Journal of Thermal Analysis and Calorimetry, Vol. 84 (2006) 2, 331–337

DSC MONITORING OF SUPERMOLECULAR STRUCTURE DAMAGE OF POLYETHYLENE PRODUCTS
Academia and industry challenges

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Investigated materials were produced from polyethylene of low density (PE-LD) and a filler: carbon black or chalk. A part of the samples was kept in ambient temperature over several months in order to study the effect of material ageing. The qualitative conclusions were drawn based on a precise analysis of shape of DSC curves and the basic investigations of PE morphologies known from literature. The influence of the thermal history and the filler contents on the amount and kind of crystal phase was established. Additionally, the effect of the measurement technique, in our case it was positron annihilation lifetime spectroscopy (PALS), on the morphological feature changes was found. The paper serves selected examples of problems solved by DSC. However, from the other hand, the authors discuss critically the opportunity given by this method.

Keywords: *DSC, morphology, PALS, PE-LD*

Introduction

A production process consisted of separate operations is a combination of actions directly connected with changing the shape, dimensions, properties and condition of a blank. The final and finishing operations of some technology very often include heat treatment, which is used to ensure the require mechanical properties of the material. Thermoanalytical techniques could play an important role in optimising the steps of the process chain. DSC is superior to other techniques because it uses small amounts of tested material and needs short time for the measurement, and also, the continuous registration of thermal parameters as a function of time is possible [1, 2]. It is known that the properties of commercial products, made from plastics, are the results of an arrangement of polymeric chains, i.e. morphological feature. In physics of polymeric material, the problem of chain rearrangement, relaxation and stability of a supermolecular structure has attracted a great interest and can be studied by many techniques. Hence, polymers are challenges for both academia and industry [3, 4]. Every technique, except DSC or DTA, very often requires special preparation of the sample. Such techniques like transmission electron microscopy (TEM), scanning electron microscopy (SEM), light microscopy, X-ray diffraction, nuclear magnetic resonance (NMR), infrared spectroscopy (IR), dielectric spectroscopy, and other one, are used under specific conditions. Unfortunately, these conditions more or less change a supermolecular structure of the studied sample in comparison with a supermolecular structure of a commercial product. The more energy is added to the system during the sample preparation the more changes occur [5]. It must be emphasised that DSC or DTA use a small sample without any special preparation and every DSC curve reflects a phase situation of the system [1, 2, 5]. These curves could play a significant role in predicting, and especially, controlling the quality of production by assessing changes in the physical or chemical nature of raw materials of intermediate and final products. DSC is the simplest technique applied for assessing phase phenomena in polymer mixtures and multi-component systems [2–4, 6, 7]. However, it is used as '…a very expensive thermometer… [3]' very often.

Polyethylene (PE) has been the subject of extensive investigation concerning its crystal structure, morphology and corresponding amorphous phase relaxation behaviour [3, 4, 8–14]. Crystallisation from the melt of polymeric material, especially linear macromolecules, permits to obtain a broad spectrum of crystal forms. These forms may range from close to equilibrium to metastable or unstable that makes rather complicated the interpretation of melting data, obtained from the DSC study. In spite of this the calorimetric studies can give some information on crystal perfection, distribution of crystals in amorphous matrix, interphase existence and an amount of crystal fraction in the material [2, 15–17]. The information can be drawn from a shape of DSC traces or temperature of transitions occurring during heating or cooling performed at a constant rate [12, 18–21].

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1388–6150/$20.00
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Springer, Dordrecht, The Netherlands

The application of DSC for monitoring the morphology feature changes of the processed polyethylene is the main topic of this paper. The relative changes of the supermolecular structure based on the changes of the thermodynamic parameters are concluded. This paper leads to a broader understanding of the relationship between processing history and morphology in the resultant engineering products. The paper will serve selected examples of problems solved by thermal analysis. Additionally, it shows how one of the measurement techniques, applied to the polymeric system, can change the material structure, and hence its properties. In order to perform the study mentioned above, the sample should have been irradiated by a positron beam. This paper gives evidences of structure damage being the consequence of the measurement technique application, which was a positron annihilation lifetime spectroscopy (PALS) [14, 22]. The structure damage, resulting from the application of different methods mentioned in this section, is revealed in the literature as a value variety of the same physical parameter, e.g. the glass transition temperature evaluated for the same, from the chemical point of view, material.

