

Fine dispersed blends for compatibilizers for laminates of immiscible polymers

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Blends of high-density polyethylene (HDPE) and isotactic polypropylene (iPP) are used to increase the strength of adhesive bonds between the immiscible polymers HDPE and iPP. Melt blended as well as solution blended material is examined for its suitability to compatibilize the interface between the bonded members. Two standard test methods, the T-peel test and the tensile test, are applied to determine the strengths of adhesive joints. Laminated samples for the peel-tests as well as specimens subjected to the tensile tests were prepared at a temperature exceeding the melting temperature of both homopolymers. TEM and LVSEM examinations were performed for characterizing the morphology of the interface with the aim to determine the parameters which significantly influence the blends' adhesive properties. The bonding strengths obtained with the blended material are discussed with respect to the morphologies of the interfaces, the degree of dispersion in the blend, and the bonding mechanisms. © 2000 Kluwer Academic Publishers

1. Introduction

Increasing the strength of adhesive bonds between immiscible polymers constitutes the foundation for many of today's applications. Especially laminated polymer films have become of technical importance due to their advantages in a broad scope of possible applications. Numerous composites contain layers of polyethylene and polypropylene, both of them being essential components of food packaging. Due to the weak adhesion between these non-polar polymers, compatibilizers have to be used to increase bonding strength. The mechanism of adhesive action is quite different for various types of adhesives and substrates.

Excluding chemical bonds between substrate and adhesive, adhesion can be explained by mechanical, molecular-physical, or thermodynamic mechanisms. In most of the cases, adhesion is interpreted as a combination of distinct interactions on the basis of different models. The molecular-physical interpretation of the interface phenomena includes three different models, ie, de Bruyne's polarization theory [1], Deryagin's electrostatic theory [2], and the diffusion theory developed by Vojutskii [3].

For the non-polar system polyethylene/polypropylene the former two can be excluded as well as any other kind of intermolecular bonds caused by polarity or high electronegativity. Thus, adhesive action between PE and PP can only be accomplished by mechanical interlocking, diffusion of macromolecules across the interface, and/or dispersion forces. As the latter are comparatively weak, just the former two are starting points to increase adhesion between the polymers investigated here. Usually, the weak interfacial adherence

of two immiscible polymers A and B is strengthened by adding an interdiffusing block copolymer A-B [4, 5].

In this work, a new approach is performed by using an interface layer of a fine dispersed blend A/B of the homopolymers A and B. In this case, a strong junction is expected to be achieved by mechanical adhesion caused by two effects. On the one hand, the effective interface area is enlarged leading to higher fracture forces related to the original surface. The effect is supposed to be equivalent to roughening where the material's surface area can be increased by a factor of 2 to 4 [6, 7]. On the other hand, blend domains will interlock with the substrate like anchors, yielding a much greater contribution to adhesion. These interlocking domains cannot be bypassed by a propagating crack, leading to a large deformation of the material when the compound is detached [8]. Failure then must occur within the same material by breaking chemical bonds resulting in a higher fracture energy.

2. Experimental

2.1. Polymers and blend preparation

The polymers investigated in our study were high density polyethylene (HDPE, Lupolen 6021D) and isotactic polypropylene (iPP, Novolen 1100H), both supplied by BASF AG. The density according to the manufacturer was 960 kg/m³ and 910 kg/m³, respectively.

Blends were prepared either by melt blending or solution blending. For melt blending, a mini twin screw extruder (DSM) was used operating at a temperature of 200 °C. The granulated homopolymers were melt mixed for approximately five minutes without any

pretreatment. The extrudate was cut into pieces and pressed to thin films in a hot press at 180 °C.

The solution blended material was obtained by dissolving the homopolymers in boiling xylene (1 wt %). The solution was either applied directly onto the samples' surfaces or, in order to obtain thin films, the blend was precipitated in cold acetone. To rule out any solvent influence on the adhesive properties, the precipitate was dried in a vacuum chamber for at least 24 hours. The blend was subsequently pressed to thin films in a hot press keeping identical conditions as for the extrudate.

