Peeling of laminated films comprising high-density polyethylene and polypropylene/low-density polyethylene blends

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The peel strength of laminated films comprising high-density polyethylene (HDPE) and blends of isotactic polypropylene (PP)/low-density polyethylene (LDPE) was studied as a function of the heat-treatment temperature, T_H, the cooling condition, and the blend composition of the substrate films, where HDPE is the peel, i.e. the film to be peeled or the flexible adherend, and the blend is the substrate (the rigid adherend). The peel strength was strongly dependent on T_H and the cooling rate. In the case of quenched films, the peel strength increased drastically for the films with T_H higher than the melting temperature of PP, $T_{m,PP}$. For slowly cooled films, however, the peel strength had a maximum for films with T_H nearly equal to $T_{m,PP}$. By varying LDPE composition in the substrate, a systematic decrease in the peel strength was observed, indicating the important role of LDPE in the PP matrix in controlling the peel strength between HDPE and PP. The adhesion mechanism and the role of LDPE are discussed from the viewpoints of (1) partial miscibility and interdiffusion among PP, HDPE and LDPE, and (2) crystallization kinetics of the component polymers.

(Keywords: peeling; adhesion; diffusion)

INTRODUCTION

Laminated films have become popular because of their properties, such as mechanical strength, ability to act as a gas barrier, heat resistance, dyeability and peeling. Among these properties, peeling involves several processes at the interface of polymer blends, namely adhesion, miscibility, interdiffusion, morphology and crystallization. In particular, blends of polyethylene (PE) and polypropylene (PP) have been studied from these viewpoints[1–13]. It is well known that PE is not miscible with PP[2], mainly because of the absence of any specific molecular interaction at a PP–PE interface other than the van der Waals interaction; however, substantial adhesion has been observed experimentally by many workers[10,11,13,14]. Adhesion between PE and ethylene copolymers and between polyolefin and butyl rubbers was also reported by Yamakawa[15] and Sung[16], respectively.

Wu[17,18] classified the types of adhesion at polymer interfaces as: (I) fracture theory; (II) weak-boundary-layer theory; (III) wetting-contact theory; (IV) diffusion theory; and (V) chemical adhesion theory. The fracture theory (I) assumes the presence of defects or microcracks at the interface, which determines the adhesive or peeling strength. The weak-boundary-layer theory (II) predicts that peeling occurs at a weak boundary layer located near the interface. Particularly in the case of polymer blends, an extracted low-molecular-weight component is localized near the interface and behaves as a weak boundary layer. The wetting-contact theory (III) is based on the thermodynamics at interfaces. The work of adhesion, W_a, is given by:

$$W_a = \gamma_A + \gamma_B - \gamma_{AB} \tag{1}$$

where γ_i (i = A or B) is the surface tension of the i component and γ_{AB} the interfacial tension between A and B. W_a has a maximum for the case of autohesion ($W_a = 2\gamma_A = 2\gamma_B$) since the interfacial tension γ_{AB} becomes zero. Because the interfacial tension is related to the solubility parameter, δ_i, the peel strength is also related to δ_i. The peel strength f_p is phenomenologically given by[18,19]:

$$f_p = a\exp[-b(\delta_i - \delta_j)] \tag{2}$$

where a and b are constants. The diffusion theory (IV) predicts time evolution of the peel strength due to interdiffusion of the polymer chains at the interface. According to Vasenin's kinetic theory[20,21] the fracture strength, f, is given by:

$$f = pt^q \tag{3}$$

where t is time of adhesion, and p and q are constants. The value of q is experimentally determined to be in the range of 0.25 to 0.20. It was also verified experimentally that the peel strength, f_p, has the same relation with t for autohesion of polyisobutylene[22]. The chemical adhesion

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theory (V) is based on an estimation of the number density and strength of the active chemical bonds bridging the two components at the interface.

In reality, the peel strength of laminated polymer films may be determined by the combination of the five types of adhesion described above. In addition, a mechanical interlocking at the interface (type VI) has been identified as a supplemental, or in some cases an essential, contributor to adhesion. An improvement of the peel strength between incompatible blends is characteristic of crystallizable blends and is insignificant in amorphous blends, since the degree of volume contraction on crystallization is much larger than that on glass transition.

In the case of PP/high-density polyethylene (HDPE) laminated films, several reinforcing mechanisms have been proposed to account for the enhanced adhesive and/or peel strengths, most of which are basically described by the adhesion types I to VI. Studies related to the wettability include a surface modification (V) and an analysis of the peel strength as a function of the contact angle (III). It is well known that polyolefin has a low wettability. Methods to improve adhesion properties of PE and PP were discussed by Brewis and Briggs[23]. They studied the peel strength of self-adhered low-density polyethylene (LDPE) pretreated with discharge of several gases including air. The peel strength increased with discharge time, suggesting the importance of the introduction of functional groups having oxygen in improving adhesion properties. Imachi studied the peel strength of LDPE and PP as a function of the bonding temperature at which the two films were laminated[10,11]. The peel strength *versus* bonding temperature curve had a peak around the melting temperature of PP, $T_{m,PP}$. He measured the contact angle of an LDPE droplet on the surface of PP or PP/LDPE and found that wettability increased remarkably around the melting temperature of PP. Thus he explained the increase in the peel strength around $T_{m,PP}$ by the wettability between LDPE and PP.

In relation to type IV, Kryszewski *et al.*[3] reported the presence of partial miscibility between PP and PE. According to their infra-red absorption study, each component mixes with the other at its critical concentration at the interface, which is on the order of 10%. Wool and co-workers[13,14] also predicted the possibility of interdiffusion of immiscible polymer blends at the interface.

Interlocking of polymers near the interface (type VI) involves contraction of polymers during crystallization. Galeski and co-workers[7–9] proposed the formation of influx at the interface, which increases the interface strength due to an increase in the interfacial area. Yuan and Wool[13] explained the enhanced interfacial strength by interlocking mechanisms, i.e. inclusion of a low-temperature crystallizable component by a high-temperature crystallizable component during spherulite formation of the latter. Rybnikar[12] reported that crystallization behaviour of HDPE in PP was markedly dependent on the thermal history of the blend. The crystallization rate of HDPE was enhanced in the blend because of heterogeneous crystallization.

In the case of amorphous blends, the adhesive and healing mechanisms are well interpreted in terms of mutual diffusion of each component (types III and IV)[14]. However, for crystallizable polymer blends, the relation between the interfacial morphology and mechanical properties has not been quantitatively elucidated, because both of them are strongly dependent on the method of blending and history of the heat treatment. In this paper, we study the adhesion mechanism of polyolefin at the interface by measuring the peel strength as a function of the heat-treatment temperature and the composition of the substrate film.