Experimental

Methods

Thermal characterisation of the samples by DSC was performed with using of a Perkin-Elmer DSC7 type and the first heating run (20 K min^{-1}) was recorded. The melting temperature (T_m) was defined as the maximum of the melting endotherm. The analyses were performed under following conditions: environment – nitrogen atmosphere; flow rate – 20 mL min^{-1}; sample pan – aluminium; reference – empty aluminium pan; sample size – about 5 mg; heating rate – 20 K min^{-1}; calibration procedure – done with indium standard according to [2]. However, in order to establish the characteristic points of the DSC curve, the first derivative of the signal was considered [6].

Sample preparation

The composite material including carbon black as a filler was produced from granulated polyethylene of low density (Lupolen 2012 D schwarz 413, BASF) as a band with a thickness of 1 mm and a width of 300 mm, samples PE(c). This investigated material was divided into three parts: the first one unprocessed, the second one drawn (40% elongation), the third one irradiated with high energy electrons, which are named in this paper as PE(c), PE(c/D), PE(c/E), respectively. The bands were produced by Instytut Chemii i Techniki Jądrowej (Warsaw, Poland). Also, 10, 20, 40 mass% of calcium carbonate (grain of 0.63 μm diameter) was added to pure PE-LD (Centrum Technologiczne, Wydział Chemii, Uniwersytet im. A. Mickiewicza, Poznań, Prof. L. Domka): samples PE(Ca/10); PE(Ca/20) and PE(Ca/40). The fillers were applied in order to improve the properties of polymeric products and to reduce the cost of produced plastic. PE-LD, type DO72, was obtained from Zakłady Chemiczne 'Blachownia' (Poland): samples named as PE.

The samples were cut out from the bands and additionally processed in our laboratory. Some parts of the samples were annealed at 373, 423 or 473 K mainly over 1 h (although the samples annealed over 5 min or 5 h were also studied). The temperatures are pointed out as a subscript (100, 150, 200). The other part was irradiated by a positron beam over 24 h. For this purpose a source of positrons was prepared (about 0.2 MBq). Several droplets of a carrier free solution of $^{22}NaCl$ were deposited and evaporated on a piece of Kapton foil. An another piece of the foil was sealed over the first one. The source was used in the positron lifetime measurement. A typical measurement run lasted 24 h [14, 22]. The source was located between two polymer samples cut out from the same band. After the positron lifetime study the positron irradiated samples were used in calorimetric study (all samples with subscript '*p*').

In order to study the effect of structure stability the samples were stored at room temperature (293 K) over six and fifteen months for PE(c) and PE(Ca), respectively.

Results and discussion

PE composites with carbon black

DSC melting endotherms recorded for PE-LD filled with carbon black at a heating rate of 20 K min^{-1} are shown in Figs 1–3. The curves are collected in three groups: PE(c) – as produced material, without extra drawing or irradiation; PE(c/D) – drawn material (40% elongation); PE(c/E) – electrons irradiated material. Owing to the fact that the shape of the endotherms was almost the same for all samples studied just after adequate process (manufacturing, drawing, electron irradiation, annealing and positron irradiation) only one of the curves representing the endotherm of the produced material is presented in the picture. However, the shape significantly varied from one specimen to another when the manufactured polymeric material had been stored, e.g. six months (it is signed by a star superscript). Therefore each picture includes one curve recorded for the sample obtained directly after the engineering process per-

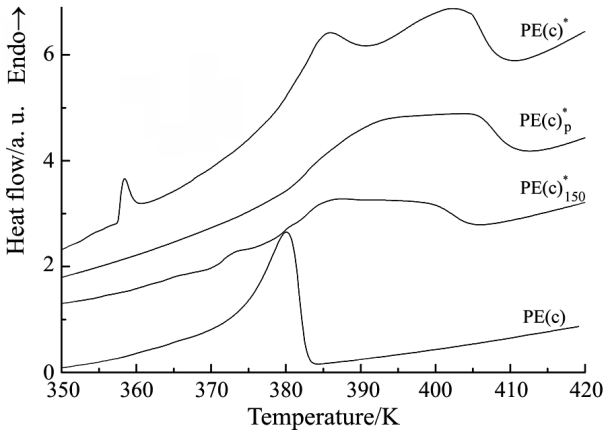

Fig. 1 DSC traces of samples cut out from as-produced material PE(c) and the materials, which were additionally treated, according to the procedure described in the text

