Changes in interface shape during crystallization in two-component polymer systems

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The interfaces between isotactic polypropylene (iPP) and polyethylene (PE) or polyoxyethylene (POE) were investigated in model sandwich-like systems by means of optical microscopy and scanning electron microscopy. It was found that during crystallization of iPP the shape of the interface undergoes significant changes. The interface surface changes from initially flat to highly developed with many deep and branched influxes of the second polymer flowing into the iPP phase. The formation of influxes is caused by the volume defect that appears during conversion of the iPP melt to crystal. The volume defect in regions of iPP melt that are closed by a continuous front of growing spherulites on one side and the interface on the other induces a deformation of the interface and flow of the melt of the second polymer into these regions. It was shown that the driving force for influx formation is the adhesion between melts of both polymers being in contact. The presence of influxes increases the interface strength mainly by increasing its area. Deformation of the interface in polymer blends can result in the deformation of the dispersed particles during crystallization of the matrix, and as a consequence in the improvement of mechanical properties of the blend.

(Keywords: blends; interface; crystallization; polypropylene)

INTRODUCTION

The production of polymer blends is one of the most explored and cheapest ways to obtain new polymeric materials with properties different from (frequently improved on) those of the polymers used for blending.

In themselves polymer blends are usually heterogeneous systems because of the immiscibility of most polymer pairs[1]. The blending process causes more or less fine dispersion in the form of droplets of one component within the other, so in blends there is a well developed interface between the components. The properties of the interface, its thickness and total area influence the properties of blends[2]. Depending on the type of polymers in a blend the interfacial layer has different thickness[3] and properties[2]. The interface can be sharp[4] or diffuse[3,5,6]. In theoretical predictions[3,7] the thickness of the interfacial layer is estimated to range from 0 to 200 Å. On the other hand some authors[5,6,8] have reported interfacial layer thicknesses of the order of several micrometres. Such large thicknesses of the interfacial layer have been attributed to mutual diffusion of the components[6,8] or formation of a microheterogeneic region with finer dispersion (emulsion-like) during melt-annealing of the blend instead of a continuous interface[9]. However, these concepts, presented without any direct evidence, do not fully account for the experimental results. It is possible that in blends there occurs additionally another, as yet unknown, phenomenon. It is necessary to note that the blends investigated in the studies mentioned above contained at least one polymer capable of undergoing crystallization: polyethylene and polyoxymethylene, in ref. 5; polyethylene (mixed with polyvinylchloride), in ref. 6; polyethylene and polypropylene, in ref. 8. Measurements of the interfacial layer thickness were carried out on solid specimens, after crystallization of the components. Thus, the crystallization of the components of the blends could have influenced their measurements.

The aim of our work was to find out what takes place at the interface between the components during solidification of the blend (if at least one of the components is a crystallizable polymer) and how it could influence the interface.

EXPERIMENTAL

The characteristic of the polymers used in the present investigations are indicated in *Table 1*.

The interface formed between isotactic polypropylene (iPP) and the other polymer, low-density of high-density polyethylene or polyoxyethylene (LDPE, HDPE or POE), was investigated during isothermal crystallization of iPP as well as after completion of solidification.

Direct observations of the interface change during crystallization were carried out by means of a phase contrast optical microscope equipped with a hot stage. The model sample was a thin (20 μm) polypropylene film in contact at its edge with a film of the other polymer. The films in contact were placed on a support glass and covered with a coverglass. In this way it was possible to observe a large, flat interface perpendicular to its surface. The model samples were melted at 190°C and then kept at constant temperature in the 130–135°C range. At such a temperature, crystallization of the second polymer is impossible. It remains molten and it is only iPP that can crystallize.

The interface was also examined after completion of crystallization in the bulk model systems. Model bulk

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Table 1 Characteristics of the polymers used in the present study

Polymer	Source and trade name	M_w	Density ($g\ cm^{-3}$)	Melt flow index (g/10 min)
Isotactic polypropylene (iPP)	Montedison, Moplen C30G		0.910	5.6
Low-density polyethylene (LDPE)	BASF, Lupolen 1800S		0.918	20
	Lupolen 1800M		0.918	8
	Lupolen 1800H		0.918	1.5
	Lupolen 2410S		0.924	20
High-density polyethylene (HDPE)	BASF, Lupolen 3010S		0.930	20
	Lupolen 6011L		0.960	5
Polyoxyethylene (POE)	Fluka AG, –	1×10^5		

samples were prepared in the form of a sandwich. Sheets (2 mm thick) of two polymers (one of which was iPP) were melted at 190°C and their surfaces brought into contact to obtain a sandwich. The sandwich obtained was cooled to 130–135°C, at which temperature only iPP could crystallize. After completion of polypropylene crystallization, the sample was rapidly cooled to room temperature whereupon sections were cut from the sample perpendicular to the interface and examined with a polarizing microscope. The shape of the interface was also examined after separation of the polymer sheets by scanning electron microscopy (SEM). In the case of iPP–POE sandwich the POE residues remaining on the interface after separation were additionally dissolved in water.

