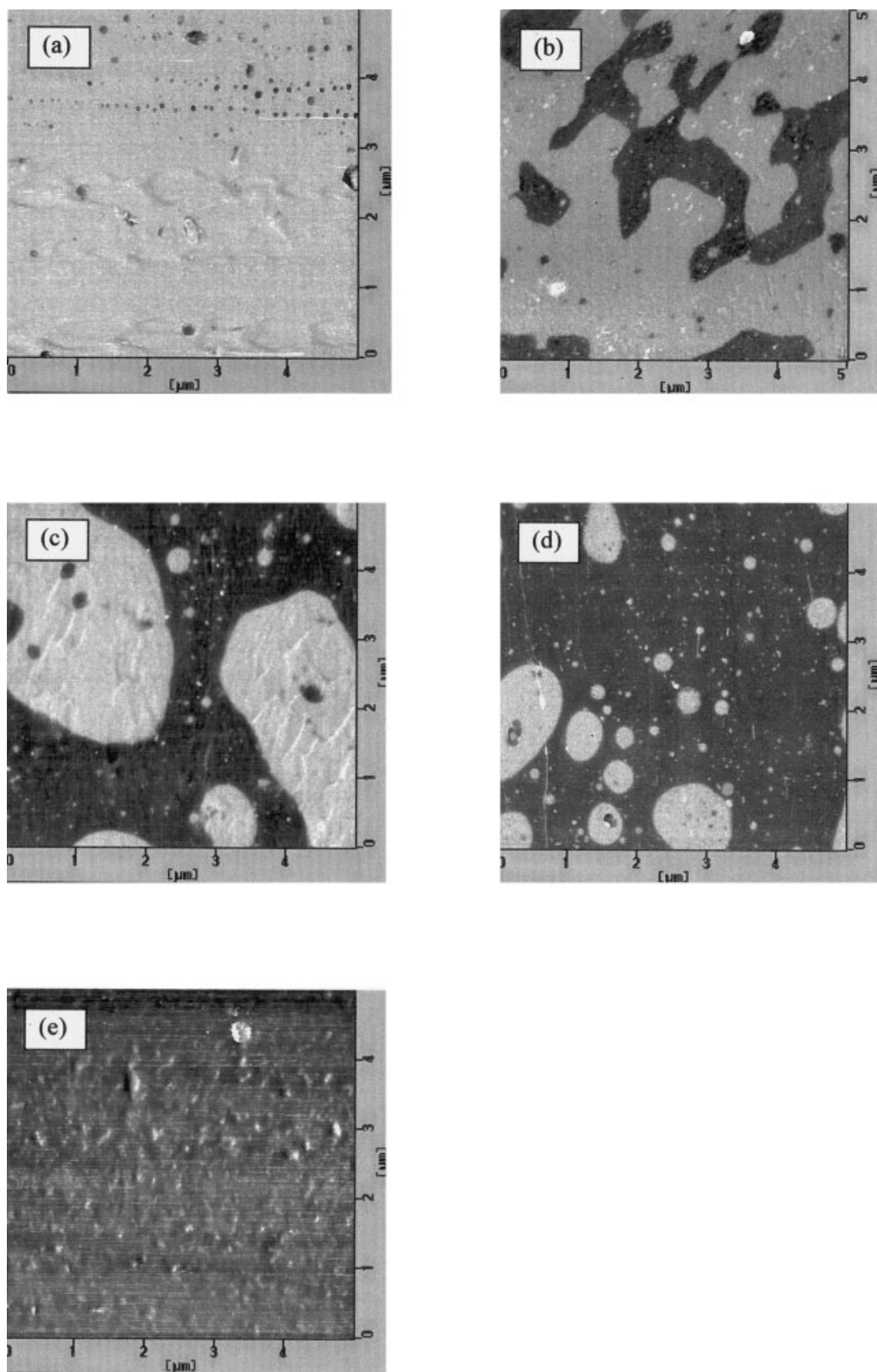
<sup>b</sup>  $\Delta H$ , hardness change.

<sup>c</sup>  $\Delta V$ , volume change.



