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In celebration of the 60^{th} birthday of Dr. Andrew K. Galwey

THERMOANALYTICAL PROCEDURES TO IDENTIFY THE MORPHOLOGY OF POLYCRYSTALLINE MATERIALS

The inhibition of reorganisation

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Abstract

Polypropylenes of differing morphologies were examined by differential thermal analysis. The problems of reordering during the programmed heating are discussed. Four potential procedures by which the reordering could be inhibited are considered, and three of these are experimentally assessed. Their advantages and deficiencies are identified. Two pretreatments, an etching and a crosslinking, are recognised as able to qualitatively characterise the initial morphology, with a preference for the former. A test to identify the occurrence of reordering is identified.

Keywords: DTA, morphology of polycrystalline materials, reorganisation

Introduction

The detailed organisation and orientation of those macromolecules within polycrystalline systems have a key influence upon the performances, particularly the physical properties, of those structures of which they are part. It is essential, therefore, that a detailed appreciation of the order and orientation in substrates be achieved. The ability to assess changes of morphology, as a consequence of treatments received and environments experienced, is also necessary.

Methods for the assessment of the molecular orientation levels of both the highly and poorly ordered volumes are established (see for example Refs [1, 2]).

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While the recognition of crystalline type and morphological form is possible by other techniques such as X-ray diffraction, and infrared spectroscopy, a full appreciation of the distribution of forms, and sizes of order requires the use of thermal methods.

Differing crystalline types, with their differing free energies, will disorder at differing temperatures. Alternative morphological forms of the same crystallinity, such as folded chain or extended chain lamellae, may also exist. Their thermodynamic stabilities are different and these forms will disorder at different temperatures. The specific sizes of each type and form of order all possess particular free energies, and will, therefore, disorder at individual temperatures related to those sizes. Further, the 'effective environment', within which an ordered volume is located, can also influence its thermal stability.

All the facets identified above describe the unique identity for each individual ordered unit within a structure. These units, and their amounts, will determine, depending upon their specific interactions and dispositions, the physical performance/properties of that structure. All the above features, with the exception of the amount, determine the temperature at which each particular ordered unit will melt.

Detailed observations of the precise temperatures at which endothermic changes are induced will reflect the distribution of the types, forms, sizes and environments of the ordered volumes within a polycrystalline substrate. This 'spectrum' of temperatures at which endothermic changes are induced can be positively provided by differential thermal analysis. The observed endothermic curve is a composite of the individual endothermic effects and is characteristic of the particular morphology of the examined sample. Although DTA is essentially a qualitative tool, when an effective resolution of the individual endothermic components is achievable, the observations do provide a 'feel' for the relative amounts of each ordered entity.

The ability to realise the full potential from DTA curves to provide morphological details, requires that during both sample preparation and the programmed heating no molecular reorganisations occur other than the induced fusions. Almost all fabricated polycrystalline structures are far removed from the equilibrium state and are metastable. Changes in these materials to more stable molecular arrangements are certain to occur, particularly with the aid of thermal energy. These products of reorganisation will disorder at higher temperatures than the original ordered element. When such reorganisations occur, the recorded DTA curve will no longer reliably reflect the initial (as presented) morphological character of the sample. The less stable (lower melting) ordered elements may, subsequent to fusion, either reform or increase in size to more thermally stable, i.e. higher melting, ordered entities. Apart from that endotherm from the additional higher stability component, a recrystallisation exotherm element may further affect the overall shape of the recorded curve. An example of such an effect is reported in the observation of two endothermic peaks from certain polyamides [3], which is interpreted by the authors, for their specific samples, on the basis of there being concurrent fusion and recrystallisation. Changes in the fraction ordered in polycrystalline materials can arise during the imposition of a higher temperature isothermal condition [4]. As well as changes to the total fraction ordered, variations in the character of that order can also occur. Lamellae are the most frequently found form of order with flexible long chain molecules. During a higher temperature isothermal annealing, increases in the fold length of folded chain lamella forms are observed [5]. In most instances these increases in fold length arise without fusion, and involve significant mass transport along the molecules through the ordered volume to adjust to the new dimensions and a lower free energy, more thermally stable state. Usually, during thermal annealing, those defects associated with the order migrate and coalesce, with an overall decrease in their numbers. The defects may be impurities, chain ends, structural irregularities, point defects, and defective stereo-regularity. Any 'frozen-in' non-equilibrium molecular arrangement can also be described as a defect. The presence of any defect will add to the total free energy of that system. An annealing may result in a decrease in free energy and enhanced thermal stability. The fold length changes on annealing may also generate voids, i.e. additional defects, within the structure. During thermal annealing, those segmental movements which extend the fold length also provide the mechanism for internal defects to move to the surface of that particular ordered entity, with a net decrease in the total free energy and an enhanced thermal stability. Once the sample temperature rises above the glass transition temperature, segmental motions will then enable internal stresses in the low order volumes to be relieved. Changes in the molecular tie segments between ordered volumes, the sizes of ordered volumes and their orientations also result. Apart from the 'internal' defects discussed above, other defects will initially be present in the surfaces of the ordered volumes. These include the chain fold itself, extended chain 'loops', chain ends, and the molecular 'tie' lengths to other ordered units. These affect the surface free energy and the effective thermal stability of those ordered volumes.

Fusion occurs over a range of temperatures for all polycrystalline macromolecular systems because of their metastable condition,.and the presence of ordered entities with a spectrum of stabilities. One further factor is relevant to the observations of fusions of macromolecular order: fusion itself is a time dependent process. To 'release' a molecular chain sequence from an ordered volume requires concerted actions with, concurrently, an available adjacent free volume of such a dimension as to be able to accommodate elements of the chain sequence as they are released. Actions are sequential, starting at folds, chain ends or other defects. The time dependent character is at its most significant in the melting of the larger and more perfectly ordered volumes. The mechanistic requirements for the disordering of macromolecular ordered structures are such that when these systems experience a dynamic heating regime (such as that imposed in a DTA observation), there is a significant time interval required for that fusion, from its onset to completion. One consequence of this time interval is that fusion is observed to occur over a significant temperature range. In contrast, the disordering of small molecule ordered systems is relatively rapid. The temperature range over which structural changes occur may be so small that the transition may be regarded as effectively isothermal.

