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Bonding of highly oriented polypropylene sheets by epitaxial crystallization of polyethylene

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The bonding of highly oriented polypropylene (PP) by means of a thin epitaxial polyethylene (PE) interlayer, was investigated. Epitaxy occurred in HDPE over a range of molecular weight, including ultra-high molecular weights. It was also observed for LDPE, although the epitaxy was less well-developed than for HDPE. Laminates of highly oriented PP thinly coated with PE and treated to induce cross-hatchng of PE showed much improved adhesion, compared with uncoated PP treated in a similar fashion. The PE epitaxy is believed to be responsible for this behaviour. The adhesive performance was also shown to be a function of the molecular weight and its distribution of PE, as well as of the annealing treatment of the PE coat.

1. Introduction

In recent years, the epitaxial deposition of material, both metal [1, 2] as well as polymer [3–9], on oriented polymeric substrates has been a subject of interest. Some property improvements as a result of such an epitaxy were demonstrated: Young's modulus and fracture stress showed a synergism [3, 5] and improved adhesion also resulted [8, 10].

We report here the effect of epitaxially crystallized polyethylene on the adhesion of highly oriented polypropylene (PP) sheet laminates. These highly oriented PP sheets or films possess desirable mechanical properties. However, when laminated into structures, adhesion is usually poor unless the laminate is subjected to heat treatment close to the melting point of polypropylene. In such an event, loss of orientation results and leads to deterioration in the original mechanical properties. The poor adhesion has been attributed to the restriction of interdiffusion because of the reduced free volume in the highly oriented material [11].

2. Experimental details

The highly oriented PP sheets used as the substrate in this investigation were supplied by the Army Materials and Mechanics Research Center in Watertown, Massachusetts, USA. The properties and characteristics of the materials have been described elsewhere [11].

We used a number of commercial polyethylenes (PEs) as the coating material. Their molecular weights, melting points and other pertinent features are described in Table I and Fig. 1. The weight average molecular weight ranged from 150 000 to nominally 4 million. Polydispersities spanned between 5 and 25. Melting points, as determined by a Perkin Elmer DSC, varied from 103 to 143° C.

The PP sheet substrate was coated in the following manner. PP films were rapidly dipped in a solution of 0.06 wt % PE in xylene. The solutions were maintained at a temperature of 110 to 120° C. The coated films were allowed to dry for at least 24 h. Weight measurements before and after dipping indicate that

TABLE I Molecular weight data of commercial polyethylenes used. For the UHMWPEs, the weight average molecular weight is taken to be equal to the measured viscosity average molecular weight

Tradename	Source	Type	M_W ($\times 10^3$)	M_N ($\times 10^3$)	M_P ($\times 10^3$)	M_W/M_N	T_M^* (°C)
Hifax	Hercules	UHMWPE	3000*	–	–	–	143.5
HB312	Hercules	UHMWPE	2570*	–	–	–	138.5
HB301	Hercules	UHMWPE	1590*	–	–	–	140
PE A	Mandelkern	HDPE	235	27	58	10.83	138
PE B	Mandelkern	HDPE	571	92.8	237	6.15	137
Dow 1	Dow Chemical	HDPE	315	21.6	43	14.55	134
Dow 3	Dow Chemical	HDPE	364	14.3	16	25.46	130
Marlex	Phillips	HDPE	315	22.4	60	14.09	133
Tenite 1550	Eastman Kodak	LDPE	299	22.4	60	13.35	103
Tenite 1810	Eastman Kodak	LDPE	150	26.4	136	5.68	110

*Melting point of as-received material.

