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THERMAL AND PHOTOCHEMICAL OXIDATION OF POLYPROPYLENE

INFLUENCE OF RESIDUAL CATALYST LEVELS IN UNSTABILISED DILUENT AND GAS PHASE POLYMERS

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Abstract—The thermal and photochemical behaviour of several unstabilised polypropylene samples made experimentally by a gas phase (GP) process has been examined and compared with those of samples made commercially by the normal diluent phase (DP) process. Higher levels of residual catalysts are shown to have a marked effect on both the thermal and photochemical processes. The initial autocatalytic growth of hydroperoxides, observed during both oven-ageing and melt processing, is considerably suppressed in GP polymer when compared to DP polymers probably because higher levels of residual catalysts are ionically inducing the decomposition of hydroperoxides thereby accelerating the subsequent thermal and photochemical breakdown of the polymer. Pre-treatment of both types of polymers with alcoholic phosphoric acid solution or sulphur dioxide produces some interesting and markedly different effects on photostability. Of the catalyst residues present, variation in titanium levels seems to be important in controlling thermal and photochemical stability; the effect of aluminium is seen but is as yet undefined.

INTRODUCTION

The thermal and photochemical oxidation of polyolefins continues to be an area of active research that poses many problems and unanswered questions [1–3]. In particular the relative importances of initiation through hydroperoxide and carbonyl groups continue to be discussed. Many workers [4–9] now firmly believe that hydroperoxides are key initiators of the photooxidation of processed polyolefins although others have proposed that carbonyl groups play a primary role by absorbing u.v. light and inducing the decomposition of hydroperoxides. In unprocessed, "hydroperoxide-free" polymer, photooxidation is believed to be induced through light absorption by oxygen–polymer (unsaturation) complexes which then generate hydroperoxides [12–14]. Thus, the general consensus of opinion is that hydroperoxides are probably the most important primary free radical producers in the oxidation of polyolefins.

Of the other types of chromophores known to be present, titanium/aluminium catalyst residues and iron contamination during manufacture/processing have also been considered to play important roles in thermal and photochemical oxidation [15], particularly in inducing cross-linking [18]. However, direct experimental evidence for this view has not been forthcoming and some workers have suggested that the concentrations of metal ions such as Ti and Fe in commercial polyolefins are too low to have any significant effects.

With the advent of new process technologies for making polyolefins [19], polymers with different types of catalyst residues are becoming available. These new types of polymers, whilst still in the experimental stage, provide an excellent opportunity for studying the influence of catalyst residues on the thermal and photochemical behaviour of polyolefins.

This paper compares the thermal and photochemical oxidations of unstabilised polypropylene samples made by both diluent phase (DP^{20}) and new gas phase (GP) processes [19]. The results indicate that high levels of catalyst residues play an important role in inducing the thermal decomposition of hydroperoxides; the importance of this process on photochemical stability is examined. Pre-treatments to reduce catalyst residue levels and decompose hydroperoxides have also been examined; evidence is presented to show that the thermal and photostability of polypropylene is related to the concentration of titanium residue. This is contrary to previous reports [1] but in line with unpublished results [24].

EXPERIMENTAL

Materials

All polypropylene samples used in this work were supplied as unstabilised powders by ICI (Petrochemicals and

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Plastics Division), Welwyn Garden City, U.K. All the DP samples were commercial samples; the GP polymers were experimental products. Catalyst concentration levels (obtained by X-ray fluorescence-XRF at ICI) are detailed in the Results and Discussion where appropriate.

Polymer films (200 μm thick) were prepared by standard compression moulding at 200° for 1 min followed by quench cooling in water. Films were thermally oxidised in circulating-air oven for various periods at the temperatures indicated. Polymer powders were also melt processed using a Brabender Plasticorder (Duisburg, W. Germany) at 200° for various periods.

Isopropanol/phosphoric acid treatment

Polymer films were immersed in isopropanol or 2% phosphoric acid in isopropanol for 4 hr in an attempt to remove some of the catalyst residues.

Sulphur dioxide treatment

Polymer films were exposed to an atmosphere of sulphur dioxide in a desiccator for 24 hr at ambient temperature to destroy hydroperoxides.

Irradiation

Polymer films were irradiated in a Microscal unit (Microscal Ltd, London) employing a 500 W high pressure Hg/W lamp (50°, relative humidity-ambient) ($\lambda \geq 300$ mm). Rates of photooxidation were measured using the well-known standard carbonyl index [1–5, 7–14] method and embrittlement was taken as the time to achieve a 0.06 carbonyl index value.

Hydroperoxide analysis

Hydroperoxide concentrations in the polymer films were estimated using the well established iodimetric method [21]. A calibration curve was obtained using cumene hydroperoxide as a standard.

RESULTS AND DISCUSSION

Influence of catalyst residues on thermal and photochemical stability

Films of DP and GP polypropylene were oven-aged at 140°. In Table 1 the times for the films to achieve 0.06 carbonyl index are compared with the known levels of titanium and aluminium as measured by XRF. It is seen that the two samples (both DP) having the lowest Ti contents were more stable than those from the GP process. The factor of two difference between the DP samples was probably caused by Al differences.

The rates of photooxidation of several polypropylene films were measured; in Table 2 the time to achieve 0.06 carbonyl units is compared with Ti and Al concentrations. The films used in this study were different from those used for thermal oxidation. In agreement with the oven-ageing data above, it is seen that polymer photostability decreases with increasing Ti concentration. Extrapolation of the GP curve gives a predicted life similar to that of DP polymer. Whilst therefore Ti in the range 25 to 80 ppm appears to have an important effect on stability, the effect of Al needs further investigation.