The thermocouple location with respect to the fusion interface, and the movement of this interface from the sample surface through its bulk to the centrally located thermocouple tip, ensures that the temperature range over which fusion is observed is smaller in a DTA based observation compared with that range recorded on the examination of the same sample, at the identical heating rate, by differential scanning calorimetry [7].

Whenever dynamic heating is applied, there will always be superheating of the metastable ordered volumes. Superheating occurs whenever the rate of fusion is so slow that the temperature of the ordered volumes exceeds the thermodynamic equilibrium fusion temperature. Restrictions upon movements in the amorphous volume will increase the effective free energy of the melt, retard the fusion, and result in an enhanced superheating.

The full potential of thermal methods for the characterisation of the detailed morphology within polycrystalline substrates can only be realised when careful attention is given to the likely distortions to observations as discussed above. Sample treatments and experimental procedures must be achieved which prevent morphological reorganisations, while concurrently avoiding the introduction of additional uncertainties. The potential for superheating should also be minimised. This paper examines both the possibilities for treatments, and procedures, using polypropylenes of different morphologies as the test substrate.

The prevention of reordering

A) The process of reordering, like that of fusion, involves mass transport which, for long chain molecules systems, means that such changes require time. When very fast heating rates are applied, the objective is to attain such sample temperatures where every ordered element, whatever its stability within the total structure, will have melted before any significant reordering has occurred. The recorded fusion behaviours should then be representative of the initial metastable morphology. The use of fast heating as an analytical procedure has been suggested by others [4]. At very slow heating rates, there is time for significant reorganisation. Comparisons of the observations at markedly different heating rates should yield clear indications of the occurence of induced reordering.

B) The major morphological forms in polycrystalline materials are folded chain lamella or extended chain lamellae. If reorganisation occurs, segments will move principally in the original chain direction. Anisotropic films or fibres should have this chain direction markedly oriented in the long length direction of the sample. At reorganisation there is a clear reduction in sample length. The holding of these substrates at constant length should markedly retard or inhibit reorganisation.

C) Reorganisations, primarily fold length changes, and defect diffusions involve molecular movement at the surfaces of ordered volume lamellae, which comprise chain folds, loops, ends and tie molecules. Through the scission of these chain folds, loops and tie segments, it is possible to suppress reorganisation [8]. The application of drastic chemical etching could not only achieve the required scissions but also might destroy the whole accessible amorphous mass. However, there is strong evidence to suggest that strained chain elements, such as those at chain folds, and in tie segments, are more rapidly attacked [9].

D) The occurrence of reordering can be prevent through physical inhibition of the essential molecular movement. The introduction of appropriately sited crosslinks between chains is one means of achieving this objective. Salovey *et al.*, [10] have shown that the formation of crosslinks in polyethylene by γ-irradiation occurs preferentially between adjacent folds and lamellae. The enhanced activity of the strained elements, such as at the fold, again suggests itself as the possible site of this action. Bair [11] has proposed that γ-irradiation provides a useful pretreatment for the characterisation of melting behaviour as any prior reorganisation is prevented by the crosslink insertion.

Experimental

Raw materials

(i) Rod

Isotactic polypropylene (ICI, GYE47) was obtained as a ca. 3 cm diameter rod within which the basic morphology was spherulitic. Using a lathe operating at minimum speed, finely divided samples were turned off the outer 2 mm sheath. The careful use of a sharp cutting tool enabled finely divided samples to be obtained from the inner 1 cm diameter core. Both these samples were separately mixed from lots extracted from equivalent locations along the rod length. Further subdivision was effected manually as required.

(ii) Slit film

This sample was a commercial product (Plasticisers PLC) designed for use as a carpet backing. The isotactic polypropylene was melt extruded as a blown film. This product was then slit to 1 cm widths and stretched ca. 6:1 in a 140–160°C air oven within which the polypropylene film surface temperature never exceeded 120°C.

(iii) Controlled fibrillation fibre

This sample, a commercial product (Plasticisers PLC) was designed for broad textile applications. The isotactic polypropylene was extruded as a film and water quenched. This film was then stretched in an air oven an 140–160°C at draw ratios of ca. 8:1. The film surface was brushed with a multipinned roller which initiated and controlled the disruption of the film into fibrillar elements that form the basic textile raw material for products such as carpet face yarns.

The stretch applied for both the slit film and controlled fibrillation materials must be sufficient to achieve products with positive fibrous (i.e. anisotropic) characteristics. The samples, in both cases, contained folded chain lamella elements within larger microfibrillar units. In contrast, the rod materials were spherulitic in which the folded chain lamellae had (as expected) their chain direction transverse to the radial directions of the spherulitic whole. X-ray diffraction observations indicate that in all samples the crystalline type was monoclinic.

Samples of both film products were subjected to either one or three minute exposures to 135°C. Further samples of the slit film were 'annealed' for two hours at 144°C.

Thermal analysis

Differential thermal analysis was utilised rather than differential scanning calorimetry. DSC is primarily a quantitative tool in both construction and operation; from the basic observations the attaining of qualitative informations is purely secondary. The consequences of the above are that the precise temperatures of any induced change and the shapes of the recorded enthalpic effects cannot be used with the same reliability as would be the case with observations from the use of instrumentation specifically designed to yield qualitative information, namely DTA. A more detailed comparison of the two techniques is examined elsewhere [7]. Reference has already been made to the sensed temperature width of an endotherm in DSC as being broader than that recorded in DTA for the same transition (loc. cit). This extra width impedes the resolution of closely occurring changes. It will result in a distortion to and a broadening of the recorded endothermal effects associated with each of the induced changes.

