

Thermo-optical, DSC and microfractographic investigation of PE–PE mixtures

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The nucleation effect of high-density polyethylene (HDPE) to low-density polyethylene (LDPE) and the structure of the resulting directional LDPE morphology was studied using thermo-optics, differential scanning calorimetry (DSC), X-ray diffraction and microfractography. Thermo-optics and DSC showed a higher nucleation activity of HDPE compared with the heterogeneities within the LDPE melt. The parallel and more perfect arrangement of the chain segments in transcrystalline LDPE resulted in a higher melting temperature, a difference in unit-cell spacing and a less ductile behaviour during fracture than with spherulitic LDPE.

1. Introduction

The crystallization of polymer melts is commonly induced by “natural” heterogeneities contained in the polymer melt. The result is a spherulitic or similar morphology. This nucleation can be improved by adding to the polymer certain substances which show higher nucleation activity, and thus start nucleation at smaller undercooling. In the same way, a surface of a material which is in contact with the polymer melt is regarded as nucleation active if its nucleation activity is higher than that of the heterogeneities of the melt. On such surfaces, a directional morphology, transcrystallinity, is generated because once the polymer is nucleated at the surface it can crystallize into the melt. This effect has been well known to exist for a long time, for many polymer/surface systems [1, 2] and has also been observed in the nucleation of low-density polyethylene (LDPE) by high-density polyethylene (HDPE) as reported earlier [3, 4].

The aim of the present work was to obtain further detail concerning whether (1) the different nucleation activities of the high-density polyethylene surface and the in-melt heterogeneities for the nucleation of low density polyethylene are detectable, (2) the nucleation at smaller undercoolings with HDPE as the nucleating surface, influences the structure of the resulting LDPE morphology, compared with the spherulitic morphology due to nucleation on in-melt heterogeneities, and (3) the differences in structure and mechanical behaviour between spherulitic and transcrystalline LDPE lead to a different microstructural deformation and fracture behaviour which is detectable by microfractography. The polyethylenes used were commercial LDPE and HDPE.

2. Nucleation activity

Two methods were used to investigate the nucleation activity: (a) thermo-optics using a transmission light

microscope with crossed polars and fitted with a heating stage, and (b) differential scanning calorimetry (Perkin-Elmer DSC 2-C).

From the appearance of a nucleation effect of HDPE on LDPE leading to transcrystallinity, it is obvious that different nucleation activities must exist between the melt-contained heterogeneities and HDPE. This becomes very clear if powders of the two polyethylenes are solid-state mixed and the mixture is melted and then cooled in a heating-stage microscope. Fig. 1 shows different steps during the cooling run between 105 and 92 °C. The HDPE insulates are solidified and after nucleation LDPE begins to crystallize on them. The growth of the spherical transcrystalline LDPE layer is stopped by small spherulites formed by nucleation on heterogeneities within the LDPE melt. DSC investigations were made also using a solid-state mixed powder mixture of both polyethylenes. Their ratio was such as to guarantee that a significant amount of transcrystallinity would be generated in the LDPE. Fig. 2a, curve 1, is the heating run whereby the powder mixture is melted. The cooling run 2, curve T, shows that nucleation and subsequent crystallization begin at a smaller undercooling as compared with the cooling run of the pure LDPE in Fig. 2b. With the cooling rate used (5 K min^{-1}) both the transcrystalline and the spherulitic morphology are generated. With isothermic crystallization at a temperature between the undercoolings necessary to activate the different nucleation sites, it should be possible to produce exclusively the transcrystalline morphology and therefore only one peak for LDPE in the thermogram. The generation of both morphologies during the DSC investigation has been proved using a sample taken off the DSC pan. Under a polarizing microscope in microtome cuts perpendicular to the flat side of the sample (Fig. 3a), and by direct inspection of thin areas of the unchanged specimen (Fig. 3b), it is seen that part of the LDPE is