EXPERIMENTAL

Samples

Three kinds of polyolefin films, high-density polyethylene (HDPE), low-density polyethylene (LDPE), and blend films of isotactic polypropylene and low-density polyethylene (PP/LDPE) were supplied by Idemitsu Petrochemical Co., Ltd. The thicknesses of these films were 80 and 200 μm. The LDPE fractions of the blend films were varied to be 0, 5, 10, 16 and 20 wt%. The characteristics of these polymers are shown in *Table 1*, where M_w and M_n are the weight- and number-average molecular weights, respectively. Pairs of films, comprising a thin film (80 μm thick) and a thick film (about 800 μm thick), were laminated in a hot press with a pressure of about 3.9 MPa for 5 min at 200°C then cooled gradually to room temperature. The cooling condition was the same as used for the slowly cooled sample, which will be specified later. The thick films were prepared by stacking four films (200 μm thick) in a hot press prior to lamination. Then these laminated films were heat treated at the heat-treatment temperature, T_H, for 10 min followed by either rapid quenching to ice–water temperature or slow cooling to room temperature. The former are designated as quenched films and the latter as slowly cooled films. The films having a thin peel (i.e. a flexible adherend) of HDPE on top of PP/LDPE blend films are coded as HD films. Similar laminated films having a thin peel of LDPE on the substrate of PP/LDPE (coded as LD films) and a control sample, which was a laminated film of thin HDPE and thick LDPE substrate (HD–LD film), were prepared in the same manner.

Cooling rate measurement

The cooling rate was measured for an HD film with the dimensions 155 mm long × 200 mm wide × 800 μm thick. A thermocouple sheet was inserted between the peel and substrate, and the laminated film was covered with two ferrotype plates. Then the film was hot pressed under the same conditions as described above. The cooling rates of the slowly cooled and quenched films were measured with an analysing recorder (Yokogawa, Co., Ltd, model 365EE).

Peel strength measurement

The peel strength was measured for a sample strip of 25 mm wide laminated film, according to the Japan Industry Standards K6854[24]. This is a 180° peel strength measurement on a partially prepeeled film with a constant stretching rate of 200 mm min^{-1}. The film length and the

Table 1 Characteristics of the sample films

Sample code	Melt index (g 10 min^{-1})	M_w ($\times 10^{-5}$)	M_n ($\times 10^{-4}$)	M_w/M_n
HDPE	1.0	1.43	2.8	5.1
LDPE	0.3	1.39	1.63	8.6
PP	0.5	6.85	9.33	7.3

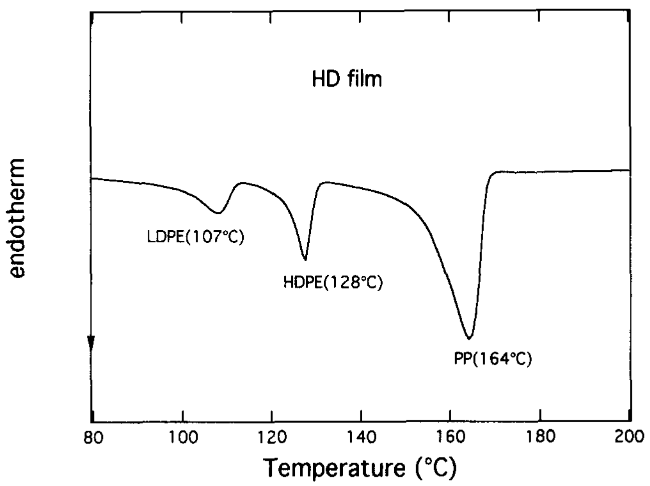

Figure 1 D.s.c. thermogram of quenched HD film with 16 wt% LDPE, on the heating process

peeling rate were modified to 50 mm (30 mm for the interchuck distance) and 100 mm min^{-1}, respectively. At least five sample strips were examined and the peel strength was evaluated by taking the average. All the measurements were conducted in a temperature-controlled room at 20°C.

Microscopy

Thin cross sections of the laminated films cut with a razor were investigated under a polarized microscope. Details of the interface were observed with a transmission electron microscope on ultramicrotomed sections of the samples stained with ruthenium tetroxide.

Calorimetry

Differential scanning calorimetry (d.s.c.) was conducted with a DSC-3100 (MAC Science, Japan) to investigate the melting and crystallization behaviour of the laminated films. The heating rate was 5°C min^{-1}, and the cooling rate was controlled to approximately 5°C min^{-1}. The sample was purged by nitrogen gas.

RESULTS AND DISCUSSION

Thermal behaviour

Figure 1 shows the d.s.c. thermogram of a laminated HD film, having 16 wt% LDPE in the substrate, on the heating process. The melting endotherms of the three components, i.e. LDPE, HDPE and PP, are clearly resolved in the thermogram. The peak melting temperatures for LDPE, HDPE and PP are determined to be $T_{\mathrm{m,LDPE}} = 107$°C, $T_{\mathrm{m,HDPE}} = 128$°C and $T_{\mathrm{m,PP}} = 164$°C.

Figure 2 shows the d.s.c. thermogram of the three homopolymers on the cooling process. Each peak indicates its crystallization exotherm. The crystallization temperature of PP was almost identical to that of HDPE, although the melting temperatures are different by about 35°C between PP and HDPE. This fact is very important for the crystallization kinetics of the laminated films, which will be discussed later.

Cooling rates

Since the cooling rate is one of the most essential factors affecting the crystallization kinetics of polymers, particularly for multicomponent polymers as studied here, the cooling rates of the quenched and slowly cooled films were measured. *Figure 3a* shows the temperature variations of the slowly cooled and quenched films with time. The time axes for the slowly cooled and quenched films are shown at the top and bottom of the figure, respectively. It should be noted that a slight shoulder appears at about 114°C for the slowly cooled film. This shoulder was reproducible when the experiment was repeated, and corresponds to the crystallization exotherm of PP and HDPE, as discussed in *Figure 2*. Although a similar shoulder was also observed for the quenched film

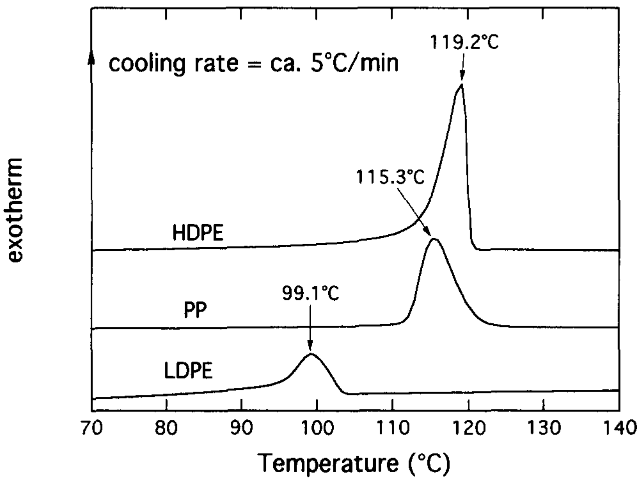

Figure 2 D.s.c. thermograms of the HDPE, LDPE and PP homopolymer films on the cooling process

