

## 폴리프로필렌/폴리에틸렌 및 폴리프로필렌/폴리에틸렌/EPDM 블렌드의 유변학적 및 기계적 물성

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### Rheological and Mechanical Properties of PP/PE Binary and PP/PE/EPDM Ternary Blends

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**요 약 :** 폴리프로필렌(PP)과 고밀도폴리에틸렌(HDPE) 혹은 저밀도폴리에틸렌(LDPE) 이성분계 및 PP/HDPE/EPDM 혹은 PP/LDPE/EPDM 삼성분계 블렌드의 유변학적 및 기계적 물성에 대한 비교연구를 행하였다. 블렌드는 압출기를 이용하여 용융혼합하여 제조하였다. PP/HDPE 및 PP/LDPE 이성분계 블렌드는 전형적인 불상용성을 보였지만 PP와 HDPE간의 계면점착력이 PP와 LDPE간의 그것보다는 양호한 것으로 나타났다. 블렌드의 점도는 EPDM 함량의 증가에 따라 증가하였다. EPDM 함량의 증가에 따라 PP/PE 이성분 블렌드의 항복응력과 탄성율은 약간 감소하였지만 충격강도는 상당히 개선되었다. EPDM에 의한 이러한 강인화 효과는 EPDM이 LDPE보다 HDPE와의 계면점착성이 좋음으로 인해 PP/LDPE 블렌드 보다 PP/HDPE 블렌드의 경우가 더 크게 나타났다.

**Abstract :** Comparative studies have been made on the rheological and mechanical properties of polypropylene(PP)/high density polyethylene(HDPE) binary blends or PP/HDPE/ethylene-propylene-diene terpolymer(EPDM) ternary blends and PP/low density polyethylene(LDPE) binary blends or PP/LDPE/EPDM ternary blends. Morphological analysis has been also performed using scanning electron microscopy. Blends have been prepared by melt mixing in an extruder. The rheological measurement and morphology showed that the interfacial adhesion between PP and HDPE was better than between PP and LDPE, even though both the PP/HDPE and PP/LDPE binary blends were typical incompatible systems. The viscosity of binary blends of PP with HDPE or LDPE increased with the addition of EPDM. The impact strength of the PP/PE binary blends were strongly improved by the addition of the EPDM at the expense of slight loss in yield strength and initial elastic modulus. It was found that the toughening effect by EPDM was more prominent in PP/HDPE blends than PP/

LDPE blends, due to the better interfacial adhesion between EPDM and HDPE than EPDM and LDPE.

## INTRODUCTION

Polymer blends have been extensively investigated because of their commercial importances as well as their theoretical interest. Among the polymer blends attracting commercial interest are polypropylene(PP)-based ones. Indeed, there are extensive literatures on the blends of polypropylene(PP)/High density polyethylene(HDPE).<sup>1-6</sup> One of the reasons for addition of HDPE to PP is improvement of its low temperature impact and environmental stress cracking properties.

Due to their inherent immiscibility, in order to enhance the ultimate properties, frequently a compatibilizer has to be used, e.g. in PP/HDPE blends 5% of ethylene-propylene rubber(EPR) was found necessary to ascertain linearity between the tensile/impact strengths and HDPE content.<sup>4,5</sup> Strange enough, however, few works have been published on the blends of PP and low density polyethylene(LDPE). Santamaria et al.<sup>7</sup> investigated on the extrudate shrinkage in the blends of PP and LDPE with approximately equal shear viscosities in capillary flow.

The objective of this work is to systematically investigate the composition dependence of properties of the PP/LDPE blends and the PP/LDPE/EPDM ternary blends and compare with those of the PP/HDPE and the PP/HDPE/EPDM ternary blends. To our knowledge, no comparative works have been reported on the rheological and mecha-

nical properties of binary blends of PP with HDPE or LDPE, and ternary blends of PP, EPDM with HDPE or LDPE, even though separate investigations have been published on the PP/HDPE, PP/LDPE blends and so on. For the purpose, we used HDPE and LDPE of very similar molecular weight characteristics except their degree of chain branching.

## EXPERIMENTAL

**Materials.** The characteristics of polyethylene and polypropylene(PP) used in this study are summarized in Table 1. The PP, high density polyethylene(HDPE), low density polyethylene(LDPE), and ethylene-propylene-diene terpolymer(EPDM) with dicyclopentadiene(DCPD) as a termonomer were all commercially available grades. The methyl contents in HDPE and LDPE were estimated from their IR spectra using the method suggested by Bryant and Vorter,<sup>8</sup> and Cross, et al.<sup>9</sup> The characteristics of EPDM are shown in Table 2.

