Polymer Vol. 37 No. 12, pp. 2323–2333, 1996
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0032-3861/96/$15.00+0.00

Thermal and photooxidation of polypropylene influence of long-term ambient oxidation: spectroscopic, thermal and light scattering studies

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(Received 23 June 1995; revised 26 July 1995)

The influence of long-term ambient storage conditions in the presence of air has been examined on the thermal and photooxidation of unstabilized polypropylene. Samples of polypropylene have been aged under ambient storage for 12 years together with a control sample kept under refrigeration at −20°C. The samples have been examined using second order-derivative absorption, fluorescence and phosphorescence spectroscopic techniques, thermal analysis (d.s.c.), light scattering and hydroperoxide analysis. All the polymer samples stored under ambient conditions exhibit significant increases in luminescent species and hydroperoxide concentrations as a consequence of slow oxidation processes. The d.s.c. and light scattering analysis show that these polymers exhibit an increase in crystallinity compared with that which has been stored by refrigeration. The data are related to the thermal and photooxidative behaviour of the polymers using Fourier transform infra-red spectroscopy (*FT*i.r.) and compared with that of a modern suspension grade polypropylene. Copyright © 1996 Elsevier Science Ltd.

(Keywords: oxidation; polypropylene; light scattering; fluorescence; phosphorescence)

INTRODUCTION

The mechanisms involved in the sunlight-induced oxidation of polyolefins have been a topic of extensive research for over 40 years. The crucial question in the initiation process is the origin of the free radical species responsible for chain degradation. Because polyolefins do not theoretically absorb light in the near u.v. region (290–380 nm), impurity chromophores (such as carbonyl groups, hydroperoxides, unsaturation and trace metal ions) are believed to be responsible for initiating radical production[1–3]. These chromophores are produced during the commercial manufacture and processing of the polymer. In fact, in processed polymer, carbonyl and hydroperoxide groups are believed to be the key initiators of photooxidation whereas, in 'pure' polymer samples containing neither of these chromophores, oxygen-polymer charge-transfer complexes are believed to be important[4–6]. In one study[5], prior destruction of the carbonyl and hydroperoxide groups in polyolefin films by irradiation in an inert atmosphere had no effect on their subsequent rates of photooxidation. Little work has been undertaken in recent years to confirm or deny the role of oxygen-polymer charge-transfer complexes in polyolefin photooxidation; though high pressure studies have been undertaken on polystyrene which showed that the rate of photooxidation was dependent on oxygen pressure[7,8].

Many workers have undertaken studies to evaluate the relative importance of different species in initiating photooxidation of polyolefins[1–3], with one study attempting to organize their relative importance in terms of quantum yields of reactivity[9]. From this work, hydroperoxides were concluded to be of primary importance, whereas in other studies unsaturated species were found to be important[10–12]. However, the two species may well be intimately involved as unsaturated hydroperoxide groups. Similarly, unsaturated carbonyl species have also been identified in polyolefins by fluorescence analysis and their concentrations are closely related to the polymer stabilities[13,14].

It is well known that unstabilized polyolefins oxidize rapidly during high temperature processing operations[1–3], with a rate dependent upon temperature and the presence of oxygen. According to the Arrhenius law at lower temperatures the rate of oxidation is expected to be significantly slower. Though it will also be impaired by the phase change to a solid material restricting radical mobility, at ambient temperatures unstabilized polyolefins will still have a minimum storage life. This was

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illustrated in one study by the observation of a higher level of fluorescence regeneration in polyolefins in an oxygen atmosphere[13]. In the present study, the effects of such long-term storage oxidation have been examined on the subsequent thermal and photochemical stability of unstabilized polypropylene powder samples. Bags of unstabilized polypropylene powders were kept in dark storage in air at ambient temperatures for 12 years, with one sample being stored in a refrigerator at −20°C. The polymers were subsequently examined by fluorescence and phosphorescence spectroscopy, hydroperoxide analysis and second-order derivative u.v. spectroscopy, and the data compared to the relative stabilities of the polymers in film form after compression moulding. Changes in the morphological properties of the polymers have been examined by thermal analysis and a new method involving light scattering in the solid-state. The data and stabilities are compared to those of a modern suspension grade of polypropylene material.

EXPERIMENTAL

Materials

Original samples of diluent phase polypropylene powder HF-20 grade were supplied by ICI Ltd. (UK) and stored for 12 years under normal ambient conditions in their paper sacks and these are numbered throughout as PP1–6. A sample of these powders was also stored under refrigeration at −20°C and this is referred to as PP control. A sample of modern suspension grade polypropylene powder was supplied by Repsol, Madrid, Spain. Samples of the powders were compression moulded at 200°C into films of 150 μm thickness. Samples of the oxidized powders were also extracted with cold hexane for 12 h. The hexane used was pretreated with silica gel to remove any polynuclear aromatics.

Polymer analysis

Samples of the polypropylene powders were analysed for hydroperoxide concentrations using the standard iodometric method[1]. Second order derivative absorption spectra were obtained using a Perkin-Elmer Lambda-7 spectrometer, fluorescence and phosphorescence spectra were obtained using a Perkin-Elmer LS50B spectrometer. Fluorescence spectra were obtained at ambient temperature and phosphorescence spectra were obtained at 77 K. Samples of film were oven aged at 130°C in a forced air draught oven and irradiated using a Microscal Light exposure unit (Microscal Ltd., London) utilizing a high pressure Hg/tungsten filament lamp ($\lambda > 300$ nm, ambient temperature and humidity). Oxidation rates were determined via the well-established carbonyl index method[1].

$$C.I. = [(\log_{10} I_0/I_t)/D] \times 100$$

where D is film thickness in μm, I_0 is the initial light intensity at 1710 cm^{-1} and I_t is the transmitted light intensity at 1710 cm^{-1}.

Light scattering measurements

Light scattering (LS) measurements were obtained using the equipment schematically represented in *Figure 1*. Polarized light from a 2 mW HeNe laser ($\theta = 6328$ Å), (P)500 : 1 (R) is monitored by a Photodiode positioned at right angles to the beam. A small fraction of light from the beam is reflected onto the photodiode by a glass plate which is orientated at 45° to the laser beam. For cloudy films which are heterogeneous, a ×4 beam expander is used to increase the beam diameter from 0.5 to 2 mm which reduces the effect of heterogeneity.

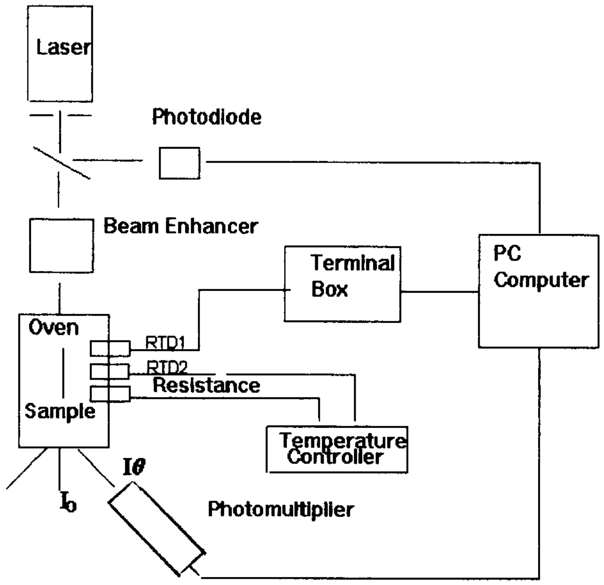

Figure 1 Light scattering device developed in-house

The beam in such conditions is incident on an aluminium sample holder. The polymer film (150 μm) is pressed homogeneously between two glasses of 0.15 mm each by a flat screw of 1 cm in the removable sample holder plate. This is housed in a heating cell controlled by an Omega CN-2010 programmable temperature controller. The oven is made of an aluminium block with a central passage for the laser light beam and side channels for heat dissipation to the air currents. Scattered light is then collected by a photomultiplier tube (PM) positioned at an angle of 10° in the XY plane and 0° in the Z direction. The PM is protected by an interference filter that transmits light only at the laser wavelength. All the mentioned signals, laser intensity, light scattering intensity and temperature are coupled to a PC computer through a terminal box. Hence, LS intensity can be monitored as a function of time and sample temperature.