The tensile experiments were carried out using an Instron Tensile Test Machine.

RESULTS AND DISCUSSION

The studies carried out on the thin model system show that during polypropylene crystallization from the melt the shape of the interface undergoes changes.

It appears that the second, molten polymer flows into the regions between iPP spherulites growing near the interface. This takes place when a region of polypropylene melt near the interface is surrounded by a continuous crystallization front on one side (an extended developed crystallization front arises from impingement of growing spherulites) and by the melt of the second polymer on the other. The deformation of the interface at such places starts at the moment when the iPP melt becomes completely occluded by spherulites and the melt of the second polymer. The deformation ends with the completion of crystallization of spherulites, when all of the polypropylene melt is converted to spherulites. In this way the interface between the two polymers becomes developed, in contrast to its initial flat shape.

It should be noted that the deformation of the interface and formation of influxes of the second polymer inside polypropylene was observed independently of the type of second polymer. We have observed the described changes in the interface for polypropylene in contact with several polyethylenes of various molecular weights and viscosities and with polyoxyethylene. The only condition for the changes to occur is that the second polymer be molten during crystallization of polypropylene.

The formation of influxes near the interface occurs not only in thin, two-dimensional systems but also in bulk, sandwich-like samples. The sandwiches of polypropylene with other polymers were crystallized in the way described in the Experimental section (crystallization of polypropylene was carried out in the temperature range 130–135°C, at which the second polymer is molten). After solidification of the sample, thin sections were cut out perpendicular to the initial interface and examined by means of a polarizing microscope. The micrographs of the sections (*Figure 1*) show many influxes of the second polymer between iPP spherulites. The influxes are often very deep, of the order of several average radii of spherulites. For the crystallization temperature of 135°C, the average depth of influxes of polyethylene into iPP is 0.34 mm, i.e. 4.7 times the average radius of polypropylene spherulites growing at that temperature. The deepest observed influx was 1.45 mm long.

The interfaces of bulk samples were also examined by means of scanning electron microscopy. The micrographs (*Figure 2*) reveal a great number of influxes in which deformed residues of the second polymer often remain after the tearing of the sandwich along the interface. Those remnants are caused by the shape of the influxes which are often pear-like (see *Figure 1*). Moreover, the influxes are frequently not separated from one another, but form large, branched subsystems near the interface. Numerous, large influxes considerably modify the shape of the interface (which was flat before crystallization).

The following explanation for the phenomenon of interface deformation and formation of influxes is offered: During the conversion of polymer melt to spherulites, its volume shrinks due to the denser packing of molecules in the crystal form than in the melt. The decrease of the specific volume of polymer due to crystallization is usually of the order of several per cent. In *Table 2* the volume defect due to crystallization of isotactic polypropylene as a function of the crystallization temperature is shown. The initial data used for the calculations were taken from refs. 10 and 11.

Spherulites occluding some region of the melt prevent any supply of new melt from the rest of the sample. Further spherulitic growth in such regions induces a volume defect due to the density change during crystallization. The volume defect is compensated by the deformation of the interface and flow of the second polymer into those regions. The formation of influxes described is shown schematically in *Figure 3*.

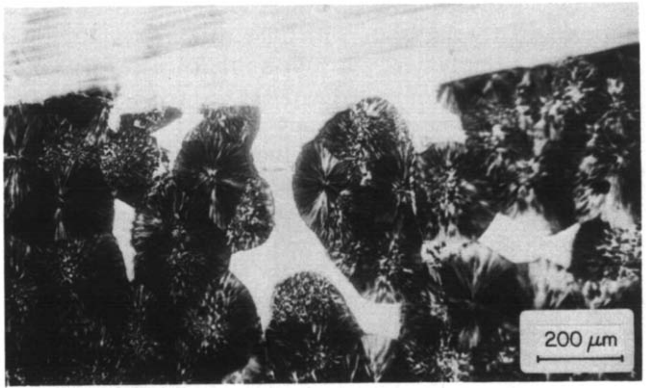

Figure 1 Optical micrograph (crossed polars) of a section cut from a sandwich of iPP and LDPE (Lupolen 2410S) isothermally crystallized at 135°C

