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A DSC STUDY OF THERMALLY TREATED AND UV-TREATED LOW-DENSITY POLYETHYLENE

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The melting behaviour of thermally and UV-treated polymer film was studied using DSC. The melting profiles was registered after periods of 24 hours of exposure. The melting profiles after the UV-exposure resembled those observed after heating at 60°. A weak shoulder was first recorded at about 50° and was observed to shift to higher temperatures with increasing exposure time. At the end of the experiments the shoulder was registered around 80°. The changes are compared with results from mechanical tensile tests.

The molecular weight and the conditions of crystallization greatly determine the ease with which the fine structures of semicrystalline polymers change. It has been shown experimentally that the crystals of polyethylene [1 – 3] and other semicrystalline polymers [4] rearrange easily during heating. Theoretically this has been regarded as a consequence of the conformational changes in the amorphous regions of the polymer [6, 7]. Gamma-radiation has been used to produce cross-links between amorphous molecules to prevent rearranging [8]. The main concern in the works mentioned has been directed to rearrangement at temperatures near or above the crystalline melting point, as well as to molecular changes in the polymer melt. In this study an effort has been made to investigate the calorimetrically observed phenomena produced by treatment at 60 to 80° and by UV-light.

Experimental

The low-density polyethylene used was a commercial grade polymer, Unifos DFDS 6600. The resin is reported [9] to have the following characteristics: density 923 kg/m^3; melt index 0.31 g/10 min, $\overline{M}_w = 159 \cdot 10^3$, $\overline{M}_n = 29 \cdot 10^3$, degree of long chain branching $1.5 \cdot 10^4$. The experimental details are described elsewhere [10]. The samples were cut from a 0.5 mm thick film extruded by Oy Wiik & Höglund Ab. According to the manufacturer the film contained no additives. All test specimens were cut in form before heat or UV-treatment.

The samples were placed on cleaned aluminium foils and heated in an oven with air circulation at 60° and 80°. The temperature stability was better than $\pm 2°$. After heating, the samples were quenched to $20 \pm 2°$ and conditioned at this tem-

perature in a desiccator overnight. A DSC run was conducted after every 24 hours of heat treatment.

For UV-treatment the samples were exposed to a UV-lamp (Hanovia Fluorescence Lamp, Modell 11, Hg-arc lamp) at a distance of 500 $\pm$ 50 mm. The exposure was extended up to 36 days. The temperature during the test was measured not to exceed 40°. The energy density of the UV-light was not measured. The samples were conditioned as described for samples with heat treatment.

The melting profiles were determined with a Perkin-Elmer DSC-1 differential scanning calorimeter. The instrument was calibrated using indium as reference material. The heating rate of 16°/min and sensitivity range 4 of the instrument were used. The DSC runs were done under a N_2 atmosphere.

Results and discussion

Heating of a polymer sample at a temperature within its melting range may result in both melting and recrystallization. The characteristic fusion profile of the polymer obtained by DSC was remarkably influenced by the thermal history of the specimens. The results observed after heat treatment at 60° are given in Fig. 1.

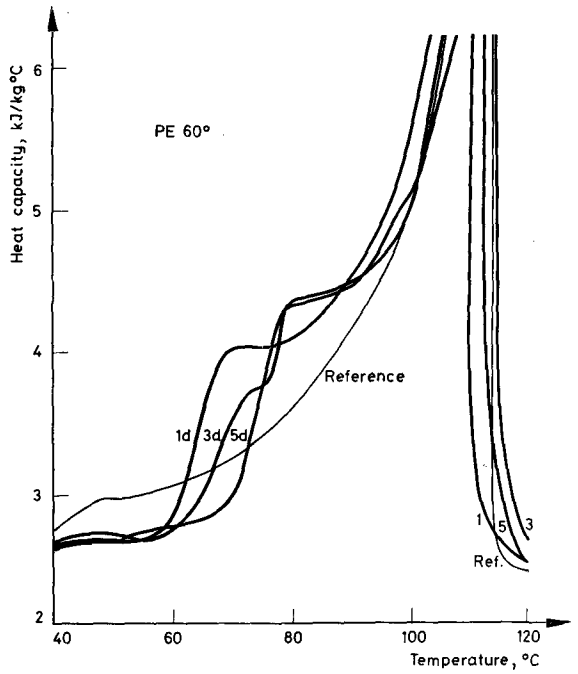

Fig. 1. DSC melting profiles of the polyethylene samples after isothermal treatment for 1, 3 and 5 days at 60°. The sample as received is marked reference

Gradual changes could be recorded in the samples in the form of a bimodal thermogram. First a single shoulder was observed slightly above the annealing temperature. Another shoulder appeared along with the first one after an exposure of about 3 days. Within 5 days the first shoulder had gradually disappeared, while the second one was steadily growing at about 80°. As a result of the treatment at 80° the curves given in Fig. 2 were observed. They indicate only a single shoulder phenomenon at about 90°.

