

Effect of Molecular Structure in Branched Polyethylene on Adhesion Properties with Polypropylene

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ABSTRACT: Adhesion properties between branched polyethylene (PE) and isotactic polypropylene (PP) were studied by a peel test and scanning electron microscopy. In this study, two types of branched PEs were used; one is a linear low density polyethylene (LLDPE) and the other is a high pressure low density polyethylene (LDPE). The adhesive strength of the LLDPE/PP is much higher than that of LDPE/PP. Furthermore, the formation of PE influxes between PP spherulites has a small effect on the adhesion. The dynamic viscoelastic measurements for the binary blends composed of branched PE and PP were also carried out to estimate the interfacial tension by using a rheological emulsion model proposed by Paliarne. The interfacial tension is 1.0 mN for LLDPE/PP and 2.1 mN for LDPE/PP, suggesting that the interfacial thickness of LLDPE/PP is about twice that of LDPE/PP. The adhesive strength between branched PE and PP will be determined by the interfacial thickness, which represents the entanglements between two polymers. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 457–463, 1998

Key words: branched polyethylene; polypropylene; adhesion; interfacial tension; dynamic viscoelastic property

INTRODUCTION

It is well known that branched polyethylenes (PEs) are classified into two types according to their molecular structure. One is called linear low density polyethylene (LLDPE) that is characterized as short chain branches; it is obtained by copolymerization of ethylene and α -olefins such as 1-butene, 1-hexene, and 1-octene. The other is called high pressure low density polyethylene (LDPE) that is characterized as long chain branches, as well as short chain branches, by chain-transfer reactions during free radical polymerization at high pressure. Both branched PEs are regarded as excellent materials for film man-

ufacture and are often used as coextrusion films with isotactic polypropylene (PP) for wrapping food. The PE layer of the coextrusion film provides good heat sealability and low temperature toughness, while the PP layer provides stiffness and heat resistance. However, branched PEs are immiscible with PP; therefore, the adhesive strength of the coextrusion films is generally poor.

According to Wool and Yuan,^{1,2} adhesive strength is dominated by the following two origins: the entanglements of PE and PP chains, and the mechanical interlocking by PE "influxes" between PP spherulites. For a long time crystallization case, mechanical interlocking has been considered to be the most effective mechanism for adhesion. Bartczak and coworkers showed the formation of PE influxes is connected with the growth of PP spherulites and the depth of the influxes increases with the size of PP spherulites.^{3,4}

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This study investigated the effect of molecular structure in branched PE on the adhesion properties with PP, which is very important for industrial applications. For the purpose of this study, two types of branched PEs were used: LLDPE and LDPE.

EXPERIMENTAL

Materials and Blend Preparation

The polymers used in this study were commercial materials. PP [TOSOH poripuro J5100A; number average molecular weight (M_n), 4.3×10^4 ; weight average molecular weight (M_w), 5.7×10^5], LLDPE (Lumitac 12-1; M_n , 3.0×10^4 ; M_w , 1.0×10^5), and LDPE (Petrocene 180R; M_n , 3.5×10^4 ; M_w , 1.4×10^5) were products of TOSOH Corp. The species and contents of branches were determined by ^{13}C -NMR spectroscopy. LLDPE is an ethylene-1-butene copolymer containing 32 ethyl branches/1000 backbone carbon atoms. LDPE has 4 methyl, 6 butyl, 1 pentyl, and 4 long (>C6) branches/1000 backbone carbon atoms.

Binary blends composed of branched PE and PP were prepared as follows. The two components were dissolved together in xylene at 403 K with a small amount of 2,6-di-*tert*-butyl-4-methyl-phenol as an oxidation inhibitor, then rapidly precipitated with methanol, and the resulting polymers dried under a vacuum. The blending ratio was 80/20 (w/w, branched PE/PP).

All polymers used in this study were melt pressed in a laboratory hot press at 473 K and 10 MPa for 5 min and quenched into ice-water bath. The thickness of the films was about 0.2 mm.