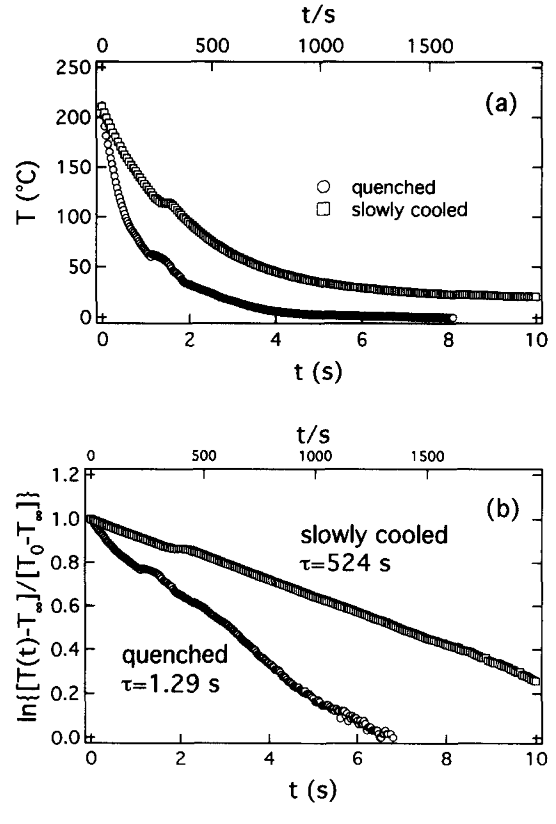

Figure 3 Time dependence of the cooling rates for the slowly cooled and quenched films: (a) linear plot; (b) semilogarithmic plot. τ denotes the characteristic time for the cooling rate defined by equation (1). The time axes for the slowly cooled and quenched films are shown at the top and bottom of each figure, respectively

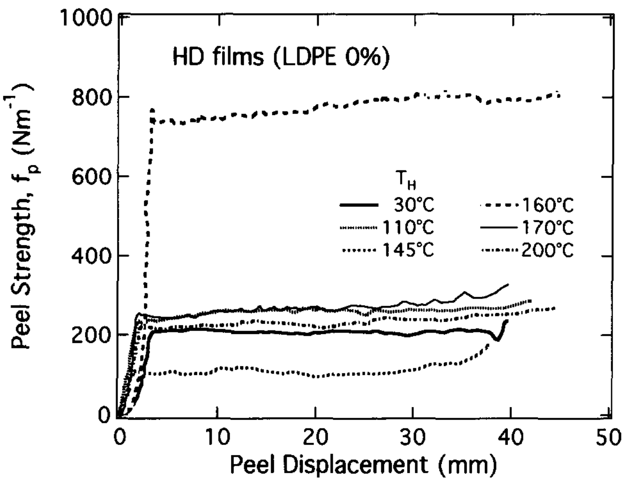

Figure 4 Peel strength–displacement behaviour for slowly cooled HD films

at about 60°C, it was not reproducible. Therefore this shoulder is not discussed, although it might also be related to crystallization.

The cooling condition can be characterized with a characteristic time for cooling. Since the lateral dimension of the film was much larger than the film thickness, one-dimensional thermal diffusion is assumed. Thus the temperature of the film at t, $T(t)$, is given approximately by:

$$T(t) = T_\infty + (T_0 - T_\infty)\exp(-t/\tau) \qquad (4)$$

where T_0 and T_∞ are the film temperature at $t=0$ and $t=\infty$, respectively, and τ is the characteristic time for thermal diffusion. It should be noted that τ is not a material constant but is dependent on the experimental condition as well. *Figure 3b* shows the plot of $\ln\{[T(t)-T_\infty]/[T_0-T_\infty]\}$ *versus* t for the quenched and slowly cooled films from $T_H = 220$°C. As expected, the temperature changes were well described by equation (4) and τ is estimated to be 1.29 and 524 s for the quenched and slowly cooled films, respectively.

Heat-treatment temperature dependence

Since it is expected that the peel strength depends on the melting temperatures of the components, six temperatures, above and below the melting temperatures of the components seen in *Figure 1*, were chosen for the heat-treatment temperatures, T_H. *Figure 4* shows the peel strength *versus* displacement behaviours for the slowly cooled HD films. Although the peel strength, f_P, depends on T_H, the peeling behaviour has a common feature. Peel strength, f_P, increased at first with the peel displacement up to about 3 mm and then reached a more or less constant value until the peel was completely taken off. This behaviour is similar to a stress–strain behaviour for semicrystalline polymer films, where the stress has a steep rise up to a yield value then maintains a plateau value before it shows a second rise related to fracturing. When a semicrystalline polymer film is stretched, neck formation is usually observed in the stress–strain behaviour. In the case of peeling behaviour, however, no neck formation is observed in the plateau region if the peeling is governed by *adhesive* failure. On the other hand, if the peeling occurs via *cohesive* failure, a flexible adherend, i.e. a peel, is elongated by neck deformation. In most cases in our study, however, no neck formation was observed unless stated. The initial upturn of the f_p is due to a bend deformation of the peel, since the 180° peel experiment was employed here. If the peel is flexible and inextensive, the peel strength f_p is related to the angle of the peel experiment, θ, as follows[18]:

$$f_p = \frac{f}{w} = \frac{G}{1-\cos\theta} \qquad (5)$$

where f, w and G are the peel force, the width of the sample film and the fracture energy per unit interfacial area, respectively. HDPE films of 80 μm thickness employed here were sufficiently thin and tough to be regarded as a flexible and inextensive adherend. Thus, for 180° peel experiments in this study, f_p is simply related to the fracture energy, G:

$$f_p = G/2 \qquad (6)$$

Therefore the peel strength indicates the fracture energy per unit area with a scale factor of 0.5.

Since the peel strength has an overshoot at the peel displacement of about 3 mm for the film of $T_H = 160$°C in *Figure 4*, a slightly higher peel strength seems to be required for the formation of the initial cleavage. A similar peeling behaviour was observed for quenched HD films. However, quenched films treated above $T_{m,PP}$ and having a low content of LDPE ($\leqslant 5\%$) had a peel strength higher than 780 N m^{-1}. In this particular case, neck formation was observed during peeling, indicating a cohesive failure at the interface. The peel strength–displacement measurements were repeated at least five times and the peel strength, f_p, was determined as an average value of the peel strengths at the plateau region.