**Table 2.** EPDM Characterization

$\eta_{inh}$ (dl/g) <sup>a</sup>	I. V. <sup>b</sup>	PE/PP <sup>c</sup> (by mol %)	ML <sup>d</sup> <sub>1+4</sub>	Source
1.52	5.1	57/43	45~55	Royalene 359 (Uniroyal)

a 0.5 g/dl xylene solution at 70°C

b by ICI titration method

c by IR analysis

d Mooney Viscosity measured at 100°C

**Table 1.** Properties and Sources of PP, HDPE, and LDPE

Polymers	Melt index (g/10 min)	Density (g/cm <sup>3</sup> )	Amount of methyl groups per 1,000 carbon atoms	Molecular weight		Sources
				$\bar{M}_n$	$\bar{M}_w$	
PP	8 <sup>a</sup>	0.90	—	90,000	200,000	4017(Kor. Petro.)
HDPE	0.8 <sup>b</sup>	0.96	2.0	42,000	100,200	E308(Kor. Petro.)
LDPE	0.8 <sup>b</sup>	0.92	14.9	33,000	81,000	5072(Hanyang)

a) measured at 230°C b) measured at 190°C

**Preparation of Blends.** Blends were prepared by melt-mixing in an 30 mm $\phi$ - single screw extruder (L/D=28.8). The temperature of two cylinders was set at 200°C and the die temperature was set at 210°C. The extrudates were injection molded to obtain the samples for tensile and Izod impact tests at 200°C.

**Measurements.** Rheological properties were measured using a capillary rheometer(Instron Model 3211) in the shear rate range of 3.5~350.5 sec<sup>-1</sup> at 200°C. The length and diameter of the capillary were 5.0925 cm and 0.1275 cm, respectively. The tensile tests were carried out using an Instron UTM(Model 4202) on the samples prepared according to ASTM D638-84. The crosshead speed was 50 mm/min, and the gauge length was 20 mm. Notched Izod impact test was measured according to the ASTM D256. For mechanical properties, six or more measurements were averaged.

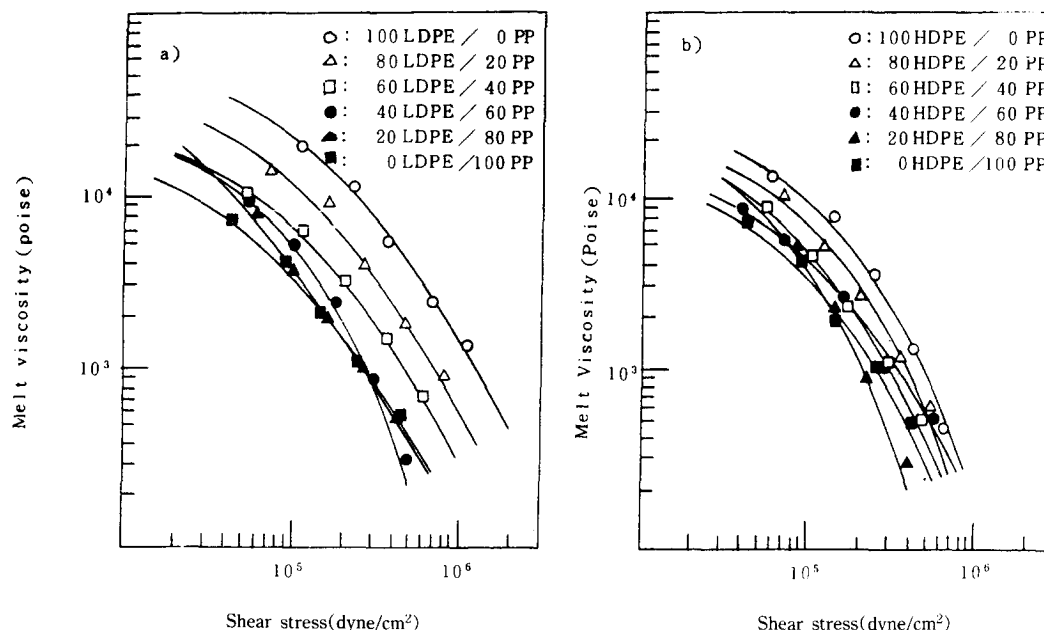
Scanning electron micrographs(SEM) were obtained by JEOL JSM35-CF SEM. Samples were cryogenically fractured in liquid nitrogen and metallized by gold coating prior to the installation in

the SEM chamber.

## RESULTS AND DISCUSSION

The rheological behaviors for PP/HDPE and PP/LDPE blends are shown in Fig. 1. It is seen that the melt viscosity decreases as the PP contents increase for both PP/HDPE and PP/LDPE blends. It is interesting is, however, that the viscosity curves for the blends of 40/60 LDPE/PP and 20/80 LDPE/PP or 20/80 HDPE/PP compositions cross that for PP homopolymer at higher shear stress. The viscosities of the blends having those compositions are slightly higher than those of PP at low shear stress, but on increasing the shear stress, the curves fall down quickly.