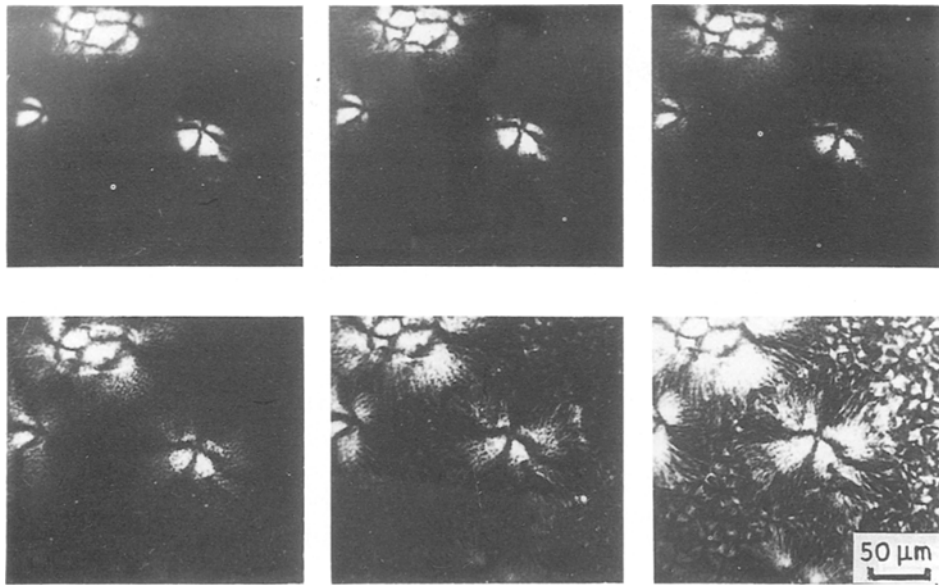


Figure 1 Different steps during cooling of a melted mixture of powders of LDPE and HDPE; a heating-stage microscope with polarized light was used.

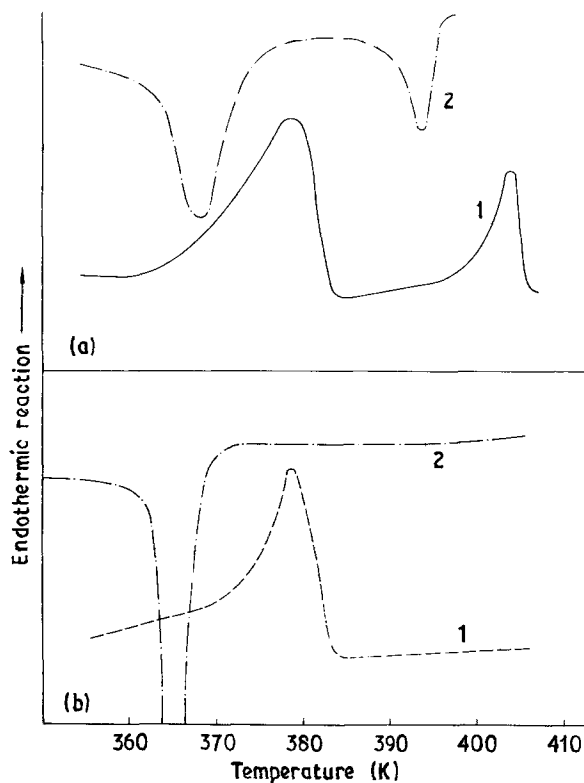


Figure 2 DSC thermograms of (a) a solid-state mixed powder mixture of LDPE and HDPE, heating run 1 and cooling run 2; (b) LDPE, heating run 1 and cooling run 2.

nucleated on HDPE insulates leading to a directed growth.