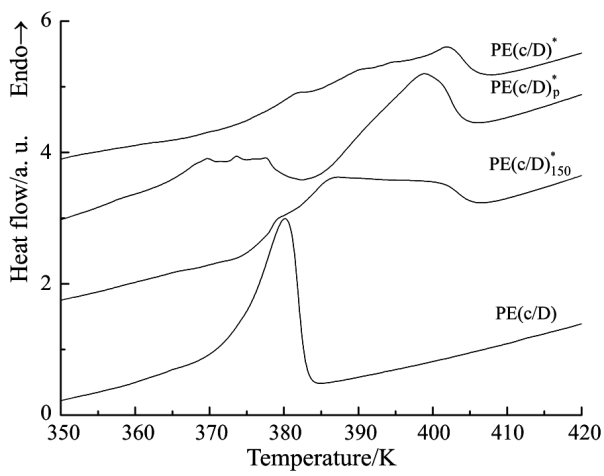

Fig. 2 DSC traces of samples cut out from drawn material PE(c/D) and the materials, which were additionally treated, according to the procedure described in the text

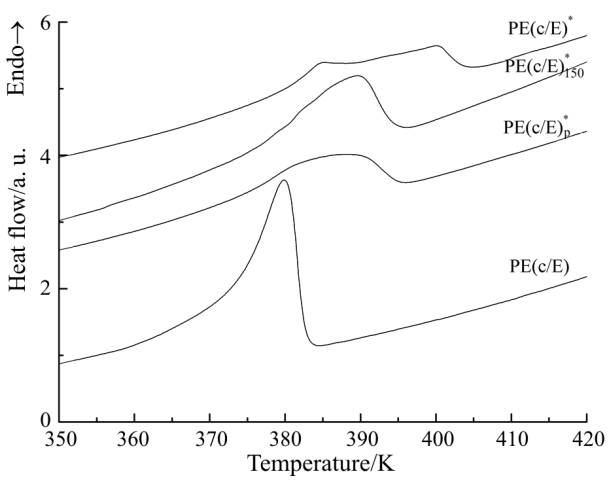

Fig. 3 DSC traces of samples cut out from high energy electron irradiated material PE(c/E) and the materials, which were additionally treated, according to the procedure described in the text

formed in factory (e.g. PE(c) in Fig. 1) and three curves recorded for the additionally treated in our laboratory samples which were stored at ambient temperature over six months (e.g. $PE(c)^*_{150}$, $PE(c)^*_p$, $PE(c)^*$ in Fig. 1). All of the curves obtained for stored specimens exhibit a more or less pronounced shoulder or double peak (e.g. curves $PE(c)^*$, $PE(c)^*_{150}$, $PE(c)^*_p$ in Fig. 1) whereas the curves for the 'fresh' material shows only a single melting peak (e.g. PE(c) in Fig. 1). In this paper the term 'fresh' means that the material was studied directly after preparation. In order to understand the origin of these complex shapes, the interpretation of melting data must thus be coupled with a detailed study of the actual morphology and molecular dynamic of PE chain that was previously described [14, 23–26]. One can easy find out from the DSC curves that the melting endotherm is a sum of three endotherms representing separate melting processes. The melting processes occur in the following temperature ranges: 353–378 and 378–393 K; 393–408°C. The recorded curves a highly similar to the curves presented earlier [18–21], which were obtained for blends of different polyethylenes. We can only see rather good separation of three processes for the sample $PE(c)^*$, which was not processed additionally. The $PE(c)^*$ sample, as produced, was storage at room temperature over six months. It is worth noticing that this temperature is much higher than the glass transition temperature of PE [26]. Likely, that material was the most susceptible to supermolecular structure changes. Owing to the fact that the endotherms, $PE(c / E)^*_p$ and $PE(c / E)^*_{150}$, are a little shifted towards higher temperature and the melting process is still reflected as a single (broad) endotherm, one might conclude that the electron irradiated material exhibited the weakest structure changes after six months.

