

# NOTES

## A Novel Gas-Barrier Elastomer Composed of Butyl Rubber and Polyamide

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### INTRODUCTION

Freon gas as chlorofluorocarbon or hydrofluorocarbon has been used as a refrigerant in air-conditioning systems. In particular, dichlorodifluoromethane (R12) and 1,1,1,2-tetrafluoroethane (R134a) have been widely used because of their outstanding chemical stability. Although they are being severely restricted because of their ability to destroy the ozone layer and their greenhouse effect potential, they are still being used in air-conditioning systems in many fields.

Generally, as a hose for an air-conditioning system is used not only for circulating the refrigerant but also for absorbing the vibration of compressor in the air-conditioning system, it must be rubbery. However, rubbery material does not have very good gas-barrier properties and the refrigerant loss by permeation is not very small during circulation in the rubber hose.

To solve this problem, there are two methods. One is the development of nonfreon gas as an alternative to R12 or R134a. However, this problem has not been thoroughly settled even today. The other is to improve the gas-barrier property of the rubber hose.

Recently, a laminate molding-hose composed of an inner tube of a thin layer of polyamide (PA) and outer tube of butyl rubber (isobutylene-isoprene copolymer, IIR) was proposed to improve the gas-barrier property. The laminated molding-hose improved the gas-barrier property considerably, but showed insufficient flexibility, which is a serious problem.

Hence, we tried to make a hose with both a good gas-barrier property and elasticity by blending rubber and plastic to solve this problem.

Recently, a polymer alloy of nylon6 (PA6)/isobutylene-methylstyrene elastomer (XP-50) was studied by using the compatibilizer derived from dynamically vulcanized polymer alloy: PA6/XP-50 plus curatives,<sup>1</sup> but no experiments have yet been made a polymer alloy of PA/IIR.

In this study, we selected IIR as a rubber and PA as a plastic. However, IIR and PA are essentially incompatible and the blend should show a lower mechanical property than that of their parents compounds because of inferior interfacial adhesion<sup>2</sup> and poor dispersion of PA in IIR.

Usually, an interfacial agent (or compatibilizer) is used to improve the interfacial adhesion and dispersion between immiscible polymers in polymer blending.<sup>3-7</sup>

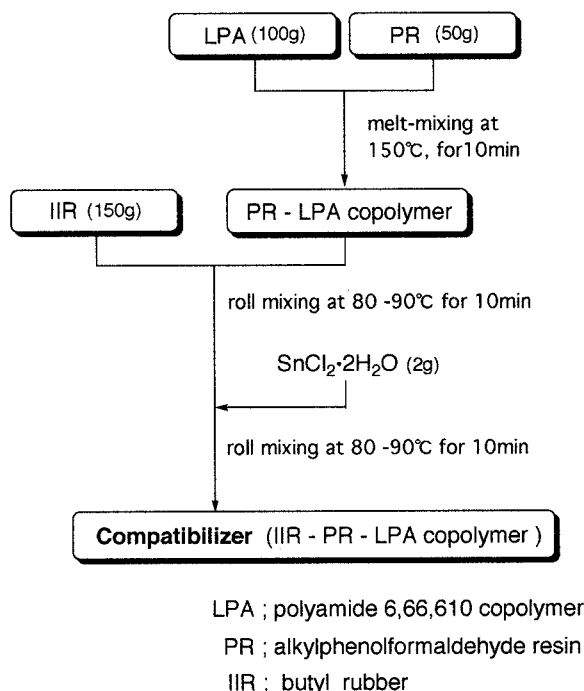
So we designed and synthesized a compatibilizer that has both an IIR and PA block by using alkylphenolformaldehyde-resin (PR) having a reactivity toward IIR and PA.

### EXPERIMENTAL

#### Materials

The butyl rubber (IIR) employed was Butyl 402 (regular type) supplied by Polysar Co. The weight average molecular weight and unsaturation concentration were  $3.35 \times 10^5$  and 2.2 mol %, respectively.