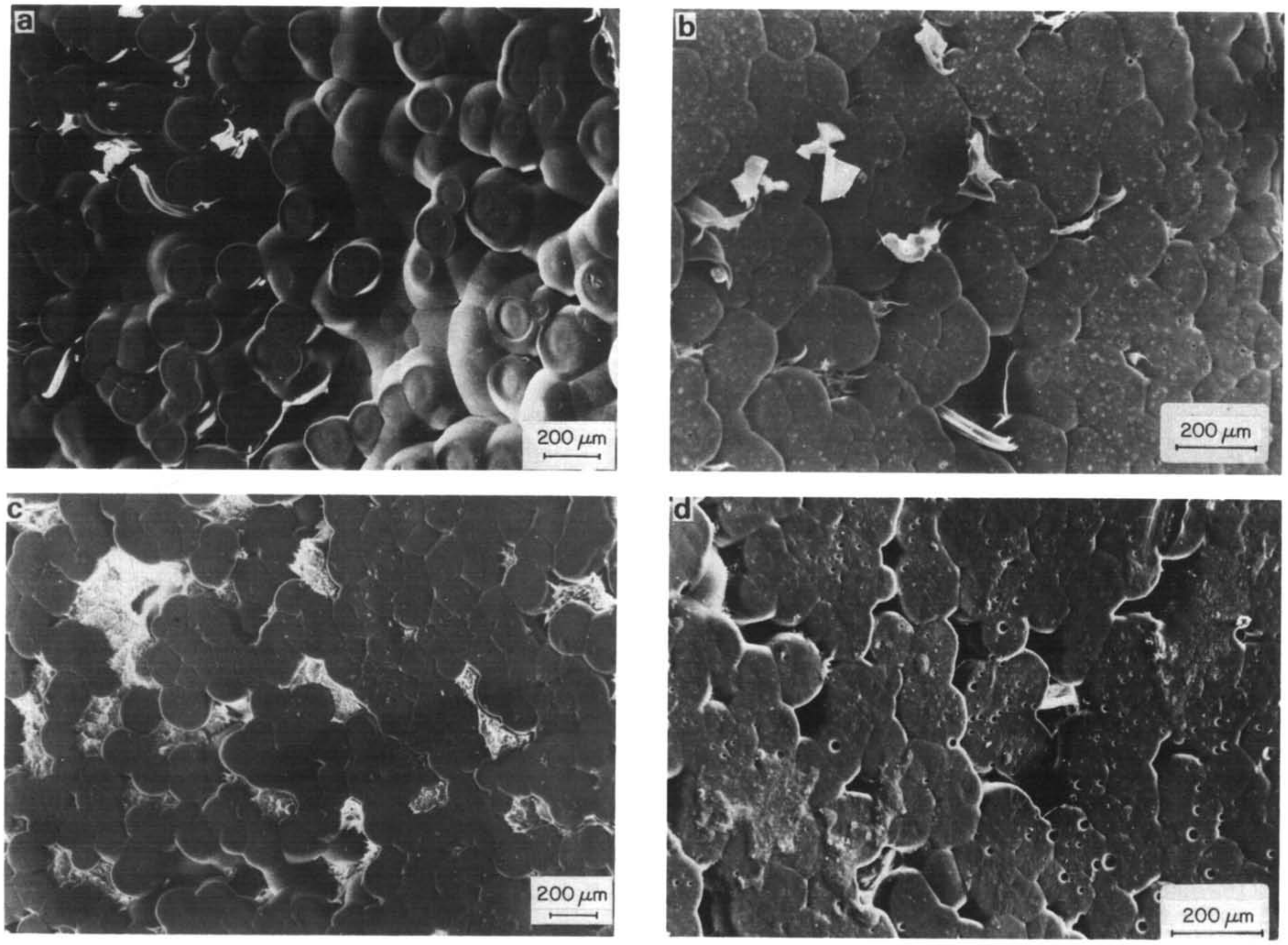

Figure 2 SEM micrographs of the interfade between iPP and: (a) LDPE (Lupolen 2410S); (b) LDPE (Lupolen 3010S); (c) HDPE (Lupolen 6011L); (d) POE