Thermal analysis

Polymer samples (6 mg) were analysed using a Perkin-Elmer DSC-7 instrument. Dynamic measurements were undertaken at a constant rate of 10°C min^{-1} under a nitrogen atmosphere. All the samples were initially thermostatted at 40°C. Initial scans were obtained from 40 to 200°C. The samples were then maintained at 200°C for 5 min in order to remove the thermal history of the polymer sample. A reverse scan was then undertaken in order to monitor the dynamic crystallization of the polymer. A final scan was then recorded under conditions where the thermal histories of the samples were maintained constant.

Microscopic analysis

Videographs of the polymer microstructure were obtained using a Sony video printer camera system attached to a Carl-Zeiss Jena (Model-Jenaval) microscope with a modified stand for transmission or reflection modes. Samples, as films of 150 μm were observed by transmission mode under polarized light with crossed polarizers as well as at different magnification levels. Interferential contrast was used for improving the image quality.

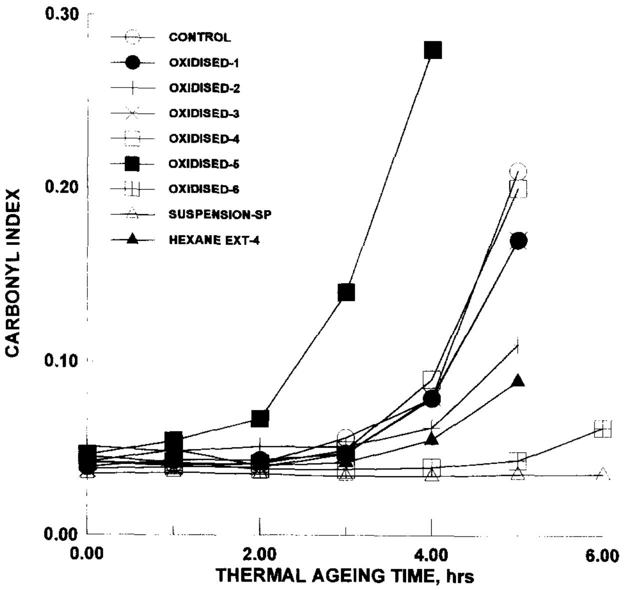

Figure 2 Carbonyl index vs oven ageing time (h) at 130°C of polypropylene film samples (○) refrigerated control, (●) oxidized-1, (+) oxidized-2, (×) oxidized-3, (□) oxidized-4, (■) oxidized-5, (⊞) oxidized-6, (▲) cold hexane extracted-4 and (△) suspension grade polymer

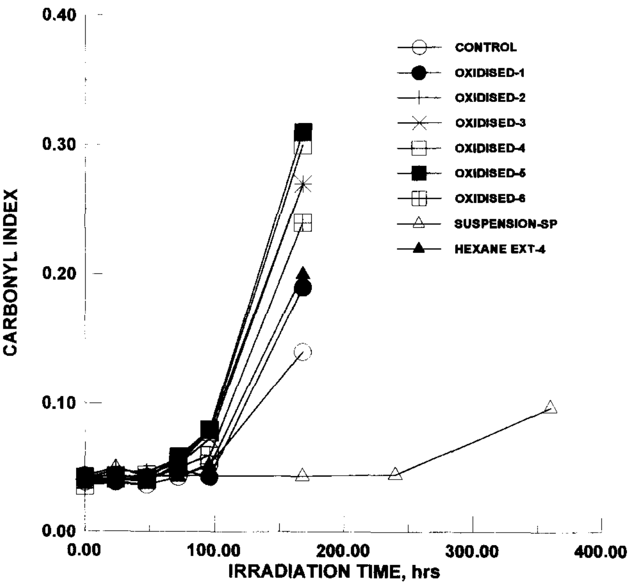

Figure 3 Carbonyl index vs irradiation time (h) of polypropylene film samples (○) refrigerated control, (●) oxidized-1, (+) oxidized-2, (×) oxidized-3, (□) oxidized-4, (■) oxidized-5, (⊞) oxidized-6, (▲) cold hexane extracted-4 and (△) suspension grade polymer

RESULTS AND DISCUSSION

Thermal and photooxidation rates

The thermal and photooxidation rates of the polypropylene film samples are compared in *Figures 2* and *3*, respectively. Samples PP oxidized 1–6 are the polymers stored in air under ambient conditions in different sacks, and make an interesting comparison with the PP control (stored under refrigeration) and suspension grade polymers. *Figure 2* shows that all the long-term aged materials thermally oxidize more rapidly than that of the fresh suspension grade polymer, with PP5 being the most unstable and PP6 the least stable. However, the control sample stored under refrigeration exhibited no increase in stability over the ambient oxidized samples PP1–6. This would suggest that species responsible for the high temperature instability of the polymer are not influenced by long-term ambient oxidation processes and may be inherent in the polymer from manufacture. Cold hexane extraction of the polymer powders gives an improvement in stability, as illustrated for sample 4. Thus, some of the species responsible for inducing thermal oxidation have been extracted. The data on photooxidation are markedly different, as shown in *Figure 3*. Here the control polymer kept under refrigeration is more stable than that of the oxidized polymers PP1–6 stored at ambient temperatures. The hexane extracted polymer is also more stable, as is the suspension grade material. In this case, it is evident that the oxidation species generated during ambient storage contribute towards initiation of the photooxidation of the polymer. As observed for thermal oxidation the least stable sample was 5. Thus, there is obviously a distinct difference between those chromophores originally present in the polymer and those generated during oxidation on storage. Spectroscopically they appear to be similar, although the latter are much more readily extractable by cold hexane treatment. This suggests that those chromophores formed by ambient oxidation are from small molecular chain fragments.

Hydroperoxide analysis

The hydroperoxide data shown in *Table 1* exhibit a number of interesting features. Firstly, all the ambient stored polymers 1–6 have oxidized compared with that of the refrigerated control. Secondly, the hexane extracted samples were found to exhibit higher levels of hydroperoxide than the non-extracted (oxidized PP-4 in Table 1) (though this may be associated with contamination from the *n*-hexane after evaporation). Thirdly, the suspension grade material exhibited a higher hydroperoxide concentration than that of the older diluent phase

Table 1 Hydroperoxide concentrations (ppm) in polypropylene powders

Sample	PPOOH (ppm)
Control	14
PP Repsol	50
1	40
2	60
3	25
4	15
5	71
6	60
Hexane ext.-4	20

control material. This increased concentration may be associated with higher oxidation levels during the manufacturing process. These results clearly suggest that overall, hydroperoxides are not the only contributing factor in inducing thermal and photooxidation of polypropylene. Whilst it may be evident that the increased hydroperoxide levels in the ambient oxidized samples could account for their poorer light stability compared with that of the refrigerated control, this is clearly not the case in thermal ageing. The effect of hexane extraction is anomalous in that the treatment may well have removed amorphous material containing active hydroperoxides, hence the improvement shown in thermal and light stability. The enhanced levels of free hydroperoxides found after the hexane treatment are not an integral part of the polymer backbone since they derive from the hexane. They are therefore, expected to be inactive[1–3] in terms of any β-chain scission processes.

