Journal of Thermal Analysis and Calorimetry, Vol. 67 (2002) 343–347

RELATIONSHIP BETWEEN THE THERMAL PROPERTIES AND THE MORPHOLOGY IN HIGH DENSITY POLYETHYLENES

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Abstract

This work presents a relationship between the thermal properties in different polyethylene samples analyzed by differential scanning calorimetry (DSC). The morphology and structural changes were studied by transmission electron microscopy (TEM). A preparative method involving surface etching was used to obtain surface replicas. The main morphological features of the samples, characterized by lamellar structure, obtained in this work by TEM give values of mean lamellar thickness from 900 to 500 Å in the highest branch content and molecular mass. Enthalpies of melting allowed to calculate crystallinity; given values in the range from 47 to 68%.

Keywords: crystallinity, lamellar thickness, morphology, polyethylene

Introduction

The physical properties of the polyethylene (PE) are influenced by their lamellar morphology which is dependent of the branch content. As predicted by theory [1], the melting temperature depends on the comonomer content. It decreases monotonically with the comonomer content and does not depend on the specific chemical nature of the counits. Previous analysis in polyethylene has shown that ethyl, propyl, hexyl and vinyl acetate branches follow the same relation. It has been pointed out that a proportion of these small groups may enter into the lattice meanwhile with side groups larger than methyl, the side groups do not enter the crystal lattice in systems crystallized from the bulk. There is a point of interest in the melting and in the morphology of the polyethylene. Transmission electron microscopy (TEM) is a very powerful tool

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1418–2874/2002/ $ 5.00
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in the polymer field. The morphology of the crystalline polyethylene corresponds to lamellar crystals with thickness that vary, depending on the crystallization conditions, in which the molecules are ordered perpendicularly to the crystalline thin sheets with a molecular pledge of the chains the nature of which has been a topic of wide controversy [2–3].

In this work a relationship between the thermal properties in different polyethylene samples analyzed by differential scanning calorimetry (DSC) is presented. The morphology and the structural changes in the polymer were studied by TEM. This comparison is important because it is linked with the final properties of the PE and with its production process variables. The lamellar thickness and the melting temperatures of commercial polyethylene was compared to samples obtained in laboratory of PE grafted with diethylmaleate (DEM) [4].

Experimental

The thermal properties of the samples were studied by a Perkin Elmer DSC-7 calorimeter, calibrated with indium. 10 to 12 mg of polyethylene samples were sealed in aluminum pans and were subjected to the following steps: heating at 10°C min^{-1} from room temperature to 170°C and, after 3 min at 170°C, cooling at 10°C min^{-1} from this temperature to 25°C and, finally, heating at 10°C min^{-1} from 25 to 170°C to obtain the melting peak temperature (T_m). Enthalpies of melting were converted to crystallinity, $(1-\lambda)_{\Delta H_u}$ from the ratio $\Delta H_a/\Delta H_u$, being ΔH_a and ΔH_u the apparent and the completely crystalline heats of fusion, respectively. Taking for the enthalpy of a polyethylene crystal, ΔH_u, the value of 289 J g^{-1} [1].

To evaluate the morphology lamellar in PE a TEM Hitachi/H-600 was used. The morphology changes were studied from surface replicas micrographs obtained by TEM. Replicas were obtained by permanganic etching. The etching solution was prepared from concentrated sulfuric acid added to orthophosphoric acid. Then potassium permanganate crystals are added to the acid mixture. After agitated for a determined time, cleaned and dried polyethylene samples (originals and grafted) were placed in the solution. Replication is originated with a platinum shady and finally with a film of coal [5]. The film once separated from the sample constitutes a detailed replica of the surface that intent reflects the lamellar morphology.

Results and discussion

The experimental melting temperatures (T_m) of the original polyethylene samples and those of the functionalized polymers depend, first on the thermal treatment of the sample, and, second, on the experimental conditions for the determination of the melting behavior. The apparent melting temperature T_m obtained shows important differences with the thermal treatment applied previously in the polyethylene (Fig. 1). The degree of crystallinity increased with the thermal treatment, in the range of 10–13% for a treatment of 24 h to 100°C and T_m increased from 126 to 130°C.

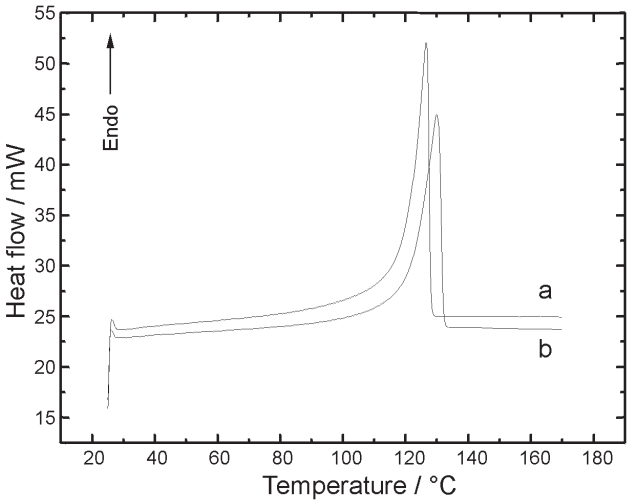

Fig. 1 Comparison of DSC endotherms for a HDPE-1 a – before and b – after a thermal treatment of 24 h to 100°C

The melting temperature is determined by the size of the crystal in the chain direction [6]. That way the thermal treatment seems to give origin of thicker lamellar populations as evidence the increment in the mean lamellar thickness for a HDPE-1 sample (Table 1). The occurrence of annealing processes during the thermal treatment is possible.