Figure 5 shows the heat-treatment temperature dependence of f_p for slowly cooled HD films. For simplicity, error bars are shown only for the HD film with 0% LDPE, which indicate the maximum and minimum values of f_p for this particular film. The magnitudes of the error bars suggest that the peel strength is determined with a high accuracy. Films with different compositions have a common feature: the presence of a strong peak of f_p at $T_H = 160$°C. Similar behaviour was observed by Imachi for LDPE and PP/LDPE laminated films[10,11]. *Figure 6* shows the heat-treatment temperature dependence of f_p for quenched HD films. Error bars are again shown for only one case, i.e. HD film with 16%

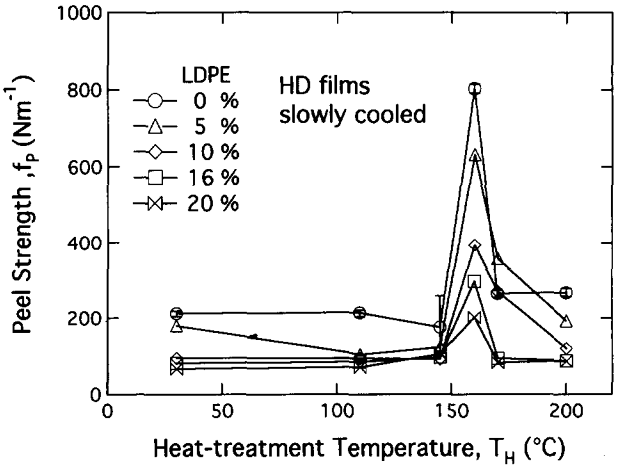

Figure 5 Heat-treatment temperature dependence of peel strength for slowly cooled HD films

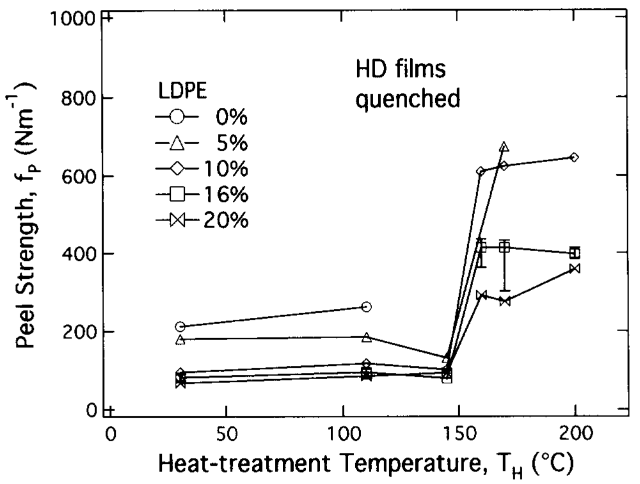

Figure 6 Heat-treatment temperature dependence of peel strength for quenched HD films

LDPE. In this case, the peel strength has a step-wise dependence on T_H. The peel strength of the films quenched from a temperature equal to and higher than $T_{m,PP}$, is much higher than those quenched from lower temperatures. This phenomenon is completely different from that in *Figure 5*. Therefore it is clear at this point that the cooling rate is one of the most important factors controlling the peel strength. It should be noted that the values of f_p for $T_H = 145°C$ are lower than those for $T_H = 110°C$ and 30°C, in most cases, for the slowly cooled and quenched films. This suggests that melting of the HDPE component also affects f_p. When only HDPE melts and recrystallizes during laminate film preparation, the interfacial structure is modified, resulting in decrease of f_p. This trend is exaggerated when the initial film is prepared by quenching instead of slow cooling[25,26].

It is obvious that the singular behaviour of f_p at $T_H = 160°C$ is related to melting of PP. However, the difference in f_p between the quenched and slowly cooled films cannot be ascribed to the crystallization temperature because HDPE and PP crystallize at almost the same temperature, even for the slowly cooled films, as shown in *Figure 2*. Note that the cooling rate for the slowly cooled films is estimated to be about 23°C min^{-1}, which is much faster than the rate employed in the d.s.c. measurement (about 5°C min^{-1}). This suggests that the difference in the crystallization temperatures between HDPE and PP is negligibly small for both slowly cooled and quenched films. Therefore the difference in the peel strength between the films quenched and slowly cooled from T_H must be ascribed to the difference in the crystallization kinetics of the component polymers, i.e. the crystallization rate and crystallization-related phenomena, for example, phase mixing or phase demixing.

Crystallization kinetics. Since there is partial miscibility between HDPE and PP in the molten state, both components may interdiffuse and form an interfacial region having a characteristic width of d_{IF} and concentrations of ϕ^*_{HDPE} and ϕ^*_{PP}, where ϕ^*_i denotes the equilibrium fraction of *i* in the other matrix[3]. According to Helfand and Tagami[27], the interfacial thickness for polymer blends, d_{IF}, is given by:

$$d_{IF} = \frac{2b}{\sqrt{6\chi_{AB}}} \tag{7}$$

where *b* is the segment length and χ_{AB} the Flory interaction parameter of A and B. Zhang and Wool[13] estimated $\chi_{PP/PE}$ at 140°C to be 0.011 and obtained $d_{IF} = 54$ Å. Since the segment length *b* of PP and HDPE is in the range 5–7 Å, d_{IF} is about 10 times larger than *b* and is thick enough to contribute to the peel strength. Therefore even though ϕ^*_i is on the order of 0.01 or less, a large number of entanglements of PP and HDPE can be created at the interface in the molten state. These entanglements are unknitted during the cooling process due to crystallization-induced phase separation. If the effective time for disentanglement of unlike polymer chains in the interfacial region of thicknsss d_{IF} is on the order of 0.1 s or seconds, a significant difference in the peel strength for quenched and slowly cooled films can be expected by either phase separation induced by crystallization or entrapment of chain entanglements. As a matter of fact, the experimental results, shown in *Figure 5*, strongly suggest that the cooling rate of quenched films might be fast enough to freeze the interfacial mixing of the components.

A typical effect of the cooling rate can be found in *Figure 5* by comparing slowly cooled HD films with $T_H = 160°C$ to those with $T_H \geqslant 170°C$. HD films with $T_H \geqslant 170°C$, at which temperature both HDPE and PP are in the molten state, are cooled after heat treatment. These films therefore experience the temperature region of 160°C. Thus one may expect that the peel strength is determined by heat treatment at 160°C, since the cooling rate is slow and the film may stay at 160°C for a reasonably long time, even for HD films with $T_H \geqslant 170°C$. However, as seen in *Figure 5*, the difference in f_p between HD films with $T_H = 160°C$ and those with $T_H \geqslant 170°C$ is significant. This might be because the cooling rate is not constant over the entire temperature range but decays logarithmically, as shown in *Figure 3*. Then the initial cooling rate is much faster than the average rate of the entire time range. Therefore, even in slowly cooled films the initial cooling rate was large enough to freeze the chain structure at the interface, whereas the rate became slow enough to allow the component chains to disentangle at the later stage. For such cases, the difference in the peeling behaviour can be ascribed mainly to the interdiffusion of unlike chains at the interface (type IV). In the case of slowly cooled HD films with $T_H \geqslant 170°C$, the contribution of interchain locking, i.e. the interdiffusion of the component polymer chains, to the peel strength is small. Thus a well-developed interface created by individual crystallization of PP and HDPE gives a lower f_p than the case of HD film with $T_H = 160°C$.