Spectroscopic analysis

In previous studies[11,12], second-order derivative u.v. absorption spectra on polyolefin films showed absorptions at 220 nm, associated with the presence of the residual unsaturation in the polymer conjugated with carbonyl groups. Examination of the polypropylene samples under study here in film form showed similar absorptions. These are illustrated in *Figures 4–6*, where marked differences in absorption spectra are observed. The spectra are shown to effect a comparison of the main band at 220 nm. The broad longer wavelength bands due to the carbonyl absorptions at 250 and 280 nm are not so evident in the spectra here, due to their lower extinction coefficients and the low sensitivity used with the instrument (±0.5). However, expansion of the spectra show that these long wavelength bands are of comparable relative intensities to higher energy transition at 220 nm. The most significant feature of these results, is the observed marked increase in absorption for all the ambient stored polymers shown in *Figures 5* and *6* when compared with the frozen control sample shown in *Figure 4*. The suspension grade of polymer exhibits a somewhat higher absorption than that of the diluent grade control (*Figure 4*). After cold hexane extraction the

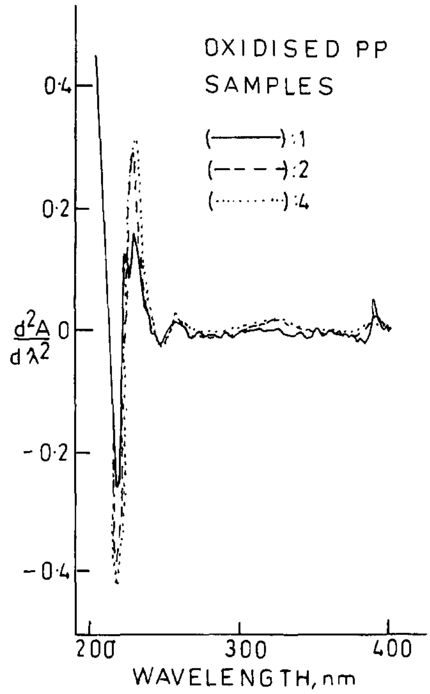

Figure 5 Second-order derivative u.v. absorption spectra of 200 μm polypropylene film samples aged under ambient conditions (——)—1, (-----)—2 and (······)—4

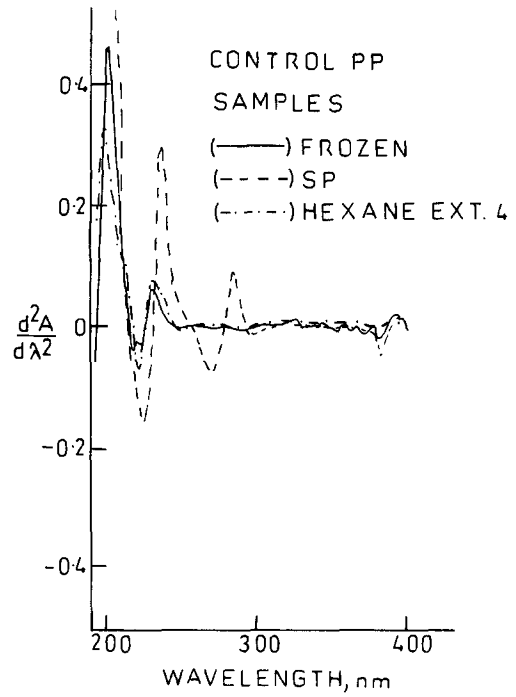

Figure 4 Second-order derivative u.v. absorption spectra of 200 μm polypropylene film samples (——) control-frozen, (-----) suspension grade and (–·–·–) hexane extracted-4

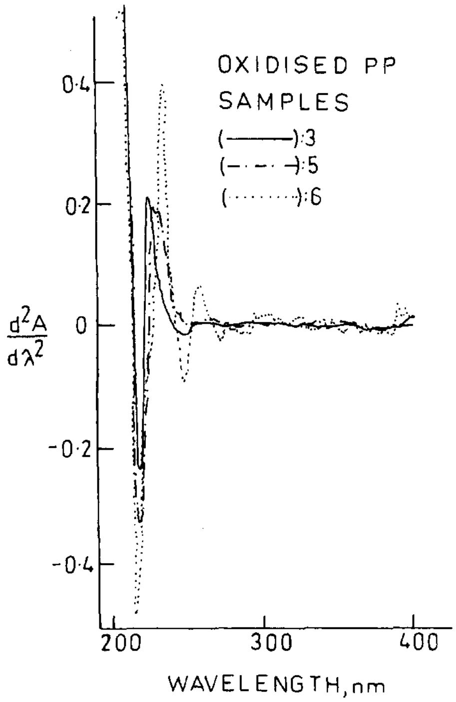

Figure 6 Second-order derivative u.v. absorption spectra of 200 μm polypropylene film samples aged under ambient conditions (——)—3, (–·–·–)—5 and (······)—6

components giving rise to these increased absorption bands are removed and the original absorption of the polymer is virtually restored. Thus, oxidation during ambient storage appears to have taken place, certainly in the amorphous regions of the polymer where extractability by cold hexane is feasible. Naphthalene uptake from the atmosphere was ruled out in earlier work[11-13]. *FT*i.r. analysis of these films was too insensitive to detect such changes although it should be pointed out that very minor growths at $1680\,\mathrm{cm}^{-1}$ were evident upon spectral expansion. The growth of these chromophores during storage would certainly be expected to contribute toward sensitizing the photooxidation of the polymers with subsequent hexane extraction improving stabilization. However, there is no exact correlation between photooxidation rates from *Figure 3* and the concentration of the species formed. Furthermore, marked differences in the levels of chromophores do not correlate with minor differences in the photooxidation rates of the polymers.