Table 2 Molar volumes of iPP melt and crystal, and relative volume defect due to crystallization at given temperature

T_c (°C)	V_{melt} (cm^3 mol^{-1})	$V_{crystal}$ (cm^3 mol^{-1})	$\Delta V/V_{melt}$
110	52.04	46.07	0.1147
115	52.19	46.14	0.1159
120	52.35	46.21	0.1173
125	52.50	46.28	0.1185
130	52.65	46.35	0.1197
135	52.81	46.42	0.1210

The mechanism of formation of influxes near the interface between two polymers is very similar to the formation of 'weak spots' with holes inside the volume of a crystallizing polymer[12]. It follows that the formation of influxes is strictly connected with the growth of the spherulitic structure. The influxes are always formed near the interface when one of the polymers crystallizes while the second is in the liquid state. Their number and dimensions depend (similarly as in formation of weak spots[12]) only on the parameters of the spherulitic structure, mainly the primary nucleation. Experiments with different polymer pairs confirm these conclusions.

Another question that arises is whether the adhesion between melts of two polymers is enough to cause the flow, or whether an additional force, e.g. external pressure, is also required. In order to answer this question we carried out crystallization of model bulk samples under low vacuum (0.5 mmHg). Examination of sections cut from the samples after solidification showed that under these conditions influxes are also formed and their dimensions are no different from those formed in samples crystallized under atmospheric pressure. The next experiment was designed to show the effect of adhesion between the two polymer melts. The polymers were separated by a thin layer of an adhesion-lowering agent, which was ethylene glycol and/or the commercial agent 'Silform' (Polish product). Examination of the interface by means of optical microscopy (sections cut perpendicular to the interface) and scanning electron microscopy (*Figure 4*) shows that the presence of an anti-adhesive agent on the interface drastically reduces the number and size of the influxes in those areas of the interface where the agent was present during crystallization. On the basis of the above experiments one can conclude that adhesion between the polymers is a sufficient driving force for the deformation of the interface and the formation of influxes.

The deformation of the interface may influence the mechanical properties of the system because of a large increase in the interface area and also its very developed shape (influxes are often pear-like, see *Figure 1*), so the separation of the polymers requires breaking of the second polymer influxes (see also *Figure 2*). Shear tests[2] (single lap joint samples, shown schematically in *Figure 5*, were used) were carried out for sandwich model samples of iPP with several polyethylenes. The samples were