Polyamide obtained from Toray Ind., Inc., were CM1021T (polyamide 6,  $M_w = 2.65 \times 10^4$ , hereafter abbreviated as PA) used for dispersed phase and CM833 (polyamide 6,6,610-copolymer,  $M_w = 1.00 \times 10^4$ , hereafter abbreviated as LPA) used for the compatibilizer.



**Scheme 1** Synthetic process of compatibilizer.

The PR used for compatibilizer was Tackirol 201 provided by Taoka Chemical Co., Ltd., which was of average molecular weight,  $4.65 \times 10^3$ .

These materials were used without further purification.

### Synthesis

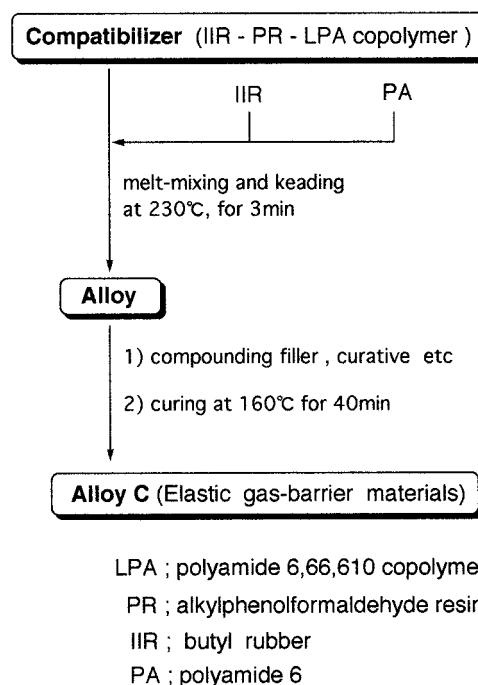
#### Compatibilizer

Scheme 1 shows the synthetic process of the compatibilizer (IIR-PR-LPA copolymer).

At first, PR-LPA copolymer was derived by adding PR chips (50 g) to molten LPA (100 g) at 150°C for 10 min. Then, the PR-LPA copolymer (150 g) was mixed with IIR (150 g) for 20 min at 80–90°C in the presence of tin dichloride (2 g) to give the IIR-PR-LPA copolymer, which is considered to work as a compatibilizer.

#### Polymer Alloy and Elastic Gas-Barrier Materials

As shown in Scheme 2, IIR, PA, and the compatibilizer were melt mixed and kneaded in a continuous extruder (KCK35-80/2, KCK Industrial Co.) to give a polymer alloy. The polymer alloy (Alloy) or polymer blend (compatibilizer free case, Blend) were compounded with HAF (High abrasion furnace black) carbon black, polymethylolphenolic resin (vulcanizer), and other ingredients listed in Table I, and cured at 160°C for 40 min.



**Scheme 2** Synthetic process of Alloy and Elastic gas-barrier material.

### Measurement

The Fourier transform IR (FTIR) spectrum was recorded on a PARAGON 1000 type FTIR spectrometer of

**Table I** Compounding Recipes

	Alloy-C	Blend-C	IIR-C	PA
Butyl Rubber (IIR)	—	—	100	—
Polyamide 6 (PA)	—	—	—	100
Alloy <sup>a</sup>	157 <sup>b</sup>	—	—	—
Blend <sup>a</sup>	—	143 <sup>c</sup>	—	—
HAF <sup>d</sup> carbon black	40	40	40	—
Zinc oxide	5	5	5	—
Stearic acid	1	1	1	—
Curative <sup>e</sup>	7	7	7	—
Antioxidant <sup>f</sup>	1	1	1	—
<b>Cure condition</b>				
Temperature (°C)	160	160	160	—
Time (min)	40	40	40	—

<sup>a</sup> Prepared by melt-mixing and kneading at 230°C for 3 min.