The fluorescence excitation and emission spectra of all the polypropylene samples in powder form are shown in *Figures 7* and *8*. These spectra were obtained using their individual wavelength maxima exciting at 230 nm and tuning in to the emission at 340 nm. The spectra, associated with the presence of α, β-unsaturated carbonyl species[13,14], show a number of interesting features. The emission spectra have wavelength maxima at 340, 395 and 435 nm. Variation of the excitation wavelength produces a similar emission spectra, but with variations in the peak heights, suggesting different types of similar chromophores[13]. The two long wavelength emission maxima do not appear to be connected with that at 340 nm, since after cold hexane extraction the latter is significantly reduced in intensity. This is also evident in the excitation spectrum where the band at 230 nm is significantly reduced in intensity. The two long wavelength emission bands are also not markedly affected by long-term ambient oxidation, whereas that at 340 nm increases significantly depending upon the polymer sample. Sample 6 exhibits the greatest fluorescence intensity

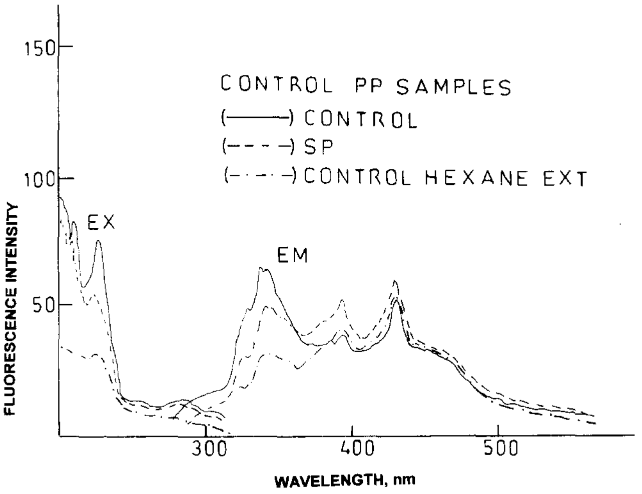

Figure 7 Fluorescence excitation and emission spectra at 300 K of polypropylene powder samples (——) control-frozen, (-----) suspension grade and (-·-·-·-) control hexane extracted

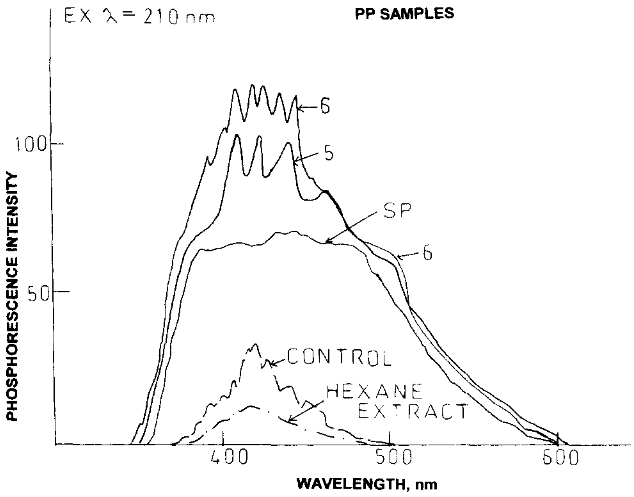

Figure 9 Phosphorescence emission spectra at 77 K (excitation at 210 nm) of polypropylene powders (——) suspension grade (SP), (-----) control frozen, (-·-·-·-) hexane extracted control and oxidized samples 5 and 6

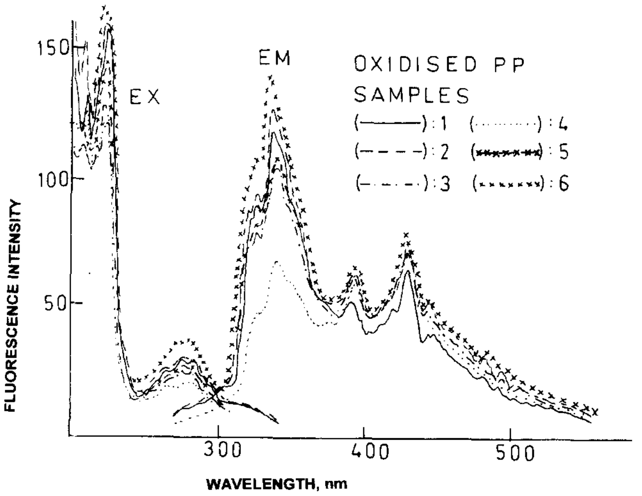

Figure 8 Fluorescence excitation and emission spectra at 300 K of long-term ambient oxidized polypropylene powder samples (——)—1, (-----)—2, (-·-·-·-)—3, (·······)—4, (x-x-x-x)—5 and (xxxxx)—6

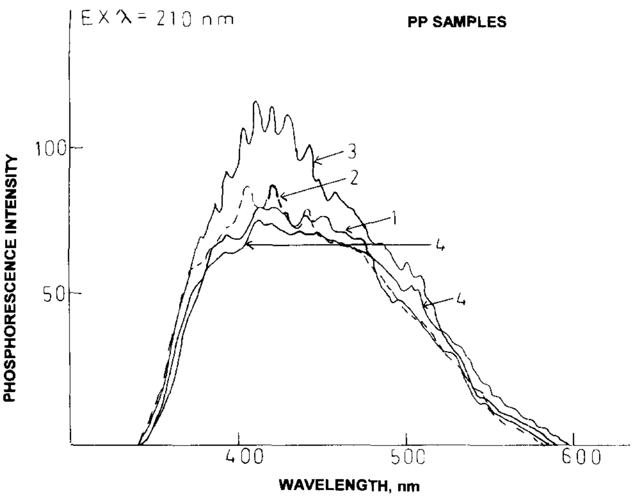

Figure 10 Phosphorescence emission spectra at 77 K (excitation at 210 nm) of oxidized polypropylene powders (——) 1, 3 and 4 and (-----) 2

and this is consistent with the second order derivative absorption spectrum (*Figure 6*). However, sample 4 appears anomalous in this regard and exhibits the lowest intensity fluorescence of the oxidized samples. Thus, on long-term storage all the polymer powder samples have acquired increased levels of fluorescent species. Again, although the differences in unoxidized, oxidized and cold hexane extracted polymer samples can be compared, there is no good correlation between the light stabilities of the oxidized film samples.

Phosphorescence emission spectra of the polymer samples in powder form at 77 K are shown in *Figures 9* and *10* exciting at 210 nm and *Figures 11* and *12* for excitation at 290 nm, respectively. Broad, but structured emission spectra, are observed in the region 380 to 650 nm. Here the species are believed to be of a similar structural type, but with an extended conjugation, i.e. α, β-dienones[13,14]. At 210 nm excitation the control sample which had been frozen exhibited a very low intensity emission compared with the oxidized samples. The suspension grade was significantly higher at this excitation wavelength, but was nevertheless lower than the oxidized samples. Cold hexane extraction of all the powders removed the phosphorescent species all at the level shown for the control polymer (*Figure 9*). It is interesting to note that at this lower excitation wavelength at 210 nm, there is little difference in intensity between the oxidized polymer samples; again sample 6 exhibiting the highest intensity emission.

At 290 nm excitation, the phosphorescence emission spectra are not unlike those of the fluorescence in terms of orders of intensity observed. All the oxidized polymer samples exhibit higher phosphorescence intensities than that of the control except sample 4. Sample 6, again exhibits the highest intensity phosphorescence with the frozen control and suspension grades exhibiting the lowest intensities. In this case there are significant increases in intensity on ambient storage associated with oxidation.

