Journal of Thermal Analysis, Vol. 36 (1990) 1675-1684

THERMOANALYTICAL INVESTIGATIONS OF SELF-REINFORCED POLYETHYLENE

*M. Prox, B. Pornnimit, J. Varga** and *G. W. Ehrenstein*

ZENTRUM FÜR KUNSTSTOFFTECHNIK FRIEDRICH-ALEXANDER-UNIVERSITY
ERLANGEN-NÜRNBERG, GERMANY
*TECHNICAL UNIVERSITY OF BUDAPEST, BUDAPEST, HUNGARY

The mechanical properties of the self-reinforced polyethylene increase due to the formation of a shish-kebab structure.

Thermal analysis demonstrated that high-strength-PE has a heat deflection temperature 20°C higher than normal PE. The DSC analyses showed that the presence of a crystalline structure exhibits high thermal stability. This structural form does not relax at high temperatures as is shown by the fact that upon re-crystallization there were enough stable nuclei to build a similar crystalline structure.

Fundamentals of self-reinforced polyethylene

The applications of polymers are continuously increasing. In order to meet increasingly demanding applications, new materials such as high performance engineering polymers are being developed but they are very expensive in relation to commodity polymers (e.g. PE, PP, ...).

In addition to foreign body reinforcement with fibres (glass, carbon, aramide, etc.), self-reinforcement of polymers (the reinforcement of polymers without a foreign body) presents an important way of increasing a polymeric material's stiffness at relatively low cost.

With the method of the self-reinforcement [1], it is possible to orientate and fix the molecules in a highly ordered form. The orientation is produced by an extensional flow, such as would be generated by a converging or stagnation flow which cause the molecules to stretch and extend. In order to prevent the relaxation of the molecular orientation from the stretched chain configuration, the molecules must be rapidly crystallized.

Increasing the pressure on the melt raises the melting point of crystals as can be seen in Fig. 1 [2]. In the case of sudden pressure increase the melt crystallizes abruptly and the orientation is frozen.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

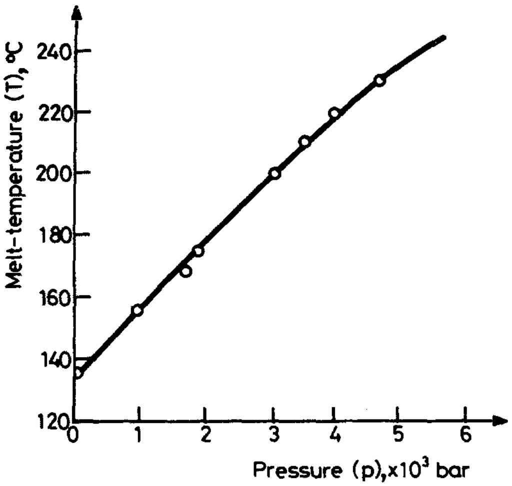

Fig. 1 Melting point as a function of pressure for polyethylene

The prerequisites for self-reinforcement are

- the generation of extensional flow to ensure chain orientation
- a processing temperature near the crystallization point
- a high pressure in the final phase to fix the orientation via pressure-induced crystallization.

The requirements for self-reinforcement can be met in either extrusion [3] or injection molding [1], allowing the technique to be used both processes.

Mechanical properties and structure of self-reinforced polyethylene

Control of the processing conditions to induce self-reinforcement can sigificantly increase the properties of PE-HD. Stiffness, strength and resistance to wear have been shown to increase by a factor of five in injection molding and by an order of ten in the extrusion process when the data are compared with the normally processed material.

Normally produced PE results in a sperulitic structure in which regions of folded crystals exist and are interconnected by regions of unoriented tie molecules. In an ordered self-reinforced material the molecules crystallize to a shish-kebab structure [4], (Fig. 2). The extended chain crystals (shishs) are the central fibrils oriented in flow-direction. The ordered lamallae (kebabs) grow in a folded form on these fibrillated nucleating sites under high pressure [5].