In the case of the HDPE–LDPE laminated film, a peeling experiment could not be conducted even for slowly cooled films, because of cohesive failure when the interface was invisible after heat treatment. This may be explained by the solubility parameter dependence of the peel strength (equation (2)). According to Iyengar and Erickson[19] cohesive failure occurs if the difference of the solubility parameters, $\Delta \equiv |\delta_A - \delta_B|$, is less than about 0.8 and interfacial failure occurs for $\Delta > 0.8$. This is type III adhesion.

It should be noted that an interdomain locking effect becomes effective if molten films are cooled much more slowly than the slowly cooled films. This condition was typically attained in a d.s.c. experiment with a constant cooling rate of 5°C min^{-1}. We prepared a 'super-slowly cooled' film by keeping a hot-pressed film in the hot press

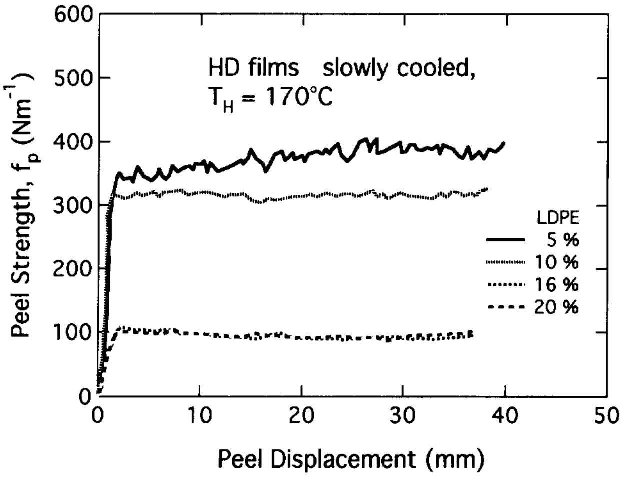

Figure 7 Peel strength–displacement behaviour for slowly cooled HD films with different LDPE fractions

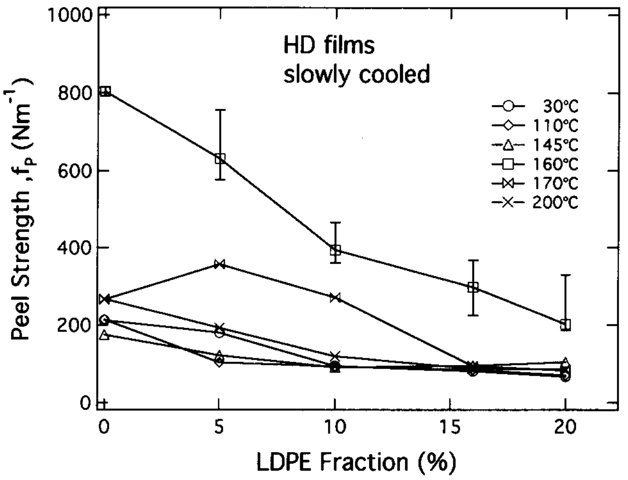

Figure 8 Composition dependence of peel strength for slowly cooled HD films

and turning off the heater. The characteristic time of cooling, τ, was estimated to be 7400 s. In this case, well-developed spherulites of PP were observed, similar to those in Figure 13 of ref. 13, with a typical morphology of interlock structure, i.e. HDPE domains buried between PP spherulites. Interdomain locking, which is an influx of molten polymers into the spherulites of the other components, is proposed by Yuan and Wool[13]. If the cooling rate is slow enough, PP crystallizes first due to heterogeneous nucleation at the PP/HDPE interface, and forms spherulites on the cooling process. Some molten HDPE at the interface is entrapped in the interspherulite regions of PP because of volume contraction during spherulite formation, resulting in the formation of an influx and/or interlock structure, which enhances the peel strength.

Substrate composition dependence

As has been shown in *Figures 5* and *6*, the peel strength decreases systematically by increasing the LDPE component in the substrate films, and this trend is observed in all the samples, independent of heat-treatment temperature.

Figure 7 shows the peel strength–displacement curves for slowly cooled HD films from $T_H = 170°C$. Peel strength, f_p, depends strongly on the LDPE composition: the lower the LDPE content, the higher f_p. Another interesting aspect in this figure is the oscillation of f_p during peeling, particularly for the film with 5% LDPE. We will discuss the origin of this oscillation in conjunction with the peeled surface morphology in a later section.

Figure 8 shows the composition dependence of f_p for slowly cooled HD films. The composition dependence is strongest for the film with $T_H = 160°C$. For quenched HD films, the peel strength behaviour is classified into two extremes, as shown in *Figure 9*. The peel strength of films with T_H less than $T_{m,PP}$ does not depend on LDPE composition. The HD films of T_H higher than $T_{m,PP}$ exhibit an almost identical behaviour with respect to LDPE fraction, i.e. the peel strength decreases more or less linearly with LDPE fraction in this concentration regime. These results (*Figures 8* and *9*) strongly indicate that the LDPE component in the substrate film decreases the peel strength of HDPE from the substrate.

In order to clarify the role of LDPE in the substrate, the peel strength was also measured for LD films, where the peel was substituted from HDPE to LDPE. *Figure 10a* shows the comparison of the peel strength between slowly cooled HD and LD films with $T_H = 160°C$. It is seen that the peel strength of the LD film does not depend on the LDPE fraction in the substrate, whereas that of the HD film decreases with LDPE fraction. A similar behaviour was observed for the quenched HD and LD films, as shown in *Figure 10b*, where cohesive failure was observed for HD films having 5% LDPE fraction or less in the substrate. A peeling experiment was also conducted on a laminated film of thin LDPE and thick HDPE, resulting in a complete moulding between the two. On the basis of the results discussed above, the following order of cohesive strength is obtained: HDPE–LDPE > HDPE–PP > LDPE–PP. Ideally, this order of peel strength should be discussed quantitatively in terms of the solubility parameters of the components. However, the literature values[19] of δ_i are spread too widely to employ the criterion of $\Delta = (\delta_{PP} - \delta_{PE}) \leq 0.8$ of equation (2). For example, according to Brandrup and Immergut[28], δ_{PE} is in the range 7.7–8.79 $(\mathrm{cal\,cm^{-3}})^{1/2}$ and δ_{PP} in the range 9.2–9.4 $(\mathrm{cal\,cm^{-3}})^{1/2}$. In addition, the value of δ_{PE} is not usually specified for either HDPE or LDPE. Because of the