Table 1 Melting temperature (T_m), enthalpies of melting (ΔH_m) and mean lamellar thickness (L) determined in polyethylene samples by DSC and TEM

Sample	T_m/°C	ΔH_m/J g^{-1}	L/Å
HDPE-1 (M_w=175 000 g mol^{-1})	126	175	600
HDPE-1 (with thermal treatment[a])	130	198	917
HDPE1-f-DEM (2 mol% DEM)	121	137	514
HDPE-2	131	179	787
HDPE-3 (M_v=1 091 477 g mol^{-1})	133	195	514

[a] Thermal treatment: 24 h to 100°C

The mean crystal thickness was obtained from TEM micrographs (Fig. 2). The main morphological features of the samples were characterized by a lamellar structure. In this sense, the mean crystal thickness obtained from the micrographs gives an important depression with the grafting (values for HDPE-f-DEM in Table 1), with values decreasing from 917 to 514 Å.

This difference is originated from the increment of the amorphous regions, because in the functionalized polyethylene the disordered material was increased with the intro-

duction of the diethylmaleate units. It is important to notice when we compare both types of samples, original and grafted, the quantity of lamellas, which were evidenced in the micrographs by area, was smaller in the last case, as it is illustrated in Fig. 3.

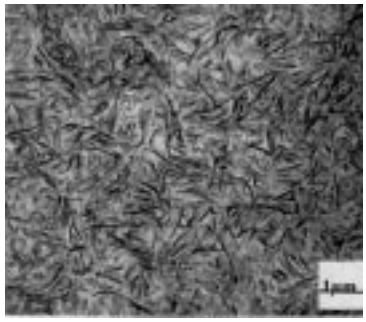

Fig. 2 Micrograph of surface replica in HDPE-1 with thermal treatment of 24 h at 100°C

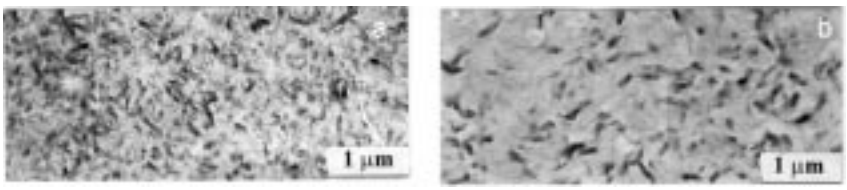

Fig. 3 Comparison of micrographs for surface replica in HDPE, (a) before and (b) after the functionalization (HDPE-f-DEM with 2 mol% DEM)

These facts are demonstrated by the decrease in the enthalpies of melting obtained by DSC in HDPE1 and HDPE1-f-DEM (Table 1). ΔH_m obtained from DSC endotherms was converted to levels of crystallinity. In this sense it was found a direct

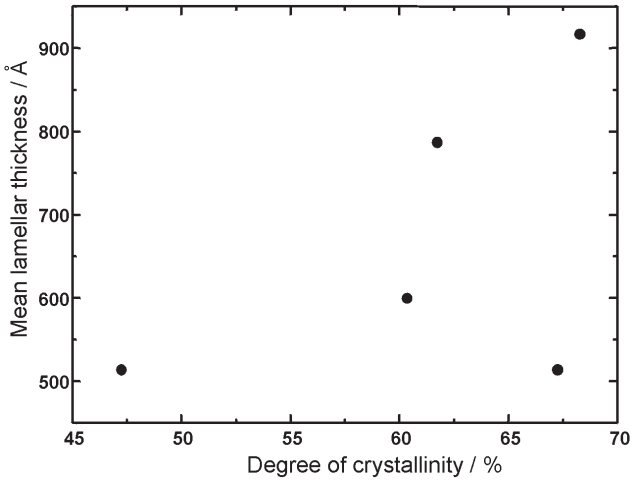

Fig. 4 Variation of the mean lamellar thickness (L) with the levels of crystallinity obtained from the enthalpies of melting (ΔH_m)

relationship between the levels of crystallinity with the mean crystal thickness measured (Fig. 4).

However, the sample HDPE-4, with a degree of crystallinity of 67%, escapes of this tendency, due probably to its high molecular mass, which affects its crystallization process. This relationship between ΔH_m and the mean lamellar thickness (L) can be useful to estimate morphological features from thermal properties.

Finally, it is important to indicate that previous works have found that the replication method, can give high lamellar spacing [7]. Due to it we are optimizing the experimental conditions to obtain values closer to SAXS spacing.

Conclusions

A relationship between the morphological measurements made from TEM micrographs and the thermal properties determined by DSC was established. The grafted polyethylene reveals an important depression in the mean lamellar thickness respect to the original sample. At the same time, the melting temperature as well as the enthalpies of melting were reduced with the modification. When comparing the micrographs of both types of samples, the quantity of crystals, which was evidenced by area, was smaller in the modified PE.

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The authors would like to thank CONICIT (National Council of Scientific Investigations) for the financial support through the project S1-98001906, as well as the UDO (University of Orient) for the financial support through the Council of Investigations, Project No. CI-5-1902-0836/98. They also thank Dr. Alejandro Müller, (USB, Caracas) for valuable discussions.

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