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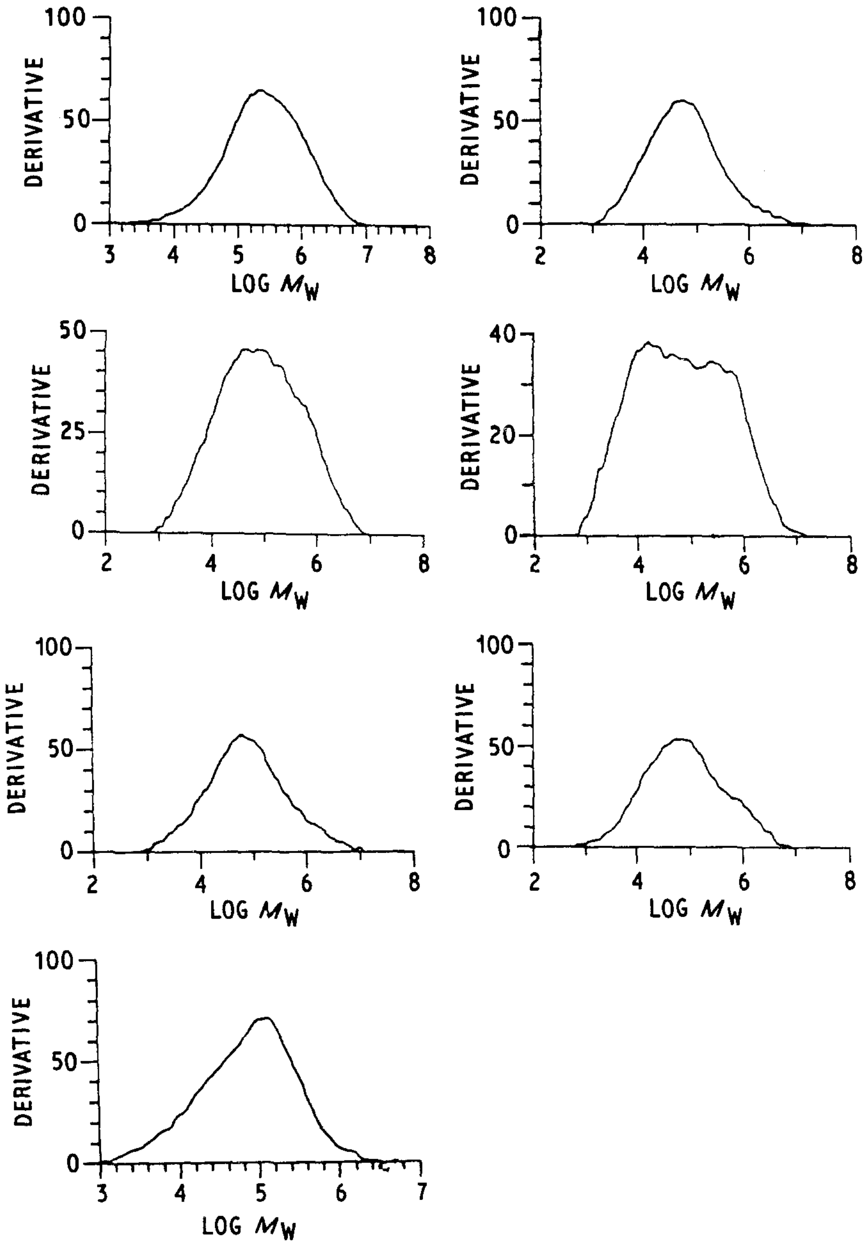


Figure 1 Molecular weight distributions for polyethylene. From left to right beginning at the top: PE B, PE A, Dow 1, Dow 3, Marlex, Tenite 1550, Tenite 1810.

the thickness of the applied coat is of the order of 0.5 to 1 μm. These sheets were then laminated and compression moulded at 159° C and 2000 p.s.i. ($\sim 13.8\,\mathrm{N\,mm^{-2}}$) for an hour. In an alternative preparation scheme, PE coats were made by melt-drawing thin films from a heated glass plate in the manner described by Petermann and Gohil [12]. Here, a small pool of 0.06% PE in xylene is spread over a thin glass plate maintained at 133° C. The solvent evaporates, leaving behind a thin molten film of PE. This film is then drawn off the heated glass plate, with the help of a pair of tweezers, on to the surface of the PP film. These films are typically some 0.5 μm thick. The treated films were then laminated and moulded as before. Annealing experiments were also carried out. Here, the moulded laminates were annealed for 1 h at 2300 p.s.i. ($\sim 15.8\,\mathrm{N\,mm^{-2}}$) at various temperatures.

