

DSC-STUDIES OF THE HIGH MOLECULAR WEIGHT POLYETHYLENE

M. KARTTUNEN¹ and P. TÖRMÄLÄ²

¹Tampere University of Technology, Institute of Materials Science,
Box 527, SF-33101 Tampere 10 (Finland)

²Tampere University of Technology, Institute of Textile Techno-
logy, Box 527, SF-33101 Tampere 10 (Finland)

ABSTRACT

Differential scanning calorimetry (DSC) was used to study the crystallization kinetics, melting points and the degree of the crystallization of thermoplastic and crosslinked high molecular weight polyethylene (HMWPE). The studied samples were prepared by extruding thermoplastic polyethylene and polyethylene-peroxide mixture into the form of tubes. The crosslinking was done at 250°C and the samples were cooled by water.

The results of DSC-investigations showed that the crosslinking changes the crystallization process of HMWPE. There seems to be a clear correlation between the degree of crystallization, the melting point and the degree of crosslinking of HMWPE.

INTRODUCTION

The morphology and the crystallinity of thermoplastics depend greatly on the rate of the nucleation and on the growth rate of spherulites. These parameters, on the other hand, depend strongly on the undercooling of the polymer melt.

The thermoplastic HMWPE crystallizes in the form of spherulites. The crosslinked HMWPE crystallizes in the spherulitic form, too. It has been shown by pressed crosslinked samples that the melting point and the crystallinity of the high density polyethylene decrease as a consequence of the crosslinking process (ref.1).

A rapid cooling will decrease the degree of crystallization of partially crystallizable polymers. During industrial production processes, such as extrusion and injection moulding, rapid cooling of plastics samples occurs. Therefore it is interesting and also important to study the crystalline structure of plastics samples produced under such conditions. Here we have studied by DSC the crystalline melting behaviour of thermoplastic and crosslinked HMWPE tubes which were rapidly cooled after extrusion (thermoplastic tubes) or after vulcanization (crosslinked tubes). Differences

in the crystallization behaviour between thermoplastic and cross-linked polyethylene were also studied.

EXPERIMENTAL

The studied samples were prepared by extruding thermoplastic HMWPE (Unifos News-1878, $M_{21} = 4$ g/10 min, 190°C) and HMWPE-peroxide (Luperox 130; 2,5-dimethyl-2,5-di(t-butyl-peroxy)hexyne-3) mixture into the form of tubes. The extruder was a single screw extruder Dolci 45-21D.

The outer diameter of tubes was 16 mm and the wall thickness was 2 mm. The thermoplastic tubes were cooled directly by means of water and the peroxide-containing tubes were first crosslinked by heating in a nitrogen atmosphere at 250°C and then cooled by water. The temperature of the waterbath was 20°C . The amount of peroxide was varied to achieve different degrees of crosslinking (ref.1).

Perkin-Elmer 2C-differential scanning calorimeter was used in the investigations of the melting and crystallizing behaviour. The used heating rate was $20^{\circ}\text{C}/\text{min}$. The areas of melt and crystallization peaks were determined by planimeter. A value 68,4 cal/g for the enthalpy of the totally crystalline polyethylene was used (ref.2). The crystallization kinetics were studied using the method which has been applied in studies of effectivity of nucleating agents in polymers (ref.3). Accordingly the thermoplastic and crosslinked polyethylene samples were heated to 190°C where they were kept 12 min to obtain samples where all crystallites were melted. After melting the samples were cooled to 50°C using the cooling rate $5^{\circ}\text{C}/\text{min}$. The weight of the DSC samples was 4.5 mg.

The DSC and extraction samples were cut from tubes perpendicular to the long axis of the tube. The degree of crosslinking was determined by method of extraction (DIN 16892).

RESULTS AND DISCUSSION

The crosslinking decreased both the enthalpy, melting point and the temperature of crystallization maximum of HMWPE as can be seen from the Fig. 1, where the melting and crystallization thermograms of a thermoplastic and a crosslinked sample (the degree of crosslinking = 95 %) are given.

Fig. 2 shows the crystallinity and the melting point of HMWPE as a function of degree of crosslinking.