3. Structure of the transcrystalline morphology

From optical studies it is known [1, 5] that the transcrystalline morphology is built up from lamellae as is the case in spherulites. X-ray investigation [5, 6] and infrared dichroism [7] show that the *b*-axis of the unit cell of the polyethylene lies parallel to the growth direction, i.e. perpendicular to the nucleating surface. Our X-ray diffraction studies on transcrystalline

LDPE support this and show that in both the spherulitic and the transcrystalline morphology the unit cell is the same, but there are differences in the lattice spacings. Debye-Scherrer patterns were taken from three areas of a specimen prepared by melting and cooling (from 220 °C to room temperature at 2.6 K min⁻¹) a combination of test bars of LDPE and HDPE. The transcrystalline layer in the LDPE was about 80 μm thick. In the diffraction pattern from the transcrystalline middle part, the interference for the lattice spacing in the *c*-axis is significantly sharper than that from the spherulitic LDPE alone. The calculated value is 0.257 nm which lies between that of spherulitic LDPE and spherulitic HDPE. Thus it can be concluded that in the transcrystalline material there is a more perfect ordering within the unit cell and not so many molecule segments misfit the ideal parallel arrangement in the lamellae. It can be assumed that the possibility of the arrangement of side groups outside the crystalline lamellae and the conformational and translational motion of polymer segments into the correct arrangement is due to the higher crystallization temperature at which transcrystallization starts, and to the fact that in this morphology the lamellae are arranged in parallel. There is no need for branching to occur for space filling as is the case in spherulites.

This more perfect arrangement is supported by the resistance of the transcrystalline morphology in LDPE to oxidizing etchants, e.g. a solution of chromium trioxide in a mixture of sulphuric and phosphoric acid, which is similar to that of spherulitic HDPE [3]. The more perfect arrangement lowers the diffusion rate in the crystalline regions and protects reactive sites within the macromolecules from attack by the agent. The inverse influence of diffusion coefficient on the amorphous part of the lamellae can be assumed but may only be confirmed by further experiments.

The results mentioned so far and the well-known fact that the crystallization temperature of polymers influences their crystallite melting point [8], suggest a

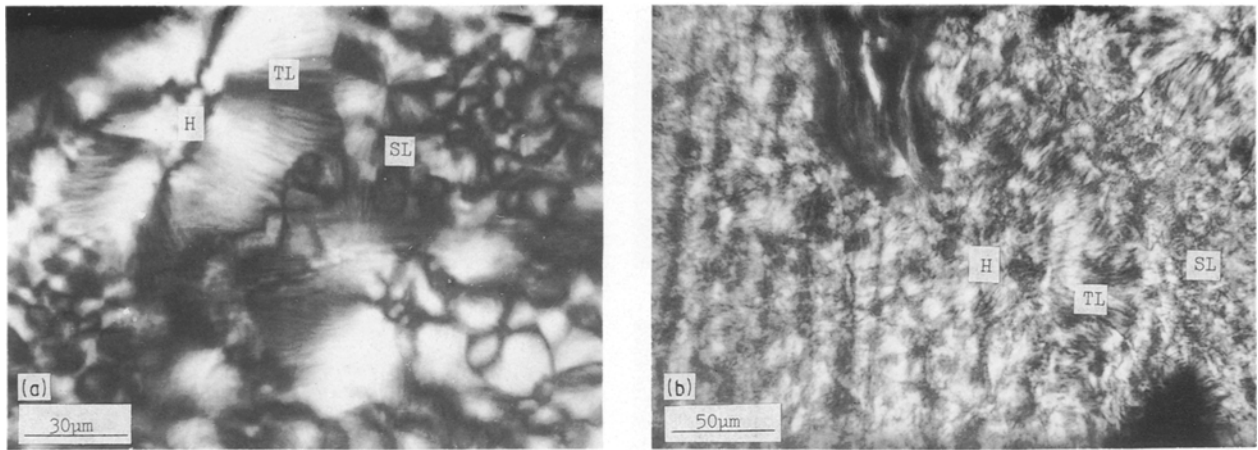


Figure 3 Cross-polarized photomicrographs of the DSC specimen according to Fig. 2a. HDPE (H), transcrystalline LDPE (TL) and spherulitic LDPE (SL) are marked. (a) Microtome cut; (b) direct visual image.

higher melting point of the transcrystalline material compared with the spherulitic material cooled at the same rate. The steps during a heating experiment under a polarizing microscope with a sample of the above specimen prepared from LDPE and HDPE bars with a transcrystalline middle part support this (Fig. 4). The spherulitic LDPE is always molten and the transcrystalline material of the same polymer begins to melt. The latter disappears at a temperature about 8 K above the spherulite melting point.