For examination by transmission electron microscopy (TEM), the PE coats were etched with a permanganate etchant for polyolefins [13]. A 7 vol % solution of $KMnO_4$ in concentrated H_2SO_4 was prepared. The coated sample was left in this solution for 15 min at room temperature. Immediately after that, the sample and solution were cooled to 0° C to halt further etching. After the sample was removed, it was washed in a pre-cooled solution of 2 parts H_2SO_4 to 7 parts water, and then allowed to warm to room temperature. It was finally rinsed in hydrogen peroxide, distilled water and acetone, in that order. Replicas of the etched surface were prepared and used.

The static mechanical properties of the laminates were measured using ASTM D 882-81. Peel strength was measured by an overlap test. Each specimen, made up of two strips of coated PP film, overlapped in part, was compression moulded under conditions described above. The energy to either debond the overlapped region, or to fracture the sample was determined by measuring the area under the stress–strain curve. The separation stress of the sample was also determined. This is the maximum force to separate the overlap area divided by that area. This quantity was calculated only for specimens that debonded at the overlap, as opposed to those that fractured. In some cases, a blocking test, ASTM D 1893-67, was also used.

Figure 2 Transmission electron micrograph of a polyethylene coat (HB 301) after coating on to the polypropylene substrate, but prior to any thermal treatment.

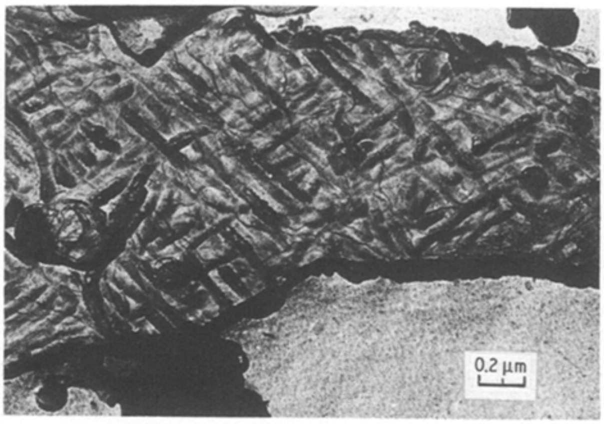


Figure 4 Transmission electron micrograph of a polyethylene coat (HB 312) after treatment at 159° C, 2000 p.s.i. ($\sim 13.8\,\mathrm{N\,mm^{-2}}$) for 1 h, and then subjected to a permanganate etch. The bidirectional "woven" structure is clearly visible.

3. Results and discussion

3.1. Transmission electron microscopy

Transmission electron micrographs show that the PE crystallites have a very different morphology when first coated on the PP substrate from solution as compared to after thermal treatment. Fig. 2 is a micrograph of the PE coat as prepared from 0.06 wt % PE in xylene. What is seen is a loose assembly of overlapping lamellar PE single crystals. After heat treatment, the single crystals of the PE coat undergo a drastic change. The PE crystallites have melted and then recrystallized, to form a cross-hatched structure. Fig. 3 shows such a morphology for an ultra-high molecular weight polyethylene (UHMWPE) coat. The lamellar thickness is found to be about 67 nm, consistent with the periodicity found in linear PE subjected to similar heat treatment [14, 15]. The lateral extension of the lamellae appears to be rather short, again in keeping with recent observations in PE that the lateral extension of the crystallites decreases a great deal with molecular weight [16]. The PE lamellae have crystallized with a definite bidirectional orientation, as noted in the figure: the crystallites are laid down with the chain axes generally between 90 and 110° to each other. A close scrutiny of the micrograph reveals that the individual lamellae are not laid down in an even fashion. A portion of one lamella may crystallize over another lamella, while a second portion may crystallize under a third. This gives a "woven" texture to the structure. Permanganate etching of the PW surface shows this feature in better detail. Fig. 4 is an electron micrograph of a surface replica of an UHMWPE (HB312) coat etched for 15 min in a permanganic solution. The woven nature of the surface is clearly visible.