In the strongly crosslinked samples (the degree of crosslinking > 90 %) the degree of crystallinity was 15-20 % lower than in the

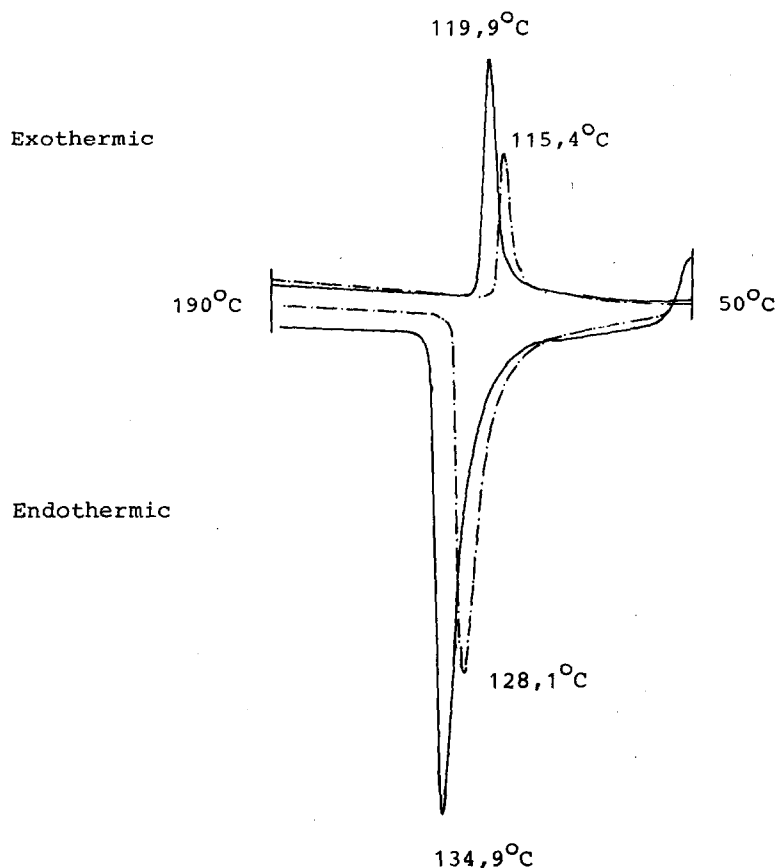


Fig. 1. Melting and crystallization thermograms of thermoplastic (—) and crosslinked (----) HMWPE (the degree of crosslinking = 95 %).

thermoplastic samples (see Fig. 2a). The melting point (the peak temperature) decreased about 11°C when HMWPE was totally crosslinked (see Fig. 2b).

On the outer surface of crosslinked tubes there was a thin layer whose degree of crosslinking was clearly lower than that in the deeper parts of the tube wall. For example in samples with degree of crosslinking of 99 % in the middle of the wall the degree of crosslinking was 55 % on the outer surface. This was evidently caused by evaporation of peroxide from the outer surface during crosslinking. The crystallinity was, however, about the same through the samples.

It is obvious that the C-C bonds which are formed between mole-

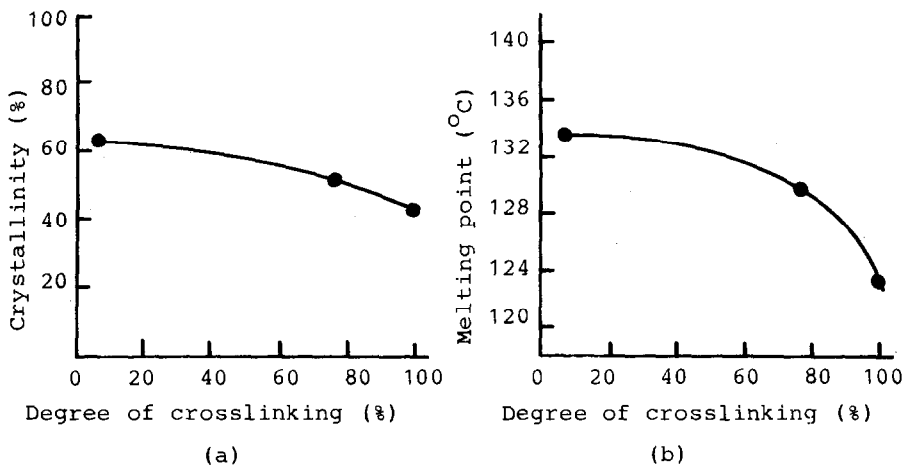


Fig. 2. (a) Crystallinity and (b) melting point of crosslinked HMWPE tube samples as a function of degree of crosslinking.

cular chains during crosslinking change crystallization process by decreasing the molecular order of the system and by decreasing the molecular mobility in the melt. The crosslinking changes probably both the rate of the nucleation of spherulites and the growth rate of spherulites. In addition, the tertiary substituted carbon atoms cannot place themselves into the crystal lattice.

The above measurements show that it is possible to estimate the degree of crosslinking of polyethylene in tube samples by measuring the degree of the crystallinity or the melting point with DSC-techniques.

REFERENCES

- 1 J. de Boer and A.J. Pennings, *Polymer*, 23 (1982) 1944-1952.
- 2 W.P. Brennan, *Thermal Analysis Application Study*, No. 22, Perkin-Elmer, Norwalk, USA, 1977.
- 3 H.N. Beck and H.D. Ledbetter, *J. Appl. Polym. Sci.*, 9 (1965) 2131-2142.