2.2. Mechanical tests

2.2.1. T-peel test

For T-peel testing, pairs of films comprising an iPP film (140–300 μm thick) and a HDPE film (10% thicker, to achieve equal stiffness of the probe arms and therewith a peel angle of 90°) were laminated in a hot press. The blend (thin film or solution) was applied in a defined section of 15 mm length, and the polymer films were melted between glass slides at 180 °C (Fig. 1). They were pressed for 3 minutes (if not noted otherwise) at 1 MPa and cooled to room temperature on a steel plate. The 200–500 μm thick laminates were cut to a width of 15 mm, their length was 50–70 mm.

To measure the peel strength, the laminated films were peeled with a constant peeling rate of 20 mm/min using a Zwick 1445 tensile testing machine. Every 25 ms a test signal was recorded from which the peel force per width was calculated. For each sample the arithmetic average of the peel force was computed as well for the blend coated section as for the untreated sections (Fig. 2). For each series of measurements containing 7 identically prepared samples, the arithmetic

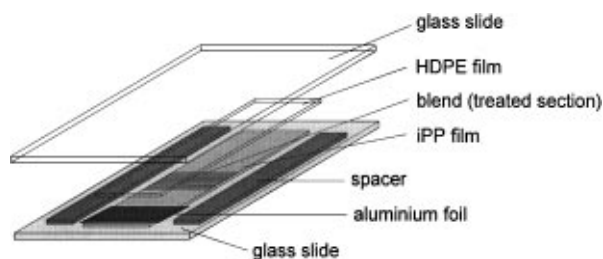


Figure 1 Preparation of the peel test laminates.

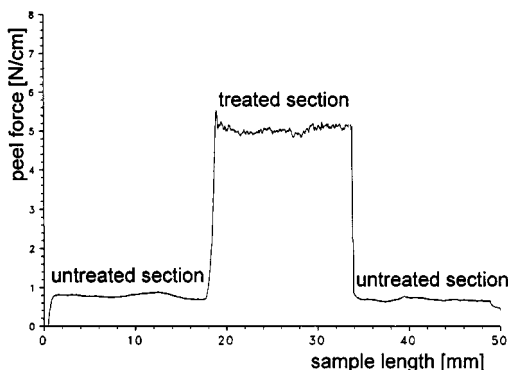


Figure 2 Peel force diagram illustrating different bonding strengths within a single sample.

averages were taken again, weighted with the number of test signals.

The sectioning of the laminate enables to observe significant differences in adhesive strength within a single sample, eliminating parameters such as film thickness or peel angle [9]. These parameters have been shown to significantly influence the measured forces [10–12] but if they are kept constant, the peel test is a sensitive test method for determining adhesive strengths.

2.2.2. Tensile test

The homopolymers were molded in a hot press to obtain bars of $6 \times 15 \times 70 \text{ mm}^3$ which were cut in half. To get a plain and smooth surfaces, a film of the corresponding polymer was attached to the cut surface on a hot glass plate. Subsequently, tensile specimens were prepared by molding half of a HDPE bar and half of an iPP bar in an aluminum form at 180 °C. The blend used as compatibilizer (thin film or solution) was applied between the smooth surfaces. By means of a spring, variable in position, a constant contact force of 12 N was applied. The specimens were tensile tested perpendicular to the joining interface at a constant stretching rate of 1,4%/min. Force measurements were conducted until failure of the samples occurred.

2.3. Microscopy

To obtain information on the interface between the substrates and the blends, multi layer sandwiches, comprising films of HDPE and iPP alternating with blended material, were prepared. Sandwiches were molded in a hot press at 180 °C. The samples as well as cross-sectional microtome cuts of these samples were etched in a 1 wt % solution of potassium permanganate in concentrated sulfuric acid and orthophosphoric acid, according to the method of Olley, Hodge, and Bassett [13]. Microtome cuts (60 μm thick) were examined in a Hitachi S 4500 field emission low-voltage scanning electron microscope (LVSEM) with an acceleration voltage of 1 kV. Low voltage technology enables to obtain a topographic image of the polymers without surface coating. Two-step replicas of the smoothed and etched surfaces of the multi layer samples were investigated in a Philips CM 200 transmission electron microscope (TEM). This technique reveals lamellar details in polyethylene as well as in polypropylene [14, 15], allowing representative studies of the melt crystallized interface morphologies.

Furthermore, the peeled surfaces of the laminated films were investigated in the LVSEM to get information on the mechanisms of adhesive bonding. These investigations were performed without etching the samples.

