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Structural changes during photodegradation of poly(ethylene terephthalate)

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An investigation has been conducted into the effects of photodegradation on the structure of poly(ethylene terephthalate) (PET). Films, with and without ultraviolet absorbers and prepared by biaxial orientation after extrusion, have been exposed in the laboratory for periods of up to 1020 hours. The samples were investigated by differential scanning calorimetry (DSC), X-ray diffraction and size exclusion chromatography. The appearance of a cold crystallization peak during DSC heating scans was noted for exposed samples and this was considered to be a result of released molecules in the amorphous region that could rearrange into a crystalline phase. From X-ray analysis, a loss of crystalline orientation was observed after degradation and an interpretation was given based on relaxation in the mesophase region. In samples containing the photostabilizer additive the magnitude of changes in structure was lower, possibly due to segregation effects during film production making the non-crystalline region relatively immune to degradation effects.

1. Introduction

The natural environment causes a number of chemical changes in polymers, leading mainly to a reduction in molecular sizes and the formation of chemical groups like carbonyls and hydroperoxides within the molecules. These changes produce unwanted effects like brittleness, yellowing, surface deterioration and loss of transparency [1–3], and are responsible for the reduction in product lifetime.

The vast majority of work published in the literature deals with the chemical aspects of polymer degradation, with very little emphasis on the effects that degradation may have on the polymer physical structure. Among these effects, a change in the crystallinity and morphology has been identified as a possible consequence. This issue has been investigated through the years and various different results have been reported, such as:

- An increase in crystallinity during photodegradation [4, 5], thermal degradation [6, 7] and high energy irradiation [8, 9];
- A decrease in crystallinity, mainly during gamma irradiation [10, 11];
- A change in morphology, like spherulite destruction, is less frequently reported [12];
- Alteration in crystal lattice [13, 14].

The scission of entanglements and tie chains molecules in a semi-crystalline polymer leads to their reorganisation into a crystalline phase resulting in the increase of crystallinity. This is frequently called chemi-crystallization [5, 15] and it has been observed with, e.g., polypropylene [16, 17], polyethylene [18, 19] and other polymers [20, 21]. In a detailed investigation, Rabello and White [4] analysed the chemi-crystallization process during polypropylene photodegradation and concluded that the gain in crystallinity starts when a drastic reduction in molecular sizes occurs and ends when the molecules are too defective to allow further ordering. They also proposed a mechanism of chemi-crystallization, based on the deposition of molecule segments released in the interphase region onto the pre-existing crystals, following the same crystal orientation distribution [4]. In thick products, where there is a difference in the extent of degradation at the surface and in deeper layers, the crystallinity increases mainly at the surface resulting in contraction that eventually causes spontaneous surface cracks [3, 12]. These cracks are the main practical consequence of chemi-crystallization and are one of the most frequent causes of premature failure of polymers.

The increase in crystallinity during exposure seems to be strongly dependent on the freedom and mobility

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of the molecules. During processing the development of entanglements hinders extensive crystallization and an amorphous phase is created, in conjunction with the crystalline phase. The molecules within the amorphous phase may be able to further crystallize if they are disentangled or if they are broken, as may happen when degradation is taking place. The rearrangement of molecule segments during exposure, however, also depends on their mobility and it is reasonable to expect that the glass temperature (T_g) is the lower limit for its occurrence. Polymers that are exposed below their glass temperature are unable to exhibit chemi-crystallization. This fact has been noted when PET, that has a T_g of 65–70°C, was exposed at room temperature [5, 22]. On the other hand, if PET films are exposed in an environment containing moisture, the water act as a plasticizer, promoting molecular mobility, and therefore chemi-crystallization can occur [23, 24].

In the case of amorphous (and undegraded) PET, an exothermic peak is observed during the heating stage of a differential scanning calorimetry (DSC) analysis, which is due to a phenomenon called *cold crystallization*. This happens when the polymer is crystallizable but the product was produced in such a way, like fast cooling, that the molecules did not have favourable condition to crystallize, being frozen in the amorphous state. When this product is heated to above its glass temperature, the chains acquire mobility and can rearrange into a crystal phase. Different from chemi-crystallization, chain scission events do not precede cold crystallization.