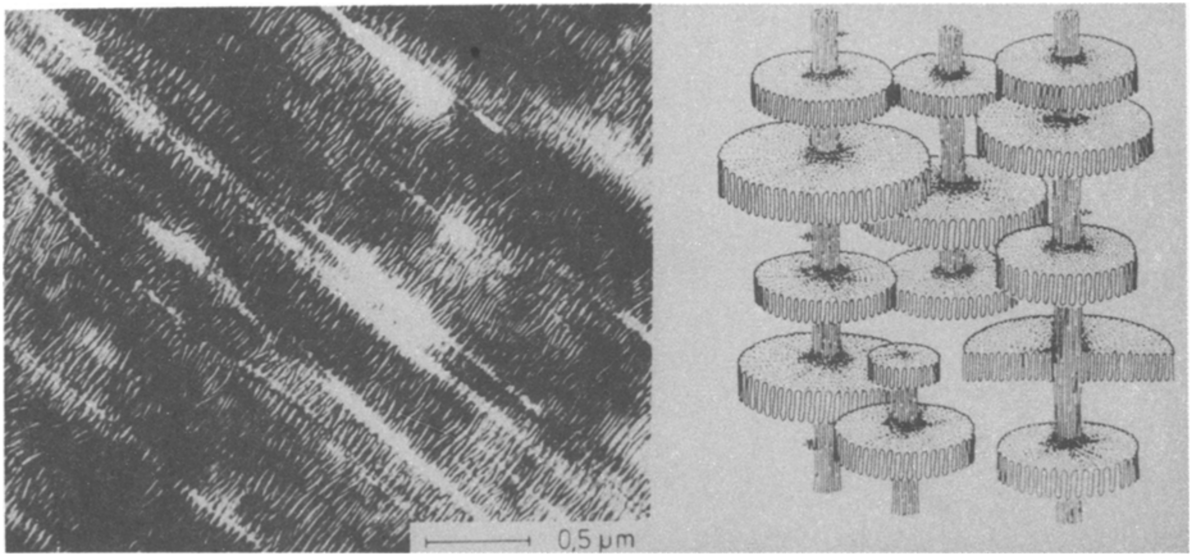

Fig. 2 Shish-Kebab structure in self-reinforced PE-HD

The result of the formation of the special shish-kebab structure is the increasing of several properties of PE. The aim of the present paper is to study the properties at high temperatures and to demonstrate the results by thermal analysis of the structure.

Experiments

Thermo-mechanical properties

The dependence of the mechanical properties on the temperature was measured in the torsional vibration test between 20° and 140° [3]. A plot of shear modulus and damping as function of temperature shows that with controlled self-reinforcement during the production process the stiffness increases as does thermal stability, Fig. 3. The temperature at which the beginning of the steep rise in damping is observed, which is a sign of softening in the material, increases by 20° to 120° in comparison to normal PE.