Measurements

The adhesive strength between branched PE and PP was evaluated with a 180° peel test. Bonding between PE and PP films, which we wrapped partially by aluminum foil as shown in Figure 1, was performed in a mold at 6 kPa for 15 min on a hot press controlled at 473 K. Various cooling conditions were taken in this study: quenched into the methanol bath with frozen carbon dioxide (233 K); quenched into the water bath of 288 K; out of the mold then cooled down in air to room temperature (296 K); and slowly cooled down in the mold to room temperature for at least 0.5 h. The bonded films were cut and separated into

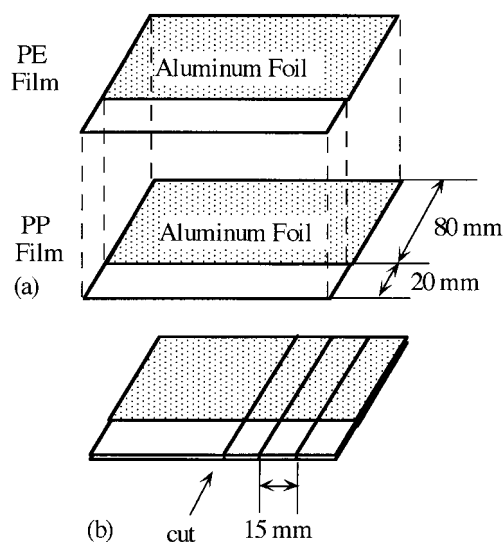


Figure 1 Preparation of bonded specimens for a peel test.

strips with a 15-mm width for a peel test. These sample specimens were subjected to the 180° peel test at 296 K. The crosshead speed was 50 mm/min. The average force was taken as the peel strength. At least 10 average values of peel strength were taken for each cooling condition.

After the peel test, the fractured surface was gold coated and the microstructure was examined by a scanning electron microscope (SEM) (model Sigma-II, Akashi Co.).

Direct observation of the interface was also carried out by a polarized microscope equipped with a hot stage. PP film was in contact at its edge with a film of branched PE. The films in contact were sandwiched between a microscope slide and a coverglass on a hot stage, heated to 500 K, and kept at this temperature for 10 min to completely melt the crystallites. Then the samples were cooled down to room temperature at a cooling rate of 2.0 or 10 K/min.

Dynamic mechanical measurements were carried out for branched PEs, PP, and their blends. Dynamic shear moduli (i.e., storage shear modulus G' and loss modulus G'') were measured at 463, 493, and 523 K using a cone-plate type rheometer (MR-500, Rheology Co., Ltd.) in the angular frequency range of 6.28×10^{-2} to $1.88 \times 10^1 \text{ s}^{-1}$. The master curves were obtained by horizontal shifts without vertical ones.

The morphology of the blends was examined by the SEM. Fractured surfaces of the blend samples were prepared by breaking in liquid nitrogen and

Table I Peel Strength Between Branched PE and PP at Various Cooling Conditions

Cooling Condition	Peeling Force (N/m)	
	LLDPE/PP	LDPE/PP
Slowly cooled in mold	400	100
Cooled in air	300	50
Quenched into water (288 K)	600	50
Quenched into methanol with frozen carbon dioxide (233 K)	600	50

sputter coating with gold. The volume-average radius of the dispersed PP domain was analyzed using a TV image processing system (model TVIP-4100, Nippon Avionics Co. Ltd.).

RESULTS AND DISCUSSION

The peel strength between branched PE and PP is summarized in Table I. It was confirmed that adhesion fracture in the interface occurred for all samples. Table I shows that the peel strength of LLDPE/PP is much higher than that of LDPE/PP at any cooling condition. Furthermore, the peel strength of the quenched samples is higher than that of the slowly cooled samples for LLDPE/PP. On the other hand, the slowly cooled sample in the mold shows the highest value of peel strength for LDPE/PP.

Scanning electron micrographs for the PE surfaces of fractured films are shown in Figure 2. These samples were slowly cooled in the mold. As seen in the figure, there are many fibrils on the surface for both branched PE films. The fibrils on the surface are due to pullout of the PE influxes that were incorporated into the space between PP spherulites.^{1,2} Furthermore, the fibrils on LDPE are the same shape as those on LLDPE, although LDPE/PP shows weak adhesive strength. The result demonstrates that the formation of influxes (mechanical interlocking mechanism) has little influence on the adhesive strength in this study. Moreover, there is no influx on PE surfaces of fractured films obtained by the other cooling conditions (but not presented here).