3. Results and discussion

3.1. Methods of blend preparation and application

To explore the influence on adhesion by different methods of blend preparation, films of melt blended as well

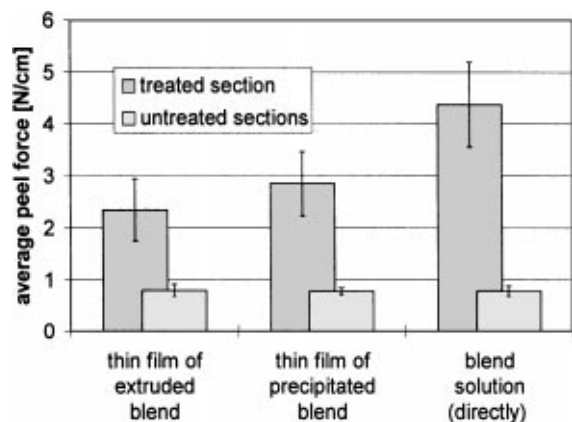


Figure 3 Influence of the method of blend preparation and application.

as of solution blended material were prepared under identical conditions and used as compatibilizers in the peel tests. In addition, the influence of blend application was investigated by conducting one series of measurements with blend solution applied directly onto the substrates. Blends containing 50 wt % HDPE and 50 wt % iPP (50 : 50 blend) were used for these experiments. In Fig. 3, the resulting peel forces (treated section) are shown, compared to the values of the pure materials (untreated sections).

In comparison to both kinds of blend films, the directly applied blend solution leads to considerably higher peel forces. This can be explained by the different dispersions of the both components in the blend resulting from the different methods of blending.

TEM as well as LVSEM examinations of the multi layer sandwiches revealed that direct application of the blend solution leads to a finer dispersion than can be achieved in blend films. The differences in dispersion are also conspicuously reflected by the number and the dimensions of the “pull outs” resulting from the deformation of the material at the peeled surfaces (Fig. 4).

(An additional series of measurements revealed that there is no difference whether the blend solution is applied onto the HDPE substrate or onto the iPP substrate. If there had been any solvent influence, the re-

sults should differ for the different substrates, because the solubility of iPP in xylene exceeds that of HDPE. Consequently, in our experiments the influence on adhesion by the solvent can be neglected.)

No remarkably different peel forces are measured for the thin films from melt blended and those from solution blended material. Values for the solution blended film are only slightly higher. Considering that solution blending goes along with a much finer dispersion than melt blending does, and that a finer dispersion leads to higher peel forces, the difference is much smaller than expected. Thus, differences in dispersion may have diminished during the melting in the thin film preparation process.

3.2. Influence of time in the molten state

Three series of measurements were taken to determine the influence of the time the blend is in the molten state during sample preparation. Therefrom information on the fundamental mechanisms can be gained of how adhesion develops with time when blends are used as compatibilizer. Peel test laminates compatibilized with films of a 50 : 50 blend were pressed for 3, 15, and 40 minutes. The resulting peel forces as a function of pressing time are shown in Fig. 5.

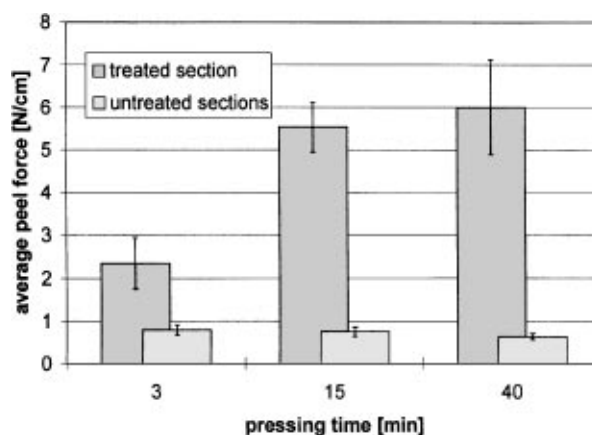
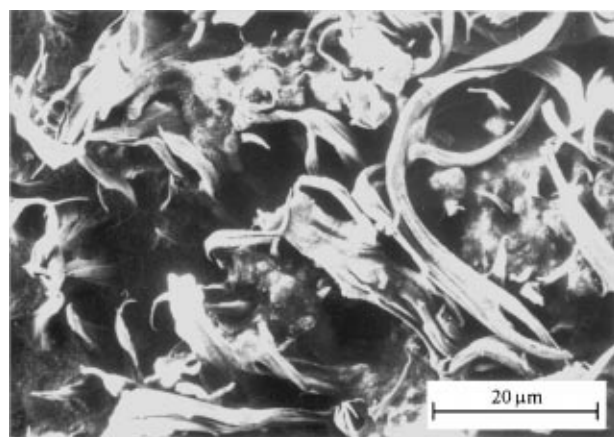
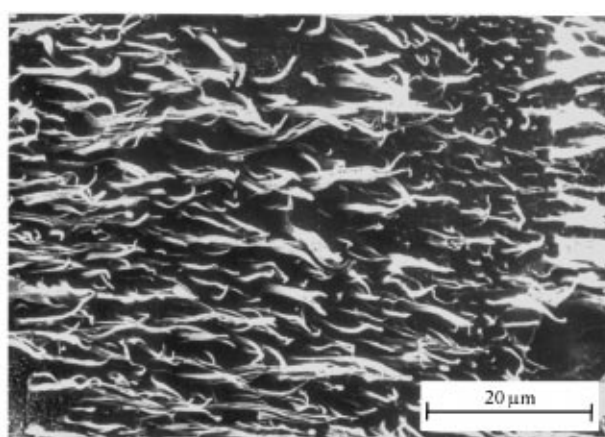