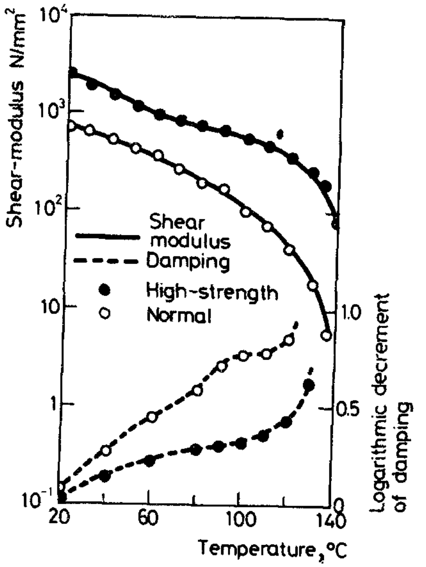

Fig. 3 Dependence of shear-modulus and damping on the temperature

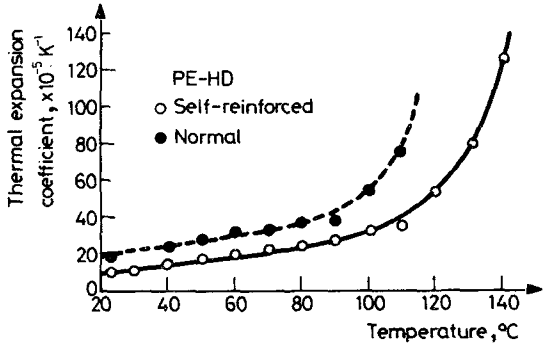

Fig. 4 Influence of self-reinforcement on the thermal expansion coefficient

This thermal shift in the material properties of about 20° is also demonstrated by the thermal expansion coefficient, as measured by TMA, Fig. 4. Below 110°, self-reinforced PE has a relatively small expansion coefficient. At temperatures above 110° the expansion coefficient increases steeply. The steep gradient in the thermal expansion coefficient plot for normal PE begins at a temperature 20° lower than for the reinforced material. The thermal expansion coefficient of self-reinforced PE in the flow direction is the same as in the direction perpendicular to flow.

This observation is confirmed by the shrinkage behavior, the results of which show high thermal stability for the high strength PE in contrast to the considerable shrinkage shown by the normal PE, Fig. 5.

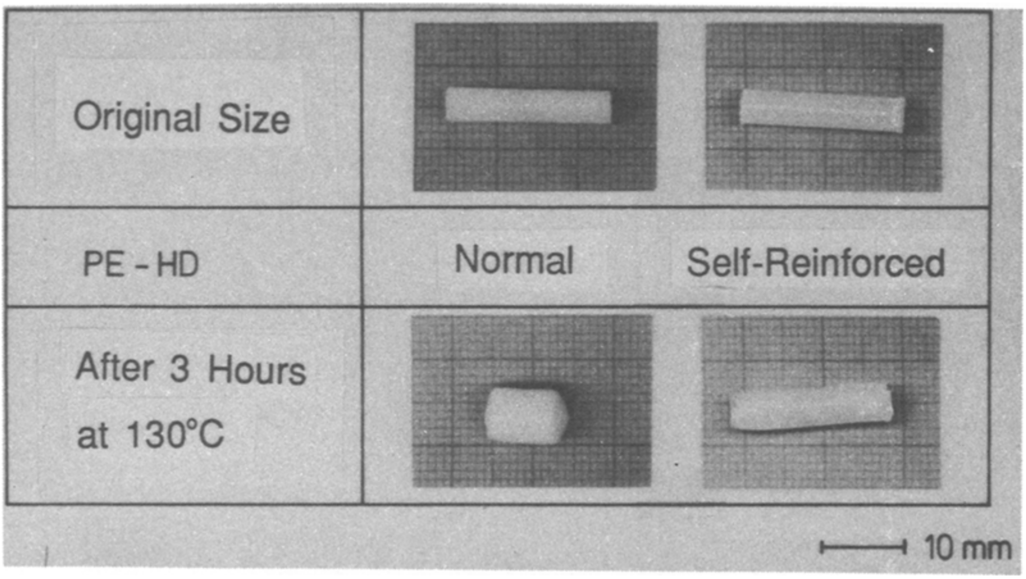

Fig. 5 Shrinkage behaviour of polyethylene

The high heat deflection temperature and the resulting mechanical strength at high temperature indicate that the increase in strength is the result of the formation of the special shish-kebab structure morphology.

DSC-measurements

The formation of different crystalline structures in high-strength material can be demonstrated with the aid of DSC-analysis. Normal PE has a small, deep melting-peak indicating a regular distribution of crystallites, Fig. 6. The self-reinforced PE has a distinctive wide peak. Since type of this structure requires considerably more thermal energy to melt the various forms of crystallites.