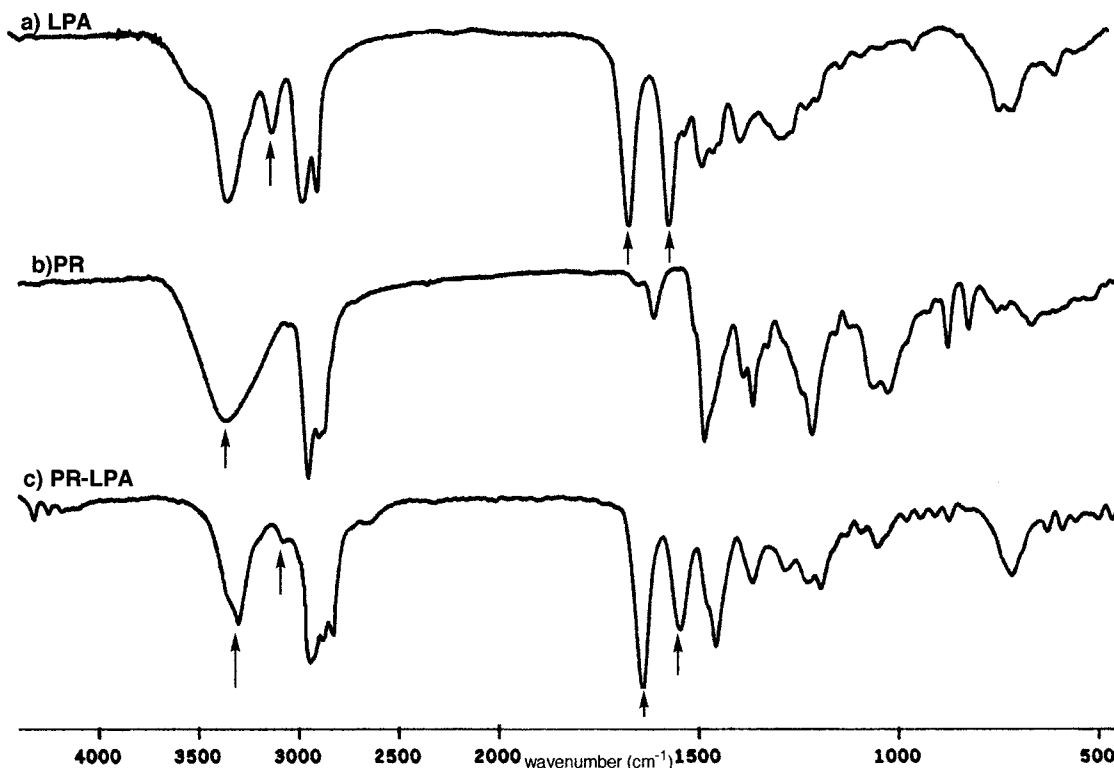
<sup>b</sup> The wt ratio of IIR : PA : compatibilizer was 70 : 30 : 10 in weight.

<sup>c</sup> The wt ratio of IIR : PA : compatibilizer was 70 : 30 : 0 in weight.