The clearly visible thermo-optically difference in the melting points cannot be seen in the DSC heating runs. Fig. 5 shows the thermograms of a sample prepared by solid-state mixing of 2.2 wt % HDPE and 97.8 wt % LDPE and filled in the DSC pan. In the second heating run only one melting peak of LDPE

without any shoulder appears. The melting peak is the same as that for the first heating run in which all LDPE is still spherulitic. A possible explanation is to assume that the increase in the lamellar melting point due to the more perfect ordering is compensated by another effect. This may be a decrease due to smaller crystallite size which, on considering the Thompson equation, should have a lower melting point. From the thermo-optic experiment, a higher melting point can be inferred. It is known that with spherulitic material the birefringence often disappears just before the DSC crystallite melting temperature is reached, because the lamellae or blocks can begin to rotate and thereby destroy any anisotropy. On the other hand, in transcrystalline material the lamellae are arranged more perfectly parallel to each other and can remain in that

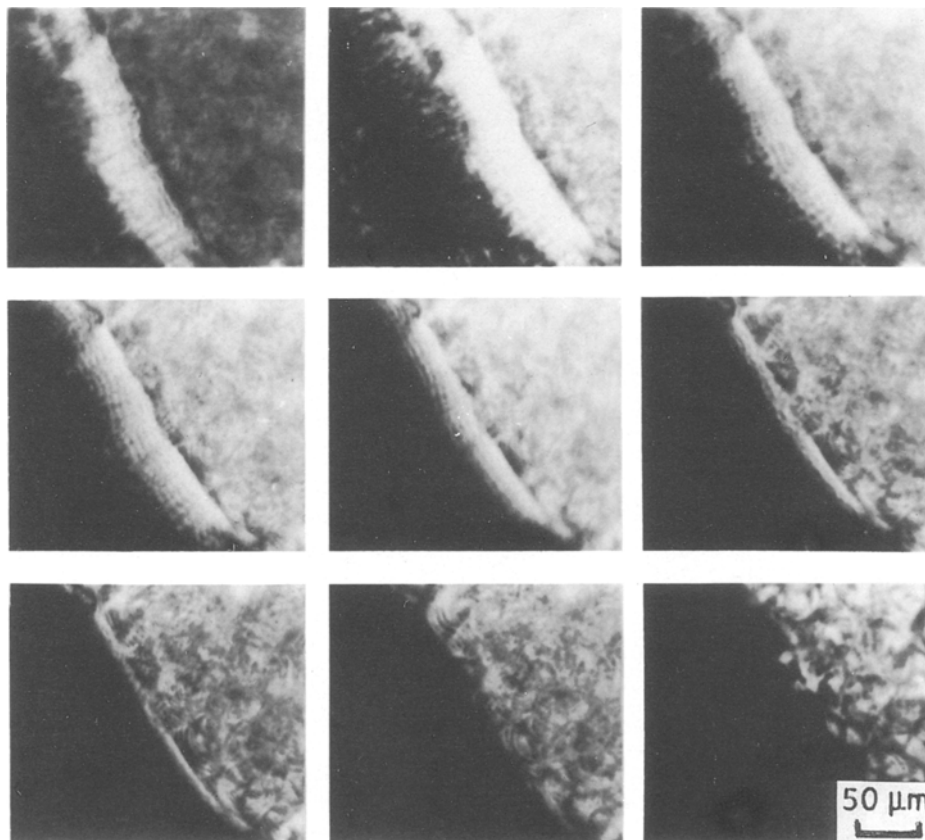


Figure 4 Different steps during the heating of a system of LDPE and HDPE bars melted together; a heating-stage microscope with polarized light was used.