Light scattering analysis

Under the conditions of analysis used here for solid-state films, the refractive index of the 'crystalline particulate' differs considerably from that of the amorphous phase; a consequence of which are significantly larger dimensions (1–100 μm) than that of the wavelength of the laser light, giving rise to Mie scattering[15]. Under our experimental conditions here the extent of laser light scattering is measured as a function of time (isothermal) and/or temperature in dynamic conditions. It is well accepted that there is a dynamic equilibrium between the amorphous and crystalline phase in a semicrystalline polymer material. This is due to the existence of a physically well defined interfacial region, of finite thickness, where momentum,

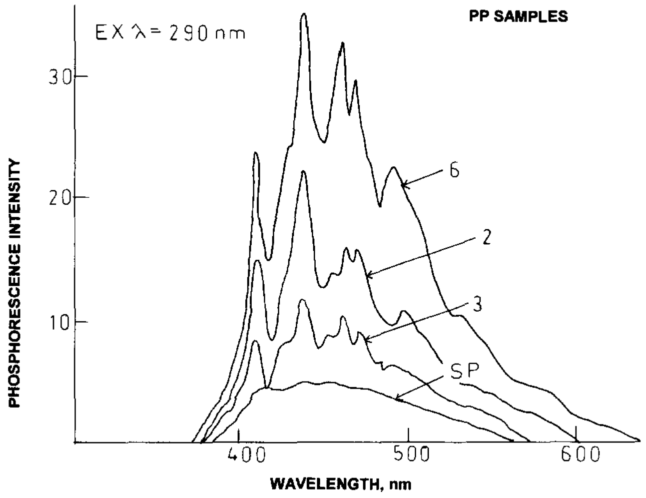

Figure 11 Phosphorescence emission spectra at 77 K (excitation at 290 nm) of polypropylene powders suspension grade (SP), and oxidized 2, 3, and 6

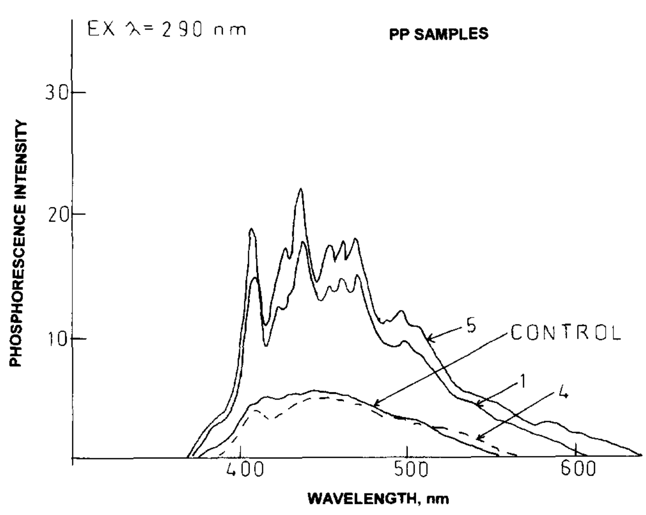

Figure 12 Phosphorescence emission spectra at 77 K (excitation at 290 nm) of polypropylene powders control, and oxidized 1 and 5 and (-----) 4

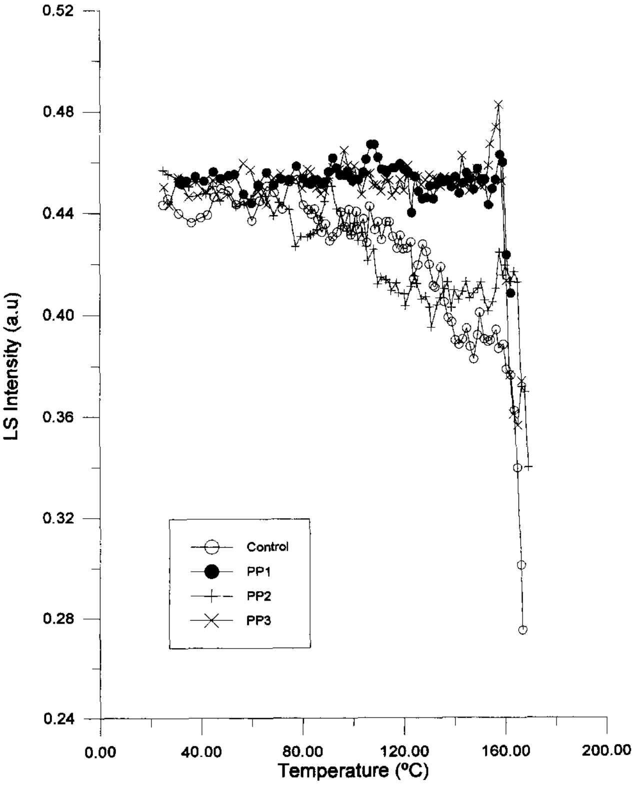

Figure 13 Light scattering intensity vs temperature at 5°C min^{-1} for (O) PP control, (O) PP1, (+) PP2 and (x) PP3 polypropylene film samples

mass and heat flows from one phase to the other. External conditions are then continuously affecting the overall thermodynamic state of the polymer system. At present we are unable to measure such interchanges in the interfacial region, though with the aid of light scattering measurements, combined with other techniques used here, it is possible to gain some understanding of the phenomena involved in the interface. The initial amount of light scattered by the polymer film provides useful indications of the general morphological state of the material. Thus, an increase in light scattering (LS) implies an increase in the size and/or percentage crystallinity in the polymer.

Figures 13 and *14* show the effect of temperature on the light scattering intensity of the polypropylene films. In the solid-state there are definite changes in light intensity where the rate of change of light scattering intensity relates to dynamic interchanges between the crystalline and amorphous phases. These results show a number of interesting features. Firstly, the control polymer which has been stored under refrigeration exhibits a marked decrease in light scattering before the melting point of the polymer (~160°C). After this point the light scattering decreases markedly due to melting and loss of crystallinity. Secondly, for the degraded samples (except PP5) light scattering intensity is maintained showing a less pronounced effect than that of the control polymer. This is an indication of the deterioration of the amorphous phase of the polymers by slow ambient thermal oxidation to give smaller chain fragments with higher crystallinity. Sample 5 appears to be erroneous and closer to that of the control. Finally, PP4 exhibits an increase in light scattering with temperature, suggesting that the polymer is more sensitive to annealing during the scan. After hexane extraction however, PP4 exhibits characteristics similar to that of the control polymer. Here extraction of low molecular weight oxidized fractions by the hexane appears to have facilitated reorganization of the morphological structure of the polymer, compensating for the effect of ambient thermal oxidation and hence, an increase in stability.

In *Table 2*, the transmitted laser light intensity (I_0), the scattered light intensity at 10° (I_θ) and the ratio of scattered light (I_θ/I_0) are shown for the control PP film

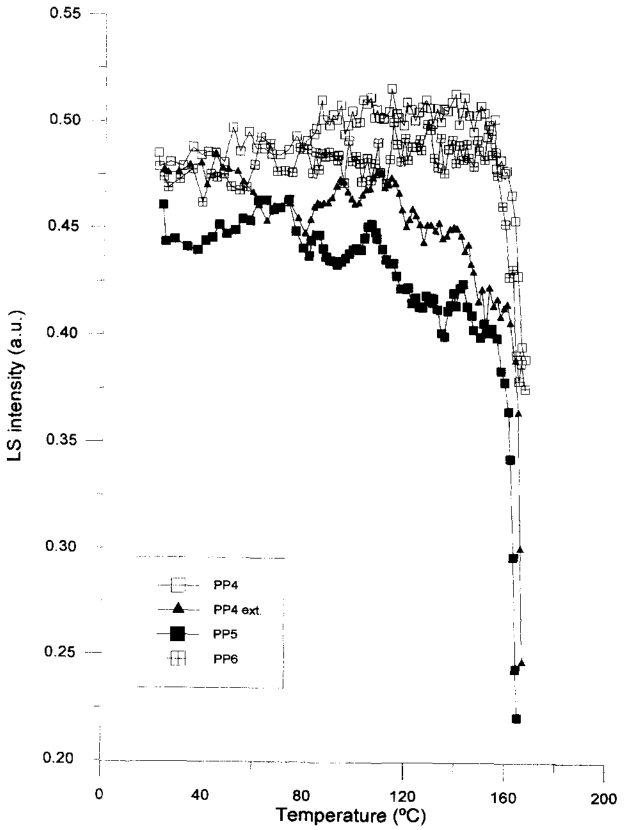

Figure 14 Light scattering intensity vs temperature at 5°C min^{-1} for (□) PP4, (▲) PP4-hexane extracted, (■) PP5 and (⊞) PP6 polypropylene film samples