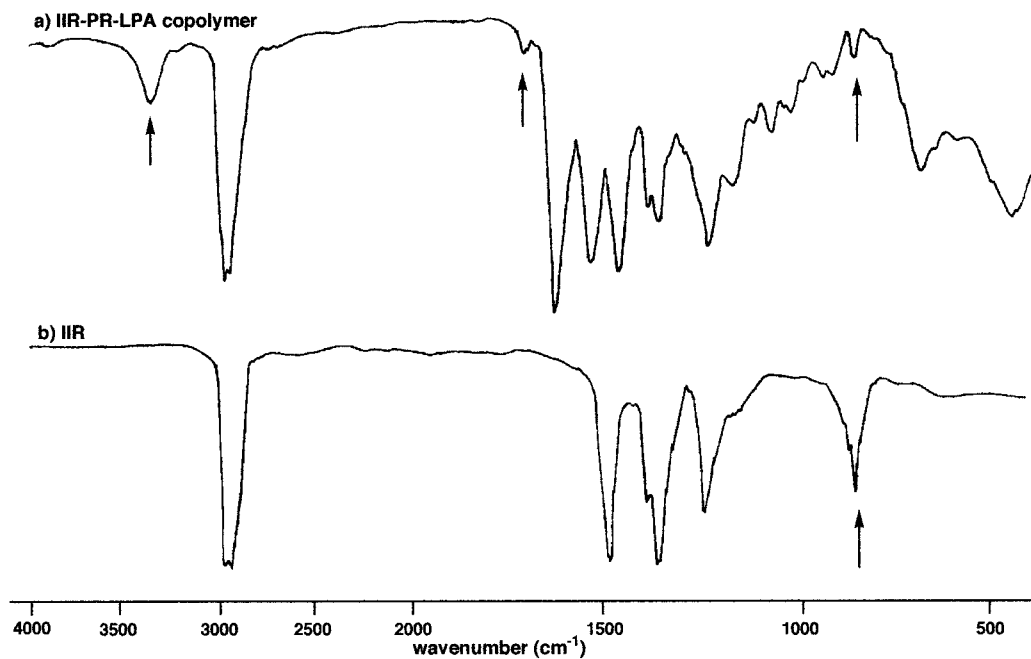
<sup>d</sup> High abrasion furnace black.

<sup>e</sup> Polymethylol phenolic resin.

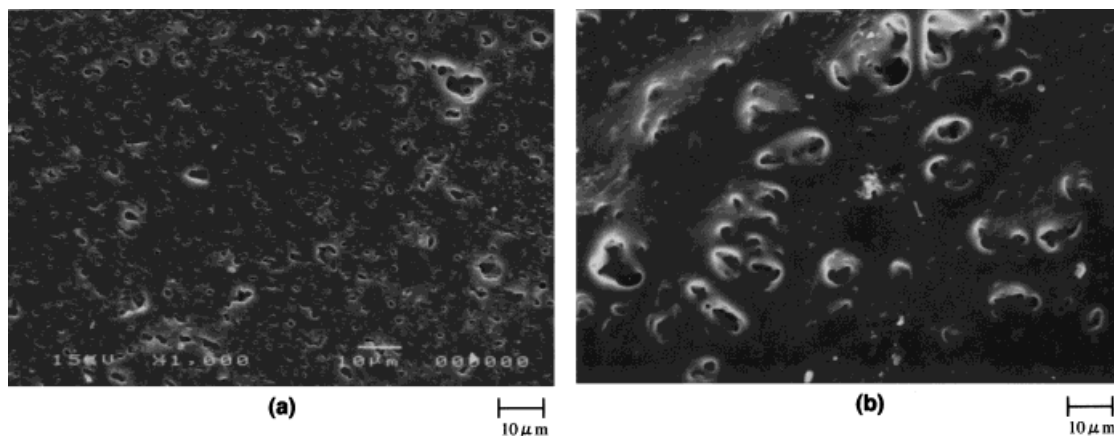
<sup>f</sup> 2,2'-methylene bis(4-methyl-6-*tert*-butylphenol).



**Figure 1** IR chart of materials used for Alloy; (a) polyamide6,66,610 (LPA), (b) Alkylphenolformaldehyde resin (PR), and (c) Reaction product of PR/LPA.



**Figure 2** IR chart of compatibilizer; (a) compatibilizer consisted of IIR and PR-LPA copolymer and (b) IIR.



**Figure 3** SEM photographs of the composites of IIR (70) and PA (30); (a) Alloy with 10 wt parts compatibilizer and (b) Blend without compatibilizer.