Figure 5 Influence of pressing time on peel force. (Treated section compatibilized with a thin film of a 50 : 50 blend.)



(a)



(b)

Figure 4 LVSEM photographs of the peeled surface treated with different compatibilizers. (a) Thin film of extruded blend; (b) Directly applied blend solution.

It is evident that pressing time does not influence the adhesion of the untreated sections, peel force for detaching the pure components always is about 0.8 N/cm. Where blend films were used as compatibilizer, peel forces are 4 to 7.5 times higher and strongly affected by pressing time. Increasing the pressing time from 3 to 15 minutes leads to a remarkable increase in peel force, while there is just a slight improvement when pressing for further 25 minutes.

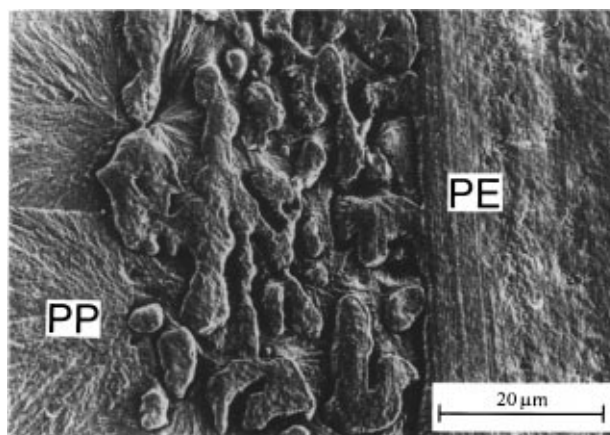
These results can be explained by the blend specific mechanisms of adhesion. When the substrates are melt pressed with the blend in between, the polymers associate with the respective component of the blend at the interface leading to mechanical adhesion. Some of the blend domains simply act as elements of roughness (see Fig. 8, marked as I), forcing a crack to bypass the obstacle. This can be considered as an enlargement of the effective interface. A much higher contribution to adhesion is yielded by those blend domains which interlock with the substrate (see Fig. 8, marked as II). To detach the interlocked parts of the substrates, forces comparable to the breaking strength of the respective component are necessary. The deformation mode can be recognized in the LVSEM pictures (see Fig. 4) in the form of material which has been pulled out of the peeled surfaces. The number of these “pull outs” represent the number of domains which had been interlocked. Fig. 6 shows the boundaries between substrate and compatibilizer, illustrating the interlocking in the μm -scale.

A necessary condition for the efficiency of such interlocking domains is the bridging of the respective interface similar to the neck formation during the sintering process of powder material [Fig. 6b and c]. For that, diffusion of polymer molecules across the interface has to take place, so that molecular entanglements or crystal interconnection can be formed. The longer the pressing time the more and the larger are the bridges and the more domains act as effective points of linkage between blend and substrate. Consequently, the force to detach the bonded members increases with pressing time. The longer the blend is in the molten state, the more the interfaces are influenced by a contrary effect. A coarsening of the bridges due to phase separation leads to a decrease in the specific interface area and therefore to a reduction of adhesive bonding strength.