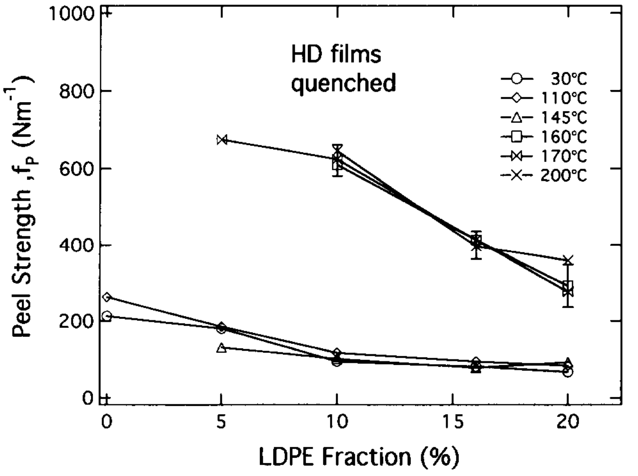

Figure 9 Composition dependence of peel strength for quenched HD films

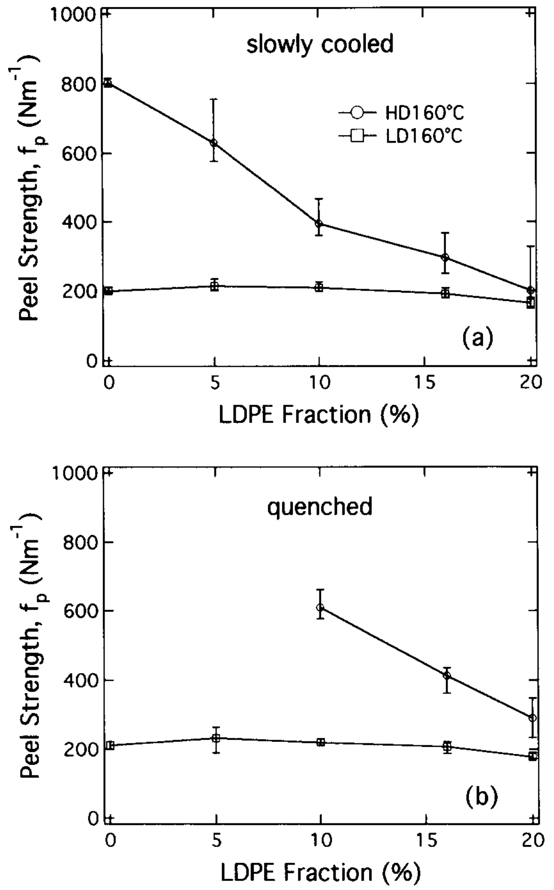

Figure 10 Comparison of the LDPE fraction dependence of peel strength between HD and LD films: (a) slowly cooled; (b) quenched

appearance of significant variation in the peel strength with LDPE fraction, it would be worth evaluating δ_{HDPE} and δ_{LDPE} precisely.

Other reasons for the LDPE fraction dependence of f_p might be found either in the difference in crystallization kinetics or in a discrete change of the interfacial tension on crystallization. Because of crystallization of PP, LDPE molecules might be excluded from the PP crystals and be located near the interface. These localized LDPE molecules may form a weak boundary layer (type II). The surface tension changes drastically at solid–liquid transition since the mass density changes discretely at the transition. For instance, polyethylene[18] has $\gamma^a = 35.7$ dyn cm^{-1} and $\gamma^c = 53.6$ dyn cm^{-1} at 20°C, where γ^a and γ^c are the surface tensions of amorphous and crystalline phases, respectively. Since the interfacial tension is related to the surface tension of the components (equation (1)), it does change discretely at the crystallization temperature. If this contribution is significant, the LDPE fraction dependence of f_p is explained by the change of wettability at the interface (type III). It is needless to say, however, that the mechanisms of both types II and III may contribute to the peeling behaviour.

Heat-treatment time dependence of the peel strength

If interdiffusion of unlike polymer chains occurs at the interface during the process of lamination, the peel strength should depend on the time of heat treatment, t_H. *Figure 11* shows this dependence for LD films treated at 170°C for a time, t_H, and then quenched to ice–water temperature. Peel strength, f_p, increased with t_H, indicating the interdiffusion of unlike polymer chains at the interface. The double logarithmic plot shows that the time evolution of f_p is roughly described by equation (3) with the exponent $q = 0.25$, which is again in good accordance with the prediction as well as the experimental results in the literature. Wool *et al.*[14] predicted average monomer interpenetration depth and number of bridges at the interface, both of which scale with $t_H^{0.25}$.

Peeled surface and interface morphology

In addition to the strong dependence of peel strength on LDPE fraction, an oscillation of the peel strength was observed in *Figure 7* for the films containing low LDPE fractions. The amplitude of the oscillation is larger for films having lower LDPE fractions. The origin of this oscillation is explained as the scission of HDPE fibrils created during the peeling process. *Figure 12* shows a series of optical micrographs of the surface of the peel having different LDPE fractions. Many fibrils are observed on the surface. The number and size of fibrils roughly increase with decreasing LDPE fraction of the substrate. These fibrils were confirmed to be HDPE fibrils from a melting point measurement of the films under a microscope.

Figure 13 shows optical micrographs of the intersections of a slowly cooled HD film (with 5% LDPE) from 170°C. The interface is indicated by the arrow. The slowly cooled film has well-grown PP spherulites in the substrate, whereas the quenched film does not. In the substrate of slowly cooled films, PP spherulites have grown and formed a truncated interface between neighbouring spherulites. During the peeling process some of the buried HDPE chains becomes fibrils, which oscillate the peel strength during the peeling process, as shown in *Figure 7*.

Figure 14 shows electron micrographs at the interface of slowly cooled HD films with $T_H = 160$°C, having 16% LDPE in the substrate. The darker phase, with many stripes, is the HDPE phase and the lighter phase is

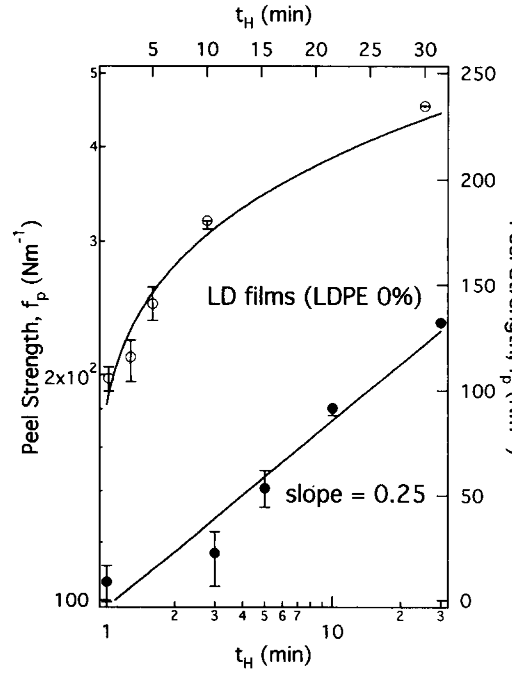

Figure 11 Heat treatment time (t_H) dependence of peel strength for LD films treated at 170°C and quenched to ice–water temperature