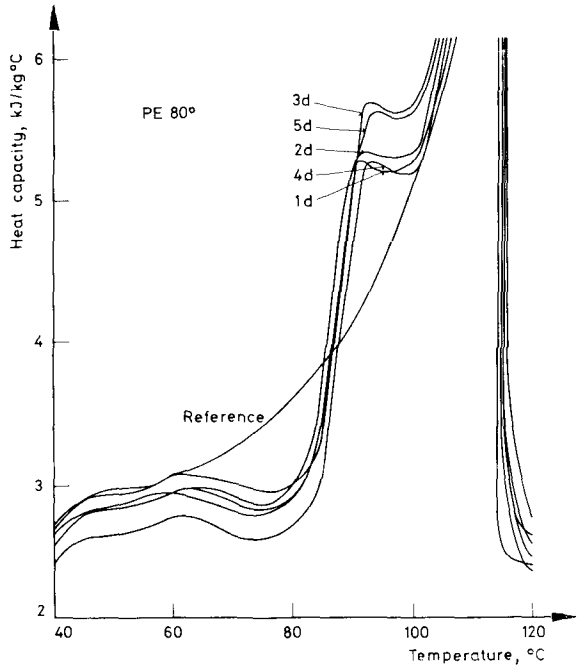

Fig. 2. DSC melting profiles of the polyethylene samples after isothermal treatment for 1 . . . 5 days at 80°

At 60° the first shoulder is presumably connected to primary recrystallization. However, the time necessary to attain thermal equilibrium at 60° is greater than the time required for primary crystallization. Apparently the results at 60° describe the transition of the sample from partial melting through primary crystallization to a rearranged physical state. The scanning rate of 16°/min and the appearing of the second shoulder first after a relatively long period of heat treatment suggest that the measured phenomenon is not only a result of superheating, but is more probably related to the real physical state of the sample.

At 80° the mobility of the amorphous or molten molecules is higher and the rearrangement takes place simultaneously with the primary crystallization. The differences between the heat-treated samples in Fig. 2 should fall within the limits of

the experimental error. The new form of the melting profile is mainly ascribed to crystalline rearrangement towards a thermally more stable crystalline morphology [11].

Quenching of the sample probably gives rise to stresses. The samples were allowed to relax after heat treatment at 80° for 9 months at 20°. Figure 3 gives the DSC curves obtained from this group of samples. A comparison of Figs 2 and 3

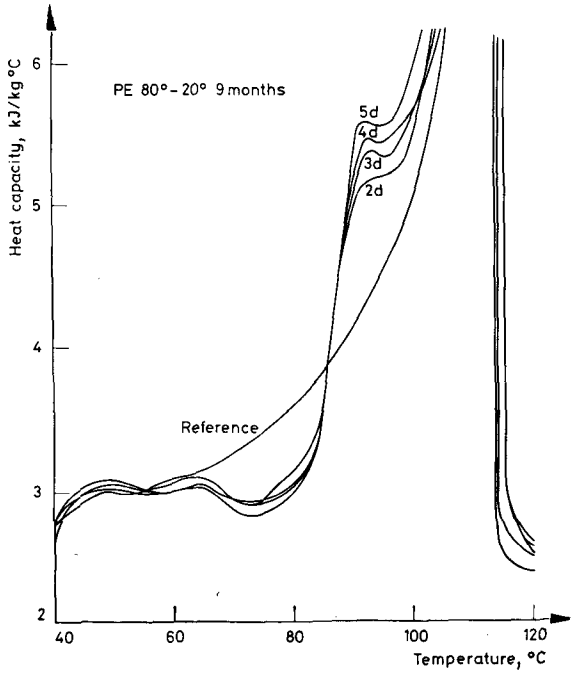

Fig. 3. DSC melting profiles of the polyethylene samples after 2 . . . 5 days of isotherma treatment at 80 °and 9 months of conditioning at 20°

indicates minor changes. The scattering of separate curves is smaller in Fig. 3 than in Fig. 2. Very strictly taken, the shoulder heights, however, are arranged according to the respective heating times at 80°. The fusion profile has retained its character.