Figure 3 shows the optical micrographs under crossed polars for the interface between PP and branched PE. As seen in the micrographs, in-

fluxes are incorporated into the space between PP spherulites. Furthermore, it is also found on the LLDPE/PP interface that a transcrystalline layer of LLDPE is formed on the PP spherulites [Fig. 3(a,b)]. On the other hand, there is no transcrystalline layer of LDPE [Fig. 3(c)]. Moreover, fast cooling (cooling rate of 10 K/min) prevents the formation of transcrystals as shown in Figure 3(d). It should be noted that the transcrystal has little influence on the adhesion in this study, because there is no transcrystal for the quenched LLDPE/PP samples that show a strong interface. The formation of a transcrystalline layer suggests that the surface of PP spherulites has nucleation activity for LLDPE rather than the "original" heterogeneities in LLDPE. This effect has been observed in the nucleation of LDPE by high-density PE (HDPE)^{5,6} and that of poly(1-butene) (PB) by

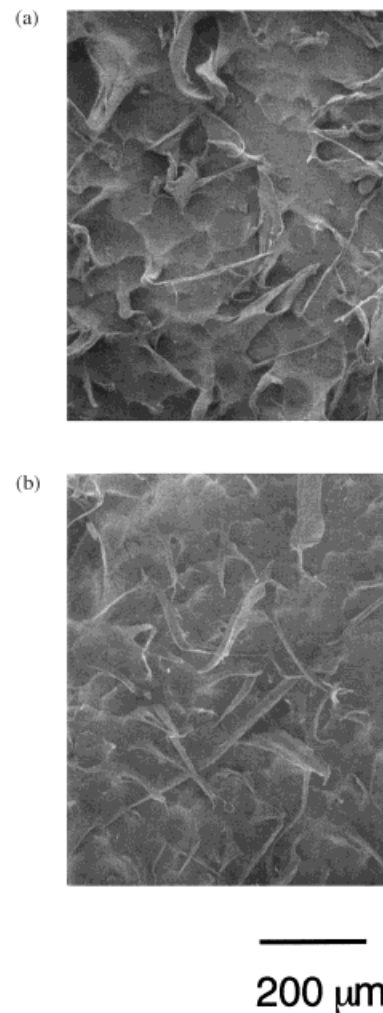


Figure 2 SEM micrographs for the fractured surface of PE films after the peel test: (a) LLDPE and (b) LDPE.