A DuPont 900 controller with a standard sample cell was used. Chromel-alumel thermocouples were centrally disposed within 4 mm glass holders.

Individual materials were cut to less than 1 mm^2 pieces and a 4 mg sample was mixed with a high viscosity, thermally stable (up to 250°C) silicone gum (Midland Silicones MS 2610) in a fibre to gum V/V ratio of 4:1. This system, when loaded into the 4 mm holder, formed a depth of 4 mm, within which the thermocouple tip was centrally located. The advantages of the gum are discussed elsewhere [7], but these include the elimination of recorded curve distortions caused by induced sample shrinkage and collapse. A more rapid relaxation post-transition stage is also achieved which will reduce peak width and improve transition resolution.

Glass beads were used as the reference, and all programmed heatings were in air at 10 deg·min^{-1}, unless indicated otherwise. All analyses were done in triplicate. A formal baseline was formed by linking the pre- and post-transition curve extrapolations with an S-shaped construction having its centre at the peak temperature. The recorded curve and constructed base line were digitised and the differences between the two calculated. The net ΔT values observed at identical sample temperatures from each of the three samples were added together. These additions were effected at fine increments across the temperature range of the experiment. The resultant combination reflected the representative DTA data for that sampled substrate. Each of these data sets was normalised using the maximum ΔT value of that specific data. The ordinate axes of the subsequently replotted data were of $\Delta T/\Delta T_{peak}$ values. The 'normalisation factor', the relative peak height, is also recorded. The replotted curves enable more facile comparisons to be made where the individual sample masses are not accurately constant.

Sample treatments

Four possible techniques were examined with polypropylenes of different morphology to assess their comparative effectiveness in preventing the occurence of reorganisation or reordering during the DTA programmed heating observations.

Method A

The time-dependent characteristics of the disordering, reordering and reorganisation processes in polycrystalline macromolecules are such that the extent of any reordering or reorganisation will be determined by the applied rate of heating. At sufficiently high heating rates it is anticipated that no reorganisation or reordering can occur before the whole system is completely fused. Programmed heating rates of 5, 10, 20 and 40 deg·min^{-1} were applied to the presented polypropylene samples to provide, by DTA curve comparisons, indicators of whether reordering or reorganisation has been prevented by the time parameters of the specific experiment.

Method B

The occurrence of reordering is usually accompanied by a shrinkage in length. Film and fibre samples, while being restrained from shrinking, were also examined by DTA. These restrained samples were prepared by winding the specified film or fibre around the outside of a 4 mm long, thin-walled aluminium tube of ca. 2 mm diameter. This 'loaded' length fitted neatly into the standard 4 mm sample holders. The remainder of the required 4 mm deep sample system volume was filled with the silicone gum. The thermocouple tip was then sited within the centre of the total volume.

Method C

The possibilities of molecular chain movement, a prerequisite for changes in the fold length of ordered lamella, can be markedly reduced by the scission of fold, loop and tie chain segments. The polypropylene samples were 'etched' in fuming nitric acid at 25°C in thermostat. Etching times of 24, 48 and 72 hours were used, after which the samples were washed initially in water, then in acetone, and finally dried.

Method D

An alternative technique for preventing the necessary molecular movement required in reordering is to introduce covalent cross links between the chains. The film and fibre samples were placed in tubes which were evacuated, sealed and then irradiated at 9 rad s^{-1} with γ-rays in a Co^{60} source (nominally 10^{4} Ci) to maximum dosage levels of either 2 to 5 Mrad. It was anticipated that crosslinking of the polypropylene would occur during the applied γ-irradiation. The specific objective of the current irradiation is to assess the influence of such a pretreatment on the subsequent DTA curves. The extent of any crosslinking was not assessed.

Results and discussion

The observed DTA curves (10 deg·min^{-1}) of the samples [the spherulitic, the slit film, and the controlled fibrillation polypropylenes] without any pretreatment are presented in Fig. 1. Although differences in the onset and peak temperatures, as well as of the shapes of the fusion endotherms, are apparent, which reflect variations in the initial sample morphologies, the detailed character of their features cannot be assessed.

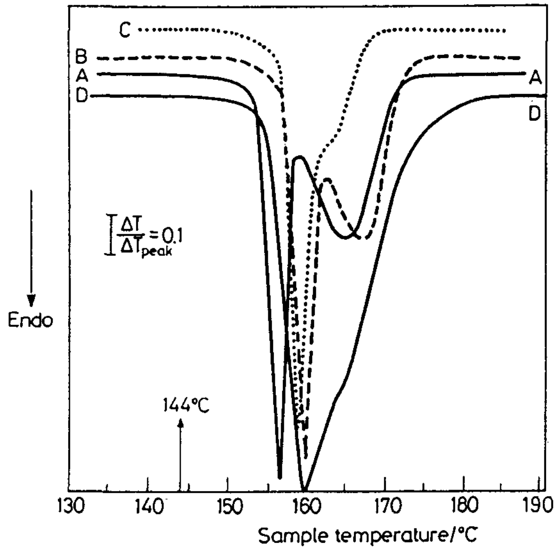

Fig. 1 DTA curves of polypropylenes of differing morphology (10 deg·min^{-1} heating rate, 4 mg in silicone gum), [(A) rod core, (B) rod sheath, (C) slit film, and (D) controlled fibrillation film fibre]

The occurrence of ordering and reordering during the programmed heating is demonstrated through the changes in the shapes and locations of the endothermic peaks recorded in the DTA curves of both the controlled fibrillation and slit film samples as respectively shown in Figs 2 and 4. The time dependent character of fusion will mean that, in the DTA experiment, the onset temperature will fall with increased heating rate, and 'the return-to-equilibrium base line' temperature will be raised.

