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EFFECT OF THERMAL HISTORY ON CRYSTALLIZATION AND MELTING BEHAVIOUR OF LLDPE

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In this paper two LLDPE samples with their own structural parameters were studied by means of DSC. Experimental results show that DSC was good for revealing slight structural difference between these two samples. Furthermore, the effect of thermal history on crystallization and melting behaviour of LLDPE was observed clearly through varying conditions of thermal treatment.

Keywords: crystallization, effect of thermal history, linear low density polyethylene

Introduction

Linear Low Density Polyethylene (LLDPE) is a low branched polyethylene with a density range between 0.918 and 0.930 g/cm^3. Compared with LPDE produced by the high pressure technology LLDPE has fewer long branched chains but some short ones which normally formed from alpha-olefin of C_4–C_8 as the comonomer with the content range of 5–10 wt% [1]. The content of short branched chains can influence the chain folding, thus the lamellar thickness. Hence the physical properties of LLDPE are closely related to the thickness and distribution of lamellae, the crystallinity and the size distribution of spherulites as well as the content and the distribution of the short side chains. Parikh *et al.* [2] reported that they had distinguished two kinds of LLDPE with little differences in density, melt index and molecular weight distribution. They observed that the one sample with melting temperature 2.5 K higher than that of the other had improved elastic performance. There is little publication regarding the effect of heat treatment on the crystallization and malting behaviour of LLDPE, particularly the thermal characterization of commercial LLDPE.

This paper is based on a collaborative investigation on 'Crystallization and Melting of Linear Low Density Polyethylene (LLDPE)' proposed by the IUPAC

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Working Party IV. 2.4. on 'Thermal Properties of Polymers' with the participation of the same authors here in DSC testing work under the specified experimental conditions. This paper extends the analysis and discussion recorded in the original report sent to the above Working Party.

Experimental

Two samples of LLDPE with different structural parameters studied in this paper are listed in Table 1.

Specimens were prepared by cutting the granular resins into slices of mass approximately 5.5 mg. A Perkin-Elmer model DSC-2C differential scanning calorimeter was used to measure the enthalpies of fusion and crystallization. Three reference materials, indium, phenyl ether and *o*-terphenyl were used for instrument calibration. The temperature range of scanning was 213 K (–60°C) to 443 K (170°C), high purity nitrogen was used as purging gas. Unless indicated the scanning rates (both heating and cooling) were 10 deg·min^{-1}.

1. For the observation of structural differences between these two LLDPE resins, identical thermal treatment were applied to all specimens in order to eliminate the thermal history caused by processing and storage conditions. Each specimen was heated up to 443 K and held at this temperature for 10 min, then cooled down to 213 K and held isothermally for 10 minutes. The DSC measurement was made during reheating to 443 K.
2. To observe the effect of heating rate on the melting behaviour, specimens were isothermally conditioned at 443 K for 10 min cooled to 213 K, then reheated up to 443 K at four separate heating rates (20, 10, 5 and 1 deg·min^{-1}). A DSC measurement was made during reheating.
3. To observe the effect of cooling rate on the crystallization behaviour, the specimens were isothermally conditioned at 443 K for 10 min then cooled to 213 K at three cooling rates (20, 10 and 1 deg·min^{-1}). Finally, the samples were reheated up to 443 K and DSC measurement recorded during this reheating cycle.
4. To observe the annealing effect on the melting behaviour, the melt specimens were cooled to four given annealing temperatures of 398 K, 393 K, 383 K and 373 K, and held at these temperatures for 10 and 120 minutes respectively. The annealed specimens were cooled to 213 K and reheated up to 443 K finally, DSC measurements being made for the final heating process.

Table 1 Structural parameters and some physical properties of two LLPEs

Commercial name	Manufacturer	Density / $g\cdot cm^{-3}$	Melt index / $g\cdot 10\ min^{-1}$ (ASTM D-1238)	Type of comonomer	Mole pct. of comonomer / %	No. of branches per 1000 C-atoms
Stamylex 1048	DSM Netherlands	0.922	4.5	Butene-1	3.2	16
Dowlex 2045	Dow Chemicals USA	0.920	1.0	Octene-1	1.7	9

Results and discussion

The results of the effects of thermal history are shown in Fig. 1.