Taking into consideration that the tendency to form a continuous phase in polymer blends is dominated by concentration and viscosity. Ramos-De Valle<sup>10</sup> explained those somewhat unexpected results as follows : When two components having different rheological characteristics flow through capillaries, the components tend to rearrange into a



**Fig. 1.** Viscosity vs. shear stress of PP/HDPE blends (a) and PP/LDPE blends (b) with different compositions.

sheath-core configuration, with the component of lower viscosity forming the sheath. This sheath will act as a lubricant between the extrudate and the capillary wall. Such trends are highly plausible at higher shear stress than at lower shear stress. Thus, more rapid reduction in melt viscosity at higher shear stress at those blend compositions may be caused presumably by the morphological changes in the blend.

Comparison of Fig. 1-a and 1-b indicates that the viscosity curves of homopolymers decreased in the order HDPE > LDPE > PP. If we consider that the HDPE and the LDPE used in this work have very similar molecular weight and molecular weight distribution, the higher viscosity of HDPE compared to LDPE is due to its larger hydrodynamic volume in a molten state because of its smaller degree of chain branching compared to LDPE.<sup>11,12</sup> LDPE contains a number of short chain and long chain

branches. It has been well established that the long-chain branched molecules are more compact and less liable to entanglements than linear polymers of similar weight, resulting in lower viscosity and melt elasticity.<sup>13</sup>

Fig. 2 shows the viscosity variations with different HDPE or LDPE composition for PP/HDPE and PP/LDPE blends. At lower shear rates, the PP/HDPE and the PP/LDPE blends showed negative deviation behavior from their additive values at higher HDPE or LDPE compositions, implying that the two blends are incompatible at higher PE compositions. One can see, however, that the blend exhibited slightly positive deviation behavior from their additive values at lower PE compositions and that the positive deviation behavior is more clearly observed in the blends of PP with HDPE than with LDPE. The result may be ascribed to the fact of the easier formation of entanglement network bet-

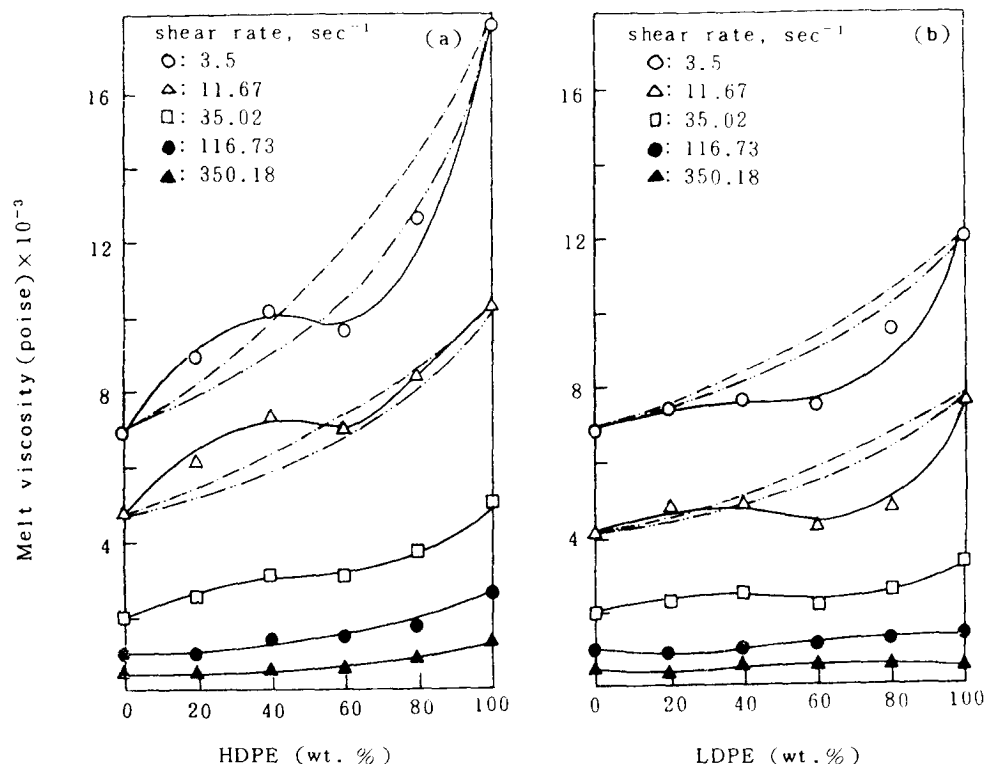


Fig. 2. Viscosity variations with different composition of PP/HDPE blends (a) and PP/LDPE blends (b) at 200°C (with various shear rate). Arrhenius ; --- Hayashida ; - - - -.

ween PP and HDPE than between PP and LDPE, since the interfacial adhesion between the former is larger than between the latter, which will be proved later in their morphology.