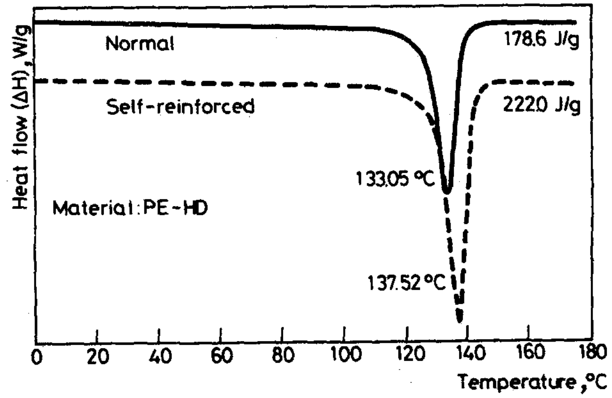

Fig. 6 Melting behaviour of self-reinforced polyethylene

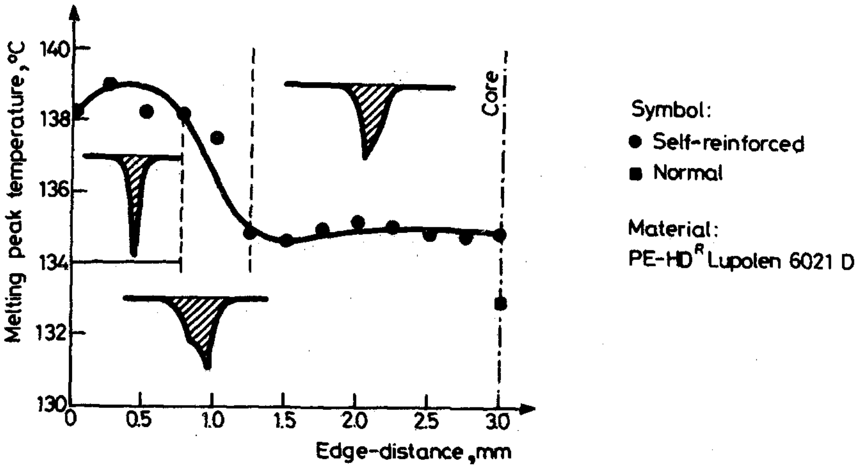

Fig. 7 DSC melting peak temperature over the cross section of high strength PE-HD

The distribution of several crystalline structures on the cross-sectional of the high strength extrudate can be demonstrated with DSC-measurements. For this studies microsections (30 μm) were cut on the cross-sectional of the extrudate and measured in the DSC. The formation of different regions (edge, transition and core) can be distinguished, Fig. 7, by the form of the peaks and the melting temperature. The edge region has a narrow peak and a high melting point while in the core region the melting temperature is 4°

lower and the peak width is larger. The transition region shows indications of the start of a double peak.

The melting peak of normal PE is at 133°. Self-reinforced PE has two distract melting peaks corresponding to two crystalline forms. The more thermally stable crystallites melt at 140° while the less stable form melts at 134°, Fig. 8. It can be seen clearly that the edge region of the high-strength PE has a higher thermal stability. The thermal stability decreases with increasing distance from edge, while the most fraction of crystalline form exhibiting lower thermal stability increases. Noteworthy in the core region are the almost constant proportions of both crystalline forms. The individual lamellae (kebabs) melt at lower temperatures, while the extended chain crystals (shishs) melt only at higher temperatures [3].