Although the effects of physical ageing on the cold crystallization behaviour of PET have already been studied [25, 26] no work has been identified relating the photodegradation with the cold crystallization. Even the investigation of the consequences of degradation on PET structure and morphology has received very little attention. In a previous work [27] the authors analysed the effects of natural exposure on the structure and properties of PET sheets.

The aim of this article is to investigate the changes in morphology during laboratory exposure of PET films with and without an ultraviolet absorber stabilizer. Industrial films were irradiated in a conventional weathering chamber for periods of up to 1020 hours and the samples were tested by DSC, X-ray diffraction and size exclusion chromatography. The effects of degradation on the extent of chemical degradation and mechanical properties of the samples dealt with here were reported in a previous publication [28].

2. Experimental

The PET was used in the form of semi-crystalline, bioriented films produced by extrusion in the industrial production line of Terphane (Brazil) using a grade with an intrinsic viscosity of 0.07 m^3/kg. According to the manufacturer, all films contained 0.06% SiO_2, used as an antiblocking agent. Two types of films were prepared: (i) the unstabilized PET and (ii) an ultraviolet stabilized PET. The latter contained an UV absorber (hydroxyphenyl triazine type) produced Ciba Speciality Chemicals with the trade name Tinuvin 1577. According to the producer it is a photostabilizer suitable for PET.

The films were exposed in a Comexin weathering chamber using Q-Panel UVA fluorescent lamps. These lamps are 1.2 m long and produce ultraviolet light that matches reasonably well with sunlight, with a cut-off at 290 nm [29]. The weathering cycle was defined as follows: 4 hours under UV light at 60°C and 4 hours in the dark under condensed water at 50°C. The films were mounted in the chamber with aluminium frames with a distance lamp to film set at 70 mm. At this distance the irradiation intensity reaching the sample surface is about 3.2 Wm^{-2}. Under these conditions the specimens are submitted to a combination of photo-, thermal and hydrolytic degradation, offering very harsh conditions to the sample deterioration. In the results shown below the exposure time is reported as number of hours under ultraviolet radiation and not the total exposure time.

After selected exposure times, the samples were tested in a Shimadzu DSC 50 differential scanning calorimeter for the following parameters: cold crystallization temperature, cold crystallization enthalpy, melting temperature and melting enthalpy. The records were done only during the first heating using a scanning rate of 10°C/min. The degree of crystallinity was taken as the well-known equation $X_c = \Delta H_m/\Delta H_u$, were ΔH_m is the measured melting enthalpy and ΔH_u is the enthalpy for the crystal phase, taken as 117 J/g [23].

The X-ray diffraction analyses were done in a Siemens D5000 diffractometer operating with a voltage of 40 kV and using a speed of 0.02°/s in the range $2\theta = 5–35°$. The samples were tested without further preparation.

A full description of the chemical changes during degradation was given elsewhere [28]. In this paper some results of size exclusion chromatography will be reported. Experiments were carried out in a Shimadzu Class LC10 operating with an UV detector set at $\lambda = 254$ nm. An experiment of UV-visible spectroscopy was done with a Perkin Elmer Lambda 6 equipment with a resolution of 2 nm.

3. Results and discussion

3.1. Thermal analysis—DSC

The DSC scans for unexposed and exposed PET are shown in Fig. 1. For the unexposed sample the only thermal transition observed is the crystalline melting region with a maximum output at approximately 255°C. The films are partially crystalline due to the procedure used in their production, which involves a biaxial orientation after extrusion. The crystals are supposed to be rather small, maintaining the desired transparency. In comparison to the amorphous PET, there are two main consequences of crystallinity in the DSC analysis: the glass transition temperature (at ∼70°C) and the cold crystallization peak (at 110–130°C) are not observed in the thermograms. The cold crystallization is a phenomenon of particular interest in PET and it occurs if heating is sufficiently slow to allow the rearrangement of the amorphous phase into a crystalline lattice [26]. The cold crystallization peak is exothermic and may be very intense, like in the example shown in Fig. 2 obtained