The transition temperatures and enthalpy changes are summarised in Table 1. The comparison between the enthalpy of melting for the processed 'fresh' material (ΔH_m) and the enthalpy for the stored material (ΔH^*_m) is presented. The percentage of the enthalpy change, given in parenthesis, shows that the most stable crystalline phases were formed in the materials which were drawn ($PE(c/D)_{150}$) or irradiated with high energy electrons ($PE(c/E)_{150}$) and additionally annealed at 423 K. It can be easy found that the enthalpy values for the stored samples are almost the same. However, it does not mean that the degrees of crystallinity are equal for these materials. The broad endotherm is a sum of at least two melting processes. It means that two crystal forms with different perfection (energy) must be taken into account. The smaller amount of a higher perfect crystal phase can give a bigger contribution to the recorded endotherm than the bigger amount of a lower perfect crystal phase

Table 1 The thermodynamic parameters of the 'fresh' samples and the samples after six months from preparation (*). The degree of destruction of the crystal fraction in the material is given in parenthesis (in %)

Samples	ΔH_m^*/J g^{-1}	ΔH_m/J g^{-1}
PE(c)	50.6 (37.6)	81.0
PE(c)$_{150}$	56.6 (37.2)	90.3
PE(c)$_p$	51.4 (26.0)	69.6
PE(c)$_{150p}$	59.1$^{\#}$ (25.4)	79.4
PE(c/D)	53.5 (25.4)	71.9
PE(c/D)$_{150}$	66.9 (16.3)	80.1
PE(c/D)$_p$	54.1 (18.4)	66.4
PE(c/E)	57.5 (26.9)	78.8
PE(c/E)$_{150}$	59.6 (12.8)	68.5
PE(c/E)$_p$	55.6 (28.4)	77.8

$^{\#}$ after 10 months

[15–17, 27–30]. Similar effect was described for the blends of polyethylenes [18, 19, 21]. Also, some co-crystallisation was found when branched and linear polyethylenes were blended [20].

The broad melting region, analysed by DSC, might be arbitrarily separated into recognisable double or multiple melting peaks, especially for the samples PE(c)*, PE(c/D)* and PE(c/E)*. One obvious reason for this separation is the presence of several different crystal forms and/or their different distribution in the amorphous matrix [3–4, 18–21]. For best separation, the produced materials were annealed at the following temperatures: 373, 423 and 473 K. Only the annealing at 373 K, that was between the melting temperature of the two crystal components for polyethylenes, was effective (Fig. 4). The temperatures of melting processes for this group of the samples correlate with the temperature ranges found for the stored samples. The splitting of the melting endotherm means that the crystalline structures due to a 5 h annealing at 373 K have been modified. The annealing over 5 min, PE(c)$^+_{100p}$, changed little a shape of the endotherm. (The endotherm of the PE composites including 10 mass% of a modified chalk as a filler, PE(CaM/10)$_{100}$ [31], is also presented in Fig. 4 for comparison.) Hence, the crystal phase of the commercial products, formed by rather one type of crystals, was transformed into the phase, which was built up by at least two various crystal forms after the samples annealing at 373 K or storage at ambient temperature. One might conclude that both treatment caused the morphological effect similar to that one found for the blends of different polyethylenes [18–21]. For the higher annealing temperatures the endotherms were similar in a shape giving a single peak.

