Polymer Bulletin 12, 269-274 (1984)

Polymer Bulletin

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.

*I. Controlled study of the chlorosulfonation technique. Colloid & Polym. Sci., 261, 412 (1983)

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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 $4x10^{-4}$nm. A Ni filtered CuK_α radiation source was used. The x-ray absorption coeffient 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 $1-(I/I_o)$ 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

TABLE I

Normalized X-ray scattering intensity, absorption coefficient, coherent diffracting length along 110, and melting temperatures of chlorosulfonated LDPE as a function of treatment-time.

Treatment-time (hours)	I/I_o	$\mu (cm^{-1})$	D_{110}(nm)	T_m(°C)	
0	1.0	3.35	32.2	130.9	-
2	0.88	3.45	32.4	130.9	
10	0.83	5.26	36.8	130.9	137.7
16	0.78	6.03	34.1	130.9	137.7
30	0.70	14.30	33.9	-	137.7
56	0.43	18.90	24.2	-	142.1
100	0.35	21.28	27.1	-	142.1

as $\sim$12% of the crystalline material has been already destroyed. The destruction of crystalline material is supported by the concurrent drastic intensity decrease of the IR doublet at 730-720 cm^{-1}(RUEDA et al, 1984). From the above results (Fig. 1) it is clear that chain packing within the unit cell does not vary during the chlorosulfonation process. This means that the attack of the material does not involve any heavy-group penetration within the lattice. Any occlusion of foreing groups in the crystals would lead to a distinct expansion of the unit cell (BALTA CALLEJA et al, 1979). The overall attack, thus proceeds gradually from the outer surface to the interior involving just a gradual destruction of crystals in the sample, contributing to the crystalline scattering intensity decrease observed. Table I shows the average initial increase and after 56 h final decrease of the coherent diffracting length in the 110 direction of the crystals as function of treatment time. This result confirms the fact that the acid attack proceeds sideways to the lamellar surface, as in the fuming nitric acid case (SCHÖNFELD et al, 1972) and that the smaller crystals are the first ones to be destroyed. In addition, since penetration of heavy groups within the lattice is discarded, the latter can only be located at the surface layer.

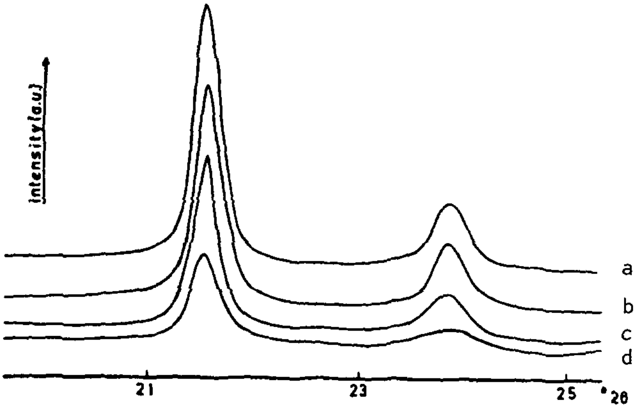

Fig. 1. Transmission X-ray diffractograms of PE chlorosulfonated samples at 45°C during various times: a) untreated, b) 10 h, c) 30 h, d) 56 h.

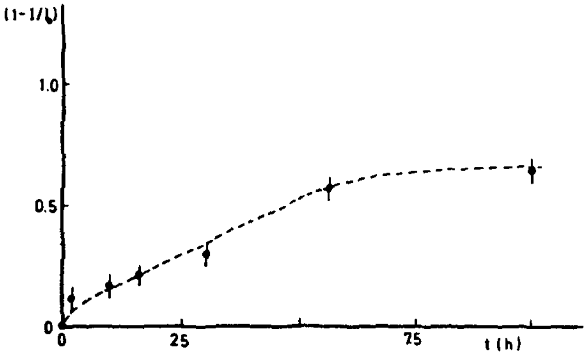

Fig. 2. Plot of $(1-I/I_o)$ vs. treatment time of chlorosulfonated PE samples.

Fig. 3 illustrates the crystal attack as revealed from DSC. In addition on the initial melting temperature peak the gradual appearance of a second melting peak at high temperature, emerging as a shoulder after 10 hours of treatment, becomes observable. After periods larger than 56 hours the high temperature peak appears as the only one in the thermogram. The peak at lower temperature corresponds to the melting of the untreated crystals. The higher temperature peak can be associated to the modified crystals having foreing groups at the surface. These contribute to the observed enhancement of microhardness previously reported (MARTINEZ-SALAZAR, RUEDA et al (1983). Finally, a broad maximum at lower temperature (<90°C) appears for the degraded material. Contrary to the high temperature peak, this maximum increases in intensity with increasing time and it could be probably related to the increasing interaction between electron dense groups, fixed after reaction, within the crystalline destroyed phase.

In conclusion, an important destruction of crystalline material occurs after chlorosulfonation treatment LDPE. According to Fig. 2 at 45°C this crystal destruction is of ~15-20% after 15 h attack. The chlorosulfonation

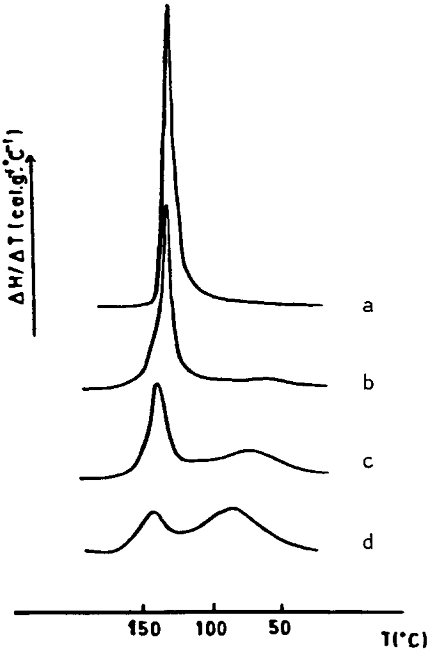

Fig. 3. DSC traces of chlorosulfonated PE sample at 45°C. Samples with similar treatment-times to Fig. 1 are shown: a) untreated, b) 10 h, c) 30 h, d) 56 h.

crystalline attack of PE proceeds into two distinguishable stages: 1) a destruction of smaller crystals and attachment of heavy groups to the surface of the remnant larger crystals and 2) progressive destruction of the larger crystals throughout a sideways degradation process.

ACKNOWLEDGMENT

Grateful acknowledgement is due to CAICYT, Madrid for the support of this investigation.

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Accepted July 7, 1984