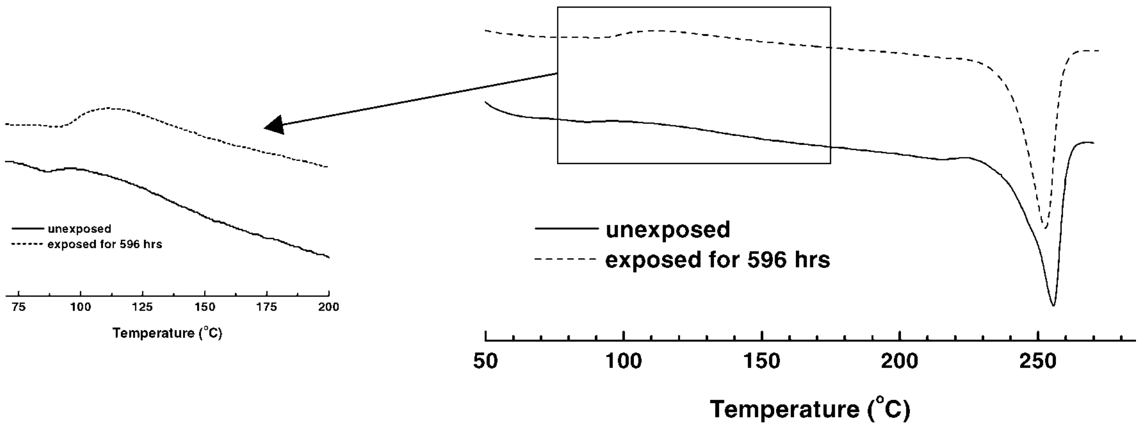

Figure 1 DSC thermograms of non-stabilized PET films. The detail shows a higher magnification of the indicated region.

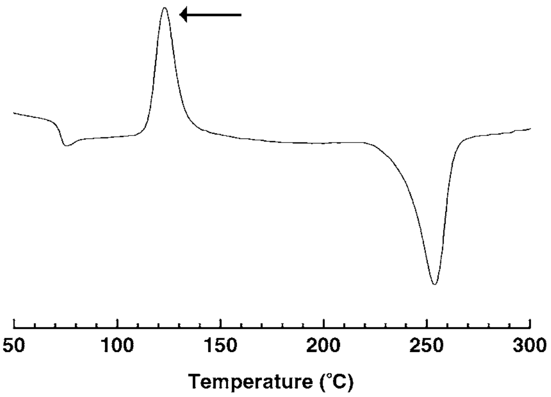

Figure 2 Example of a DSC heating scan of an amorphous PET. The cold crystallization peak is indicated with an arrow.

from an amorphous and unoriented sample. The degraded films had a distinctive behaviour. After exposure to 596 hours a weak exothermic band in the range of cold crystallization is noted (see the detail in Fig. 1. A similar feature can be observed with the sample containing the UV stabilizer (Fig. 3) but in the latter the thermal output seems to be less intense.

The appearance of an exothermic peak due to cold crystallization in exposed films raises an issue on the mechanism of PET photodegradation. According to Ping and Dezh [30], the amorphous fraction corresponding to the interlamellar region is more likely to crystallize during the DSC heating than the one in the interspherulitic region. The reason is that between lamellae there is already a certain degree of molecular packing [30]. The cold crystallization band that appeared in the degraded samples (Figs 1 and 3) would be due to the scission of entanglements in the interlamellar region (caused by degradation) and these segments could have sufficient mobility to crystallize during the heating step of a DSC experiment. Actually, this phenomenon seems to be similar to what happens when the exposure occurs above the glass transition of semi-crystalline polymers, where the scission of taut molecules increases the crystallinity during exposure, a process mentioned before and named chemicrystallization [31]. In the case of PET, however, the scission of entanglements and tie chain molecules does not increase the crystallinity during exposure because at this temperature (50–60°C) there is very little molecular mobility [23]. Nevertheless, when this sample is heated during DSC analysis, there is a small gain in enthalpy as a consequence of cold crystallization (see Table I). The melting enthalpy of the exposed samples, therefore, is slightly higher because it has two contributions: (i) the melting of original crystals produced during processing, and (ii) the melting of crystals formed during DSC heating (cold crystallization). To calculate the degree of crystallinity, the value of melting enthalpy was taken as the measured melting enthalpy subtracted by the value of cold crystallization enthalpy. It is clear in Table I that exposure did not increase the crystallinity of the as-exposed samples and, therefore, confirms the arguments stated above that chemi-crystallization does not occur below T_g.