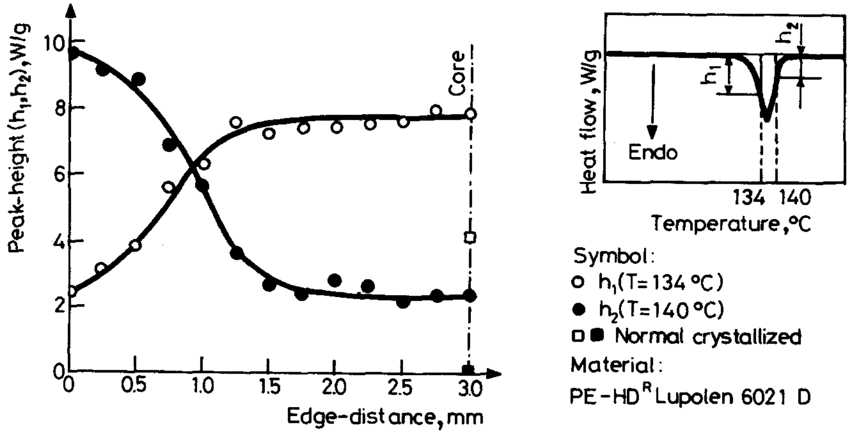

Fig. 8 Relative proportions of crystalline forms in the cross section of high strength PE-HD

Hot stage experiments

The melting and subsequent re-crystallization behaviour of the self-reinforced material as a function of final temperature of heating (T_F) was determined with the aid of a hot stage [6]. The structural memory effect [6] allows statements to be made about thermal properties and the form of the original structure. Micromoted slices were heated at a temperature gradient of 2 deg/min to several different temperatures above the melting point and the resulting re-crystallization was observed. Upon heating to $T_F = 150^{\circ}$ all crystallites were molten. After an isothermal crystallization at 128° for 2 min,

