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Crosslinking of oriented polyethylene by electron beam radiation.
Influence of morphology induced by drawing

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The influence of drawing on the crosslinking efficiency for electron beam radiation is reported for solution-crystallized ultra-high molecular weight polyethylene. A maximum in crosslinking efficiency is found at a draw ratio of approximately five, indicating an optimum morphology for inducing crosslinks during the hot-drawing process.

(Keywords: crosslinking; electron beam radiation; UHMW-PE; ultra-drawing)

Introduction

Oriented polyethylene (PE) fibres produced via melt spinning/drawing\(^1,2\) and solution spinning (gel spinning)/drawing\(^3,4\) possess favourable properties such as high specific moduli, toughness, chemical and light resistance\(^5\).

Unfortunately, however, since oriented PE fibres/tapes are obtained via solid-state drawing at elevated temperatures, close to but below the melting temperature, these structures are inherently less stable with respect to static loading for prolonged times.

A lot of studies have been carried out to improve the long-term properties of oriented PE fibres, i.e. to reduce the level of creep. By using copolymers with a small degree of branching or by crosslinking, creep can be reduced\(^6\). Woods, Busfield and Ward\(^7\) have shown a drastic reduction by crosslinking oriented PE fibres using electron beam (EB) radiation and acetylene gas as a sensitizing agent. In the case of solution-spin (gel spun) fibres, based on ultra-high molecular weight PE (UHMW-PE), no successful reports have been presented with respect to radiation-crosslinking of these oriented structures. De Boer and Pennings reported considerable decreases in tenacity when gel spun UHMW-PE fibres were irradiated\(^8\). Since both high energy y and EB radiation not only result in the formation of crosslinks but also in chain scission\(^9\) (the relative ratio depending on chemical structure and morphology), they attributed the reduction in tenacity to chain scission\(^8\).

To overcome the intrinsic problem of extensive chain scission in oriented, highly crystalline gel spun PE fibres, Hikmet et al.\(^10\) used EB radiation to induce crosslinks prior to the drawing process. In this mode of operation, oriented crosslinked PE structures could be obtained with a 10-fold decrease in creep rate if compared with uncrosslinked counterparts at identical values for the Young’s modulus.

It is well known that the efficiency of the radiation in forming mechanically effective crosslinks will depend strongly on the polymer morphology\(^11\). Up to now very little attention has been focused on the study of the influence of drawing on the crosslinking efficiency. Since during the drawing process of a polymer like PE rather drastic morphological changes occur\(^12,13\), crosslinking during an intermediate stage of drawing will allow a greater understanding about the effect of irradiation on crosslinking. Furthermore, it could be of industrial importance to know at which stage of the drawing process the crosslinking is most efficient, in order to optimize the possible use of irradiation facilities within a continuous fibre or tape production process. Moreover, effective crosslinking not only improves the creep resistance but also the maximum use temperature of the material\(^14\).

Experimental

Hostalen-Gur 412 (Hoechst/Ruhrchemie) was used as starting material for these studies; \(M_w \approx 1500 \text{ kg mol}^{-1}\), \(M_m \approx 200 \text{ kg mol}^{-1}\). Films were cast from 1.5% solution in xylene as described previously\(^12\). The dried films were extracted in n-hexane at room temperature to remove the last traces of solvent (xylene) and stabilizers. In order to obtain flat and void-free homogeneous samples, the films were finally pressed at room temperature. These films were used as a precursor for the radiation studies. The use of cast-films instead of as-spun fibres was simply related to the fact that drawn tapes prepared from these films are easier to handle in laboratory measurements such as swelling (see below). Strips cut from the films were drawn manually at 120°C and the draw ratio was determined from the displacement of ink marks originally placed 1 mm apart. Unfortunately, however, due to necking it was impossible to obtain drawn tapes with a homogeneous draw ratio between 1 and 5. Finally it should be noted that the undrawn tape (\(\lambda = 1\)) was also kept at the drawing temperature for a short time in order to have similar temperature history for both undrawn and drawn samples.