PE composites with chalk

Representative DSC curves for the PE(Ca) products are shown in Fig. 5. The curves are presented in a temperature range, which only includes the melting process. It is seen that the shapes of the melting endotherms differ and depend on the thermal history of the composites. The curves for PE and PE* differ drastically. Whereas the PE* curve reflects only one melting process, the PE curve exhibits that the crystalline phase is not homogenous and two melting processes occur. All of the stored products gave the same shape of the DSC curves. It would mean that the morphology of the PE crystallites and their distribution in the amorphous matrix for each products was similar. The question on the polycrystallinity must be better solved by X-ray measurements. However, the DSC study exhibits distinctly that room temperature is sufficient for changing the arrangement of chains in the crystalline domains of PE-LD. It is worth noticing that the annealing at 373 K does not change the endotherm

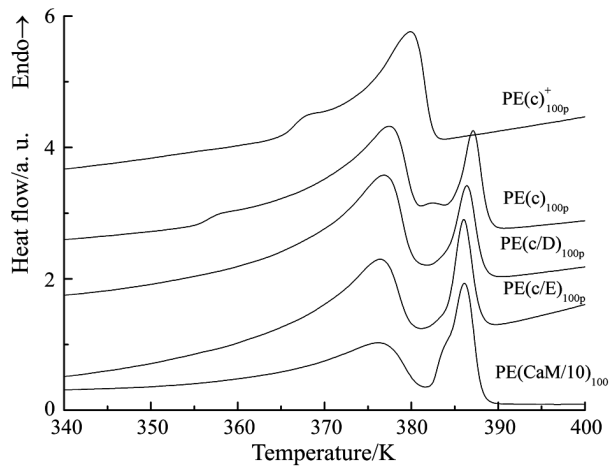

Fig. 4 DSC traces of samples cut out from as produced, drawn and electron irradiated materials annealed at 373 K over 1 h

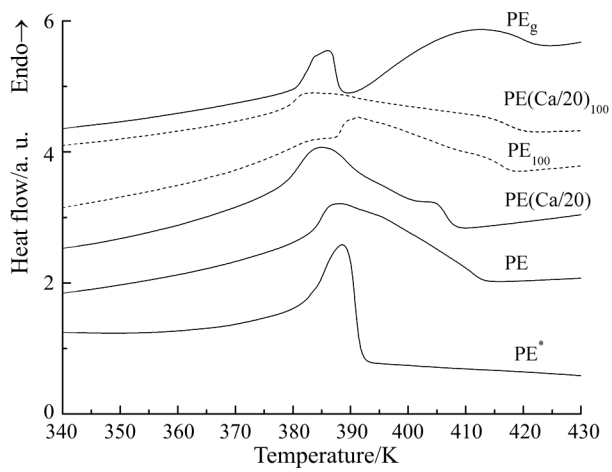

Fig. 5 Representative DSC traces of PE composites with chalk

shape too much, except the curves for the composites including the modified chalk [31]. A small change of the amount of the crystalline phase was observed when 10, 20 and 40 mass% of the filler had been added, Table 2. It means that the filler did not disturb too much the crystallisation process of PE-LD, occurring during the composites production. Most likely, only a small number of defects was created in the crystalline domains. However, the crystal-amorphous interphase was disturbed by the presence of the filler [25–26, 32].

The measurements were also performed 15 months after the production (Table 2). Most of the parameters had the same values for the composites, independently on the chalk amount. It would suggest that due to some process, most likely structural relaxation of PE, the supermolecular structures formed after 15 months exhibit the same feature despites of various chemical composition of the composites. Hence, it means that the polymer and chalk formed their structures as separated phases, and polymer arrangement was independent on the amount of the chalk.

The data for annealed samples are collected in Table 3. One can find that structural changes occurred in the crystalline domains. Except the pure polyethylene annealed sample, PE_{100}, all melting enthalpies were almost equal 83.9±1.4 kJ mol^{-1} (SD is given as an error). It is seen that the value is a little lower than the values obtained for the unannealed samples. Owing to the fact that the T_m values has also decreased, it might mean that the annealing not only increased the number of crystals but also modified the crystalline domains.

Table 2 The thermodynamic parameters of the 'fresh' samples and the stored samples (*), cut out from PE-LD/chalk composites. The endotherms of the stored samples exhibited only one minimum: PE–T_m^*=388.6 K; PE(Ca/10/20/40)–T_m^*=385.2 K. The second minimum of the endotherms are given in parenthesis

Samples	ΔH_m^*/J g^{-1}	T_m/K	ΔH_m/J g^{-1}
PE	111.1	387.2(408.1)	105.4
		387.0(402.5)$^+$	88.2$^+$
PE(Ca/10)	105.7	383.8(405.2)	97.5
PE(Ca/20)	108.2	384.6(403.4)	96.8
PE(Ca/40)	102.1	383.5(402.4)	99.6