Perkin Elmer Co., Ltd. The spectra of the LPA, PR, and PR-LPA copolymer were taken by the cast film method, respectively. The IIR-PR-LPA copolymer and IIR were molded in the hot press, and the spectra were taken by the attenuated total reflection method.

The morphology was observed with a JEOL JSM-T330A scanning electron microscope (SEM). The samples were fractured at the liquid nitrogen temperature and the fracture surface was treated with hot formic acid in order to remove PA phase.

The rheological property was measured from  $-150$  to  $180^{\circ}\text{C}$  at a heating rate of  $2^{\circ}\text{C}/\text{min}$  and at a frequency of  $1\text{ Hz}$  by using a Seiko Instruments, Inc., type DMS120 spectrometer.

Tensile strength and elongation at break were measured on a Shimadzu tensile testing machine (AG-50kNE).

Gas-barrier properties were estimated by JIS (Japan Industrial Standard) Z 0208-1976 testing method (dish method) to measure the amount of transmitted gas through the elastic gas-barrier materials adjusted to  $2\text{ mm}$  in thickness.

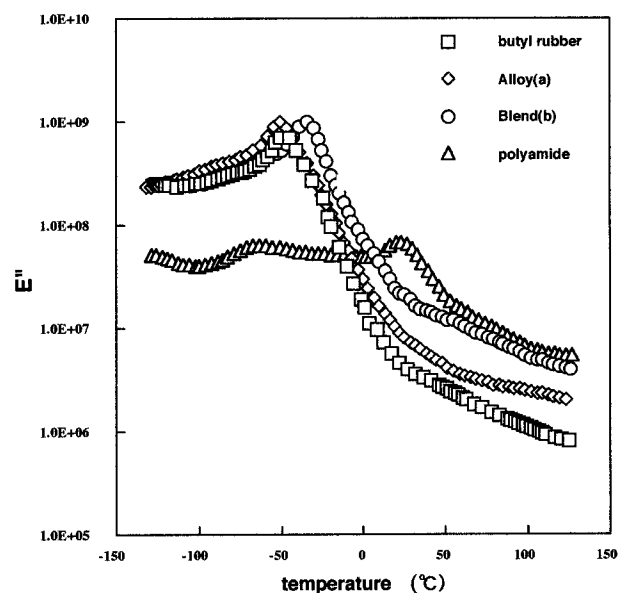
## RESULTS AND DISCUSSION

### Compatibilizer

IR spectra of LPA, PR, and PR-LPA copolymer are shown in Figures 1(a), 1(b), and 1(c), respectively. After the reaction of LPA with PR, the peaks at  $1548\text{ cm}^{-1}$  (NH bending) and  $1647\text{ cm}^{-1}$  (C=O stretching) of LPA shifted by the reaction to  $1542$  and  $1640\text{ cm}^{-1}$ , respectively. In addition, the peak intensity of the NH bending deformation of the amide group at  $1548$  and  $3085\text{ cm}^{-1}$  relative to that of  $\text{CH}_2$  stretching at  $2950\text{ cm}^{-1}$  decreased, and a peak of  $\text{CH}_2\text{OH}$  of the PR-LPA copolymer at  $3372\text{ cm}^{-1}$  decreased a little from PR. From

these results, we considered that the hydroxyl group in PR reacts with the amide group in LPA to afford copolymer, as reported by Takeyama.<sup>8</sup> It can be assumed that a peak of the third amide group at  $1650\text{ cm}^{-1}$ , which may be formed by a reaction, gives an overlap with that of C=O stretching of LPA at  $1640\text{ cm}^{-1}$ .