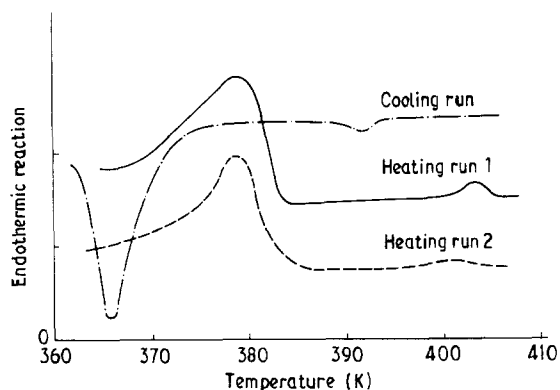


Figure 5 DSC thermogram of a specimen consisting of a solid-state mixture of LDPE and HDPE.

position until a higher temperature is reached. The oriented chain arrangement within the transcrystalline morphology results in a greater thermal expansion coefficient perpendicular to the surface normal than that parallel to it [9]. It seems possible that a quasi-thermotropic behaviour may be assumed, i.e. the lamellae and polymer chains retain their positions relative to each other just above the crystallite melting point, leading to remanent birefringence, as is the case in liquid crystalline substances.

4. Microfractography of transcrystalline LDPE

Taking into account the differences in crystallization kinetics, the structure and morphology between spherulitic and transcrystalline morphologies, it can be assumed that both morphologies will show different mechanical properties. Therefore, a knowledge of transcrystalline morphology and its mechanical properties is necessary for two reasons. First, this morphology can grow to macroscopic thickness and then be the main or only morphology in a polymer part, e.g. in a film. Second, transcrystalline morphology can be regarded as a nucleation-induced interfacial region or

mesophase, as reported by Theocaris [10] and therefore it can play an important role in polymer matrix composites or blends because the microstructural steps of deformation and fracture in the mesophase can influence or determine the integral properties of the polymer part as a whole. From this point of view the fractographic behaviour of transcrystalline LDPE was studied by SEM. The specimens were bulky ones prepared from bars of both polyethylenes melted together as described above for the X-ray studies.

Fig. 6a and b give microfractographies of the middle part of a fracture surface as-received by notch-bend impact test at room temperature with a razor blade notch. Obviously the transcrystalline LDPE is less ductile than the spherulitic material of both polyethylenes. The typical dimples and stretched fibres are absent. A greater strength and a smaller elongation at yield point can be assumed. The greater strength agrees with the greater Young's modulus of the transcrystalline LDPE as compared with the spherulitic material, as found by other authors with films containing both polyethylene morphologies [11].

The relatively low impact depth and elongation at yield point can be compared with those of coarse-grained spherulitic morphologies which are known to show less impact depth and greater strength than small-grained spherulitic material [12].

The deformation and fracture behaviour of the transcrystalline material is due to the more perfect ordering within the lamellae and to their preferential parallel arrangement, whereas in spherulites the lamellae are branched for space filling. Another point is that transcrystalline material from this point of view can be regarded as a single-crystal-like bulk, i.e. there are no grain boundaries such as are present between spherulites. The latter are regions of relatively weak mechanical bondings and therefore easily plastically deformable under dynamic stress. From this arises the high energy dissipation and high toughness of small-grained spherulitic morphologies [12]. The lack of such weak boundaries seems to be the most important factor for the low ductility of the transcrystalline region as shown in Fig. 6a and b.