Fig. 5 is a micrograph in which patches of uncovered PP substrate may be observed. Here one sees the PE lamella "straddling" several PP lamellae. The direction of the PE chain axis is at an angle approximately 45 to 55° to the draw direction of the PP axis, i.e. to the *c*-axis orientation of PP.

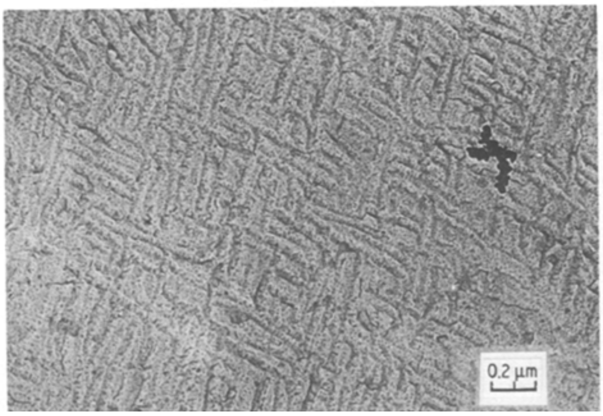


Figure 3 Transmission electron micrograph of a polyethylene coat (HB 312) after treatment at 159° C, 2000 p.s.i. ($\sim 13.8\,\mathrm{N\,mm^{-2}}$) for 1 h. The polyethylene coat has not been rearranged epitaxially.

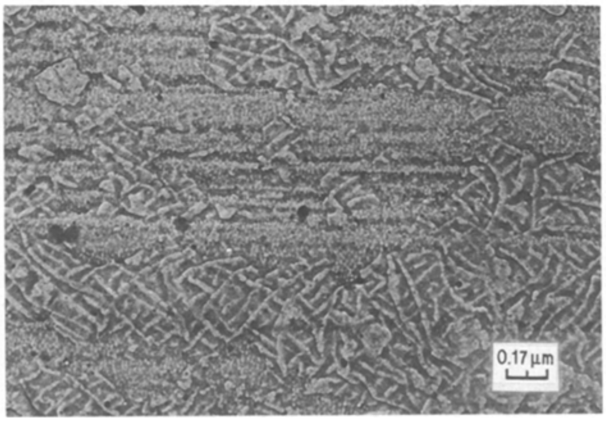
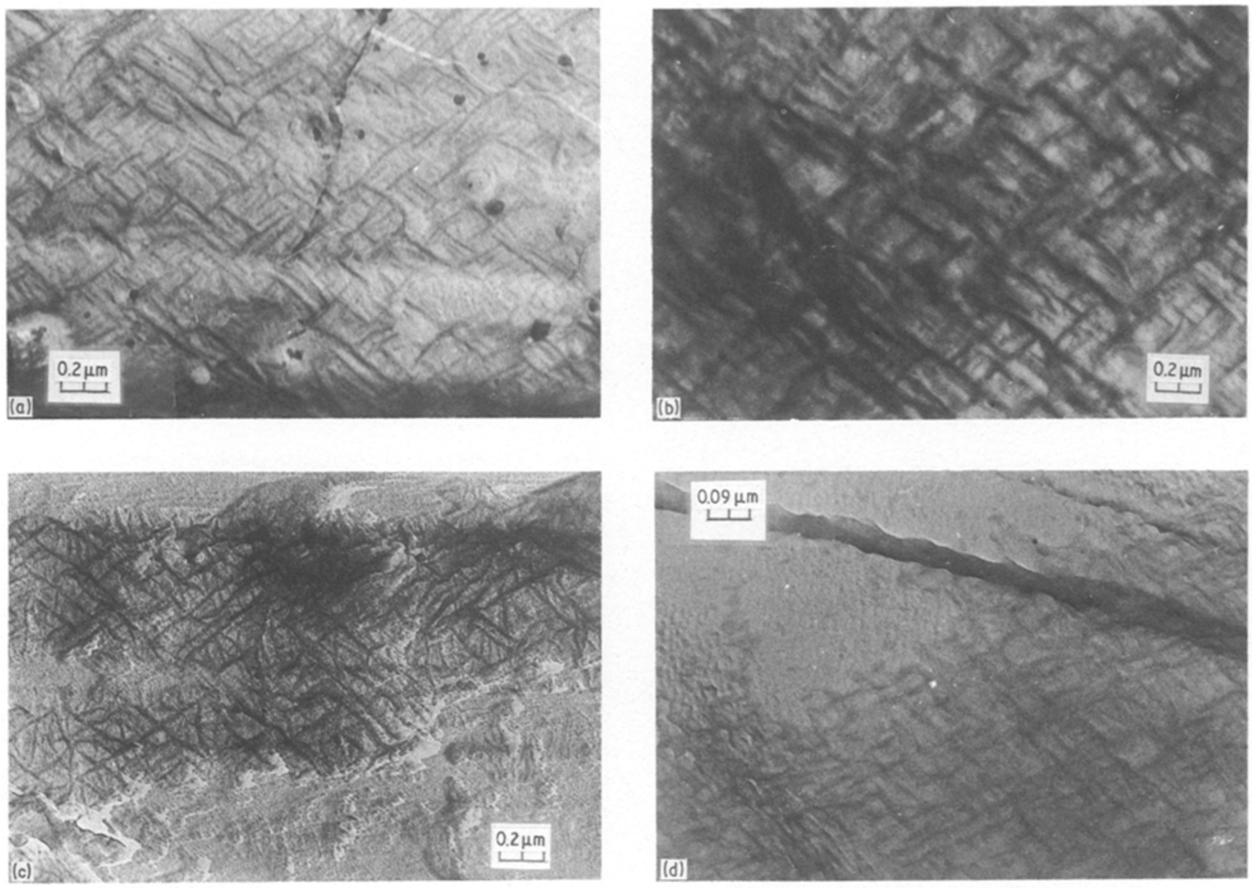