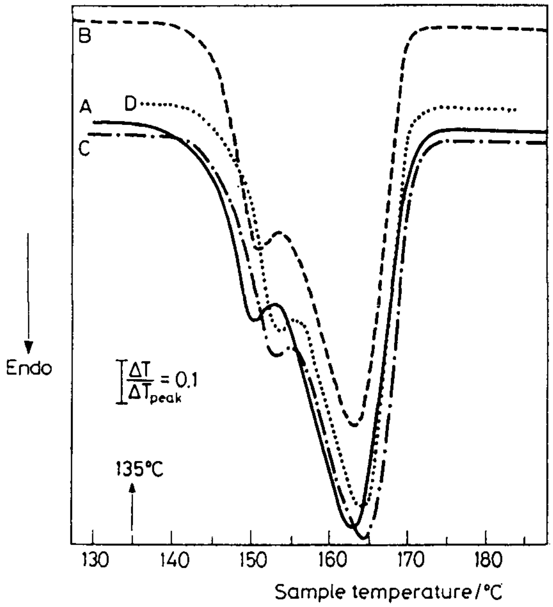

Fig. 2 DTA curves of controlled fibrillation film polypropylene: the effects of heating rate and restraint. [(A) 5 deg·min^{-1}, (B) 10 deg·min^{-1}, (C) 20 deg·min^{-1}, (D) 40 deg·min^{-1}, and (E) restrained and 10 deg·min^{-1}]

When there is no reordering within the sample, there should be little movement in the sample temperatures at the endothermic peaks with change of heating rate. The observed shift to higher temperatures at the slower heating rates arises as a consequence of the concurrent reordering to more thermally stable ordered volumes.

The shift in peak temperatures to lower values at higher heating rates can be used as an indicator of the occurrence of reordering. Although the faster heatings result in fusion with reduced reordering, the ultimate peak widths associated with the 'loss' of each size and type of order are broader. Their consequent independent resolution from the net endotherm becomes impossible. The loss of the low temperature shoulder in the 40 deg·min^{-1} heating rate DTA curve in Fig. 2 reflects this situation for the controlled fibrillation sample.

The use of 'restrained' samples as a possible means for preventing reorganisation generates DTA curves which are associated, not just with the size and type of order, but also with variations in the levels of orientation of all the ordered elements. The existence of a strain upon the less ordered volumes raises the free energies of these components. This shifts fusions of those ordered elements with which they are related to higher temperatures. Changes in the form and location of the DTA endotherm for 'restrained' samples of controlled fibril-

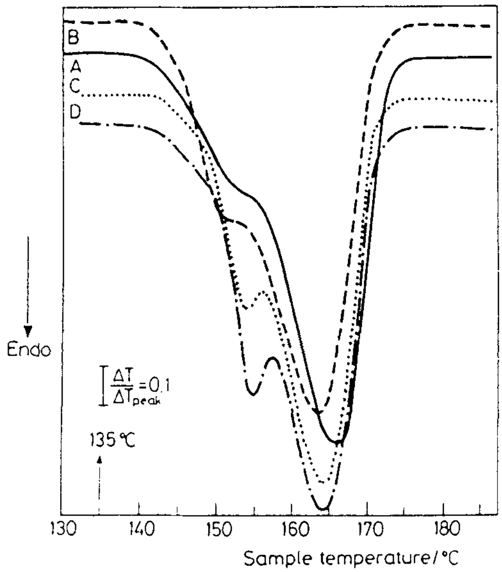

Fig. 3 DTA curves of controlled fibrillation and spherulitic polypropylene: the influence of γ-irradiation to crosslink (10 deg·min^{-1} [(A) controlled fibrillation untreated, (B) controlled fibrillation –2 Mrad γ, (C) rod sheath untreated, (D) rod sheath –2 Mrad γ, and (E) rod sheath 5 Mrad γ]

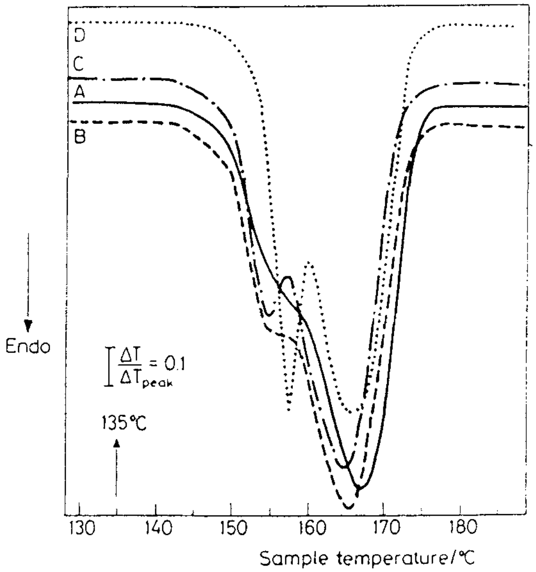

Fig. 4 DTA curves of slit film polypropylene: the influences of γ-irradiation to crosslink and restrain (10 deg·min^{-1}) [(A) untreated, (B) 2 Mrad γ, (C) 5 Mrad γ, and (D) restrained]

lation and slit film polypropylene are shown in Figs 2 and 4, respectively. This technique can only be employed if the samples for study are of the appropriate physical form. This latter constraint, combined with the existence of factors other than the basic morphology which can determine the ultimate DTA curve, led to the rejection of this procedure as a technique of general utility.

The influences of crosslinking by γ-irradiation upon the observed DTA curves are shown in Fig. 3 for the controlled fibrillation polypropylene, and in Fig. 4 for the slit film sample. There is a shift of peak temperatures to lower values with the appearance of either a more marked shoulder, or an additional peak, both of which reflect the existence of elements of lower thermal stability. The higher dose (5 Mrad) γ-irradiated slit film sample shows a DTA curve with a lower temperature endotherm which is much larger than the second peak. This latter high temperature peak is more relatable to the major fusion endotherms shown in those curves from the reference (untreated) and 2 Mrad irradiation substrates. Those samples with a spherulitic morphology after irradiation show only a progressive fall in the peak temperatures with increasing irradiation dose. The possibility of there being concurrent degradation and crosslinking must be borne in mind, particularly during extended irradiations.