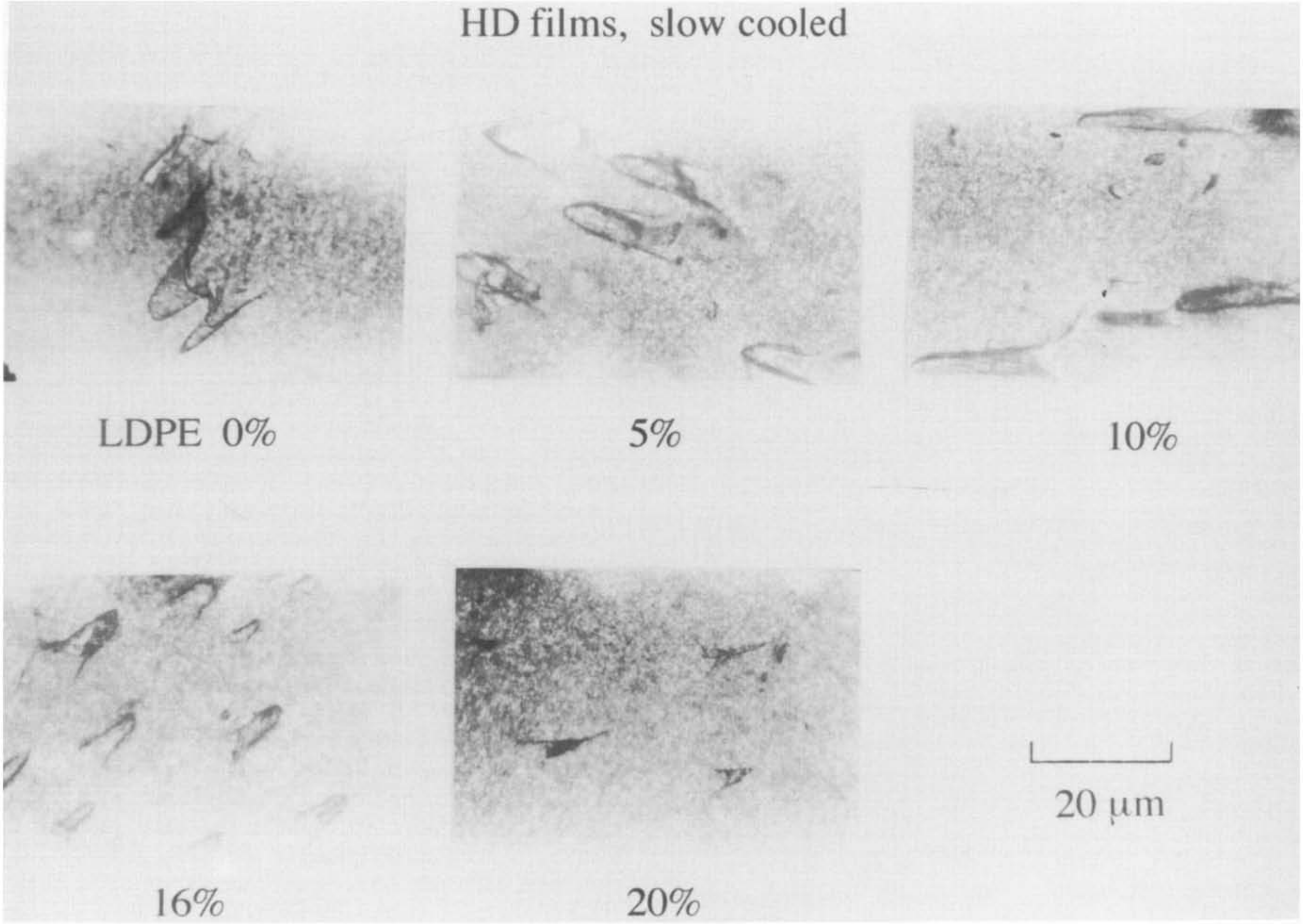

Figure 12 Optical micrographs of the peeled surfaces of the HDPE side (peel)

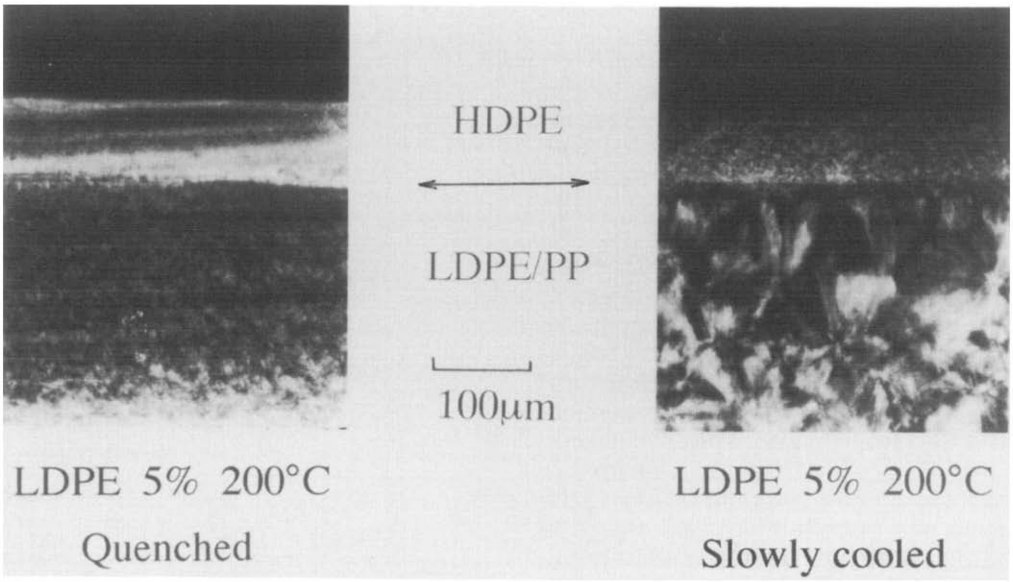

Figure 13 Polarized optical micrographs of the interfaces for slowly cooled and quenched HD films having 5% LDPE in the substrate

PP/LDPE. The stripes seen in both phases are crystalline lamellae. There are many islands of HDPE and/or LDPE in the PP/LDPE phases. Note that the interface is rather smooth and no traces of influx structures of PP spherulites can be found. Therefore the high peel strength observed in this film cannot be ascribed to the interlock structure. It should also be noted that the interface area is stained darker than the bulk phases. This might be an indication of the LDPE excluded from the substrate. If so, it is very reasonable to assume that the LDPE plays an important role in the peeling properties of PP/HDPE laminated films, since it can be a weak boundary layer between the substrate and peel. Therefore it is relevant to deduce that peeling takes place at the interface between LDPE and PP rather than at the interface between PP and HDPE, if LDPE is present in the substrate.