**Figure 2** Phase images of the polymer blend materials. Dark regions correspond to HNBR phases. FKM/HNBR = (a)100/0, (b)70/30, (c)50/50, (d)30/70, (e) 0/100.





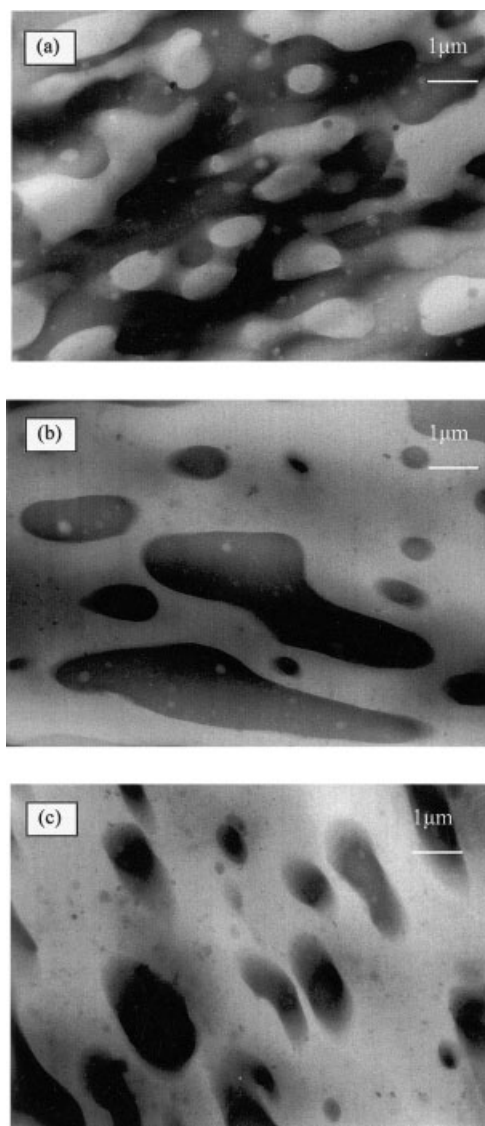
**Figure 3** Phase images of the polymer blend materials. Dark regions correspond to HNBR phases. FKM/HNBR = (a)100/0, (b)70/30, (c)50/50, (d)30/70, (e) 0/100.

(Figure 2a and e, respectively) showed almost uniform contrast except for small particles that are suspected to be artifacts induced by sectioning. On the other hand, the phase separation structure that is categorized as the sea-island morphology was evidently recognized in the polymer blend. Because the dark regions increased the total area with increasing fraction of HNBR, the dark and the bright regions should correspond to the HNBR and FKM phases, respectively. The dimensions of the islands were widely dispersed; the diameter of the small ones was less than 100 nm and that of the large ones was 5–10  $\mu\text{m}$ . Figure 3 shows the phase image of the same samples at higher resolution (for a smaller scanning area). In Figure 2, both the sea and the islands regions had appeared to be composed mainly of the single phase. However, detailed inspection of Figure 3 revealed that much smaller (100 nm or less) islands of the other component existed both in the sea and in the islands regions.

Figure 4 shows TEM images of blend samples 2–4. Similar sea-island morphology was observed also in these images. Because the dark contrast in this kind of TEM image comes from the larger scattering factor of the constituent atoms, and the scattering factor increases with the atomic number, the dark regions in this figure are certainly attributed to FKM; FKM contains fluorine, a heavier element than carbon. It should be noted that the contrast is occasionally reversed in phase images of AFM because the origin of contrast in the phase image is very complicated.<sup>6</sup> Therefore, there was a possibility of allocating the wrong constituents to the sea and islands regions only based on the phase images by AFM, especially when the blend ratio was 50/50 (v/v). In this case, however, the islands certainly corresponded to FKM even when the blend ratio is 50/50 according to the TEM images.