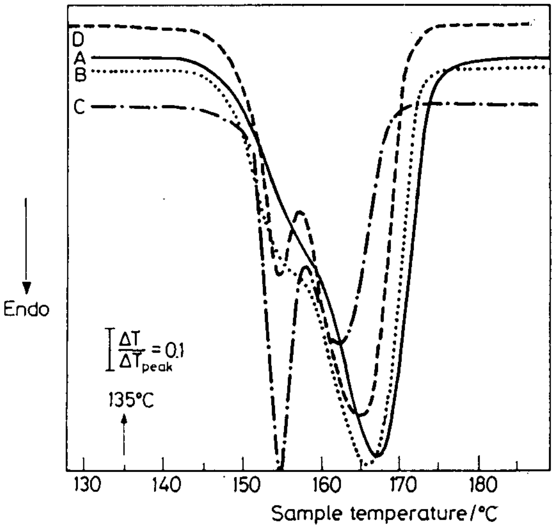

Fig. 5 DTA curves of controlled fibrillation polypropylene: the effect of nitric acid etching times at 25°C (10 deg·min^{-1}) [(A) untreated, (B) 24 h, (C) 48 h, and (D) 72 h]

The consequences of the chain scissions by nitric acid oxidation are shown in Fig. 5 and Table 1. When reorganisation is inhibited, the DTA fusion peak is expected to shift to lower temperatures. Oxidative etching, we here propose, is

Table 1 Some DTA observations from polypropylenes of differing morphology: 'averaged' data for the principal endotherm

Sample	Pretreatment	Heating rate/ deg·min^{-1}	Relative peak height	Peak onset/ °C	Peak max./ °C	Peak return/ °C
Spherulitic (Rod sheath)	–	5	93	127.0	167.0	174.0
	–	10	105	130.0	166.0	175.5
	–	20	85	130.5	167.0	178.0
	–	40	77	127.5	164.5	181.0
	2 Mrad γ	10	108	129.0	165.5	173.0
	5 Mrad γ	10	67	130.0	163.8	170.0
	24 h etching	10	83	129.0	166.0	173.0
	48 h etching	10	95	130.0	166.0	174.0
	72 h etching	10	86	130.0	166.2	175.0
Fibrillar (Slit film)	–	5	55	146.5	167.0	175.5
	–	10	71	139.5	165.0	175.5
	–	20	98	137.0	164.0	178.0
	–	40	88	137.0	161.4	186.0
	2 h at 144°C	10	186	149.0	156.5	175.0
	2 h at 144°C and 5 Mrad γ	10	115	151.0	159.0	170.0
	2 h at 144°C and 48 h etching	10	120	151.0	160.0	175.5
Fibrillar (Controlled fibrillation fibre)	48 h etching	5	24	141.5	166.0	172.5
	48 h etching	10	44	142.0	165.0	174.0
	48 h etching	20	36	143.0	163.5	176.5
	48 h etching	40	59	134.5	161.4	179.5
	1 min at 135°C	10	50	140.0	165.8	174.0
	3 min at 135°C	10	58	139.0	163.5	172.5
	1 min at 135°C and 2 Mrad γ	10	41	140.0	163.5	173.0
	3 min at 135°C and 2 Mrad γ	10	45	140.0	163.0	178.0
	1 min at 135°C and 24 h etching	10	68	139.5	164.2	174.0
	1 min at 135°C and 48 h etching	10	56	142.5	164.2	173.0
	3 min at 135°C and 48 h etching	10	63	143.4	164.2	171.5
	1 min at 135°C and 72 h etching	10	63	144.0	164.2	173.0

initially occurring at the strained fold and tie chain elements in the accessible volumes. These sites represent a significant proportion of those molecular components likely to be involved in reorganisations. The controlled fibrillation

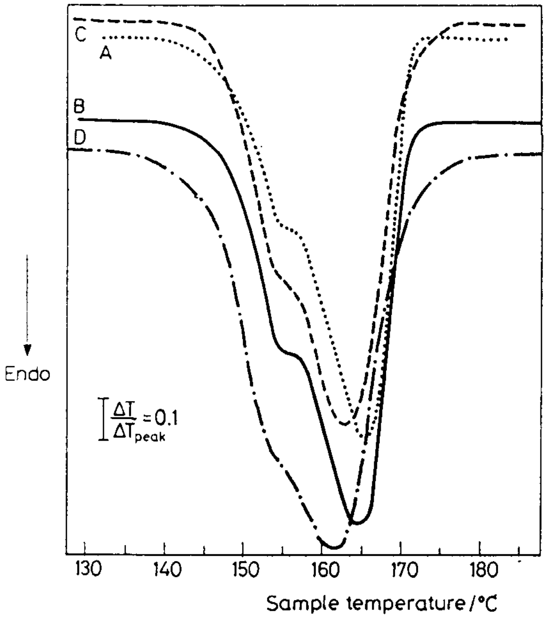

Fig. 6 DTA curves of spherulitic polypropylene (rod core): the effect of nitric acid etching times at 25°C (10 deg·min^{-1}) [(A) untreated, (B) 24 h, (C) 48 h, and (D) 72 h]