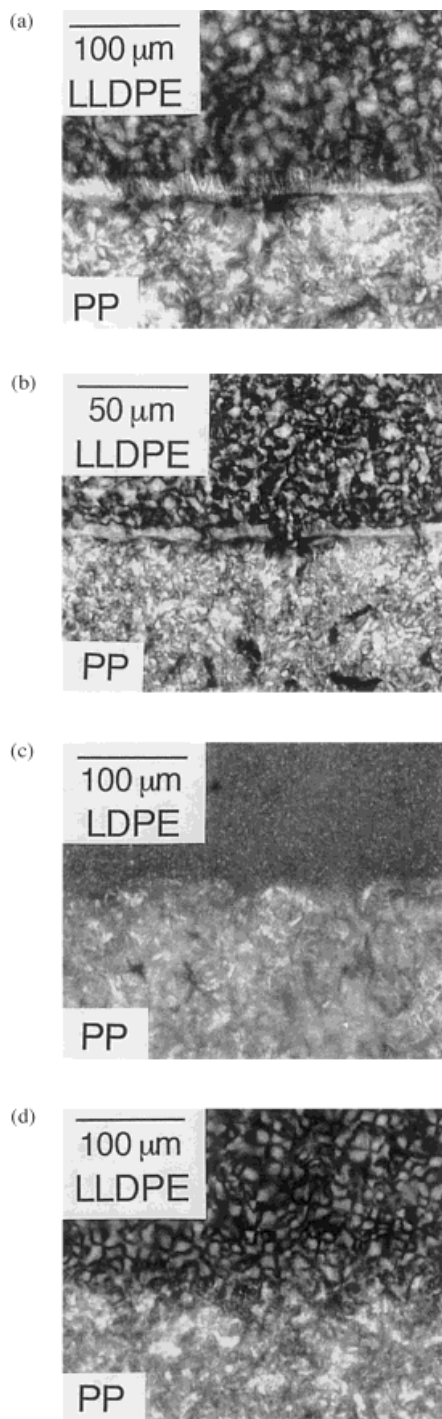


Figure 3 Optical micrographs for the interface of branched PE and PP under crossed polars: (a) LLDPE/PP, cooling rate 2 K/min, high magnification; (b) LLDPE/PP, cooling rate 2 K/min, low magnification; (c) LDPE/PP, cooling rate 2 K/min; and (d) LLDPE/PP, cooling rate 10 K/min.

PP.⁷⁻⁹ It is well known that LDPE/HDPE and PB/PP show good compatibility and/or miscibility in the molten state. In this study, the formation of a transcrystalline layer of LLDPE on the PP spherulites indicates that the interfacial tension between LLDPE and PP is very small, although LLDPE and PP are thermodynamically immiscible.

To clarify the effect of molecular structure in branched PEs on the interfacial tension with PP, dynamic viscoelastic measurements were carried out. Figure 4 shows the master curves of G' and G'' for branched PEs, PP, and 80/20 PE/PP (w/w) blends at the reference temperature of 463 K. The time-temperature superposition principle was applicable to the frequency dependence of the dynamic moduli for both blends, as well as PP and branched PEs, indicating that the molecular aggregation state for the blend samples is stable over the entire experimental regions of frequency or temperature. The dynamic moduli for LDPE and LLDPE are higher than those for PP in the measured frequency region. Furthermore, the storage moduli for the blends are higher than those for each component at the low frequency region, suggesting the existence of the secondary plateau.

According to Palierne, linear viscoelastic properties for incompatible polymer blends in the molten state are well expressed by a rheological emulsion model.¹⁰ Furthermore, the analysis can be used as a method to determine the interfacial tension between two polymer melts.¹⁰⁻¹² The emulsion model is given as the following relation:

$$G^*(\omega) = G_m^*(\omega) \frac{1 + 3\phi H(\omega)}{1 - 2\phi H(\omega)}$$

$$H(\omega) = \frac{4\left(\frac{\gamma}{R}\right)\{2G_m^*(\omega) + 5G_d^*(\omega)\} + \{G_d^*(\omega) - G_m^*(\omega)\}\{16G_m^*(\omega) + 19G_d^*(\omega)\}}{40\left(\frac{\gamma}{R}\right)\{G_m^*(\omega) + G_d^*(\omega)\} + \{2G_d^*(\omega) + 3G_m^*(\omega)\}\{16G_m^*(\omega) + 19G_d^*(\omega)\}}$$
(1)

where $G_d^*(\omega)$, $G_m^*(\omega)$, and $G^*(\omega)$ are the respective complex moduli of the dispersed phase, matrix, and blend at angular frequency ω ; γ is the interfacial tension; and ϕ and R are the volume fraction and the volume average radius, respectively, of the dispersed phase.