The summary of results obtained from DSC measurements is also given in Table I. The aim here is to show only selected results (the maximum exposure time for each type of sample) since these properties had only subtle variations with exposure time. A more detailed description on the extent of chemical degradation and mechanical properties of these samples was given elsewhere [28]. Note in Table I that the temperature of cold crystallization, T_{cc}, is slightly higher for the unstabilized PET. This is possibly a consequence of a higher concentration of chemical impurities caused

TABLE I Polymer thermal properties obtained from DSC experiments. The exposure times reported were the maximum for each type of sample [28]

Sample	Exposure time (hrs)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_m (J/g)	X_c (%)[a]
Unstabilized	0	–	–	255.3 ± 0.5	34.65 ± 1.96	29.5 ± 1.7
Unstabilized	596	112.1 ± 1.5	6.06 ± 0.08	252.7 ± 0.6	40.04 ± 1.55	28.9 ± 1.3
Stabilized	0	–	–	254.2 ± 0.6	37.50 ± 1.17	31.9 ± 1.0
Stabilized	1020	107.2 ± 1.9	3.30 ± 0.79	254.9 ± 0.2	39.58 ± 1.67	30.9 ± 0.7

[a] The values of crystallinity (X_c) were obtained from a modified $\Delta H^*_m : \Delta H^*_m = \Delta H_m - \Delta H_{cc}$.

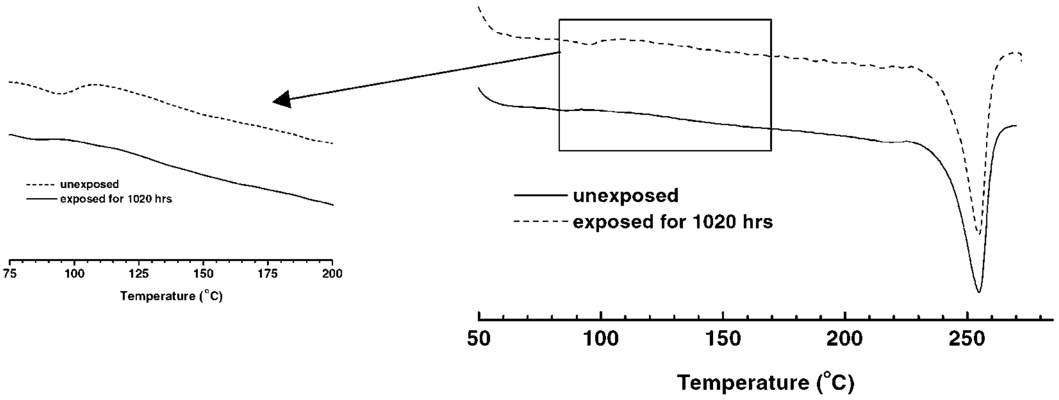

Figure 3 DSC thermograms of PET films containing the UV absorber. The detail shows a higher magnification of the indicated region.

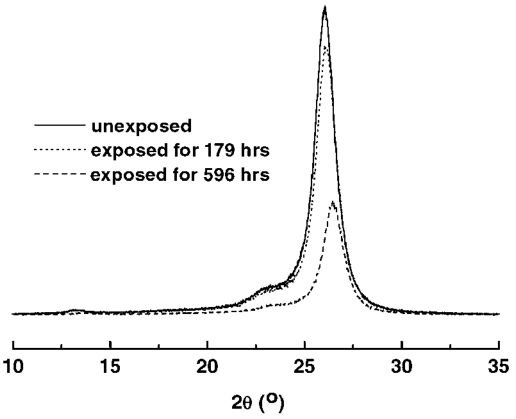

Figure 4 X-ray diffractograms of unstabilized PET.

by photodegradation leading to a lower rate of crystallization, as observed with other polymers [32]. Another aspect that should be noted in Table I is the little change in melting temperature with exposure. In polymers like polyethylene and polypropylene, the degradation causes a significant decrease in melting temperature—a fact that was attributed to molecular scission in crystal fold surface, increasing the crystal free energy [33]. In these polymers, the decrease in T_{m} can be so significant that it can be used as a method to follow the extent of chemical degradation [32, 34]. In the case of PET, the crystal stability suggests that either the fold surfaces are not attacked or their contribution to the melting temperature is not as high as in other polymers.