In general, however, the overall minima and maxima behaviors with different shear rates in the viscosity-composition plot are attributed to the change of morphology, caused by the change of the domain size and shape, and interfacial energy in a molten state depending on the shear rates. Tokita<sup>14</sup> reported that the domain size( $R$ ) in heterogeneous blend systems was given by the following equation :

$$R = \frac{12 P \gamma_{12} \phi_2}{\pi \eta_b \dot{\gamma}} \left( 1 + \frac{4 P \phi_2 E_{2k}}{\pi \eta_b \dot{\gamma}} \right) \quad (1)$$

where  $P$  is the probability of reaggregation of domain particles,  $\phi_2$  is the volume fraction of domain phase,  $E_{2j}$  is the fracture energy of domain phase,  $\eta_b$  is the viscosity of a blend,  $\dot{\gamma}$  is the shear rate during mixing,  $\gamma_{12}$  is the interfacial tension between component polymer 1 and 2. The Tokita equation shows that  $R$  is reduced as  $\eta_b$  or  $\dot{\gamma}$  is large and  $P$  or  $\gamma_{12}$  is small, leading to the enhanced interfacial adhesion between the domain and con-

tinuous phase polymers. Since the interfacial adhesion between PP and HDPE phases is larger than that between PP and LDPE, the sizes of domain( $R$ ) in PP/HDPE blends are smaller than those in PP/LDPE blends. The morphological results will be described later.

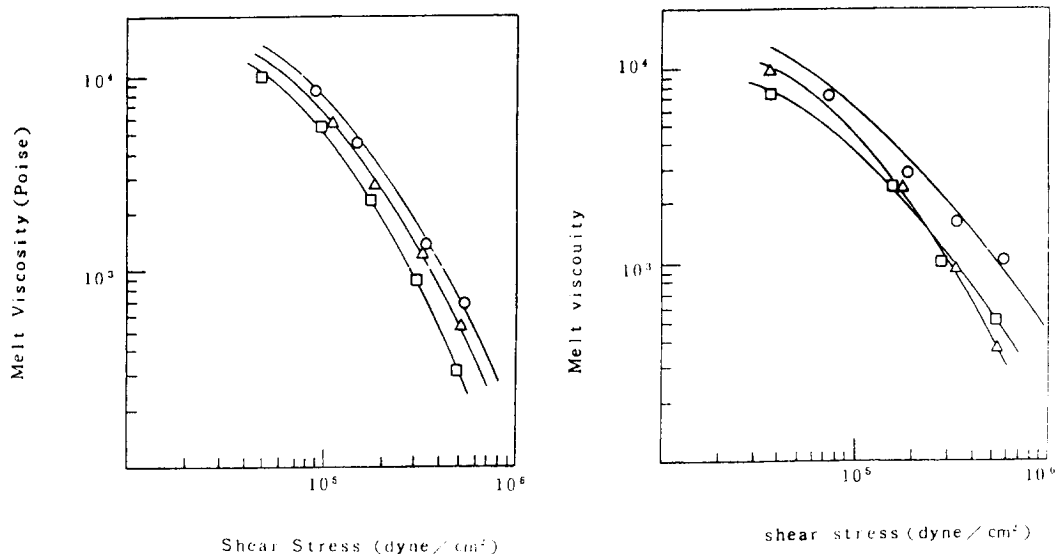
Two kinds of additive rules were denoted in Fig. 2. One is the Hayashida<sup>15</sup> equation(2) and the other is the Arrhenius equation (3).

$$1/\eta_b = \omega_1/\eta_1 + \omega_2/\eta_2 \quad (2)$$

$$\eta_b = \eta_1^{w_1} \cdot \eta_2^{w_2} \quad (3)$$

where  $\omega_i$  is the weight fraction of  $i$  component in the blend,  $\eta_i$  and  $\eta_b$  are the melt viscosities of  $i$  component and blend, respectively. In the PP/HDPE blends, the observed viscosities fit the Hayashida additive rule better than the Arrhenius additive rule. Fig. 3 shows the effect of EPDM addition on the melt viscosity of PP/LDPE and PP/HDPE blends. It is generally seen that the viscosity increases with increasing EPDM contents.

Fig. 4 shows typical stress-strain curves of homopolymers and blends. It is seen that the tensile strength and modulus of PP/LDPE or PP/HDPE



**Fig. 3.** Melt viscosity vs. shear stress of PP/HDPE blends (a) and PP/LDPE blends (b) with various EPDM content.  $\square$  : 0% EPDM,  $\triangle$  : 5% EPDM,  $\circ$  : 10% EPDM.