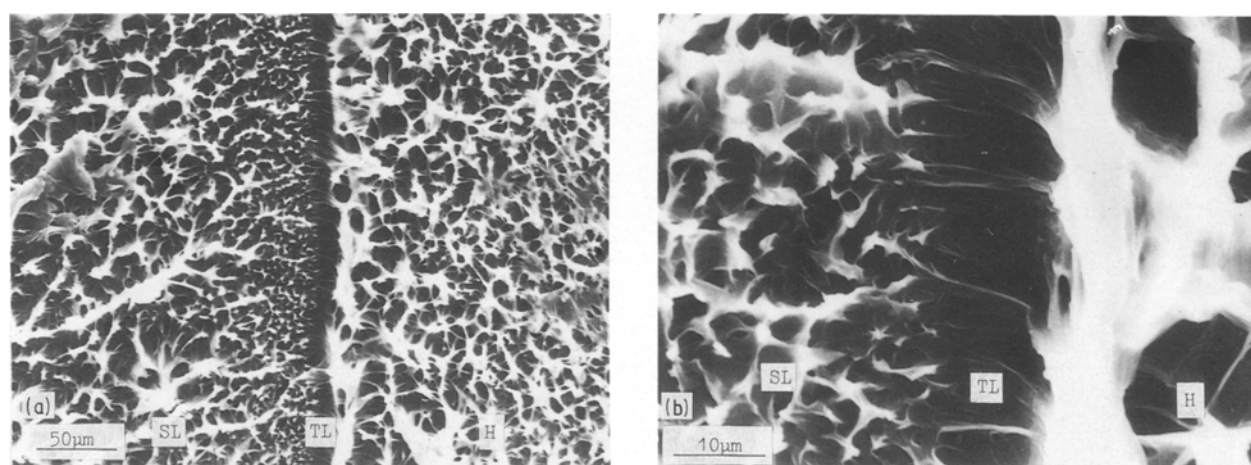


Figure 6 (a, b) Microfractographies of the transcrystalline LDPE middle part (TL) and adjacent spherulitic LDPE (SL) and HDPE (H); the specimen was prepared by melting and crystallization of bars of both polyethylenes in contact with each other; the impact test was used with a razor-blade notched specimen.

5. Conclusion

The greater nucleation activity of HDPE surfaces to LDPE compared with that of the heterogeneities within the LDPE melt can be shown directly by heating-stage experiments and DSC studies. At the interface between LDPE and HDPE the crystallization begins at a lower undercooling, as in the LDPE bulk. This effect is only detectable with DSC samples in which a large contact surface between the two polymers exists, as is the case in solid-state mixed powder mixtures. In such samples, as well as in massive samples prepared by melting and cooling solid-state mixed powders of both polyethylenes in a mould, the HDPE particles are surrounded by transcrystalline LDPE. Spherulitic and transcrystalline LDPE have the same unit cell but with small differences in the *c*-axis spacing. The differences in structure of both morphologies should result in different melting points of the crystalline regions but are only detectable by heating stage experiments. In DSC thermograms this difference cannot be seen. If this discrepancy is due to the thermotropic behaviour of the transcrystalline morphology and its smaller crystallites, the final conclusion can only be drawn if the microscopic structure is known. Therefore, transmission electron microscopy and small-angle X-ray diffraction studies must be undertaken.

The differences in structure between transcrystalline and spherulitic LDPE result in different mechanical properties as shown by microfractography. The transcrystalline morphology is less ductile than the spherulitic one, a result which is in agreement with the higher Young's modulus of transcrystalline LDPE, as known from the literature for films [11].

The nature of the nucleation sites for LDPE at the interface to HDPE is still unknown. As a working hypothesis, it can be assumed that a limited interdiffusion or mixing of both polyethylenes takes place. In this way some LDPE chain segments can be built into the crystallizing HDPE. The immobilization of these segments lowers the activation energy for nucleation.

The possibility of the generation of a transcrystalline mesophase has to be taken into account in the development of composites and blends. Owing to its mechanical properties and thermal expansibility different from those of the unaffected bulk material, it can influence the properties of the whole composite. For mathematical modelling of the macroscopic thermal and deformation behaviour of composites or blends, the level of the mechanical properties and its anisotropy, as well as the thickness of the transcrystalline mesophase, must be measured. The different thermal expansibility parallel and perpendicular to the nucleation surface can lead to the generation of internal stress within the mesophase during cooling.

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