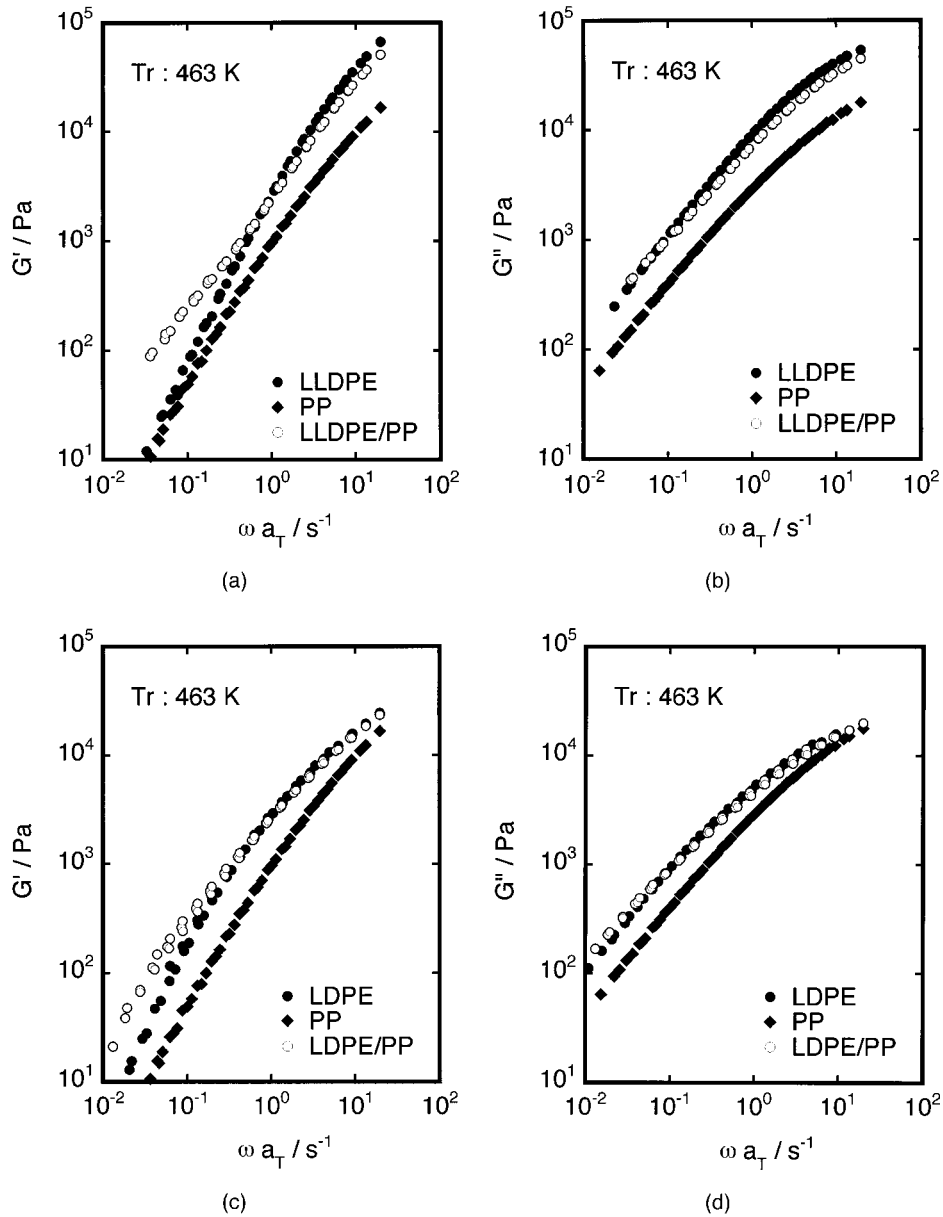


Figure 4 Frequency dependence of the dynamic moduli: (a) storage modulus G' for LLDPE, PP, and LLDPE/PP blend; (b) loss modulus G'' for LLDPE, PP, and LLDPE/PP blend; (c) storage modulus G' for LDPE, PP, and LDPE/PP blend; and (d) loss modulus G'' for LDPE, PP, and LDPE/PP blend.

Figure 5 compares the dynamic moduli calculated by the emulsion model and the experienced values. As seen in the figure, the calculated values are in good agreement with the present results. Furthermore, the volume average radii of the dispersed phase for the blends were found to be $1.2 \mu\text{m}$ for the LLDPE/PP blend and $1.7 \mu\text{m}$ for the LDPE/PP blend by

SEM observation. Consequently, the interfacial tension between LLDPE and PP is estimated to be 1.0 mN/m and that between LDPE and PP to be 2.1 mN/m .

According to Helfand and Tagami,^{13,14} the equilibrium interfacial thickness λ and the interfacial tension γ between two immiscible polymers of infinite molecular weight are expressed as