Irradiation was carried out at room temperature using the 3 MeV electron beam (High Voltage Engineering unit) at the Interuniversitair Reactor Instituut, Delft.

Swelling measurements on the irradiated materials were carried out after removal of the sol-fraction by Soxhlet extraction for about 60 h, using xylene as refluxing agent. The crosslinked gel was equilibrated in xylene at 120°C for 5 h, transferred quickly into a stopped flask and weighed \((W_w)\). Subsequently the swollen material was dried under vacuum at 50°C and weighed \((W_d)\). Finally the swelling ratio (SR) at 120°C was calculated assuming additivity of volume in the swollen gel:

\[
SR = 1 + \frac{W_{sw} - W_{dr}}{W_{sr}} \frac{\rho_s}{\rho_p} \tag{1}
\]

where \(\rho_s\) and \(\rho_p\) are the densities at 120°C of the polymer and the solvent, respectively \((\rho_s = 0.908 \text{ g cm}^{-3}; \rho_p = 0.768 \text{ g cm}^{-3})\). The swelling ratio given for each sample is the average of five to seven measurements.
The corresponding average molecular weight between the crosslinks, $M_e$, was estimated from the equilibrium swelling ratio using the Flory-Rehner equation:

$$\frac{\rho_p V}{M_e} \cdot \frac{V}{2} = \frac{V}{3} = \ln(1-v) + v + \mu v^3$$

where $\rho_p$ is the density of the dry polymer (0.908 g cm$^{-3}$ at 120°C), $V$ the molar volume of the solvent (138 cm$^3$ mol$^{-1}$ for xylene), $v$ the polymer volume fraction which corresponds to SR$^{-1}$ and $\mu$ the Flory-Huggins polymer/solvent interaction parameter given by 0.33 + 0.55v at 120°C$^{16}$. However, since this Flory-Rehner equation was developed from statistical mechanics, in which network imperfections such as chain end segments were not taken into account, a modified equation was used. This modified equation (3) proposed by Flory$^{17}$ makes allowance for such imperfections:

$$M'_e = \frac{M_e M_e}{(M_e + 2M_e)}$$

where $M'_e$ is the true average molecular weight of effective chains, $M_e$ the number average molecular weight of the uncrosslinked polymer (200 kg mol$^{-1}$) and $M_e$ the average molecular weight between crosslinks calculated via equation (2).

**Results and Discussion**

Figure 1 shows the $M'_e$ values, derived from the experimental swelling ratios according to equations (2) and (3) for different EB radiation doses. For convenience the experimental swelling ratios (SR) are indicated on the right-hand vertical axis. As can be clearly observed, a pronounced minimum occurs at a draw ratio $\lambda$ close to 5.

Another measure for crosslinking efficiency can be defined as follows. The maximum isothermal draw ratio, $\lambda_{max}$, for a two-stage drawing process, using the same drawing speed, can be defined as:

$$\lambda_{max} = \lambda_1 \lambda_2$$

in which $\lambda_1$ is the initial draw ratio and $\lambda_2$ corresponds to the second draw ratio up to break. In the case of a 1.5 wt% solution crystallized UHMW-PE sample, $\lambda_{max}$ is found to be approximately 110 at a drawing temperature of 120°C. However, if the sample is irradiated after an initial drawing to an intermediate draw ratio $\lambda_1$, the second draw ratio $\lambda_2$ will be influenced due to crosslinking, resulting in a decrease of $\lambda_2$. This decrease will be higher whenever the sample is crosslinked more. Therefore a crosslinking efficiency can be deduced by determination of $X_{eff}$, according to:

$$X_{eff} = \frac{\lambda_{max}}{\lambda_1 \lambda_2}$$

in which $\lambda_2^e$ is the second draw ratio up to break after irradiation. In Figure 2, $X_{eff}$ is plotted against the initial draw ratio for three different radiation doses. These results are completely consistent with the results from Figure 1 and thus underline the presence of an effective crosslinking morphology at a draw ratio of approximately 5.