Table 2 Light scattering intensities of PP films

Sample	I_0 (V)	I_θ (V)	I_θ/I_0 (%)
Control	0.583	0.008	1.4
PP1	0.552	0.021	3.8
PP2	0.560	0.014	2.5
PP3	0.360	0.009	2.5
PP4	0.330	0.016	4.8
PP4extr.	0.406	0.023	5.7
PP5	0.404	0.022	5.4
PP6	0.424	0.010	2.4
PP Repsol	0.401	0.010	2.5
Annealing 6h at 156°C			
PP1 deg LS	0.560	0.004	0.7

$\theta = 10°$

Table 3 Initial fusion process by d.s.c. of polypropylene films

Sample	T_{m1}	T_m	Onset	ΔH_m	% Crystallinity
Control	130.6	162.5	150.8	66.5	31.8
PP1	130.0	161.9	150.3	79.7	38.1
PP2	130.0	161.9	149.0	81.0	38.8
PP3	128.3	162.7	149.4	77.6	37.1
PP4	130.0	163.0	150.5	77.2	36.9
PP4 extr.	133.0	161.8	147.4	73.3	35.1
PP5	130.0	161.4	148.1	70.5	33.7
PP6	131.7	161.9	148.7	77.5	37.1
PP Repsol	133.0	163.3	150.6	78.0	37.3
PP1 deg LS	155.0	166.8	158.5	67.3	32.2

T in °C, ΔH in J g^{-1}

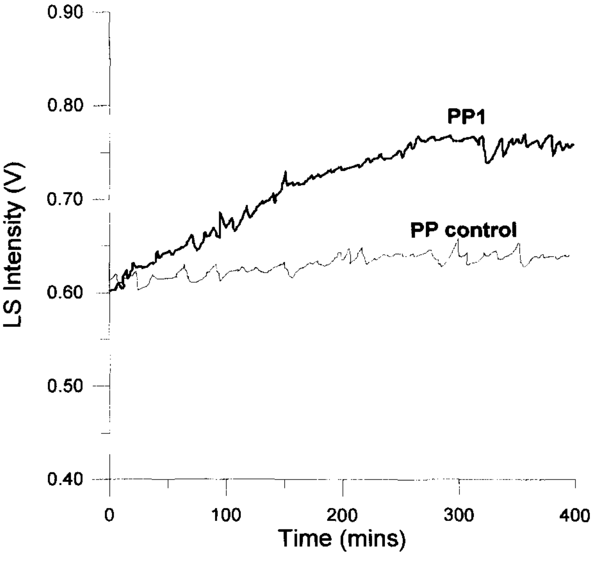

Figure 15 Light scattering intensity (V) vs time in min at 156°C for PP control and PP1 polypropylene film samples

and the degraded samples 1–6. The long-term oxidation of the polymer increases the initial scattered light fraction of the films and this fact can be related with the general increase in crystallinity, as illustrated by the d.s.c. data in *Table 3* (to be discussed later). PP1 exhibits a decrease in LS after annealing for 6 h at 156°C confirming the reorganization of the morphological structure, giving rise to a decrease in crystallinity.

Isothermal changes in the light scattering intensity with time for the PP control and PP1 samples are compared in *Figure 15*. Here the temperature was maintained constant at 156°C, close to the T_m. Under this condition, the degree of light scattering of the control remained constant upto a period of 400 min. In contrast, the PP1 sample exhibited an increase in light scattering due to the annealing of the oxidized chain fragments in the amorphous phase of the polymer, which is not present in the control sample.

Colour videomicrographs of the polymer film samples were also produced and examples of these are shown in *Figure 16*. The micrograph of isotactic polypropylene shows typical large birefringent spherulitic structures. This was a specially prepared highly isotactic film sample where the crystal aggregates are clearly shown for comparative purposes only. The PP control film sample under our experimental conditions exhibits the same morphological features that are typical of developing spherulites. In the micrographs, birefringence is alternating with shadows suggesting different sub-levels arising due to developing spherulites, which are only evident at sub-microscopic levels. In contrast the PP1 film sample exhibits a loss of definition giving rise to a less distinct image confirming deterioration in the amorphous phase as well as the presence of impurities which absorb the u.v. analysing light. After 6 h of annealing (at the end of the period of light scattering measurement obtained in *Figure 15*), PP1 shows an enhancement in the order of the crystalline phase due to reorganization through the dynamic interphase. This correlates with the increase in light scattering shown in *Figure 15*.

D.s.c. analysis

D.s.c. thermograms were obtained for all the polypropylene film samples. A typical thermogram for PP1 is illustrated in *Figure 17*. Here an initial (first) fusion run followed by a crystallization scan after 5 min in the molten state and then a second fusion scan was undertaken on the polymer film. From the first fusion scan