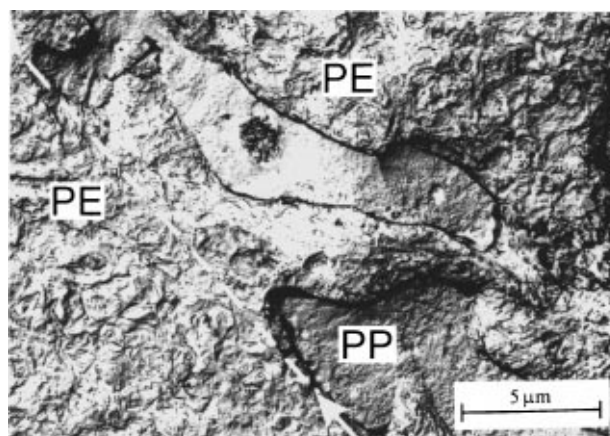
For verification of this separation process, blends which have been in the molten state at $T = 180^\circ\text{C}$ for different times were examined in the TEM. Fig. 7a and b show a 50 : 50 blend after extrusion and a 50 : 50 blend film, which has been kept in the molten state for 30 minutes after extrusion, respectively. After the heat treatment, the domain sizes of the blend components have nearly doubled.

From these considerations it may be concluded that adhesion reaches a maximum with pressing time, leveling off to the values of the pure components due to a complete loss of the bridges after infinite time (t_∞ in Fig. 8).

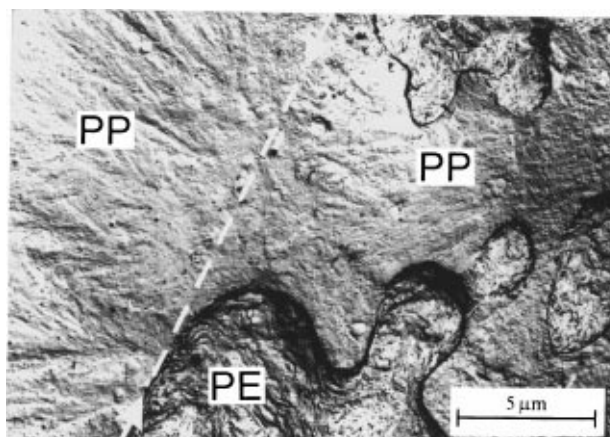
The basic mechanisms discussed above are schematically illustrated in Fig. 8. At the time t_{opt} the maximum of adhesion is reached, at longer pressing times the number of interlocking domains will be reduced due



(a)



(b)



(c)

Figure 6 Boundaries between homopolymers and blend in a multi layer sandwich (view perpendicular to interfaces, original boundary marked by white line). (a) LVSEM photograph of both of the boundaries; (b) TEM photograph of the boundary between HDPE and blend; (c) TEM photograph of the boundary between iPP and blend.

to phase separation. The components of the blend are then assumed to separate in layers, as this requires the shortest diffusion distances.

3.3. Gradient blends

The LVSEM examinations of the peeled surfaces demonstrated that fracture occurred at the interface between the blend and one of the substrates. Therefore, to improve the consistency of the compound material, these weakest points have to be strengthened.