3.2. X-Ray diffraction and molecular weight

The ability of a material to diffract X-rays in certain directions is associated to the existence of a crystal lattice, i.e., regions of a long-range ordering. By using X-ray diffraction, the changes in PET structure with degradation can be monitored. Fig. 4 shows diffractograms of unexposed and exposed samples, where two main diffraction peaks are seen. The most intense one, centred at $2\theta = 26.06^\circ$ is related to (100) planes whereas the one at $2\theta = 23.23^\circ$ is due to $(\bar{1}10)$planes [35]. After irradiation, both peaks decrease in intensity in the same proportion to reach about 35% of the original height. A small shift of peak maximum towards high angles can also be noted.

At first thought, the reduction in peak intensity could be attributed to a reduction in the degree of crystallinity caused by, for instance, crystal destruction as already observed with other types of polymers [12, 36, 37]. However, DSC results did not indicate a decrease in crystallinity with exposure (Table I), not even a reduction in melting temperature. According to Ajji *et al.* [38] PET films, oriented during processing, have three distinct regions: (i) a crystalline phase, formed by all-trans conformation chains (see Fig. 5) which is organised in the form of small crystals; (ii) a mesophase, formed by chains in trans conformation with a certain degree of orientation that link the crystalline to the amorphous region; and (iii) a wholly disordered region formed mainly by gauche chains (Fig. 5). The intensity of an X-ray diffraction peak is highly dependent on the crystal orientation distribution. The strong intensity of

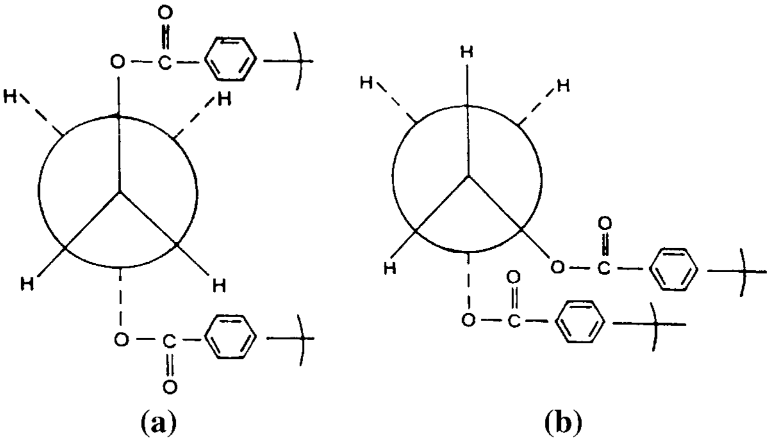

Figure 5 Isomers of ethylene glycol in the PET molecule. (a) trans conformation. (b) gauche conformation.

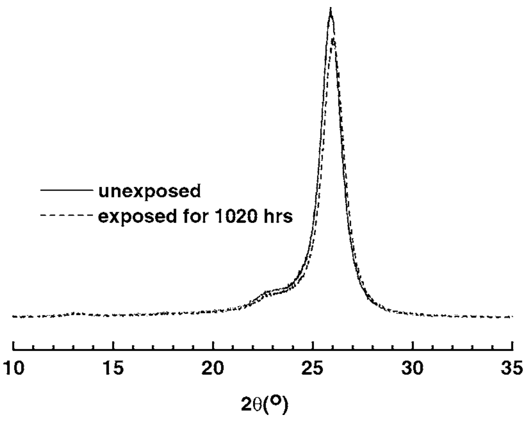

Figure 6 X-ray diffractograms of PET films containing a UV absorber.

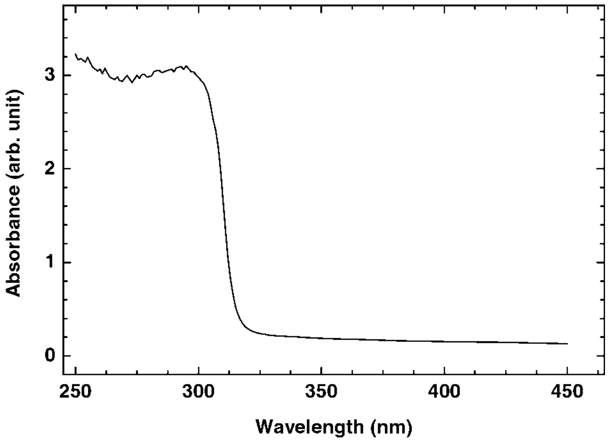

Figure 7 UV-visible spectrum of unstabilized PET films.

the (100) planes for the unexposed PET implies that crystal a-axes are oriented preferentially parallel to the film normal [39, 40]. Therefore, the *c*-axis, i.e., the chain direction, is along film main surface, as would be expected from the bi-axial orientation obtained during processing. In another work, Matthews *et al.* [41] showed that when oriented PET films are heated to a temperature slightly above T_g, there is a decrease in X-ray peak intensities due to a reduction in molecular orientation in the mesophase region. From this observation, it can speculated that the reduction in X-ray intensities of (100) and ($\bar{1}10$) planes shown in Fig. 4 is due to a loss of chain orientation in the mesophase region caused by molecule scissions during photodegradation.