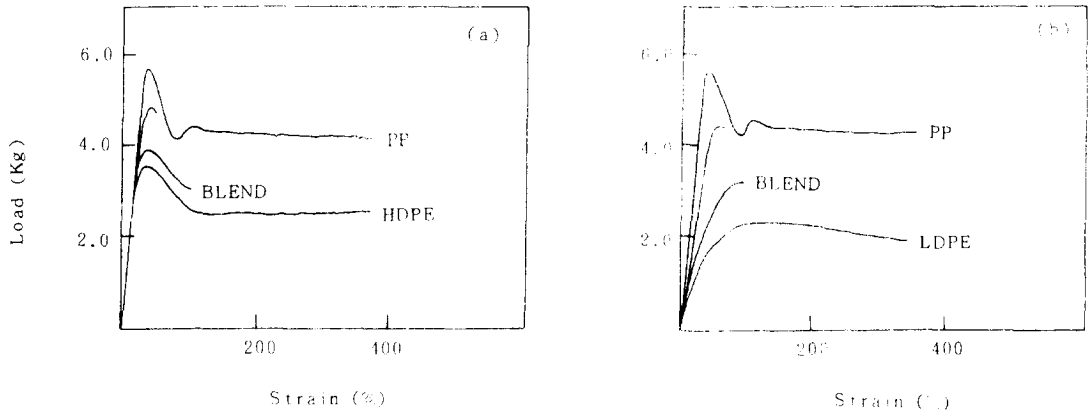


Fig. 4. Stress-strain curves of homopolymer and polyblends : (a) PP/HDPE, (b) PP/LDPE.

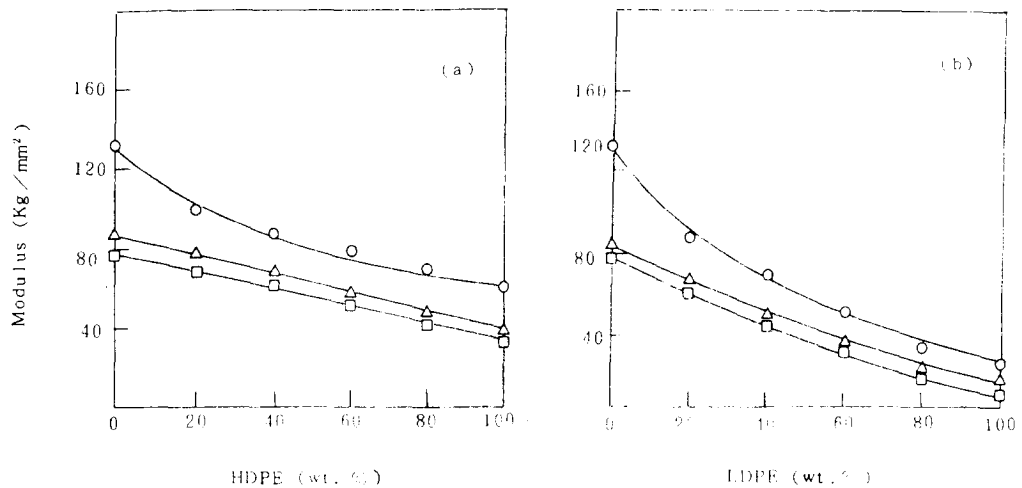


Fig. 5. Moduli of PP/HDPE blends (a) and PP/LDPE blends (b) with various EPDM content. ○ : 0% EPDM, △ : 5% EPDM, □ : 10% EPDM.

blends are the intermediate values between those of homopolymers, whereas the elongation at break of the blends was significantly smaller compared to that of homopolymers, due to the inherent incompatibility between the components.<sup>16</sup> Fig. 5 shows the effect of EPDM addition on the modulus of PP/LDPE and PP/HDPE blends. The moduli of the blends decrease with increasing HDPE and LDPE compositions.

The composition dependences of the observed moduli of PP/HDPE blends were in accord with those of Robertson and Paul<sup>17</sup> and those of PP/LDPE blends were in agreement with those of Teh

<sup>18</sup> and Deanin and Sansone.<sup>19</sup> In our work, however, the modulus did not show a maximum around 10 wt % of HDPE in PP/HDPE blends, which was reported by Lovinger and Williams<sup>16</sup> and Noel and Carley.<sup>20</sup> Instead, it should be noted that the composition dependences of the modulus for both PP/HDPE and PP/LDPE blends in this work observe very well the Simplex equation (4) suggested by Utracki,<sup>21</sup> as shown in Fig. 6.

$$P = P_1\phi_1 + P_2\phi_2 + \beta\phi_1\phi_2 \quad (4)$$

where  $P$  and  $P_i$  are the property (e.g. modulus in Fig. 6) of a blend and  $i$  component, respectively.