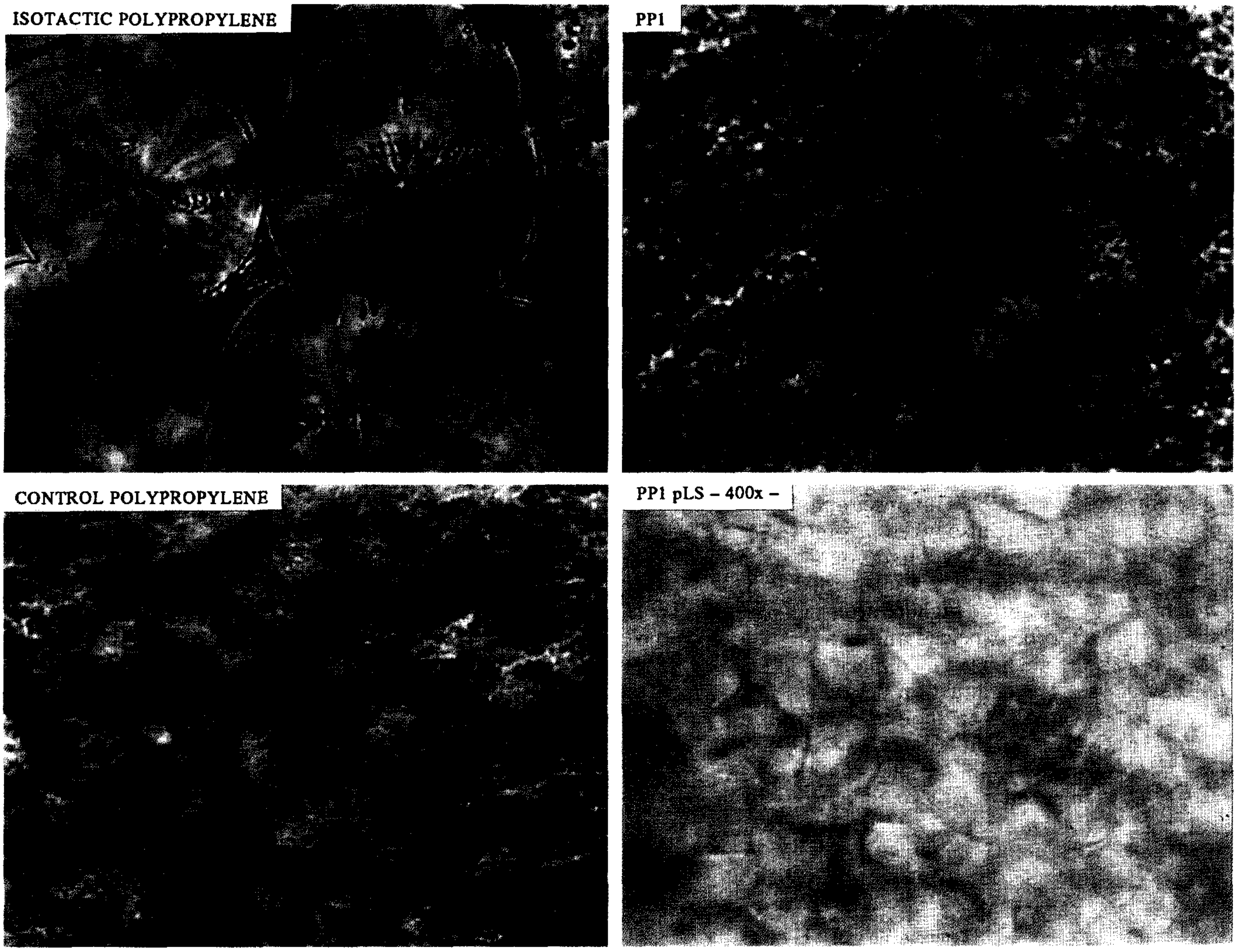

Figure 16 Colour videographs of polypropylene film samples (100 μm thick) at 400 × magnification level observed in transmission mode under polarized light

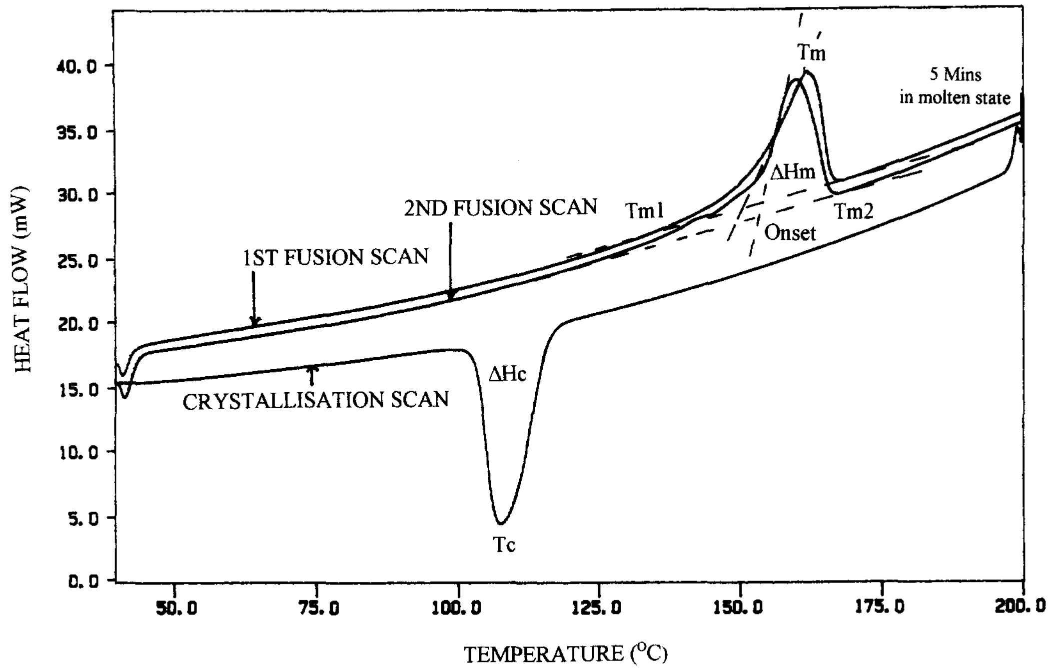

Figure 17 D.s.c. thermogram of PP1 illustrating a first fusion run followed by a crystallization scan after 5 min in the molten state and then a second fusion scan

Table 4 D.s.c. crystallization process of PP samples after 5 min in molten state at 200°C

Sample	T_c	ΔH_c	% Crystallinity
Control	108.5	78.8	37.7
PP1	107.9	94.1	45.0
PP2	107.6	98.6	47.2
PP3	107.0	93.5	44.7
PP4	107.5	90.5	43.3
PP4 extr.	107.8	88.3	42.2
PP5	107.2	84.3	40.3
PP6	108.2	93.0	44.5
PP Repsol	109.1	94.1	45.0
PP1 deg LS	103.4	54.0	25.8

T in °C, ΔH in J g^{-1}

Table 5 D.s.c. 2nd fusion process after crystallization

Sample	T_{m1} (2)	T_m (2)	Onset (2)	ΔH_m (2)	% Crystallinity (2)
Control	127.3	158.5	152.8	68.0	32.5
PP1	127.3	160.0	152.8	81.5	39.0
PP2	132.6	161.5	153.3	81.9	39.2
PP3	126.9	159.0	153.0	80.4	38.5
PP4	130.0	161.2	154.6	78.9	37.8
PP4 extr.	129.9	157.9	152.5	76.4	36.6
PP5	132.3	157.7	152.1	71.2	34.1
PP6	131.9	159.0	152.9	78.0	37.3
PP Repsol	130.3	161.5	154.6	82.3	39.4
PP1 deg LS	127.3	151.8	141.6	41.0	19.6

T in °C, ΔH in J g^{-1}

data on the melting peak (T_m), enthalphy of melting (ΔH_m) and percentage crystallinity were obtained[16] and are compiled in *Table 3*. The onset and first integration limit temperatures are also given. From the T_m data, it is evident that the values are what would be expected for commercial polypropylenes, except for the T_m of PP1, which is significantly higher after annealing. This annealing was to be expected and is associated with the reorganization which has taken place during the annealing, due to a closer interaction between the amorphous and crystalline regions in the polymer across the interface. Meanwhile, the difference between the onset and the T_m (1) in the PP1 film sample is about 20°C, whereas in the PP1 annealed sample it has been reduced by a factor of 50%. This will give rise to a reduction in the percentage crystallinity similar to that of the PP control i.e. ~30%. For all the other samples which have been oxidized, the percentage crystallinity is higher, as seen from the light scattering data (*Figures 13* and *14* and *Table 2*). It is also interesting to note that, sample PP5 is again anomalous with a percentage crystallinity approaching that of the PP control.

After the first fusion process, samples were maintained in the molten state for 5 min and then the crystallization process was followed, as shown in *Figure 17*. The results for the crystallization temperature (T_c), enthalpy of crystallization (ΔH_c) and percentage of crystallinity[16] are compiled in *Table 4*. Here the enthalpy of crystallization is higher for the oxidized PP samples compared with that of the PP control, except for the PP1 annealed sample. However, for all the samples the enthalpy of crystallization and percentage crystallinity values are higher than those obtained in the first fusion process. This fact is in agreement with that expected and the well-known reorganization possibilities of the crystalline phase according to most fundamental studies in this area[17,18]. It should be noted that when the polymer is held in the molten state for 5 min any morphological or thermal prehistories in the PP samples will be eradicated.