Figure 5 Transmission electron micrograph of a polyethylene coat with patches of polypropylene substrate visible. The *c*-axis of the polypropylene lamellae is parallel to the horizontal direction.



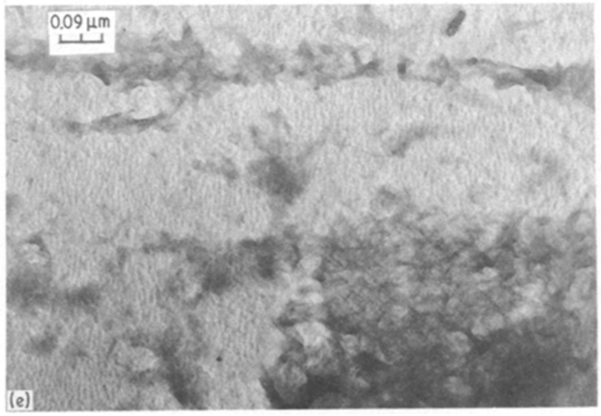


Figure 6 Transmission electron micrographs of polyethylene coats: (a) Dow 1, (b) Dow 3, (c) Marlex, (d) Tenite 1550, (e) Tenite 1810.

The epitaxial relationship is also preserved for the normal molecular weight high-density polyethylene (HDPE), as indicated in Fig. 6. The morphology of low-density polyethylene (LDPE) coats is also shown in this figure. In contrast to previous reports [5, 8], a cross-hatch structure for LDPE is present, although the lamellae are smaller and the structure less well developed than in HDPE.

The reasons for the epitaxial behaviour are still unclear. Lotz and Wittman [3, 9] have postulated a lattice plane interaction between the (1 0 0) PE and (0 1 0) PP contact planes. Petermann *et al.* [8] have argued that, on this basis, PE should, but does not, show a similar texture on hexagonal PP by virtue of the $(1\,0\,\bar{1}\,0)$ PP and (1 1 0) PE planes. Petermann and Broza [2] demonstrated in the case of metal deposition that, despite differences in interplanar spacings, unit cells and conformations, the same preferred orientation for the same metal on different substrates is observed.