$^+$measurement was performed four months later
*15 months after the production

Table 3 Enthalpies and temperatures of melting obtained for the annealed samples cut out from PE-LD/chalk composites. The temperatures of the second (and the third in the case of PE_{100}) melting transition are given in parenthesis

Samples	T_m/K	ΔH_m/J g^{-1}
PE_{100}	383.6 (391.1;412.6)	89.3
$PE(Ca/10)_{100}$	382.4 (414.1)	82.5
$PE(Ca/20)_{100}$	383.0 (413.1)	85.3
$PE(Ca/40)_{100}$	383.0 (404.9)	83.9

Curve shape interpretation

Most of authors, in order to determine the degree of crystallinity, compare the melting enthalpy of the studied polymeric system with the melting enthalpy of the same polymer of 100% crystallinity. They use so-called 'the best value' found in the data bank. It must be emphasised that such a procedure do not take into account the crystals polymorphism and the change of the system volume. Moreover, the problem with the base line stability, faced by different authors during DSC measurement, and the curves 'improvement' are not considered. However, it is generally known that some correlation with the X-ray procedure exists, although the calculations, based on the X-ray and DSC data, are performed with some procedure errors. In our previous paper [33], we gave another example how the amount of crystals in the polymeric system might be evaluated, and the comparison of the calculations based on the DSC and PALS data were presented for PMP systems.

One can easy find that we do not apply any action in order to improve the curves. Some authors subtract, smooth or apply 'other tricks' in order to show nice curves. In our opinion, it is not necessary when the measurement is performed accordingly with the art of calorimetry [2]. DSC is a differential technique, hence, subtracting the contribution of an empty pan run is not necessary. However, using DSC commercial software, one must be careful because it is very easy to evaluate the values of the melting enthalpy differing more than 100% when we apply improper baseline subtraction. Also, the calculation of the crystallinity degree, using 'the best value' obtained for 100% crystallised polymer, is a mistake. Firstly, there is only one value in the data bank for each polymer although the polymer may crystallise to several forms (units), e.g. PMP possess 6 forms. Secondly, the best value was established as an extrapolated value from the values measured for low-mass molecular substance. Thirdly, we should distinguishe whether it was DSC or DTA technique? Fourthly, we should take the sample amount as small as it is require by the method. Finally, we may not additionally process the studied sample before the DSC run and the sample storage should be short.

Effect of the measurement technique

In order to study the effect of positron irradiation on various morphological features, the specimens, taken

from three groups of the commercial products including carbon black, were annealed at 373, 432 or 473 K over 5 h and irradiated with positron over 24 h (the irradiation took place during the positron annihilation measurements [14, 22, 23]). The results of DSC measurements are collected in Table 4. Also, the comparison of the melting enthalpies obtained before and after such irradiation is given in parenthesis. One can see that the values in parenthesis for the samples from the PE(c/E) group are the smallest that would indicate the lowest damage of the crystalline domains. It means that the crystals were little affected by the positron irradiation. Most likely, the change after melting was significantly inhibited due to cross-linking of the polymeric networks. The influence of the positron beam on the PE material require a separate study that is in progress.

Recrystallisation of the electron irradiated material (PE(c/E), Table 4) led to the sharply lower enthalpy due to the interference of the cross-links with the crystallisation process. However, there is the evidence that the applied positron radiation dose increased ΔH_m value for the unannealed sample ($PE(c/E)_p$) in comparison with the non-irradiated by electrons sample ($PE(c)_p$). There seems also no universal dose limit above which reorganisation is stopped completely and effects on the melt and crystal are negligible [34]. The presented values show the variation of a positron irradiation effect for PE prepared as commercial products. Cross-linking of the polymeric network of the products before analysis could stabilise the supermolecular structure and prevent the crystal phase. An overriding effect, however, will increase the activation enthalpy of the structural or local relaxation due to the presence of strained, amorphous tie molecules. This effect was discussed together with the results obtained by mechanical spectroscopy [26].