In Fig. 6 the X-ray diffractograms of UV stabilized films also show a reduction in peak intensities but with a much lower magnitude in comparison to the unstabilized PET. It is possible that in the mesophase region, which may be ultimately responsible for the loss of orientation [41], the extent of degradation was lower because it is protected by stabilizer molecules. The location of stabilizers in the mesophase and in the amorphous region is a consequence of additive segregation during crystallization, which is rather common in polymers [32, 42, 43]. During crystal growing, the stabilizer molecules are expelled and, hence, become concentrated in these regions. Accordingly, the number of scission events are lower, causing less decay in orientation.

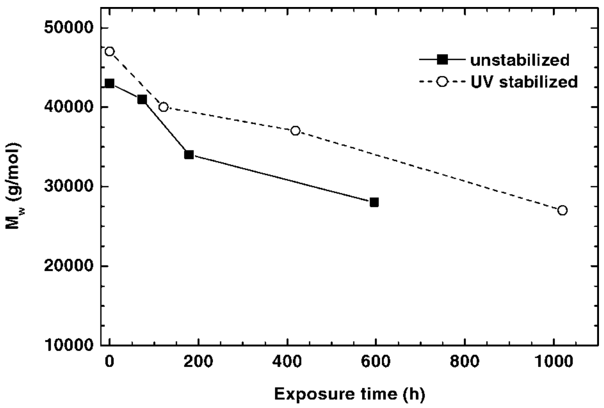

Figure 8 Weight average molecular weight (M_w) obtained from SEC analyses.

If the non-crystalline regions remain protected from degradation, as a result of stabilizer segregation, a point that must be explained is the large decrease in molecular weight in samples containing the UV absorbers (as seen in Fig. 8). It is generally accepted that the crystalline phase is much less affected by degradation because it is less permeable to oxygen and, consequently, the degradation is restricted to the amorphous phase. This is true for the polymers like polypropylene, polyethylene and PVC, that do not suffer homolytic scission by direct absorption of ultraviolet radiation from sunlight [2, 44]. The chain scission in these polymers depends on the reaction with species containing oxygen, like hydroperoxides and carbonyls. This is not the case for heterocyclic polymers like PET in which the main chain molecules can absorb directly the UV light in an amount that can cause bond breakage [44]. In Fig. 7 the UV absorption characteristic of PET shows that in wavelengths lower than 315 nm the polymer absorbs strongly. According to this idea, it is reasonable to admit that chain scission may take place within the crystal phase of PET, leading to a reduction in molecular sizes, as observed in Fig. 8. When this happens, the change in mechanical properties is expected to be much lower than when chain scissions occur also in the amorphous region because in the latter the load bearing taut molecules are broken. Actually, the loss of mechanical properties was much lower in PET containing ultraviolet stabilizers, as reported in a previous publication [28].

4. Conclusions

Some changes in PET structure caused by exposure in the laboratory have been detected. The films exposed below the polymer glass temperature did not show an increase in crystallinity during exposure. However, when these films were tested in the DSC, the released molecule segments in the amorphous region had sufficient mobility to rearrange into a crystalline phase and an exothermic response was seen in the DSC thermograms. This peak was due to cold crystallization and its magnitude was higher in PET films without ultraviolet stabilizers.

The as-moulded films had a very strong crystal orientation, with their *a*-axis parallel to the film surface, as a result of the stretching process during their production.

When these films were exposed, a clear loss in X-ray peak intensities was noted. This was attributed to a loss in orientation, caused possibly by relaxation in the mesophase region. Again, the samples with an additive stabilizer had much lower changes even when they were exposed for longer periods. The stabilized films had a large reduction in molecular sizes and this was considered to be a consequence of chain scission that occurred within the unprotected crystal phase.

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