3.2. Mechanical properties

The adhesive strength of the PE-coated laminate was measured in two ways: by a blocking test and by an overlap test. Results of the blocking force measurements for the UHMWPE-coated laminates are shown in Table II. The uncoated PP and a LDPE-coated laminate is included for comparison. It is obvious from the table that the UHMWPE-coated laminates possess much higher adhesive strength.

The effect of annealing of the UHMWPE coat on the adhesive strength was also investigated. The coated films were made up into laminates, compression moulded at 158° C and 2200 p.s.i. ($\sim 15\,\mathrm{N\,mm^{-3}}$) for 1 h, and then water-cooled quickly in the press. After that, the laminates were subjected to annealing for 1 h at temperatures of 72, 92, 113, 125 and 136° C. In addition to this, another laminate, compression moulded under identical conditions, was allowed to cool naturally (unforced), instead of being water cooled. The results of peel testing the laminates are plotted in Fig. 7. The rapidly cooled and unannealed

TABLE II Blocking force for polypropylene laminates coated with polyethylene. Moulding conditions: 158° C, 2200 p.s.i. ($\sim 15\,\mathrm{N\,mm^{-2}}$)

PE coat	Blocking force ($\mathrm{g\,cm^{-1}}$)
Uncoated PP	10 ± 3
HB312	477 ± 74
HB301	420 ± 72
Tenite 1550	13 ± 3

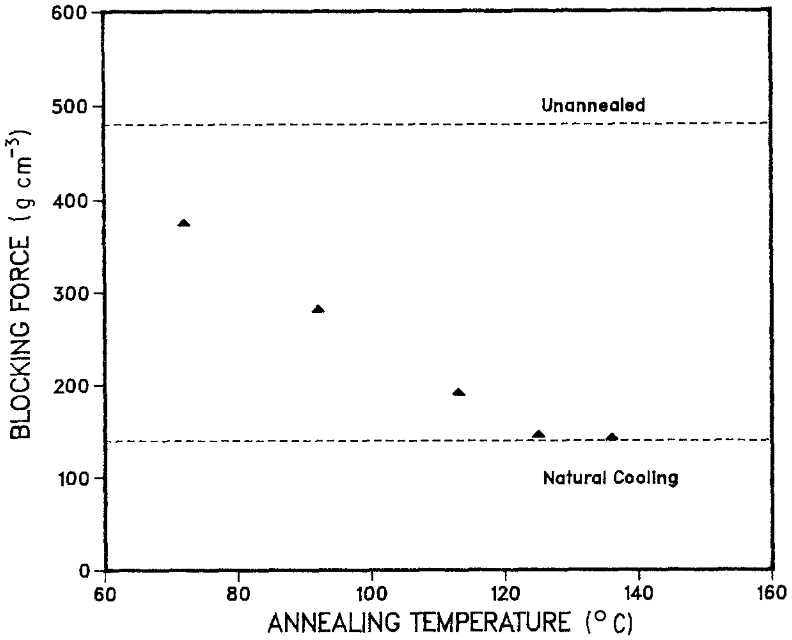


Figure 7 Blocking force of UHMWPE-coated polypropylene laminates as a function of annealing time. Moulding conditions: 158° C, 2200 p.s.i. ($\sim 15\,\mathrm{N\,mm^{-2}}$), 1 h. Annealing conditions: 1 h, 2200 p.s.i.

laminate shows the highest adhesive strength, whereas the laminate subjected to unforced cooling exhibits the lowest adhesive strength. It is noteworthy that this latter value is still much higher than that for the uncoated PP laminate. The adhesive strengths of the laminates annealed at different temperatures lie between those of the unannealed laminate and the slowly cooled laminate. As the annealing temperature increases, the blocking force gradually drops and approaches the lower bound set by the laminate subjected to unforced cooling.

The effect of the molecular weight of PE on the adhesive performance was investigated. In this case, the overlap test was employed, because of the limited quantities of some of the PE samples supplied. The coated specimens were compression moulded at 154° C and 2200 p.s.i. ($\sim 15\,\mathrm{N\,mm^{-2}}$) for 1 h. The results of overlap testing are shown in Table III. Uncoated PP moulded under identical conditions has been included.