Data from the second fusion process are shown in *Table 5*. Again, there are significant differences (around 25%) in the enthalpy (ΔH_m) and percentage crystallization values for the PP control and oxidized PP samples. This confirms that the ambient oxidized PP samples contain

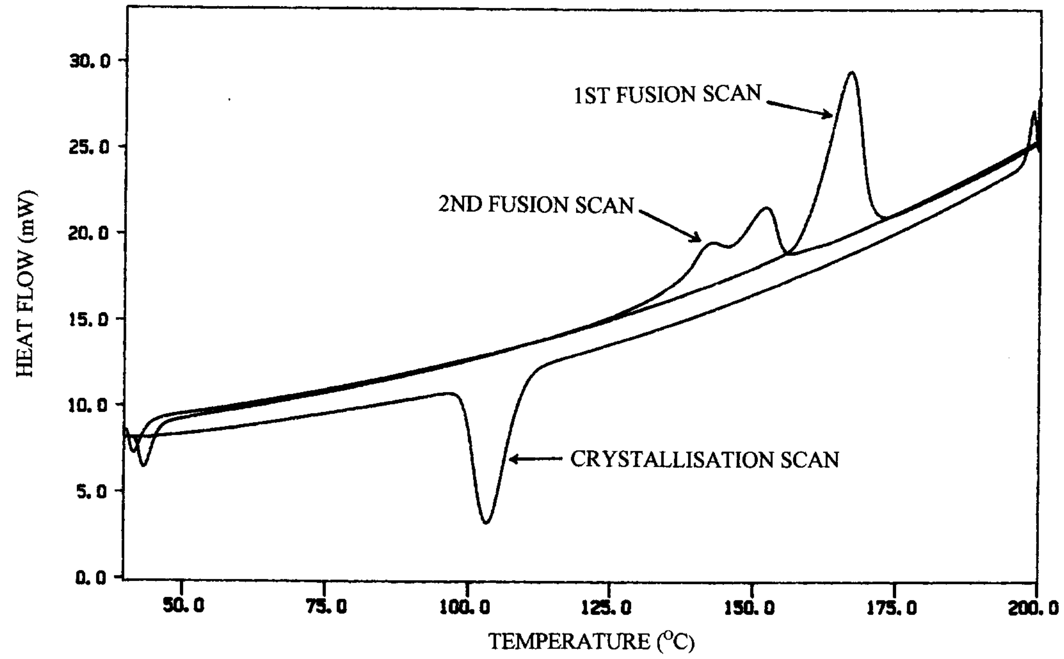

Figure 18 D.s.c. thermogram of PP1 film after 6 h annealing at 156°C showing a first fusion run followed by a crystallization scan after 5 min in the molten state and then a second fusion scan

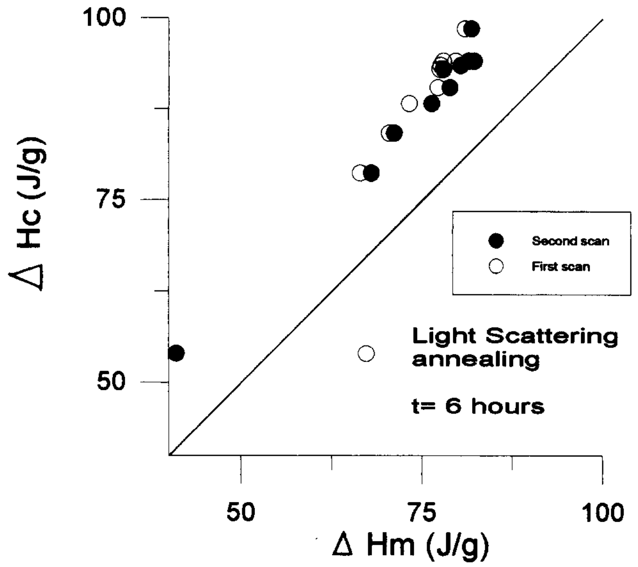

Figure 19 Crystallization enthalphy vs fusion enthalpy for the first and second scans of the examined PP samples

smaller oxidized chain fragments which are capable of reorganization into crystallites. For the sample PP1 after annealing there is a greater degree of degradation as shown by the much lower T_m value, as well as the lower crystallinity. *Figure 18* shows the d.s.c. thermogram for the PP1 sample after 6 h of annealing at 156°C. In the second fusion scan two lower T_m peaks are observed. The general response of the material under dynamic conditions is obtained, exhibiting a 20°C difference between the onset and T_m (1). The suspension grade of PP exhibits properties similar to those of the oxidized samples and is included for comparison purposes only; in any case the newer gas phase polymerization process will produce a higher molecular weight material than that of the older diluent grade samples.

One important feature of the data is the value of the enthalpy of fusion being lower than that of the enthalpy of crystallization. Consequently, this is typical of isotactic polypropylene where the helical arrangement of the chains hinders the dynamic equilibrium between the amorphous and crystalline phases. *Figure 19* shows the relationship between both types of enthalpy for the PP samples. For the first and second scans the enthalpy of crystallization is higher than the enthalpy of fusion except in the case of PP1 after annealing for 6 h at 156°C. The latter is associated with a decrease in the molecular weight of the polymer causing lower T_m and crystallinity values for the reasons previously given. In the second scan the enthalpy of crystallization remains larger than the enthalpy of fusion, but with a lower overall value (as discussed for *Table 5*).

CONCLUSIONS

The hydroperoxide data clearly show that unstabilized polypropylene is susceptible to oxidation processes upon storage under ambient conditions. This is clearly evidenced in the spectroscopic data which show the formation of unsaturated carbonyl species with prominent absorption maxima in the regions 230 and 290 nm. Removal of these species by cold hexane extraction strongly suggests their presence in the amorphous regions of the polymer where oxidation is more likely to occur. This prior treatment gives rise to a marked increase in both the thermal and light stability of the polymer.

The technique of light scattering used here coupled with that of the d.s.c. shows that the PP samples stored in air have undergone oxidation under ambient conditions to give changes in their morphological structure. Here the amorphous phase appears to have oxidized to give smaller molecular chain fragments which have recompacted into crystallites.

Though the formation of the hydroperoxide and carbonyl species may be inter-related, marked differences in the levels of chromophores do not correlate with minor differences in photooxidation rates of the polymers. Also, whilst the increased oxidation levels would be expected to give rise to smaller molecular fragments, the increased crystallinity is inconsistent with the reduction in light stability[1–3]. However, the morphological reorganization, as shown in *Figure 16*, would be expected to contribute to a much easier diffusion of oxygen through the film material and hence, an increase in oxidation rate.

In conclusion, for chromophore generation, other factors would appear to be more important in controlling the overall photooxidation rate of the polymer. This inherent instability may, as concluded earlier, be associated with the role of the original initiation sites in the polymer from manufacture or unsaturation/polymer-oxygen complexes[3,11,12]. Alternatively, there may be other, as yet, unidentified chromophores.

ACKNOWLEDGEMENTS

The authors would like to thank Dr T. J. Henman of Cambridge Polymer Consultants for storing and supplying the bags of polypropylene powder material used in this work. They are also grateful to REPSOL in Madrid, Spain for supplying the suspension grade polymer material and for development of the light scattering system. The authors also thank the Spanish Ministry of Science and Education for a grant to T. Corrales.

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