Morphological studies on ultra-drawing of solution crystallized UHMW-PE have shown that the lamella-fibril transformation is completed at a draw ratio of 5-6 (refs 12 and 13). At this draw ratio, the tautening of the tie molecules just starts and the fraction of less ordered molecules is at a maximum. Furthermore, crystallinity measurements via differential scanning calorimetry as well as via infra-red spectroscopy, show a minimum in crystallinity at the same draw ratio (i.e. 5-6)$^{18}$. Apparently the crosslinking efficiency of EB radiation is directly related to the morphology and the crystallinity of the sample.
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Summarizing, we can conclude that crosslinking is most efficient at the initial stages of drawing, i.e. $\lambda < 0.5$. Combining these results with the knowledge obtained from detailed morphological studies as discussed before, one is tempted to conclude a maximum efficiency at $\lambda \approx 0.5$.

This implies that the introduction of crosslinking via EB radiation within a continuous spinning/drawing process is most efficient in the initial stages of the drawing process. Of course one has to optimize the radiation dose in view of the aim of the desired product properties.

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References


Influence of the temperature on the structure of poly(p-phenylene) (PPP) films formed by electropolymerization of benzene on platinum electrodes in sulphur dioxide medium

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Long regular poly(p-phenylene) (PPP) chains are obtained by electrochemical oxidation of benzene at a Pt electrode in very pure sulphur dioxide in the presence of 0.1 M N(Bu$_4$)BF$_4$. At a very low temperature ($-75^\circ$C) the chains are linear and consist of about 16 phenyl units; at $-20^\circ$C there are about 30 phenyl units, but the linearity is not as good as that observed at the lower temperature. In both cases the length and the linearity of the chains are far better than those previously obtained in different organic solvents.

(Keywords: polymer film; poly(p-phenylene) (PPP); electropolymerization; sulphur dioxide; i.r. spectroscopy)

Over the last few years, several papers related to the electrochemical synthesis of poly(p-phenylene) (PPP) by anodic electropolymerization of benzene or biphenyl have emerged in the literature. Various experimental conditions have been advocated by different authors, but very little information has been given about the structure of the chains and their degree of polymerization\(^1\)–\(^9\).

In a previous exploratory work we showed the possibility of obtaining dendritic PPP deposits by electrochemical oxidation of benzene or biphenyl on Pt and by using liquid SO$_2$ at $-20^\circ$C as the solvent.\(^7\) I.r. spectra for these polymerized products showed that the chains were not very long, about 10 phenyl rings for one polymer chain, and these polymers appeared highly crosslinked.

Recently, in a preliminary note, PPP films were also obtained by electro-oxidation of benzene or biphenyl in SO$_2$ containing P$_2$O$_5$ at low temperature ($-45^\circ$C) for the purpose of making electrodes for rechargeable accumulators.\(^8\) Since this work had an applied objective no structural results about the polyphenylene chains were given.

By carrying out the oxidation of benzene or biphenyl in different 'acidic' solvents (according to the Lewis concept), such as CH$_3$CN, CH$_2$Cl$_2$, CH$_3$NO$_2$ etc., we observed that the degree of polymerization of the PPP did not exceed about 10 phenyl rings per chain. The structure of the chains was irregular, and this linearity defect was believed to be due to a secondary substitution at the ortho-position which produced a crosslinked structure.\(^10\)

By reconsidering the problem of the electrochemical polymerization of benzene in liquid SO$_2$, using a very anhydrous (C$_{H_2}O \leq 10^{-2}$ M) high-purity solvent, and without adding any dehydrating reagent to the electrolytic medium, we found the formation of homogeneous PPP films which adhered firmly to the electrode surface. Different ammonium salts with fluorinated anions were used to observe the formation of electroactive films. With typical medium conditions corresponding to 0.1 M N(Bu$_4$)BF$_4$ and 0.1 M benzene in