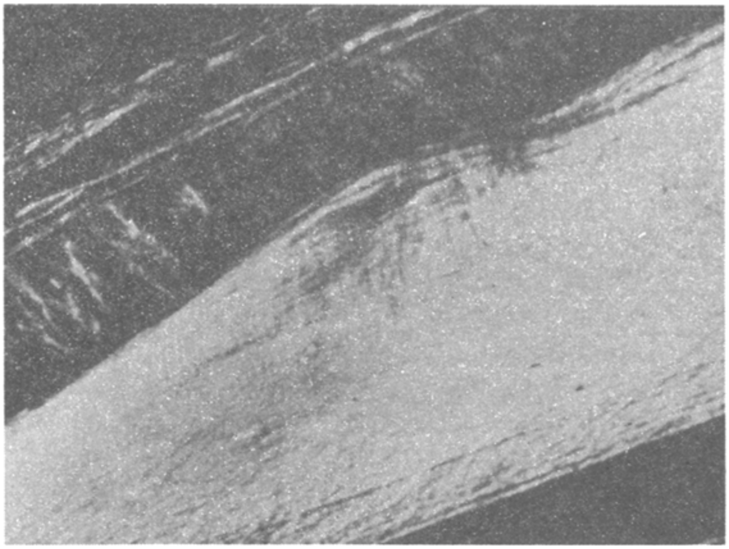

Fig. 9 Light-microscope, hot stage experiments on PE-HD at 150°C

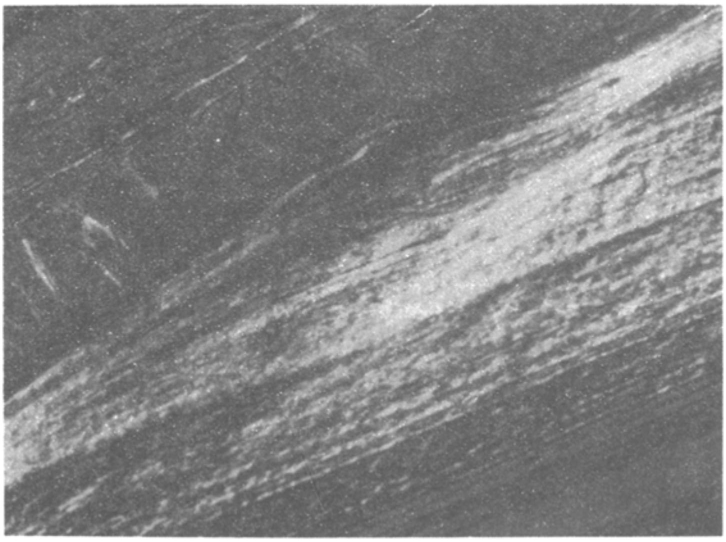

Fig. 10 Light-microscope, hot stage experiments on PE-HD at 170°C

Fig. 9, large regions were crystallized. The regions that were originally highly birefringence crystallized first. These regions also demonstrate a high birefringence after re-crystallization. After heating to $T_F = 170^\circ$ birefringent areas could still be observed, Fig. 10. Not until heating to $T_F = 220^\circ$ all of the stable nuclei of the original structure become molten and the previously observed memory effect partially disappear, Fig. 11.

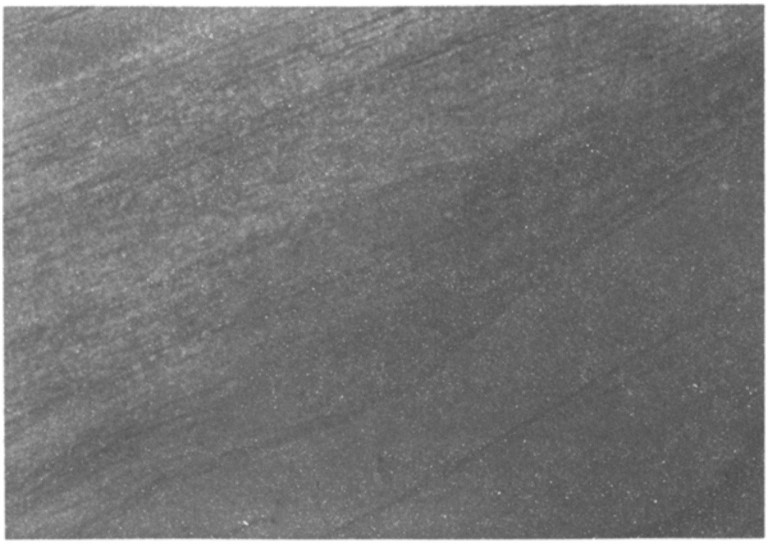

Fig. 11 Light-microscope, hot stage experiments on PE-HD at 220°C

* * *

The authors would like to thank Professor J. Petermann (TU Hamburg-Harburg) and Professor A. J. McHugh (University of Illinois) for their help in explaining the morphology and especially Mr. D. Tree, M. Sc. (University of Illinois) for the correction of the manuscript.

References

1 Cl. G. Maertin, PhD-Thesis. Universität (Gh) Kassel 1988.
2 J. Osugi, K. Hara, The Review of Physical Chemistry of Japan., 36 (1966).
3 B. Pornnimit, G. W. Ehrenstein, Kunststoffe, 79 (1989) 631-636.

4 G. W. Ehrenstein, Cl. Maertin, Kunststoffe, 75 (1985) 105.
5 A. J. McHugh, Personal Communications, 1988.
6 J. Varga, Periodica Polytechnica Chem., Eng, 28 (1984) 117.

Zusammenfassung — Die Sseigerung der mechanischen Eigenschaften von eigenverstärktem Polyethylen (PE-HD) wird durch die Ausbildung einer Shish-Kebab-Struktur erreicht.

Die durchgeführten thermo-analytischen Untersuchungen weisen für das hochfeste PE-HD gegenüber normalen PE-HD eine um 20°C höhere Wärmeformbeständigkeit nach. Die DSC-Untersuchungen zeigen, daß eine kristalline Struktur hoher thermischer Stabilität existiert. Diese morphologische Form relaxiert bei höheren Temperaturen nicht sofort; bei der Rekristallisation sind genügend stabile Keime vorhanden, um wieder eine ähnliche Kristallstruktur zu bilden.