The effect of the UV-treatment on the DSC curves of polyethylene samples is illustrated in Fig. 4. The UV-light also induced a weak shoulder first recorded at about 50°. This was observed to shift to higher temperatures with increasing exposure time. These changes are hardly connected to melting. It is more likely that UV-light has induced oxidation which leads to a diminishing of the molecular size or also to cross-linking. The shift of the heat consumption maximum towards higher temperatures in the DSC curve probably supports the latter assumption.

Annealing at 65° has been observed [12] to influence the mechanical properties of a non-crystalline PVC-polymer. Conventional tensile tests were also conducted

in this study. In these experiments the heat treatment was not observed to produce changes in the stress or elongation values. The UV-irradiation, however, diminished the elongation at rupture while the yield stress remained relatively unchanged.

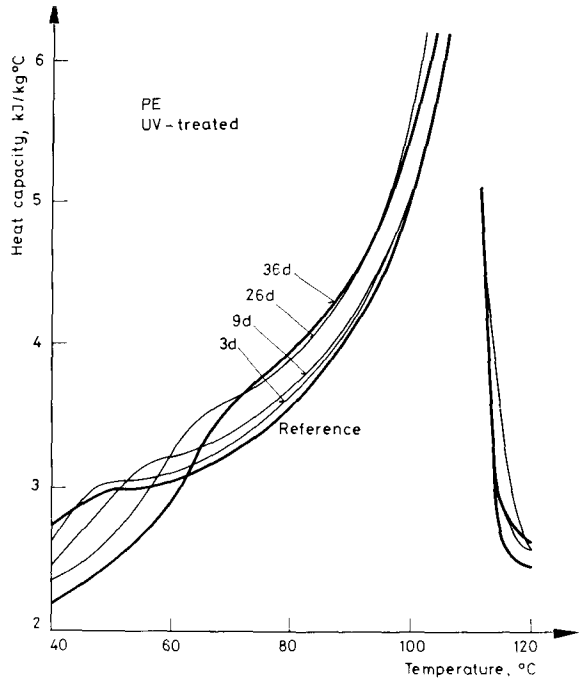

Fig. 4. DSC melting profiles of the polyethylene samples after 3, 9, 26 and 36 days of UV-treatment

Conclusions

The results illustrate that specimens with different histories may have fusion profiles with common features. If it is taken into account that the physical states of the samples may differ considerably, an integrated study seems to be a necessity.

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RÉSUMÉ — On a étudié par analyse calorimétrique différentielle (DSC) le comportement pendant la fusion d'un polymère en film soumis à un traitement thermique et par UV. Les profils de fusion ont été enregistrés après des périodes d'exposition de 24 h. Les profils de fusion après traitement UV ressemblent à ceux obtenus après chauffage à 60 °C. Un faible épaulement vers 50° est d'abord enregistré puis il se déplace vers les températures plus élevées, quand la durée d'exposition augmente. En fin d'expérience l'épaulement se situe vers 80°. Ces modifications sont comparées avec les résultats obtenus à partir des essais mécaniques de traction.

ZUSAMMENFASSUNG — Das Schmelzverhalten eines thermisch und UV-behandelten Polymerfilms wurde unter Anwendung der DSC untersucht. Das Schmelzprofil wurde nach 24-stündiger Behandlung registriert. Die Schmelzprofile nach UV-Behandlung ähnelten jeden, die nach Erwärmung auf 60° erhalten worden waren. Eine schwache "Schulter" wurde zuerst bei etwa 50° beobachtet, welche bei steigender Behandlungszeit in Richtung der höheren Temperaturen verschoben wurde. Am Ende der Versuche wurde die "Schulter" bei etwa 80° registriert. Die Änderungen wurden mit den Ergebnissen mechanischer Dehnteste verglichen.

Резюме — Используя ДСК был изучен режим плавления полимерной пленки, обработанной термически и облученной ультрафиолетовым светом. Контур плавления после выдержки под ультрафиолетом напоминает то, что наблюдалось после нагревания при 60°. Сначала было зарегистрировано слабое плечо около 50°, которое с увеличением времени выдержки сдвигалось в сторону более высоких температур. В конце экспериментов это плечо было зарегистрировано около 80°. Эти изменения сопоставлены с результатами механических испытаний на разрыв.