In most cases, it was difficult to detect visually whether the adhesive failed at the interface or cohesively, because a degreee of very fine "fibrillation" of the PP substrate generally occurred during testing.

The separation energy is plotted as a function of weight average molecular weight of PE in Fig. 8. The separation energy, and thus the adhesive performance, of the laminate goes up with molecular weight of PE. The exception to this is LDPE, which in one case (Tenite 1810) demonstrates excellent bonding at the lower end of the molecular weight scale. Fig. 9 shows the separation energy plotted against the polydispersity of PE. A continuous downward trend with polydispersity is noted. Both LDPE and HDPE follow this behaviour. UHMWPE is not included, since we have no information on the polydispersity.

These results give rise to an interesting conjecture. The much improved adhesion in the PE-coated laminates cannot be caused by interdiffusion of PE into the

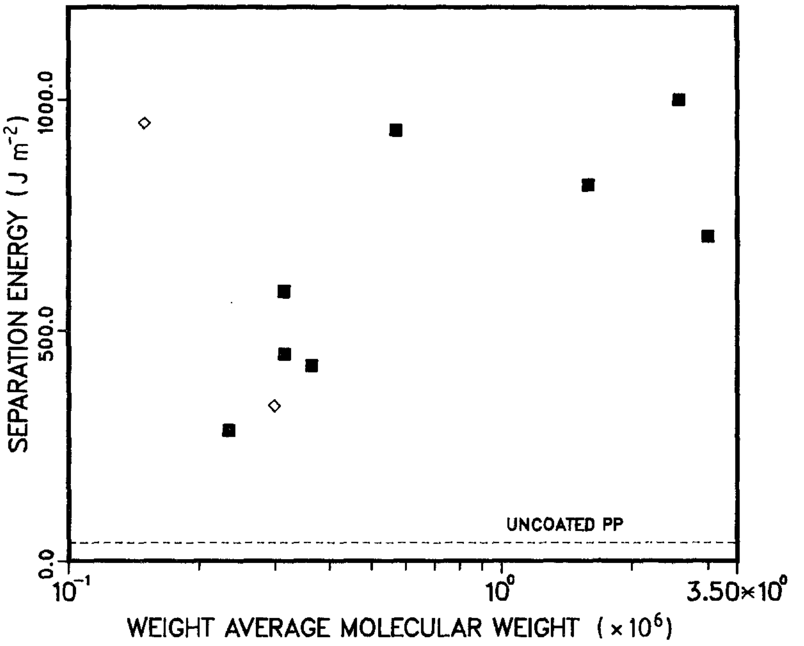


Figure 8 Separation energy as a function of weight average molecular weight of polyethylene. (◇) LDPE, (■) HDPE.

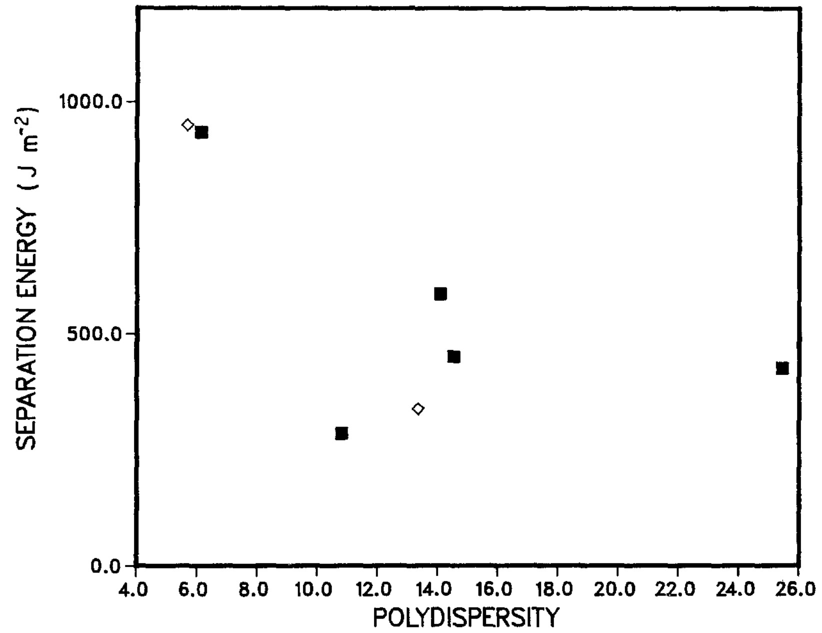


Figure 9 Separation energy as a function of polydispersity of polyethylene. (■) HDPE, (◇) LDPE.