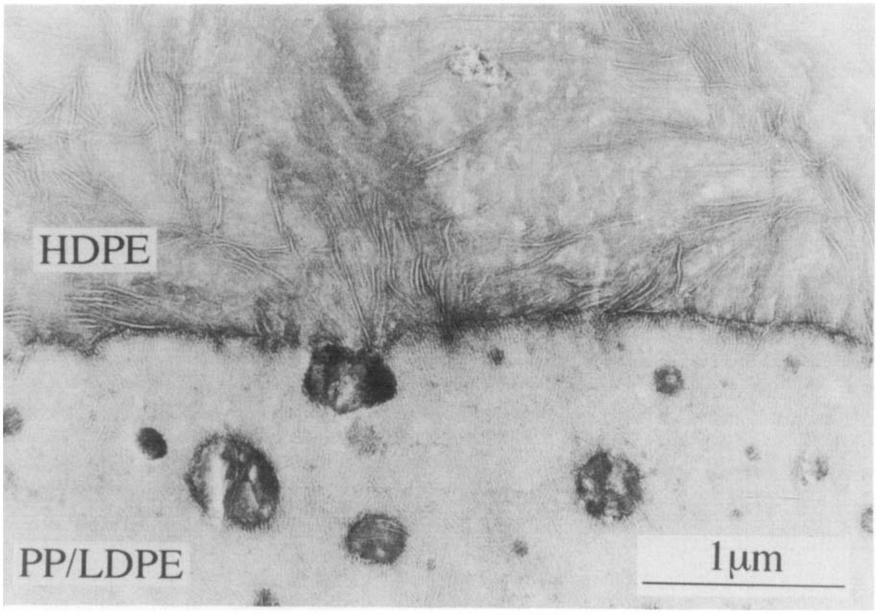

Figure 14 Transmission electron micrographs showing the interface region of HD films having 16% LDPE in the substrate. The darker phase containing many stripes of crystalline lamellae is the HDPE phase, and the ligher phase is PP/LDPE

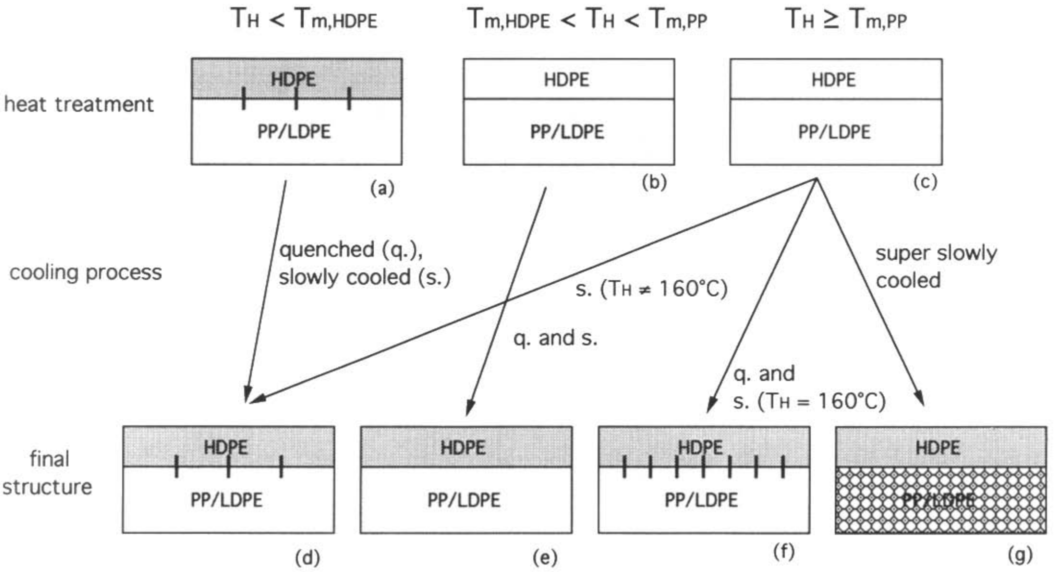

Figure 15 Structure and states of HDPE phase and PP-rich phase around the interface. The figures in the upper row show the state of the films during heat treatment, which are dependent on T_H. The lower row shows the final structures. The shaded and open rectangles indicate crystalline and molten phases, respectively. The thick solid lines across the interface denote entrapped chains due to interdiffusion of component polymer chains. The area marked with circles and dots in (g) indicates PP spherulites. The changes of sutructures and states caused by cooling are indicated by arrows

Peeling mechanisms

On the basis of the experimental findings discussed above, peeling mechanisms of the HD films are summarized with respect to the cooling rates. *Figure 15* shows the structure and states of HDPE phase and PP-rich phase around the interface. In the case of quenched films (*Figures 15a, c*) and slowly cooled film from $T_H = 160°C$, f_p recovers to the same value as the as-prepared film. If T_H is between $T_{m,HDPE}$ and $T_{m,PP}$, only HDPE melts and interdiffused chains are excluded on the crystallization of HDPE, resulting in a lack of bridged chains in the final state; this lowers f_p. Films with $T_H \geq T_{m,PP}$ show different peeling behaviours depending on the cooling rate. In the case of a quenched film, it goes to the structure shown in *Figure 15f*, which has a large number of bridged chains. However, if the film is cooled at a much slower rate ('super-slowly cooled'), the formation of PP spherulites entraps molten HDPE and thus the mechanical interlock structure is created.

CONCLUSION

The peel strength of laminated films of HDPE and blends of PP and LDPE has been investigated and the peeling mechanism discussed. The peel strength is strongly dependent on the heat-treatment temperature and cooling rate. For the quenched films, the interchain locked structure created during the quenching process contributes substantially to the net peel strength. In order to obtain such an effect, the film has to be quenched from temperatures higher than the melting temperature of PP, $T_{m,PP}$. In the case of slowly cooled films, this interchain locked structure is expected exclusively for a film heat treated at $T_{m,PP}$. Otherwise, phase separation between PP and HDPE takes place, which reduces the interfacial strength.

The peel strength was also observed to be dependent on the heat-treatment time, t_H. The peel strength is well described by $f_p \sim t_H^{0.25}$, which is in accordance with the literature. Mechanical interlocked structures due to formation of PP spherulites were not observed for quenched and slowly cooled films. This was the case of a slowly cooled film with a much slower rate ($\tau = 7400$ s).

The LDPE component in the substrate films plays an important role in controlling the peel strength. The larger the LDPE component, the lower the peel strength. The lowering of peel strength was successfully explained by a peeling mechanism involving LDPE at the interface. The peeling takes place preferentially at the interface of LDPE and PP instead of HDPE and PP if LDPE is present in the substrate.

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