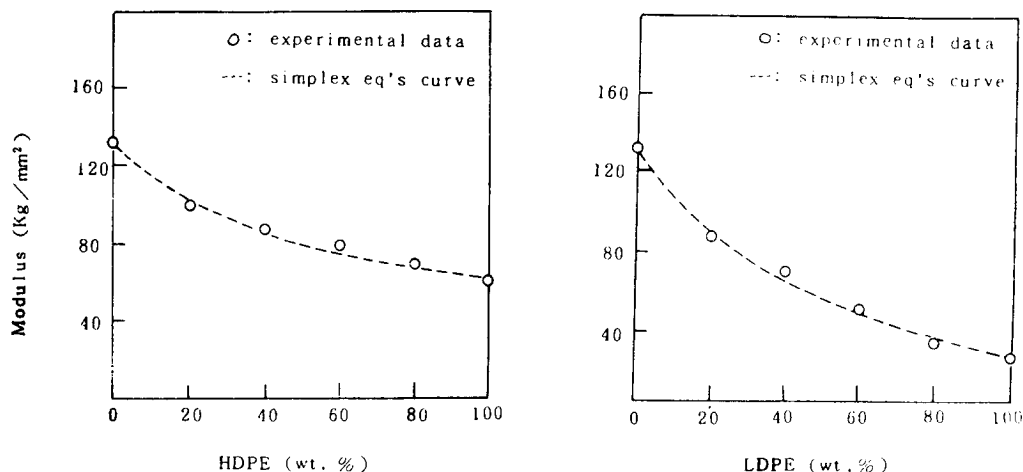


Fig. 6. Comparison of the experimental modulus data with simplex equation's curve. PP/HDPE blends (a) and PP/LDPE blends (b).

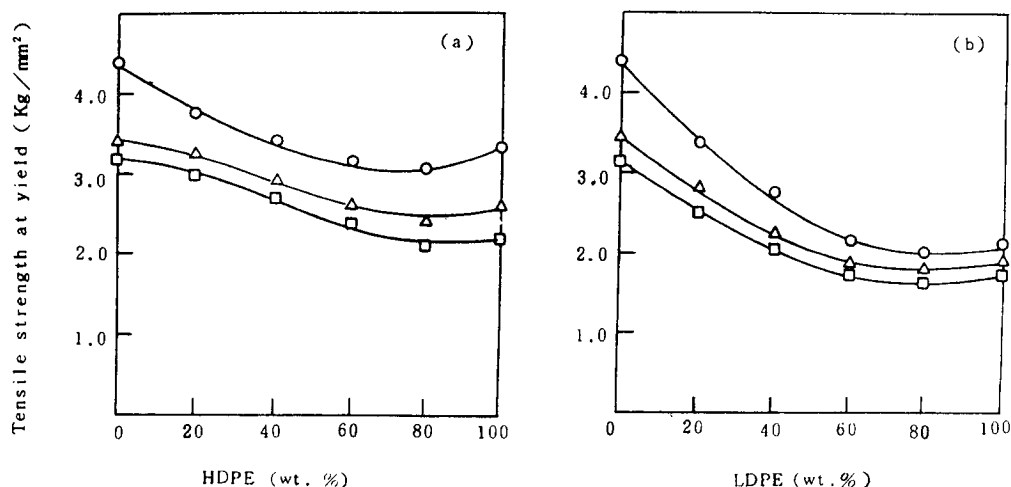


Fig. 7. Tensile strength at yield of PP/HDPE blends (a) and PP/LDPE blends (b) with various EPDM content.  $\square$  : 0% EPDM,  $\triangle$  : 5% EPDM,  $\circ$  : 10% EPDM.

$\phi_i$  is the volume or weight fraction of  $i$  component and  $\beta$  is a constant. In this Simplex equation, positive deviation (synergistic effect) is observed in the case of  $\beta > 0$  but negative deviation (anti-synergistic effect) is observed in the case of  $\beta < 0$ , whereas a simple additive rule holds for  $\beta = 0$ . The linear regression for the experimentally observed modulus data referred to in Fig. 6 gave  $\beta$  as  $-50 \text{ kg/mm}^2$  and  $-90 \text{ kg/mm}^2$  for PP/HDPE and PP/LDPE blends, respectively. In Fig. 5, the addition

of EPDM decreased the moduli of both PP/HDPE and PP/LDPE blends over the entire concentration ranges. The tensile strength at yield point showed the same trends, as shown in Fig. 7.

It is interesting to note that the impact strength of PP is improved as the HDPE and LDPE compositions increase and that the impact strength of the PP/LDPE or PP/HDPE blends was greatly enhanced by the addition of small amount of EPDM, as shown in Fig. 8. Careful inspection of Fig. 8a and