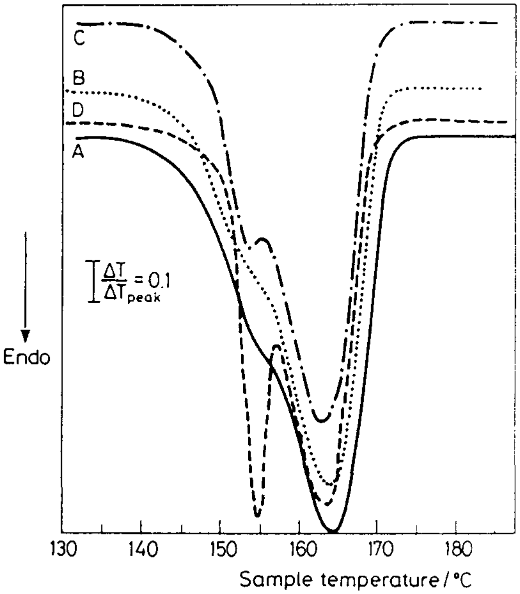

Fig. 7 DTA curves of slit film polypropylene: the effect of nitric acid etching times at 25°C (10 deg·min^{-1}) [(A) untreated, (B) 24 h, (C) 48 h, and (D) 72 h]

film, after etching, shows a more prominent lower thermal stability component (as a shoulder) after both 24 h and 48 h etchings at 25°C, and a main peak shift to lower temperature. After a 72 h etching, however, this shoulder is transformed into a peak at a higher temperature, while the main fusion peak also appears at a higher temperature. Both the spherulitic samples (Fig. 6) show the existence of a less stable ordered component, but the resolution does not improve with extended irradiation. The sample temperatures of the peaks show no change following etching. The slit film samples (Fig. 7) show a small shift in the peak temperatures to lower values and the 'translation' of the low temperature shoulder into a peak after the 48 hours etching. After the 72 h etching, the low temperature peak becomes the dominant feature, similar to that recorded after the 5 Mrad and irradiation of an equivalent sample. The shoulder and increasing peak size at the lower temperature appears to be fixed in its sample temperature location, while the high temperature peak does move to slightly lower temperatures following increased periods of etching.

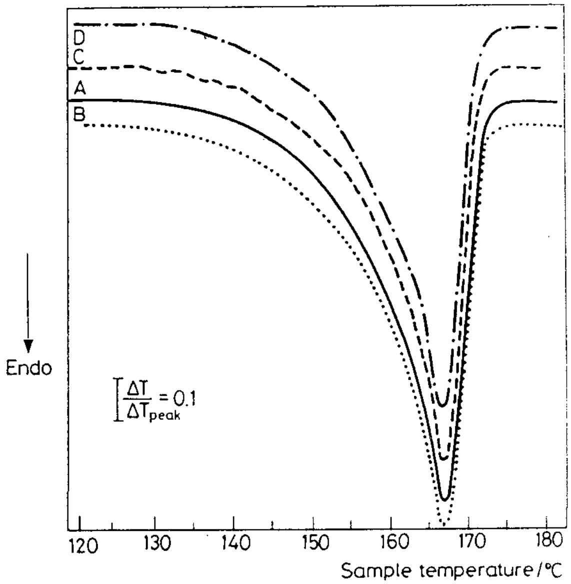

Fig. 8 DTA curves of controlled fibrillation polypropylene after 48 h etching with nitric acid: the effects of heating rate: [(A) 5 deg·min^{-1}, (B) 10 deg·min^{-1}, (C) 20 deg·min^{-1}, and (D) 40 deg·min^{-1}]

Extended etching times can achieve several changes. The desired scissions of chains at the fold (order) surface, the ties and the loops will result in a fall in the surface free energy component of the order. This fall should be observed as an enhanced thermal stability. The recorded stability shifts suggest that this free

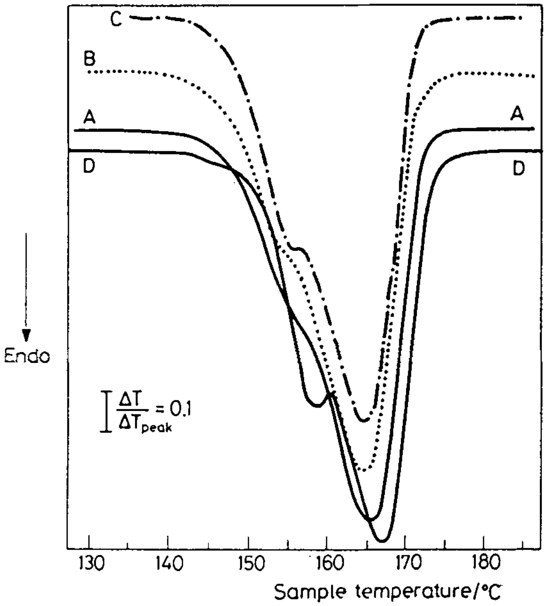

Fig. 9 DTA curves of slit film polypropylene after a 1 min annealing at 135°C: comparison of pre-analysis treatments (10 deg·min^{-1}) [(A) no treatment, (B) 2 Mrad γ, (C) 5 Mrad γ, (D) 48 h nitric acid etching]

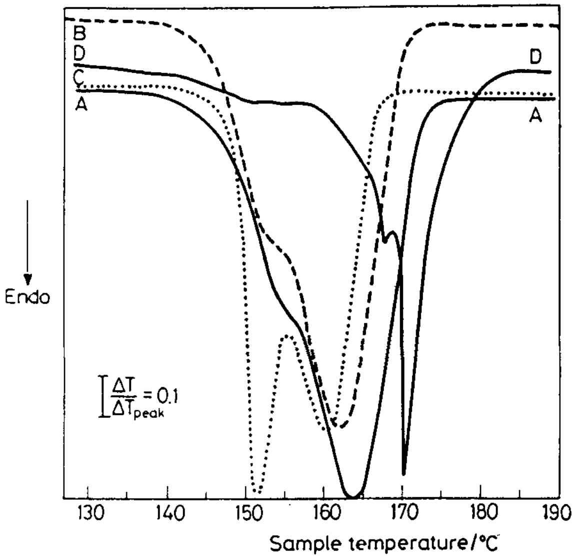

Fig. 10 DTA curves of slit film polypropylene after a 3 min annealing at 135°C: a comparison of pre-analysis treatments (10 deg·min^{-1}) [(A) no treatment, (B) 2 Mrad γ, (C) 48 h etching and (D) 72 h etching]