In Figures 2 and 3, the polymer compounding ratio had an almost linear relationship with the areal ratio of sea and island regions. When the volume ratio was 50/50, FKM and HNBR had the tendency to become the islands and the sea, respectively. This phenomenon is supposed to come from the higher surface tension of FKM than of HNBR.<sup>7</sup>

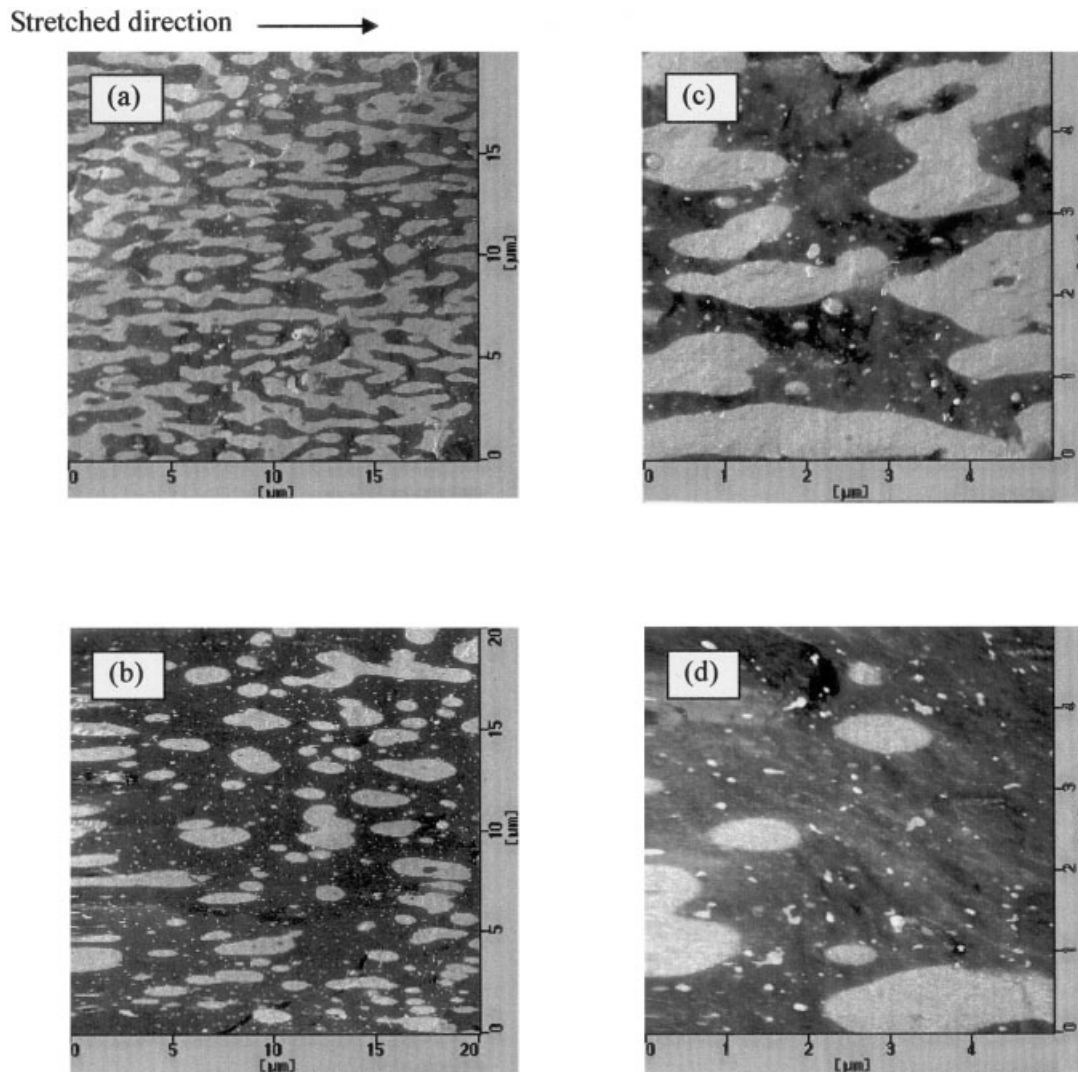
Figure 5 shows the phase images of stretched samples 3 and 4 by AFM. Even when the samples were stretched, the areal ratio of the sea and islands appeared unchanged. Both the sea and the islands regions were obviously elongated compared to the unstretched samples in Figures 2 and 3. No gaps or crazing were observed at the interface in the blend materials, two types of phases were similarly extended. If the interface of the two types of phases were weak without any molecular bonding, color variation by a deep ruggedness in the gap or crazing part would be observed at the interface. These results indicate the existence of relatively strong bonding between the FKM and HNBR phases, that is to say, the bonding by



**Figure 4** TEM images of the polymer blend materials. Dark regions correspond to FKM phases. FKM/HNBR = (a) 70/30, (b) 50/50, (c) 30/70.

mutual penetration of the molecules to the other constituent phase, by chemical bonding between FKM and HNBR, and so on.