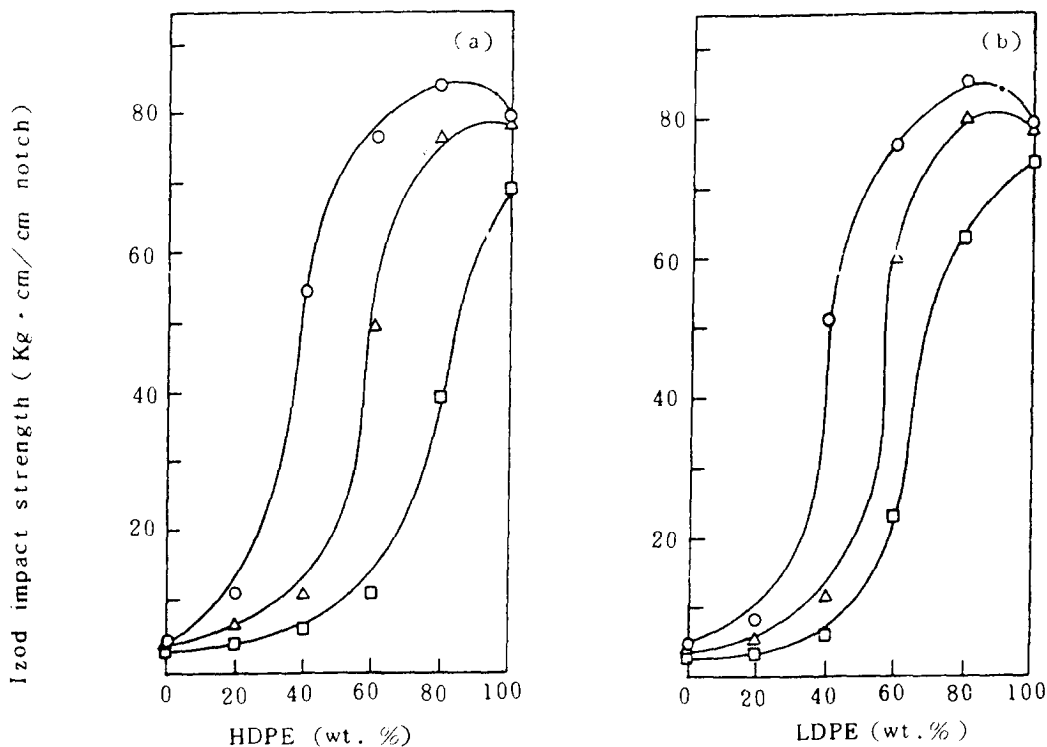


Fig. 8. Impact strength of PP/HDPE blends (a) and PP/LDPE blends (b) with various EPDM content. □ : 0% EPDM, △ : 5% EPDM, ○ : 10% EPDM.

8b shows that the increases of Izod impact strength of PP/HDPE blends by the addition of EPDM are slightly higher than those of PP/LDPE blends at the same EPDM concentrations. The result may be due to the more preferential adhesion between HDPE and EPDM than LDPE and EPDM.<sup>22,23</sup> Such kind of preferential adhesion between components can be seen more clearly in their morphology.