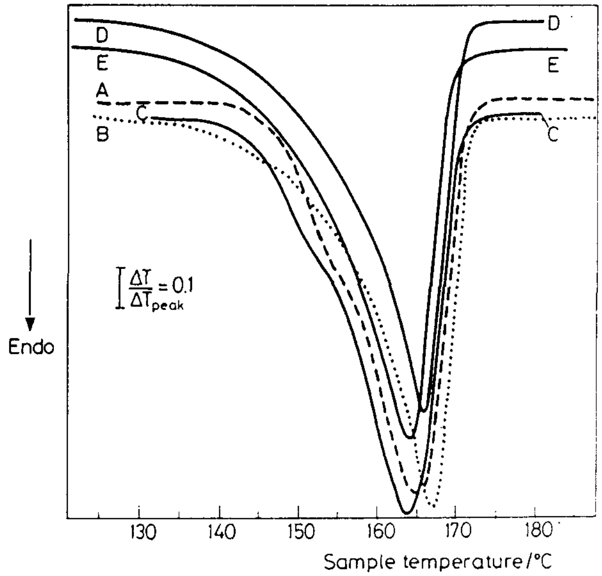

Fig. 11 DTA curves of controlled fibrillation polypropylene after 1 min annealing at 135°C: a comparison of pre-analysis treatments (10 deg·min^{-1}), [(A) no treatment, (B) 2 Mrad γ, (C) 48 h etching and, (D) 72 h etching]

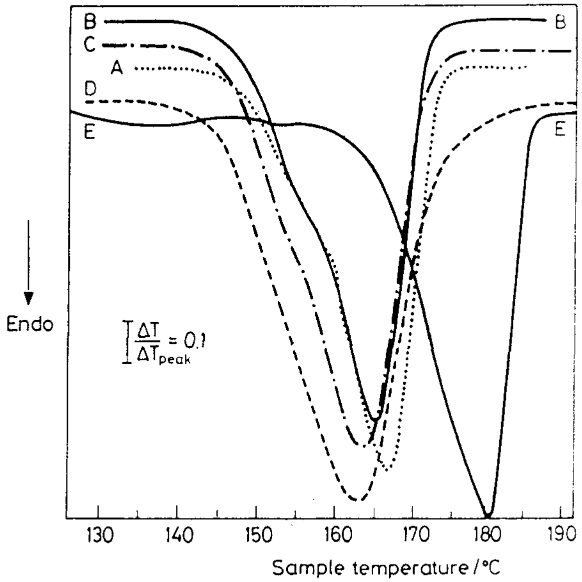

Fig. 12 DTA curves of controlled fibrillation polypropylene after 3 min annealing at 135°C: a comparison of preanalysis treatments (10 deg·min^{-1}), [(A) no treatment, (B) 2 Mrad γ, (C) 24 h etching and, (D) 48 h etching]

energy change is only a minor part of the total. Oxidation can also degrade and remove all accessible volumes; this likelihood will increase with increased etching times. The ordered volume may also contract in size by a slow incremental degradation from the chain ends at the ordered surface. The potential of a 48 h etch for totally inhibiting thermally induced reordering during the programmed heating was assessed using a comparison of the observed DTA curves at different heating rates for the treated controlled fibrillation samples. This comparison (Fig. 8) shows that even after 48 h, with the specific morphology which existed in the original sample, some reordering still occurs. The continued existence of reordering could be a consequence of accessibility, or that the lamella surfaces do not carry a high proportion of the activated chain folds i.e. the lamellae are more like that form initially described by Flory and recently revived by Willis *et al.* [12].

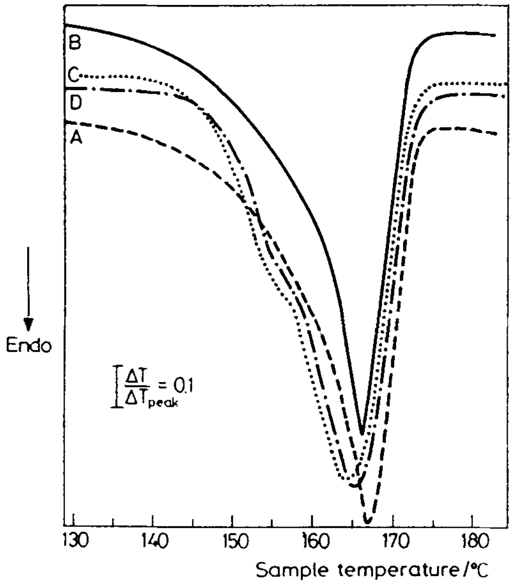

Fig. 13 DTA curves of slit film polypropylene after 2 h annealing at 144°C: a comparison of pre-analysis treatments (standard, 10 deg·min^{-1}), and effect of heating rate, [(A) no treatment, (B) 48 h etching, (C) 5 Mrad γ, and (D) no treatment but 40 deg·min^{-1} heating.]

The slit film and controlled fibrillation products which had been annealed at 135°C for 1 minute and 3 minutes, and also the slit film after annealing for two hours at 144°C, were examined by DTA after either etching or γ-irradiation treatments. Slit film sample annealed for one minute at 135°C prior to examination are compared in Fig. 9. Those samples annealed for three minutes at 135°C are compared in Fig. 10. The equivalent observations of the identically annealed and subsequently either irradiated or etched samples of the controlled fibrillation polypropylene are shown in Figs 11 and 12. Observations of the slit film samples after an annealing at 144°C for two hours, followed by either a 48 h nitric acid etch or a 5 Mrad γ-irradiation, are presented in Fig. 13. Data extracted from these recorded endothermic peaks are compared in Table 1. The slit films, after annealing, but without any subsequent treatment to prevent reordering, show shifts in the endotherm location to higher temperatures. After treating the film for two hours at 144°C, the occurrance of a morphological change is reflected by the presence of a significantly lower temperature endotherm. Both the etching and the γ-irradiations of the film annealed at 135°C show a more pronounced low temperature shoulder or peaks in the subsequent DTA curves, compared with those from equivalent unannealed samples.