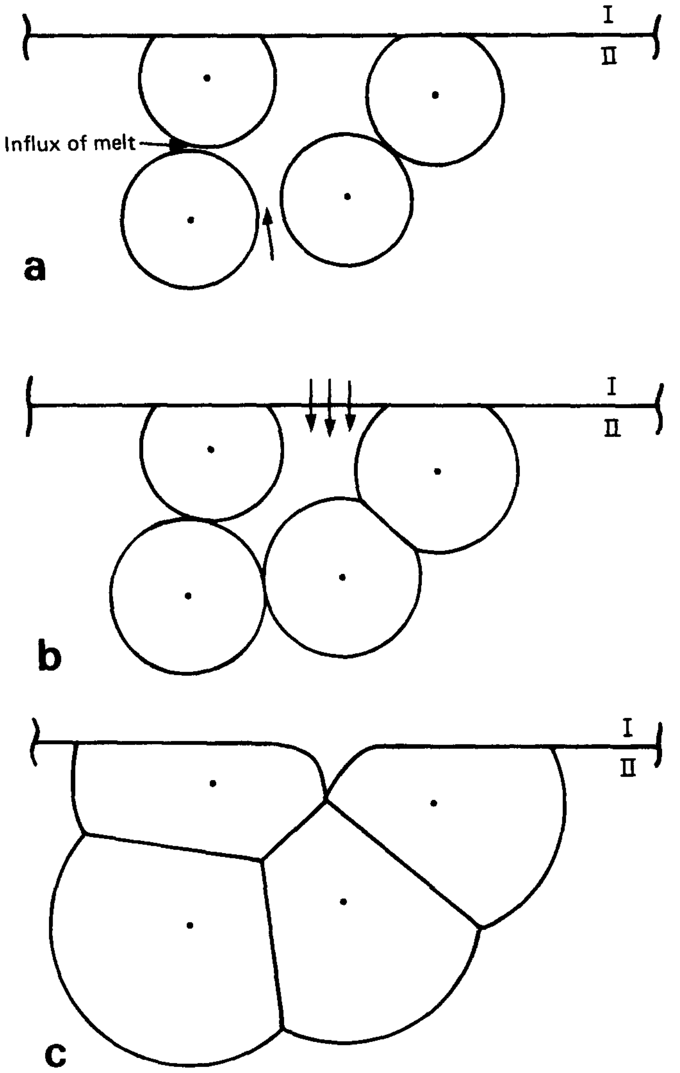

Figure 3 Schematic representation of subsequent stages of influx formation: (a) Situation before the beginning of interface deformation—melt of crystallizing polymer is able to flow into the region surrounded by the spherulites. (b) The region is completely occluded by the spherulites and the deformation of interface starts to proceed. (c) Final stage—spherulitic crystallization is completed and the influx of non-crystallizing polymer melt has formed. (I = melt of polymer not able to crystallize at a given temperature, II = polymer able to crystallize at this temperature)

prepared in two ways: one set of samples was crystallized isothermally at 135°C and then cooled to room temperature, and the other set was quenched from the melt. In the samples crystallized isothermally many influxes were present, whereas the quenched samples had an almost flat interface, without influxes. Drawing of the samples caused separation of the components along the interface. The stresses causing separation of the sandwich components are presented in *Table 3*. It is seen that for all compositions studied the stress increases by about three times if the interface is developed with influxes, so the influxes have a great influence on the mechanical properties of the contact between polymers. It is necessary to remark that the adhesion strength between polymers is the same in both crystallized and quenched samples, but the change in the interface shape causes an increase in the stress required to separate the lap joint. Frequently formed ties (pear-like influxes) must be broken in order to separate both polymers completely.

Deformation of the interface during crystallization was investigated in model systems but it also occurs in real blends, when the size of the inclusions is comparable to the spherulite size. It sometimes happens that inclusion of the non-crystallizable or molten component of the blend shuts in some part of the melt of the crystallizing matrix surrounded on the other side by the growing spherulites. Deformation of the drop-like inclusion occurs during further growth of spherulites in the same way as in the model systems tested. The situation is shown schematically in *Figure 6*. The deformation can also break the inclusion into separate parts. In order to demonstrate this effect a model sandwich of iPP and LDPE (Lupolen 2410S) was melted and isothermally crystallized several times. The large influxes formed during the first crystallization process may break into droplets in a subsequent melting and crystallization cycle. In the course of further crystallization such droplets could be deformed. Sections were cut from the sample after the last round of crystallization and examined by means of a polarizing microscope. The micrograph (*Figure 7*) shows such a deformed inclusion at a large distance from the initial interface. Examination of the neighbouring sections indicates that it is a real inclusion, not an influx. Its deformation is so high that it looks like branching.

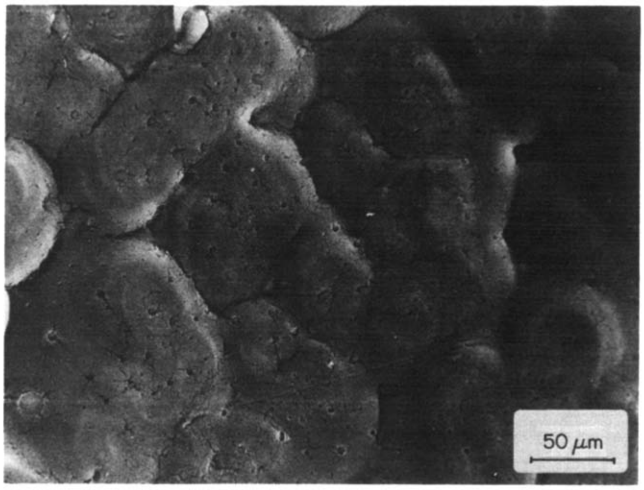

Figure 4 SEM micrograph of the interface between iPP and HDPE (Lupolen 6011L) in the presence of anti-adhesive agent ('Silform')

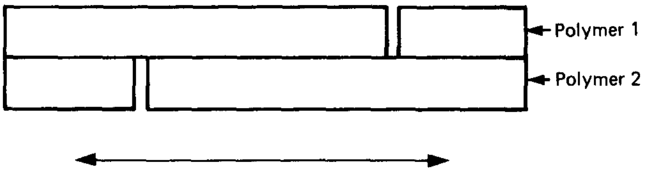

Figure 5 Scheme of the sample in shear tests (single lap joint sample)

Table 3 Stress (calculated per unit surface area of interface) required for separation of polymers in shear tests (single lap joint) for several polymer pairs