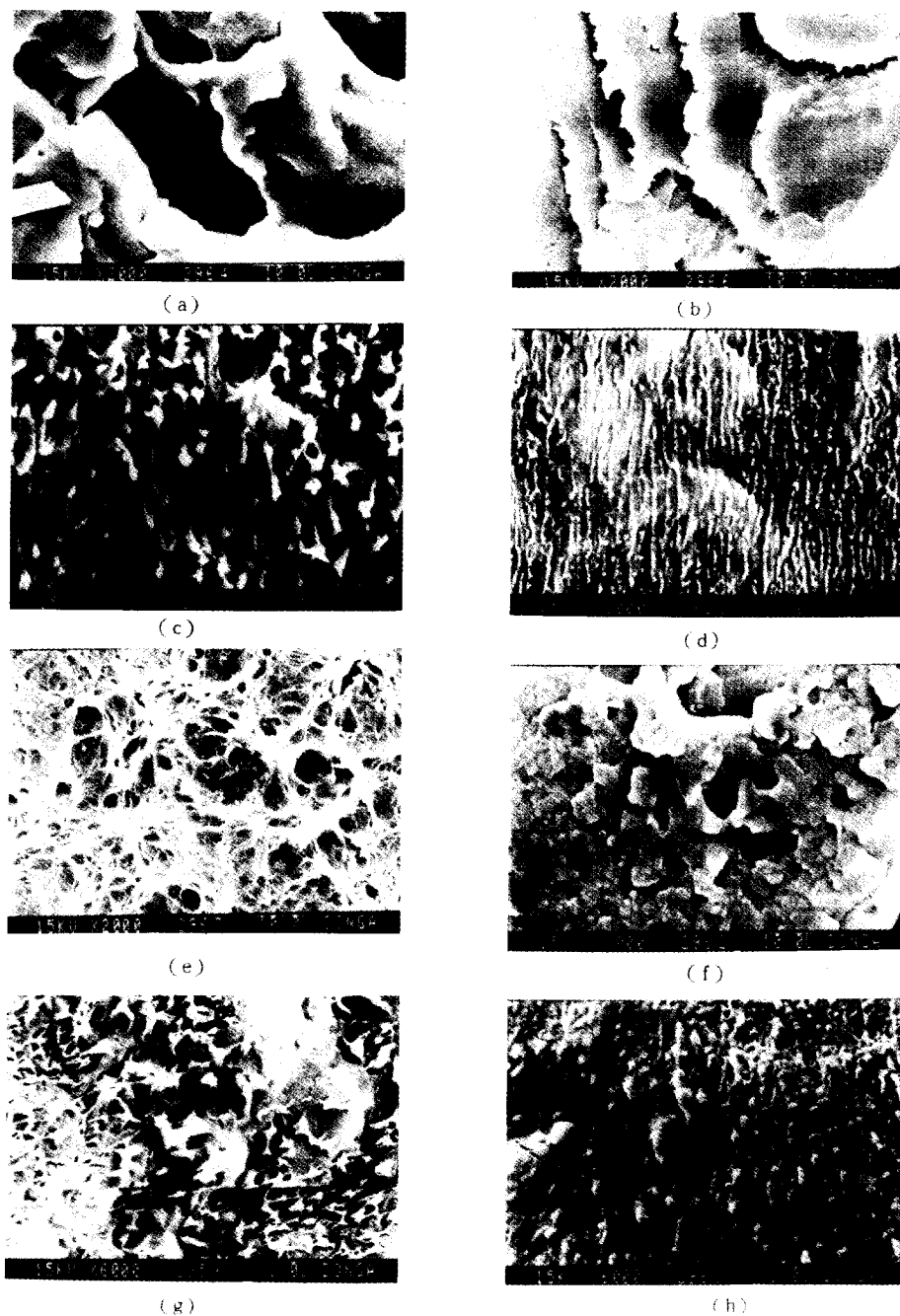
The morphology of the PP/LDPE or PP/HDPE binary blends and PP/LDPE/EPDM or PP/LDPE/EPDM ternary blends by SEM was analyzed. For PP/PE blends, as shown in Fig. 9-c and 9-d, PP and LDPE or HDPE are incompatible and their phases are grossly separated. One can see, however, that interfacial adhesion between domain and continuous phases are observed to some degree for the PP/HDPE blend having 40/60 composition by weight %, whereas such adhesion is not obser-

ved for the PP/LDPE blend of the same composition. For reference, the morphology of HDPE and LDPE homopolymers were shown in Fig. 9-a and 9-b. For comparison, the blends of 100/10 HDPE/EPDM and 100/10 LDPE/EPDM blends are prepared and their morphology were also presented in Fig. 9-e and 9-f. It is seen that HDPE and EPDM shows somewhat interconnected morphology between the components whereas LDPE and EPDM shows grossly phase separation. Thus, the finer and more interconnected domain structure of PP/HDPE/EPDM ternary blends than that of PP/LDPE/EPDM, as shown in Fig. 9-g and 9-h, can be explained by the preferential adhesion of EPDM to HDPE compared to LDPE.

## CONCLUSIONS

The composition dependence of properties of





**Fig. 9.** SEM micrographs of fractured surfaces of homopolymers and polyblends. a) HDPE, b) LDPE, c) PP/HDPE(40/60), d) PP/LDPE(40/60), e) HDPE/EPDM(100/10), f) LDPE/EPDM(100/10), g) PP/EPDM/HDPE(40/10/60), h) PP/EPDM/LDPE(40/10/60).

PP/LDPE blends and PP/LDPE/EPDM ternary blends has been investigated and compared with those of PP/HDPE and PP/HDPE/EPDM ternary blends. The results obtained was discussed in terms of the effect of chain branching and the different interfacial adhesion between components on those properties.

The rheological measurement showed that the interfacial adhesion between PP and HDPE is larger than between PP and LDPE, even though both of the binary blends were typical incompatible systems and that the viscosity of blends increased with the addition of EPDM. In the PP/HDPE blends, the melt viscosities observed fairly the Haya-shida additive rule,  $1/\eta_b = \omega_1/\eta_1 + \omega_2/\eta_2$ . The composition dependences of the modulus for both PP/HDPE and PP/LDPE blends observed very well the Simplex equation of the following functional form ;  $P = P_1\phi_1 + P_2\phi_2 + \beta\phi_1\phi_2$ . The linear regression for the experimentally observed modulus data gave  $\beta$  as  $-50 \text{ kg/mm}^2$  and  $-90 \text{ kg/mm}^2$  for PP/HDPE and PP/LDPE blends, respectively.

It was found that the impact strength of the PP/PE binary blends were strongly improved by the addition of the EPDM at the expense of slight loss in yield strength and initial elastic modulus. The increases of Izod impact strength of PP/HDPE blend by the addition of EPDM are slightly higher than those of PP/LDPE blend at the same EPDM concentrations. The result was explained by the more preferential adhesion between HDPE and EPDM than LDPE and EPDM.

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