Comparing the peak shape of the two LLDPE samples as received in Fig. 1, it can be seen that more comonomer content in LLDPE leads to a broader peak and lower peak temperature. The amount of comonomer in Dowlex 2045 is less than that in Stamylex 1048, i.e. the degree of linearity for Dowlex 2045 is higher than that for Stamylex 1048. This is in accord with the structural parameters listed in Table 1. The melting temperatures of both LLDPE samples measured after eliminating thermal history were a little higher than those measured before. These indicate that the crystalline integrity of both LLDPE increased during the new thermal history. The changes of peak shape illustrate that the size distribution of crystallites also changed. The changes of fusion enthalphy, ΔH_f, for Stamylex 1048 were slightly higher than those for Dowlex 2045 before and after elimination of the thermal history effect. These reflected the small difference in crystallinity between these two samples. The effect of heating rate on melting behaviour is shown in Fig. 2. It can be seen that the lower the heating rate, the better the peak resolution, and consequently the clearer the shoulder peak. This may be interpreted that the slower heating rates enable a semicrystalline polymer to have more time for crystal growth prior to final melting. Curve 'a' in Fig. 2 illustrates

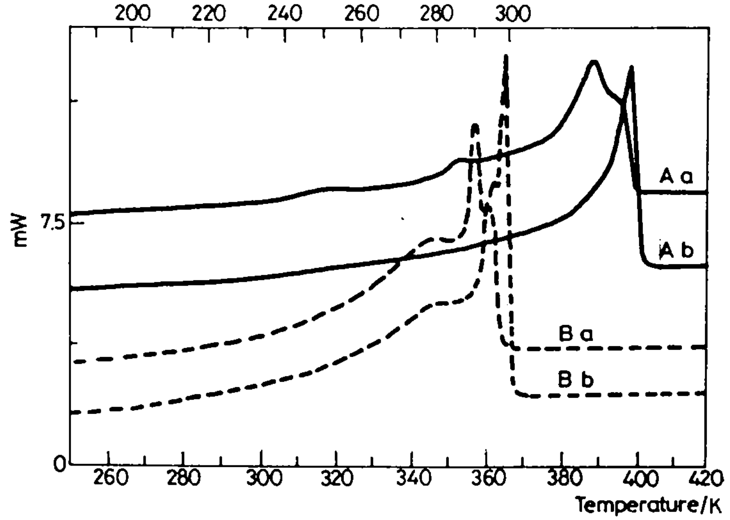

Fig. 1 DSC curves of Stamylex 1048 and Dowlex 2045 before and after eliminating thermal history: *A* denotes Stamylex 1048 while *B* denotes Dowlex 2045, *a* represents data obtained before eliminating thermal history while, *b* represents data obtained after eliminating thermal history

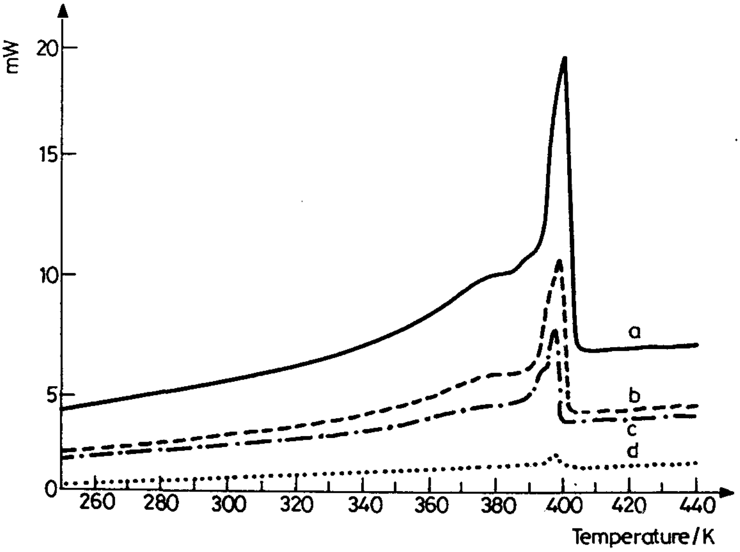

Fig. 2 DSC curves of Stamylex 1048 at different heating rates: *a*, *b*, *c* and *d* denote the four heating rates of 20, 10, 5 and 1 deg·min^{-1} respectively

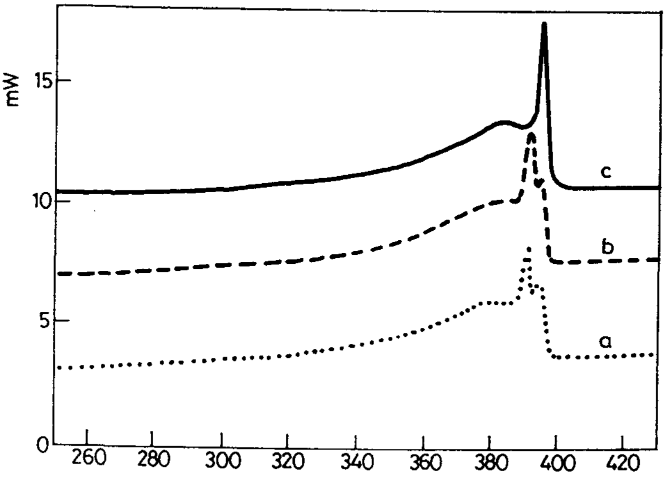

Fig. 3 DSC curves of Stamylex 1048 reheating after cooled from the melt at different cooling rates: *a*, *b* and *c* denote the three cooling rates of 20, 10 and 1 deg·min^{-1} respectively