IR spectra of the IIR-PR-LPA copolymer and IIR are shown in Figures 2(a) and 2(b), respectively. By comparing Figures 1(c), 2(a), and 2(b), we found that the peak intensity of the double bond at  $890\text{ cm}^{-1}$  and that of  $\text{CH}_2\text{OH}$  at  $3372\text{ cm}^{-1}$  relative to  $\text{CH}_2$  bending at  $2950\text{ cm}^{-1}$  decreased, respectively. And a peak of chro-



**Figure 4** Temperature dependencies of dynamic loss moduli ( $E''$ ) of the composites of IIR (70) and PA (30); (a) Alloy with 10 wt parts compatibilizer and (b) blend without compatibilizer.

**Table II Physical Properties of Elastic Gas-Barrier Materials**

Samples	Tensile Strength (MPa)	Tensile Elongation (%)	Gas Permeability <sup>a</sup> (g/m <sup>2</sup> · 24 h)
Alloy-C <sup>b</sup>	13.7	150	25
Blend-C <sup>c</sup>	9.8	110	41
IIR-C	5.9	240	57
PA	73.4	120	8
Conventional <sup>d</sup>	13.8	260	41

<sup>a</sup> Permeability for freon gas was measured at 100°C by JIS Z 0208-1976 testing method (dish method). The thickness of samples were adjusted to 2 mm.

<sup>b</sup> IIR/PA/compatibilizer = 70/30/10.

<sup>c</sup> IIR/PA/compatibilizer = 70/30/0.

<sup>d</sup> The commercial hose.

man ring-related structure at 1750 cm<sup>-1</sup> in Figure 2(a) was observed. It seems to be most probable that the reaction of PR in the PR-LPA copolymer with IIR proceeds through the mechanism of the Diels-Alder type 4 + 2 cycloaddition of quinon methine moiety toward double bond in IIR to give chroman ring.<sup>9</sup>

### Polymer Alloy

As shown in Scheme 2, the IIR, PA, and IIR-PR-LPA copolymer were melt-mixed and kneaded by the weight ratio of 70 : 30 : 10 or 70 : 30 : 0 in a continuous extruder (KCK35-80/2, KCK Industrial Co.) to give blend. Hereafter the former is called "Alloy" and the later is called "Blend."

Figure 3 shows scanning electron microscopy (SEM) photographs of (a) Alloy and (b) Blend. As shown in Figure 3(b), marked segregation of the PA phase (5–20 μm in diameter) is observed in the absence of the IIR-PR-LPA copolymer. However, as shown in Figure 3(a), comparatively small PA domains (0.1–10 μm in diameter) dispersed uniformly in IIR matrix in the presence of the IIR-PR-LPA copolymer. These results indicate the IIR-PR-LPA copolymer makes the dispersion of PA in IIR matrix better and works as a compatibilizer to give a polymer alloy.

Dynamic loss moduli  $E''$  of Alloy, Blend, IIR, and PA are plotted against temperature in Figure 4. As shown in Figure 4, the peak temperature of  $E''$  of the Alloy was -50°C, which was close to IIR. The  $E''$  peak of the PA domain at 25°C was absorbed in the relaxation region of the IIR matrix and not observed independently in both Alloy and Blend. These results mean that the matrix and the dispersed phase are IIR and PA, respectively, and that PA plays an important role in the matrix phase in the rubbery region, especially lower  $E''$  of Alloy than Blend indicates stronger reinforcing effect on Alloy than on Blend.

### Gas-Barrier and Physical Properties of Elastic Gas-Barrier Materials

The Alloy, Blend, and IIR were compounded with HAF carbon black, polymethylolphenolic resin (vulcanizer), and the other ingredients listed in Table I, and cured at 160°C to give Alloy-C, Blend-C, and IIR-C.

Gas-barrier and physical properties of the thus obtained materials were estimated by the method described in the experimental section. The results are listed in Table II.

As shown in Table II, although the gas permeability of Alloy-C is larger than that of PA, it is much smaller than those of Conventional (commercial hose), Blend-C, and IIR-C. Moreover, the tensile strength and tensile elongation of Alloy-C are better than those of them. Hence we think the Alloy-C to be useful for a gas-barrier hose.

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