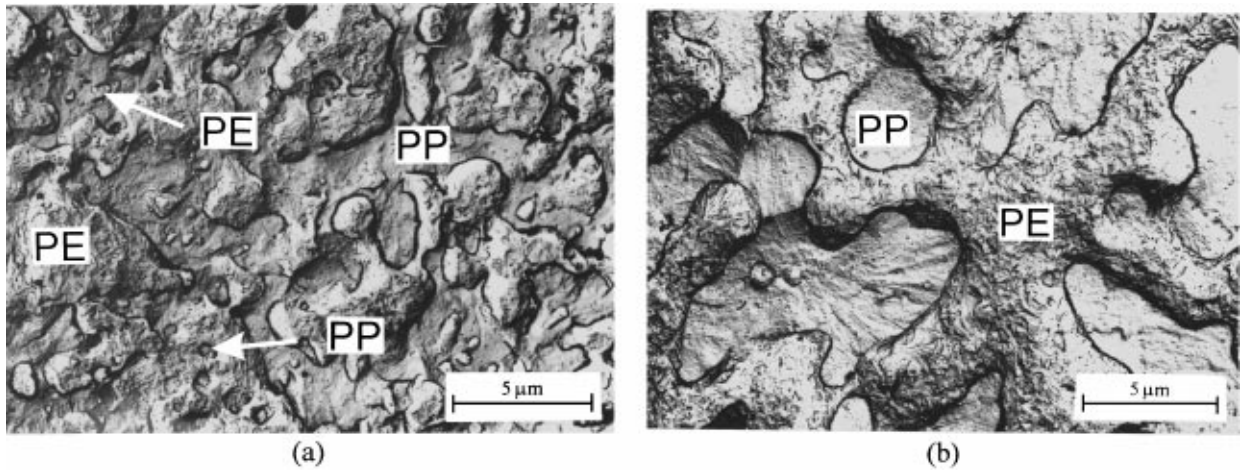


Figure 7 TEM photograph of an extruded 50 : 50 blend. (a) Cross section of the extrudate; (b) Same sample, kept in the molten state for 30 min after extrusion.

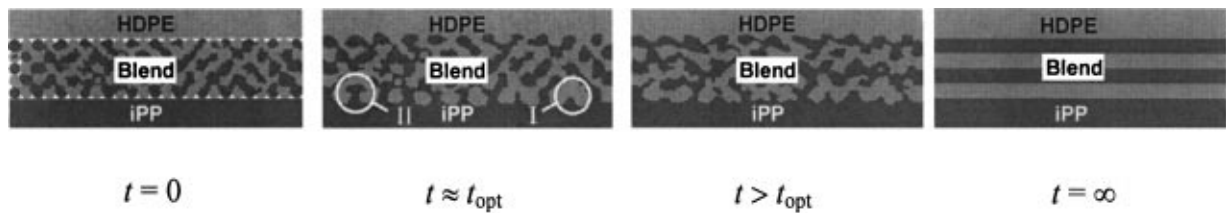


Figure 8 Time dependent development of interlocking domains between blend and substrates. I: element of roughness, II: interlocking domain.

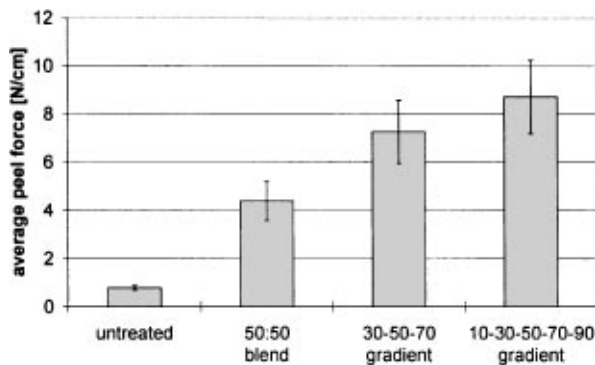


Figure 9 Comparison of compound blends in the peel test (blend application as solution).

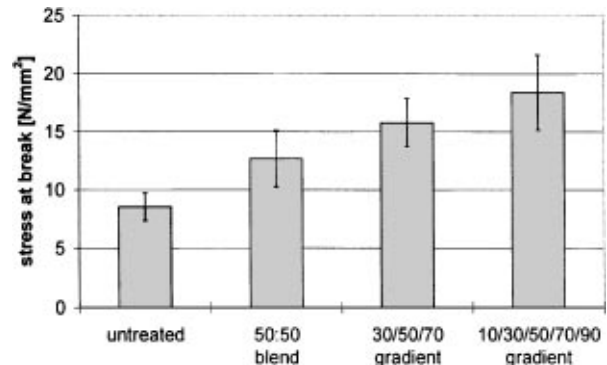


Figure 10 Comparison of compound blends in the tensile test (blend application as film).

This can be achieved with blends in which the composition changes gradually from the one pure component (HDPE) to the other (iPP). Two types of such gradient blends were examined in the peel test (Fig. 9), as well as in the tensile test (Fig. 10). The three step gradient consists of three blend layers containing 30, 50, and 70 wt % of one of the polymers, respectively. By adding two more layers (10 and 90 wt % of one component), a five step gradient is obtained.

Both test methods reveal the distinct improvement of the adhesive strength in comparison to a 50 : 50 blend. Using a three step gradient, the peel force can be increased by more than 50%, with a five step gradient, the force can even be doubled compared to a 50 : 50 blend. In the tensile test experiments, the differences in the interface strengths are less pronounced, but follow the same tendency.