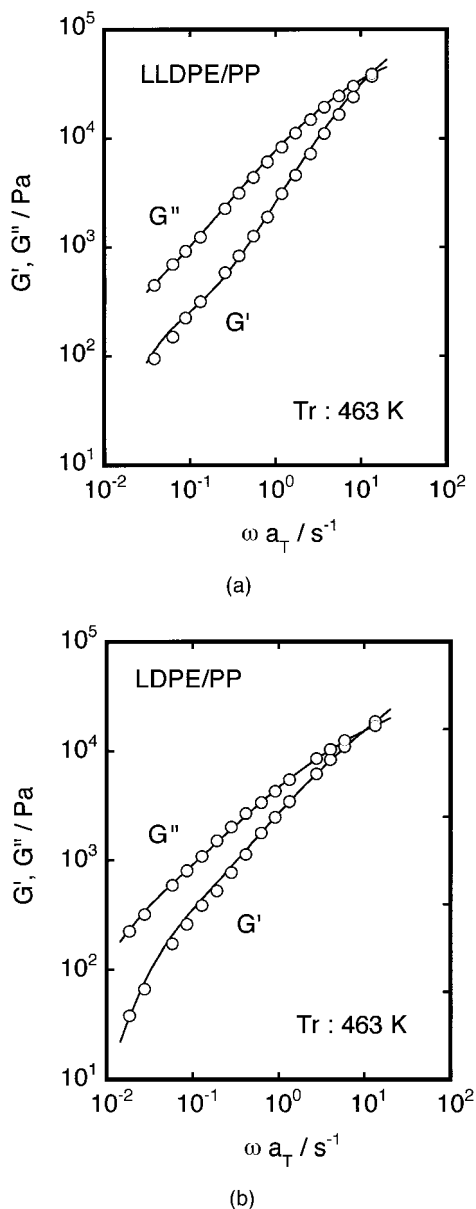


Figure 5 Comparison of calculated and experimental dynamic moduli for (a) LLDPE/PP blend and (b) LDPE/PP blend. (—) The calculated values using the rheological emulsion model and (○) the experimental values.

$$\lambda = \frac{2b}{(6\chi)^{1/2}} \quad (2)$$

$$\gamma = \frac{kT}{b^2} \left(\frac{\chi}{6} \right)^{1/2} \quad (3)$$

where b is the statistical segment step length, χ is the Flory–Huggins interaction parameter,¹⁵ and

k is the Boltzmann constant. Therefore, the interfacial thickness is expressed using the interfacial tension as

$$\lambda = \frac{kT}{3b\gamma} \quad (4)$$

Equation (4) shows the interfacial thickness is proportional to the inverse of the interfacial tension. Thus, the interfacial thickness of LLDPE/PP will be about twice as large as that of LDPE/PP. As the interfacial thickness increases, entanglements between two polymers increase. As is well known for immiscible amorphous polymer pairs, the adhesive strength increases with increasing interfacial thickness due to the increase in entanglements between two polymers.^{1,16–19} Also, adhesive strength between branched PE and PP, which are semicrystalline polymers, was determined by the entanglements between the two polymers in this study, not by the formation of PE influxes between PP spherulites.

Recently, short chain branches in LLDPE were found to play an important role for the compatibility and/or miscibility with PP.^{20–22} The χ parameter decreases with increasing short chain branches in LLDPE.^{21,22} In particular, ethyl and butyl branches have significant effects on the compatibility and/or miscibility; on the other hand, methyl branches have little influence on the compatibility with PP.^{20,22} As shown in the Experimental section, LLDPE has more ethyl branches than LDPE. The short chain branching in branched PE will be a significant parameter that determines the adhesion properties with PP.

CONCLUSION

In the present study, we investigated the effect of molecular structure in branched PE on the adhesion properties with PP. It was found that the adhesive strength of LLDPE/PP is much higher than that of LDPE/PP. Furthermore, adhesive strength is hardly affected by the formation of PE influxes between PP spherulites. It was also found that LLDPE crystallizes at the surface of PP spherulites at the slowly cooling condition and forms the transcristalline layer.

The viscoelastic measurements in the molten state for the binary blends composed of branched

PE and PP were also carried out, and the interfacial tension between the two polymers was estimated using a rheological emulsion model proposed by Palierne.¹⁰ As a result, the interfacial tension was found to be 1.0 mN for LLDPE/PP and 2.1 mN for LDPE/PP, suggesting that the interfacial thickness of LLDPE/PP is about twice that of LDPE/PP. These results demonstrate that entanglements between branched PE and PP have significant effects on the adhesive strength in this study. Furthermore, ethyl and/or butyl branches in branched PE will be responsible for the adhesion strength with PP.

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