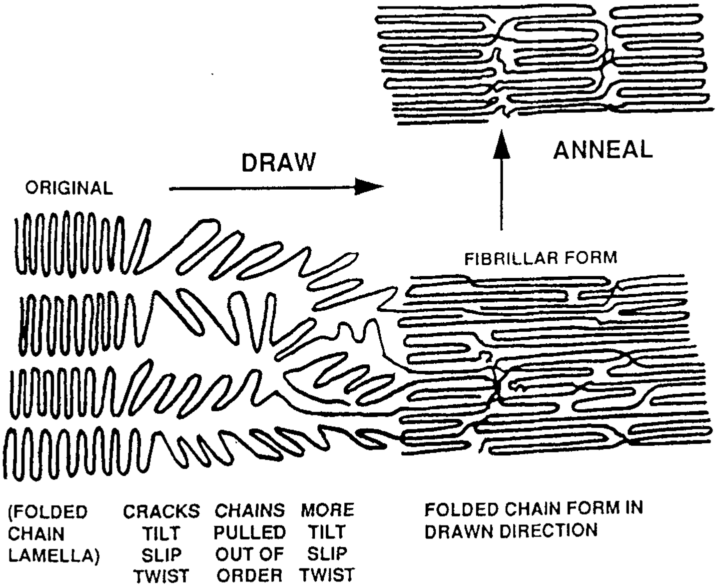

Fig. 14 A simplified representation of morphological changes: the drawing of folded chain lamellae, and their subsequent annealing

The initial polypropylene films contain folded chain lamellae in spherulitic entities. In the drawing step, these fold chain elements undergo tilting, slippage and twisting. Cracks form as a result in the initial morphology, and some chain elements are pulled out of the ordered volumes. More tilting, slippage and twisting occurs which ultimately result in fibrillar elements and with the average chain direction essentially now in the stretch direction, see Fig. 14. Greater stretch ratios are applied to form the controlled fibrillation products, within which there exists a relatively high order matrix with a concurrent high defect concentration. The defects (chain folds, loops, chain ends and tie molecules) are not random, and the oriented folded chain order yields microfibrillar entities, of ca. 10 nm width, which are apparent from X-ray diffraction observations. These structures, the products of mechanical processing, are metastable. Such deformed materials, due to the decreased stability of that morphology created in the stretching, will undergo marked changes on annealing. No large-scale disordering or ordering occurs, but there is a positive increase in the transverse lamella structure, the density and the observed long period. An enhanced separation of the centres of gravity of the order along the draw direction is also noted. The outlined change is schematically depicted in Fig. 14. These changes during annealing do mean that subsequent etching treatments are more effective in accessing fold, loop, and tie chain elements. The more marked effect of etching upon the subsequent DTA curves of the annealed samples of the slit and fibrillated film polypropylenes can therefore be appreciated. Even without a preanalysis treatment, the more severely deformed (fibrillation) sample, after a three minute annealing at 135°C, yields a lower temperature endothermic peak.

Conclusions

Four possible procedures to inhibit reordering of the polycrystalline morphology in differing polypropylenes were examined. The restraining method was not considered as reliable, due to the potential increase in the number of factors which will influence and distort the observed thermally-induced fusion behaviour, e.g. order orientation, and possible induced ordering of less ordered chain sections initiated from other less ordered chains now oriented by the restraint. These latter act as potential nuclei for further ordering. The additional effects of changing stress levels which arise as the glass transition is passed, and as subsequently ordered elements disorder, may also affect the overall melting behaviour. The existence of restraint within the amorphous volumes will also constrain segmental movement and also therefore fusion. One result of this will be enhanced levels of superheating.

The use of faster heating rates, such that no time is allowed for reorganisation, is not acceptable because:

(1) there will be a greater level of superheating,

(2) temperature gradients across the sample at the onset of fusion will be larger, and

(3) the post-fusion temperature breadth, before the return to equilibrium, will also be greater

Apart from the direct influence upon the identified transition temperatures, the increased peak widths will also result in reduced resolution and the loss of key detail. However, the influence of heating rate on peak location provides a useful tool to identify whether reordering occurs.

Crosslinking by γ-irradiation does appear to be effective in the reduction/inhibition of reordering. However, above levels of irradiation of ca. 2 Mrad, care must be exercised to ensure that degradation does not distort the observations and invalidate subsequent interpretations. The introduction of crosslinks into substrates like polypropylene, with tertiary hydrogens in abundance, makes this polymer particularly easy to crosslink and degrade. The presence of crosslinks in the volume elements at the order/low order interface, a particularly likely site because of the reactivity at the strained fold segments, will result in a slowing of the disordering process. A consequence of this latter will, however, be an enhanced superheating.

Scission/etching of the activated chain elements at the folds of ordered volumes is a potentially effective procedure to prevent reorganisation. The effectiveness of such a treatment does depend upon the acessibility of the etching probe molecule to all the appropriate locations. If the specific morphology is such as to limit access to fold or tie elements, then etching will be less efficient. It is advisable to 'test' that the proposed etching treatment is effective by examining the effect of differing heating rates upon the endothermic peaks from subsequent DTA curves. The rate of fusion depends upon co-operative segmental movements at the order/low order interface.

If chain scissions have been effected to inhibit reordering, then, in contrast to the influence of introduced crosslinks, the level of superheating should be reduced. When the heating rate test demonstrates that no reordering occurs at the 'to be employed rate' with the proposed etching conditions, and these latter conditions do not degrade the dimensions of the ordered volumes, then etching is the treatment of choice.

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Zusammenfassung — Mittels DTA wurden Polypropylene unterschiedlicher Morphologie untersucht. Es werden die Probleme der Neustrukturierung während des programmierten Erhitzens diskutiert. Dabei werden vier potentielle Prozeduren in Betracht gezogen, durch die die Neustrukturierung ausgelöst werden kann und drei davon wurden experimentell bewertet, sowie deren Vorteile und Mängel festgestellt. Zwei Vorbehandlungen, ein Ätzen und eine Vernetzung wurden als fähig erkannt, die anfängliche Morphologie qualitativ zu beschreiben. Weiterhin wird ein Test zur Feststellung vorkommender Neustrukturierung beschrieben.