	Stress (MN m^{-2})		
Polymer pair	Crystallized sample	Quenched sample	Ratio of stresses
iPP–LDPE (Lupolen 1800S)	1.04	0.30	3.49
iPP–LDPE (Lupolen 1800M)	1.43	0.45	3.16
iPP–LDPE (Lupolen 1800H)	1.24	0.45	2.74
iPP–LDPE (Lupolen 3010S)	1.02	0.33	3.10
iPP–HDPE (Lupolen 6011L)	3.33	0.94	3.47

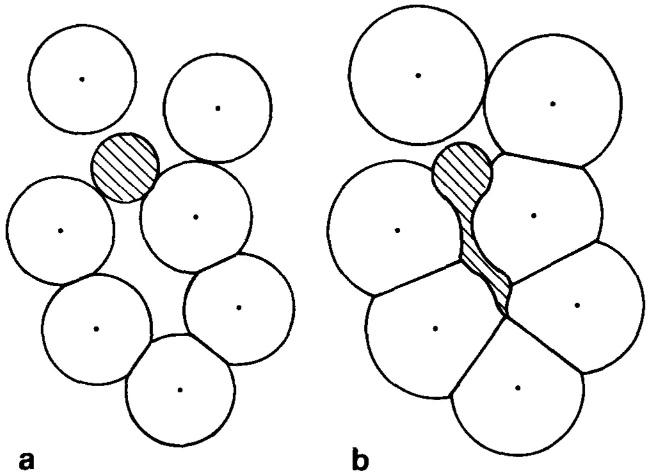

Figure 6 Schematic representation of drop-like inclusion deformation during crystallization of the matrix: (a) melt completely occluded by spherulites and the inclusion—their deformation starts; (b) deformed inclusion after completion of crystallization

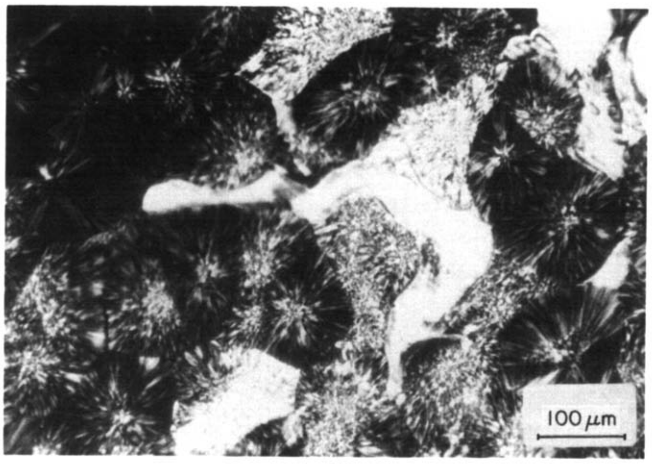

Figure 7 Optical micrograph (crossed polars) of deformed LDPE inclusion in iPP matrix

The deformation and branching of inclusions in blends improves the mechanical properties of the blend in the same way as was described above for model systems (lap joint samples).

CONCLUSIONS

On the basis of the results of this study the following conclusions can be drawn:

Spherulitic crystallization of a polymer near the interface with another polymer causes deformation of the interface in the form of numerous, deep influxes.

The deformation is caused by the change in polymer density during conversion of the melt to solid. The volume defect that arises is compensated by the second polymer flowing into the regions where this defect cannot be compensated by the flow of melt of the crystallizing polymer, this being prevented by spherulites surrounding these regions.

Deformation of the interface is conditioned only by the formation of the spherulite structure of the crystallizing polymer. The type of second polymer in contact plays no role in the flow phenomenon. It is only required that this second polymer be in the molten state during crystallization of the first one. The primary nucleation process in the crystallizing polymer decides the distribution and dimensions of the influxes.

Deformation of the interface explains the large thickening of the interface between crystallizable polymers observed by other authors[5,6,8]. Such an explanation is proposed to replace the one made in terms of mutual diffusion of polymers in contact during melt-annealing.

As a result of interface deformation, its area strongly increases. This leads to considerable improvement of the mechanical properties of the interface region.

The influx formation takes place not only in model systems but also in blends. The phenomenon can cause deformation of inclusions of the second polymer dispersed in the crystallizing matrix. This, in turn, leads to improvement of the tensile and impact properties of the blend. In some cases breaking of inclusions into separate droplets can occur, which causes better dispersion of the inclusions in the matrix.

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