The micrographs taken from a multi layer sandwich (Fig. 11) exhibit the almost continuous transition region

in morphology attainable by a five step gradient blend. Thereby the abrupt change in morphology formed at the interface between a single layer of a 50 : 50 blend and the pure components is prevented.

3.4. Comparison with copolymer

Considering the current method of using copolymers of the respective components as compatibilizers, comparable bonding strengths are achieved when blend systems are used. This is illustrated in Fig. 12. For a direct comparison, a blend containing the same weight fraction of the components (80 wt % PE, 20 wt % PP) as the copolymer (Vestolen P 7700, DSM Polymers) is also shown in the diagram.

The advantage of blend systems is their simple preparation, whereas copolymers have to be expensively synthesized and specially adapted to the specific system in

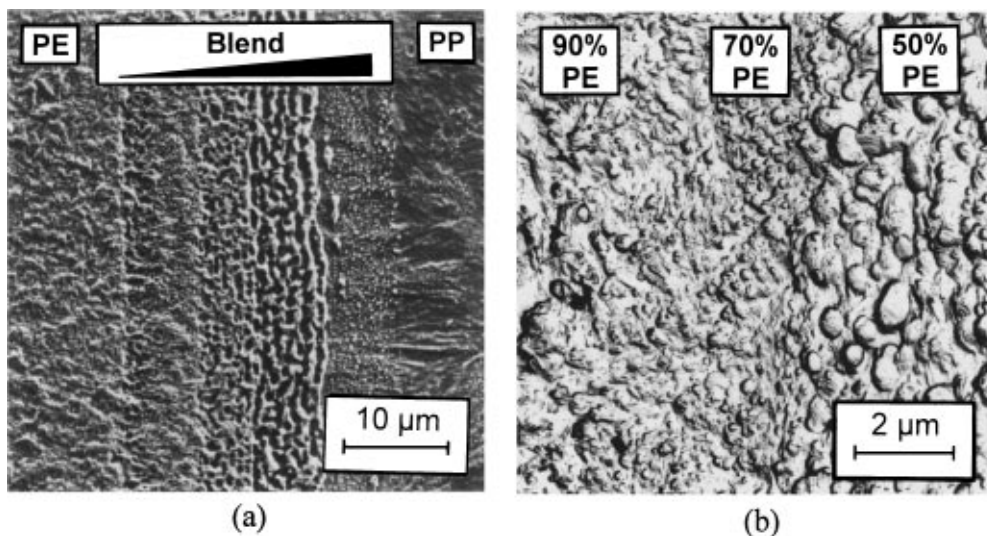


Figure 11 Interface compatibilized with a five step gradient blend (view perpendicular to interfaces). (a) LVSEM micrograph of the entire region including both of the homopolymers; (b) Magnified section (TEM) of the region between 90% HDPE and 50:50 blend.

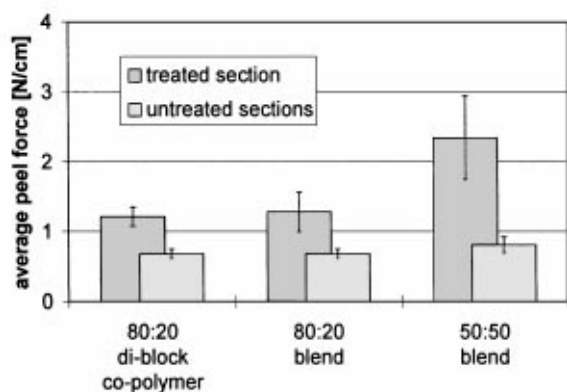


Figure 12 Comparison of peel strength achieved by blend and co-polymer.

their properties such as molecular weight and block length.

4. Conclusions

The results reported in this paper show that junctions of HDPE and iPP can be considerably strengthened by using HDPE/iPP blends for compatibilization of the interfaces.

The strengthening is caused by two effects which cannot be clearly separated with our experiments: On the one hand, the joint is strengthened by an enlargement of the specific surface areas. On the other hand, mechanical interlocking in a μm -scale is built up leading to higher separation forces, as fracture occurs within the same material.

The parameters significantly influencing the adhesive properties are the dispersion in the blend and the pressing time. The former determines the number of the possible points of linkage whereas the latter decides on the efficiency of these connecting bridges.

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