In addition, detailed inspection of Figure 5 led us to an interesting finding. In the images before stretching (Figures 2 and 3), both the sea and the islands regions had almost uniform darkness. However, the stretched samples in Figure 5 present fluctuation of the darkness in both the sea and the island regions, especially in Figure 5c and d. This observation suggests the possibility that a small amount of the other constituent had been contained in each region. Before stretching, the major and the minor constituents in each of the region should have been miscible and uniformly dissolved with each other. However, because the variable of state has been changed by stretching, the system is



**Figure 5** Phase images of the stretched polymer blend materials. Fluctuation of darkness appeared both in the dark and in the bright regions. FKM/HNBR = (a) 50/50, (b) 30/70, (c) 50/50, (d) 30/70.

thought to have shifted from the miscible state to the immiscible one. As a result, new regions with different homopolymer composition may have appeared.

According to the above-mentioned discussions, the strong bonding at the interface of the two phases and the inclusion of a small amount of the other constituent in each of the phases may have led the temperature dependence of  $\tan \delta$  to have a single peak and to shift to the low-temperature side for the blend materials.

Because there should be the strong bonding at the interface of the FKM and HNBR phases, some FKM and HNBR is presumed to have reacted and formed chemical bonds to be a compatibilizer. If the chemical structure was changed by the formation of the chemical bonds, new peaks might be found using infrared spectroscopy analysis. However, in our tentative infrared analysis, no new peaks that indicate the formation of the chemical bonds were detected. The relative

amount of the new bonds could have been too small to be detected. More detailed analysis of this problem will be performed.

## CONCLUSION

The physical properties of the polymer blend materials of FKM and HNBR were evaluated. Internal structures of the blend materials were also analyzed by AFM and TEM. The following results were obtained.

- The results of DMA demonstrated the great improvement of low-temperature characteristics for the polymer blend material (FKM/HNBR = 30/70).
- The results of AFM and TEM showed that the polymer blend materials have phase-separated structures with the sea-island morphology. The sea regions were HNBR and the island regions

were FKM for the samples containing less than 50% FKM. On the other hand, the sea region was FKM for the sample containing 70% FKM.

- Even in the stretched polymer blend, no gap or crazing was observed at the interface of FKM and HNBR. Therefore, some kind of strong bonding was presumed to exist between the two types of phases.
- In the stretched polymer blend, the inhomogeneous structures were observed both in the sea and in the islands regions. The structures were supposed to be due to the phase separation of the other constituent that was induced by the stretching.
- The strong bonding at the interface of the two types of phases and the inclusion of a small amount of the other constituent in each of the phases were thought to have led the temperature dependence of  $\tan \delta$  to have a single peak and to shift to the low-temperature side for the blend materials.

More detailed inspections of the phase-separated structures in relation to the excellent low-temperature characteristics of the polymer blend materials are in progress.

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## References

1. Recchio, M. J. SAE Technical Paper Series, **SAE-942428**, 1994.
2. Sano, H.; Usami T.; Nakagawa, H. *Polymer* 1986, 27, 1497.
3. Tsou, A. H.; Waddell, W. H. *Kautschuk Gummi Kunststoffe* 2002, 55, 382.
4. Kader, M. A.; Bhowmick, A. K. *J Mater Sci* 2002, 37, 1503.
5. Mazich, K. A.; Samus, M. A.; Killgoar, P. C. Jr.; Plummer, H. K. Jr., *Rubber Chem Technol* 1986, 59, 623.
6. James, P. J.; Antognozzi, M.; Tamayo, J.; McMaster, T. J.; Newton, J. M.; Miles, M. J. *Langmuir* 2001, 17, 349.
7. Ooyanagi, Y. *Jissen Polymer Alloy*; Agne. Tokyo, 1993.