PP substrate. Some reasons may be cited for this. The highly oriented PP substrate is impermeable, because of the drastic reduction in free volume during orientation. It is also well known that PE is incompatible with PP. The interpenetration zone between the two cannot be very large. We propose that the epitaxial behaviour of PE on PP is responsible for the improved performance.

Both the molecular weight characteristics and annealing treatment of PE affect the adhesive performance. The higher the molecular weight, the better the performance. In addition, the narrower the molecular weight distribution, the higher the peel energies. This suggests that the cohesive strength of PE is involved. Both molecular weight and its distribution have been shown to affect tensile strength in a similar fashion [15]. If cohesive failure is indeed the case, this implies that the strength of the interfacial interaction between PP and PE must be far higher than the cohesive strength of PE, including UHMWPE. The annealing behaviour of UHMWPE, in which the adhesive strength of the laminate dropped as annealing temperature was increased, is likely also due to changes in the cohesive behaviour of the PE layer. Annealing should promote additional crystallization of PE [17, 18]. However, the first-formed PE crystals are strongly bound to the PP crystal and are not free to move together to relieve strains associated with the specific volume decrease. Such effects are known to produce large internal strains in PE which has been drawn, relaxed and clamped [19, 20]. Further, internal stresses are documented in the PP phase of PP/PE blends with more than 20% PE [21]. In that case, it is likely that secondary crystallization and/or physical ageing in PP is constrained by the presence of the thicker PE crystals. In the present case, it is the thin PE layer which should be constrained by the massive PP sheets between which it is sandwiched.

TABLE III Energy required to separate polyethylene-coated overlap samples

PE Coat	Description	Number of tests	Energy (J m^{-2})
	uncoated PP	7	40 ± 4
Hifax	UHMWPE	12	705 ± 208
HB312	UHMWPE	17	1000 ± 199
HB301	UHMWPE	8	816 ± 104
PE A	HDPE	9	285 ± 107
PE B	HDPE	7	934 ± 86
Dow 1	HDPE	9	450 ± 198
Dow 3	HDPE	8	425 ± 118
Marlex	HDPE	9	585 ± 169
Tenite 1550	LDPE	10	338 ± 130
Tenite 1810	LDPE	8	949 ± 193

The mechanical properties of the laminates were measured. Table IV compares the elastic modulus and fracture strength between the coated and uncoated laminates. It shows them to be identical. Thus, coating the highly oriented PP with PE improves adhesion without adversely affecting its mechanical properties. The synergism observed by Petermann *et al.* [4, 6], is not expected to be seen here, because, unlike their sandwiches, which comprised identically thick PP and PE layers, the PE coats account for about only 2 vol % of the laminate.

4. Conclusion

PE, after deposition on highly oriented PP, rearranges itself into an epitaxial formation when treated at temperatures above its melting point but below that of PP. In this formation, the PE chain axis lies at approximately 45 to 55° to the PP chain axis. This behaviour has been observed for both HDPE and LDPE, although it is not as well developed in the latter. It has also been seen over a range of PE molecular weights, including ultra-high molecular weights.

A highly oriented PP laminate coated with PE and

TABLE IV Comparison of properties between coated and uncoated laminates

	PP	PP/PE	PP/atactic PP
Blocking force (g cm^{-1})	20	477	55
Elastic modulus (GPa)	6.6	6.8	
Fracture stress (GPa)	0.25	0.25	

*Tested 24 h after moulding.

treated as described shows much improved adhesion over the uncoated laminate. The epitaxy is believed to be responsible for this behaviour. The adhesive performance has also been correlated to the molecular weight of PE and its distribution, as well as the annealing treatment of the PE coat.

Acknowledgement

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