Destruction Level of Crystalline Material

Lamellar Structure in Melt Crystallized Low Density Polyethylene.*

2. Study of the Crystalline Phase After Chlorosulfonation


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SUMMARY

A combined X-ray diffraction and DSC investigation of the crystalline phase in lamellar low density polyethylene after conventional chlorosulfonation treatment has been carried out. Our results indicate that the acid attack does not involve any heavy group penetration within the lattice. The location of these groups at the basal crystal surface contributes, however, to an enhancement of the melting temperature of the modified lamellae. It turns out that the destruction level of crystalline material at 45°C, after 15-20 h is of the order of 20% and progressively increases for longer periods of time.

INTRODUCTION

In a previous study the kinetics of chlorosulfonation of polyethylene (PE) was investigated to establish the optimum conditions to adequately observe the lamellar morphology by transmission electron-microscopy (TEM) (MARTINEZ-SALAZAR, KELLER et al, 1983). No modification of lamellar thickness throughout the range of treatment times used (0-100 h) was detected. The lamellar periodicities measured from TEM were consistent with the long period constancy observed by small angle X-ray diffraction (SAXD). The lateral dimensions of the lamellae were, however, markedly reduced after long fixation times. Furthermore, as a consequence of the chlorosulfonation treatment the surface hardening of the samples was quantitatively evidenced (MARTINEZ-SALAZAR, RUEDA et al, 1983). The rate of hardness increase turned out to be larger for samples with a higher initial volume crystallinity. This increase was explained in terms of a lamellar hardening owing to a surface attachment of heavy groups and eventual chemical crosslinking at the crystals' surface and within the surface layer.


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The purpose of this study is to examine the influence of the chlorosulfonation treatment on the crystalline phase by means of a combined wide angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC) study. We believe that this investigation is of major interest in relation to the question on whether any substantial destruction of the crystalline phase during PE chlorosulfonation occurs.

EXPERIMENTAL

Details about the chlorosulfonation of the samples have been described previously (MARTINEZ-SALAZAR, KELLER et al, 1983). The data presented in this paper refer to a commercial PE sample (Hostalen GC, M_w=50x10^3, and 0.28 branches per 100 carbons. Treatment temperatures of 45°C and 60°C and times ranging up to 100 hours were selected. Wide angle X-ray diffraction patterns were recorded at room temperature by the beam transmission technique. A position sensitive counter was mounted onto a horizontal Rigaku goniometer at the desired angular interval (14-30°(2θ)). The spectral resolution at the counter is 108 μm which is equivalent to 4x10^-4nm. A Ni filtered CuKα radiation source was used. The x-ray absorption coefficient of each sample was determined experimentally. The measured intensities of the scattering patterns were normalized to the untreated sample after correction for absorption and thickness effects. For the determination of the integral breadth a standard sample (CaWO_4) was used. The melting behaviour was investigated using a Mettler differential scanning calorimeter. A heating rate of 10°C/min was used. A nitrogen flux of 50 cm^3/s was sent through the samples during the heating and cooling experiments.

RESULTS AND DISCUSSION

Fig. 1 shows the 110 and 200 wide-angle diffraction peaks of PE as a function of chlorosulfonation treatment time. The intensities here are corrected for absorption and thickness effects. The most important result is that the position of the maxima after chlorosulfonation remains unchanged within the experimental resolution. Furthermore the integrated scattering intensity, I, drastically diminishes with increasing time (Table I). The amount of destroyed material given by 1-(I/I_0) is shown in Fig. 2. The increase of destroyed material under the acid attack is apparently linear with time for the first 60 hours showing thereafter a leveling-off tendency. This behaviour parallels the weight-increase, previously reported (MARTINEZ-SALAZAR, KELLER et al, 1983) attributable to the filling up of the surface layer with electron dense atoms. It is interesting to note that after two hours of treatment as much