that due to the higher heating rate there was insufficient time for crystal rearranging to occur so that the shoulder peak, representing the melting behaviour of certain rearranged crystals disappeared.

The melting behaviour of LLDPE not only depends on the type and amount of comonomer, the distribution of the short branches, but also to thermal history. It is obvious that the lower the cooling rate, the weaker the supercooling. With the result that more time for crystallizing from the melt must be beneficial to the growth and perfectness of crystallites. This effect of cooling rate on the melt crystallization can be clearly observed from Fig. 3. The small inflection on the high temperature side of the melting endotherm on curves ‘a’ and ‘b’ changed to very sharp one on curve ‘c’ with decreasing the cooling rate, while the sharp peaks on curves ‘a’ and ‘b’ weakened to almost vanishing on curve ‘c’. The similar tendency can also be observed for Dowlex 2045.

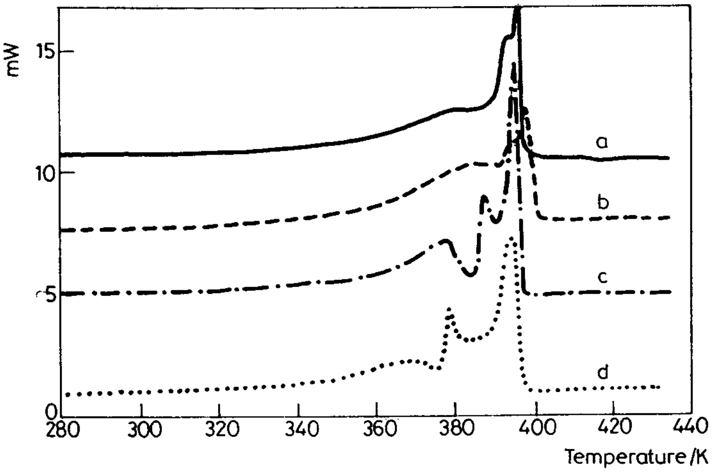

Fig. 4 DSC curves of Dowles 2045 reheating after annealed at different temperatures for 120 minutes: *a*, *b*, *c* and *d* denote the four annealing temperatures of 398, 393, 383 and 373 K

The effect of thermal history of annealing can be seen in Fig. 4. It is notable that there are always crystallites formed correspondingly to every annealing temperature. The size and perfectness of each group of crystallites were peculiar to the corresponding temperature. During reheating of the annealed sample, the DSC trace exhibited an endotherm corresponding to a certain annealing temperature appeared first and then an exotherm. This indicated that there was a recrystallization process immediately following the melting process. In this process a number metastable crystallites with smaller size or some defect would melt and then generate a new, a number of more perfect crystallites. With a rise in temperature other groups of crystallites will start melting and then recrystallizing in succession corresponding to the previous annealing temperature sequence so that a multipeak graph appeared showing the uncontinuous distribution of crystal size [3]. As for the annealing time, ten minutes is sufficient because there were little difference between the enthalpies measured from 10 and 120 minutes for both samples.

Conclusions

Experimental results show that the slight structural differences between these two LLDPE studied can be revealed easily by analyzing the peak shape, peak area and peak temperature on the DSC curve obtained. This is helpful for quality assurance in polymer conversion processes.

The effect of thermal history on crystallization and melting behaviour of LLDPE resins can be observed clearly enough varying conditions of thermal treatment. Experimental results show that DSC is not only good for monitoring the thermodynamic parameters but also for simulating and then optimizing the processing technology for polymers. That proves that DSC is a useful quality control technique in the plastic processing industry.

References

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Zusammenfassung — Mittels DSC werden zwei LLDPE-Proben mit ihren eigenen Strukturparametern untersucht. Die Versuchsergebnisse zeigen, daß sich DSC gut eignet, um geringfügige Unterschiede dieser zwei Proben nachzuweisen. Weiterhin wurde unter verschiedenen Bedingungen der Einfluß der thermischen Vorgeschichte auf das Kristallisations- und Schmelzverhalten von LLDPE untersucht.