Table 4 The thermodynamic parameters of the samples after positron radiation (*p*) obtained from DSC traces. The degree of destruction of the crystal fractions, as compared with the adequate sample non-positron irradiated, is given in parenthesis (in %)

Sample	T_m/K	ΔH_m/J g^{-1}
$PE(c)_p$	380.0	69.6 (14.1)
$PE(c)^+_{100p}$	379.9	65.8
$PE(c)_{100p}$	377.2 (386.3)	79.1
$PE(c)_{150p}$	380.2	79.4 (12.1)
$PE(c)_{200p}$	379.8	69.7
$PE(c/D)_p$	380.4	66.5 (7.5)
$PE(c/D)_{100p}$	376.8 (387.0)	78.4
$PE(c/D)_{150p}$	379.8	73.6 (8.1)
$PE(c/D)_{200p}$	380.6	79.6
$PE(c/E)_p$	379.2	77.8 (1.3)
$PE(c/E)_{100p}$	379.2 (386.1)	65.7
$PE(c/E)_{150p}$	379.9	67.0 (2.2)
$PE(c/E)_{200p}$	380.7	55.6

$^+$sample annealed 5 min

Conclusions

It was shown that the effect of the technological processes drastically changed the material morphology. Not only the thermal treatment but also the drawing and irradiation with electrons (and/or positrons) affect the polymer supermolecular structure, significantly. One can easy find that the supermolecular structures (properties) of polyethylene prepared under various conditions differ. Hence, conclusion drawn for raw PE (obtained in laboratory) might not be spread directly on its products (produced by industry). Chalk or carbon black as a filler of PE-LD gives the products which properties are not stable in time and temperature. Moreover, a component separation in the composites after the annealing and storage exhibits that the chalk, used in our study, modifies the polymer supermolecular structure only during the production. It would mean that PE is a strong component, which adopts its own supermolecular structure, removing the chalk filler outside the polymer domains where grains of chalk form aggregates. In contrary, carbon black seems to be better disperse in the polymer. It locates both in the amorphous, as well as, the crystalline domains. Most likely it is the question of the grain size.

Thermal analysis (DSC, DTA, TG) seems to be one of best methods, if not the best one, which is able to predict and control the quality of the final production. We do not need to prepare the tested sample in some special way. The small piece of the tested product cut out directly from the processed material, during any steps of the technological process, is sufficient for such an analysis. It is important that the removing of the piece of the material does not disturb the physical and chemical stability of the produced material in any way.

It was shown that one must be careful when the radiation techniques are applied. In such cases, very often, long time of the measurement is required to obtain a readable pattern, which is sufficient for the properties description. Moreover, the specimens used for those techniques must possess a special shape or dimensions. It requires a special treatment, which is not the same as in the technological process to be performed. That means different supermolecular structure, and hence different material properties.

Although DSC (DTA) seems to be a suitable method for the quick and cheap structure analysis, there is one problem faced. It is a question of material homogeneity and whether the results obtained for the small part of the material can be extended on the whole

final product. However, this problem can be resolved by testing several pieces cut out from different parts of the same product. It is possible if we take into account that the mass of one piece can be less than one milligram for a high quality calorimeter. It must be emphasised that we do not describe the supermolecular structure of the PE system in this paper, at all. For this, DSC is not proper, as one has been able to easy find. We describe the relative changes of the structure of the PE products based on the changes of the thermodynamic parameter and the general knowledge on the possible PE morphology. The morphology description by means of DSC is speculative as much as every description done for other experimental technique. However, for the property description of plastic commercial products, we propose to use very simple and cheap method (it is not time consuming), DSC or DTA, against very expensive, e.g. TEM or SEM, additionally knowing, that the latter ones require the sample preparation that drastically changes a polymer structure. In conclusion, we should consider the influence of some techniques on the obtained results at last.

Acknowledgements

It is pleasure to thank Professor V. B. F. Mathot (DSC Research, The Netherlands) for stimulating discussion about many issues addressed here. Helpful comments by Professor Ch. Schick (Rostock Univ., Germany) and his stimulating correspondence are acknowledged with pleasure.

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Received: January 20, 2005
Accepted: May 24, 2005
OnlineFirst: January 11, 2006

DOI: 10.1007/s10973-005-6846-x