Table 1. Comparison of embrittlement times during oven-ageing at 140° with catalyst residues for polypropylene samples

Polymer				
Type	Sample	T 0.06 (min)	[Ti] (ppm)	[Al] (ppm)
DP	A	150	25	30
	B	85	25	140
GP	A	75	40	200
	B	65	50	230
	C	40	65	200

Table 2. Comparison of embrittlement times during photooxidation with catalyst residues for polypropylene samples

Polymer				
Type	Sample	T 0.06 (hr)	[Ti] (ppm)	[Al] (ppm)
DP	C	140	25	140
GP	D	125	30	230
	E	125	30	180
	F	90	65	200
	G	80	70	260

It is evident from these results that Ti residues play a key role in either initiating or controlling the thermal and photochemical stability of polypropylene. These findings contradict the earlier results of Carlsson and Wiles [1] who conclude that variations in Ti levels below 100 ppm have no important role in the photoinitiated oxidation of polypropylene. Gugumus [22] failed to obtain a correlation between the u.v. stability of stabilised polypropylene multifilaments and Ti content, although considering that the total Ti content should play a role.

Influence of isopropanol/phosphoric acid treatment

Figure 1 shows the effect of treating DP/GP polymer films with isopropanol and 2% *o*-phosphoric acid in isopropanol on the rate of photooxidation. It is seen that, for DP polymer, isopropanol treatment alone has a destabilising effect (although DP polymers had received an alcohol treatment during production) but the addition of 2% *o*-phosphoric acid improves the light stability. It was found previously that *n*-hexane extraction destabilises polypropylene [14]. In the case of GP polymers, treatment by isopropanol with or without 2% *o*-phosphoric acid

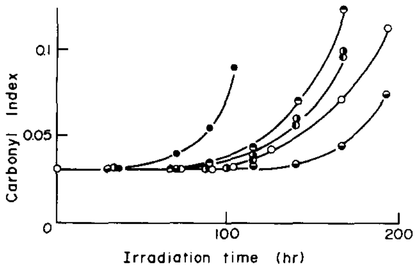

Fig. 1. Rate of photooxidation during irradiation of polypropylene films in Microscal unit: (◑) DP(D) control; (◒) DP(D) treated isopropanol; (○) DP(D) treated 2% H_3PO_4 in isopropanol; (●) GP(A) control; ( ) GP(A) treated isopropanol; (◑) GP(A) treated 2% H_3PO_4 in isopropanol.

Table 3. Effect of oven-ageing at (140°) on the photooxidative stabilities and hydroperoxide concentrations of polypropylene films

Polymer		Unheated		15 min		30 min		60 min
Type	Sample	T*	[ROOH]	T%	[ROOH]	T%	[ROOH]	[ROOH]
GP	D	126	45	28	30	18	50	1800
	I	126	40	26	10	39	50	540
	H	156	25	42	20	72	25	790
DP	D	160	65	21	100	41	240	3400

* T = time (hr to 0.06% oxygen as carbonyl). [ROOH] in μg/g. T% = % reduction in T.

markedly improves the photostability, the latter treatment being more effective. The results indicate that catalyst residues can play an important role in controlling light stability of polymer and treatment with *o*-phosphoric acid is quite an effective method of decreasing their effect. The mechanism through which catalyst residues operate as sensitisers is uncertain. Some workers [18] have suggested that they are able to abstract hydrogen atoms and can induce higher levels of cross-linking. However, transition metal ions also are able to catalyse the decomposition of hydroperoxides to alkoxy or peroxy radicals by processes such as:

$$RO_2H + M^{2+} \rightarrow RO^{\cdot} + OH^- + M^{3+} \quad (1)$$

$$RO_2H + M^{3+} \rightarrow RO_2^{\cdot} + H^+ + M^{2+} \quad (2)$$

$$(2RO_2H \rightarrow RO^{\cdot} + RO_2^{\cdot} + H_2O)$$

and may therefore accelerate the thermal and photochemical oxidation of the polymer through such mechanisms. This effect will be examined in the next section.

Development of hydroperoxides

Oven-Ageing. The influence of oven-ageing on the development of hydroperoxides in DP/GP polymers is shown in Table 3. The light stabilities of the unheated and heated films, as measured by the time to achieve 0.06 carbonyl units, are also compared. Here it is seen that all the GP polymers contain lower initial levels of hydroperoxides compared to DP polymers. Furthermore, on heating GP polymers in air for 15 min at 140°, the hydroperoxide concentrations are reduced whereas in the DP polymers the concentrations are markedly increased. After 1 hr heating the hydroperoxide concentrations show a large increase in GP and especially DP polymers. Thus mechanisms (1) and (2) above could well be operative in these polymers and could account for the differences in thermal stability.

Thermal pre-oxidation of DP polymer is seen to cause a marked increase in hydroperoxide concentration, not observed for GP polymers. These results do not rule out the importance of hydroperoxides as photoinitiators; they merely indicate that there is a critical level for hydroperoxides above which the rate is probably controlled more by morphological factors and perhaps, more importantly, by their decomposition products. This is particularly seen after 30 min peroxidation when the hydroperoxide concentrations in GP polymers are similar to their initial values but the embrittlement times have been substantially reduced.

Processing history. Figure 2 shows the relationship between the hydroperoxide concentration and melt processing time for two DP polymers. Both show increased hydroperoxide concentrations after 10 min processing followed by a decrease during the next 10 min, but a recovery over the following 10 min. This behaviour is well-known for polypropylene [1–3, 5, 7].

The GP polymer showed a different pattern of behaviour (Fig. 3). Whilst two of the polymers showed maximum hydroperoxide formation after 10 min processing, there was a steady reduction on further pro-

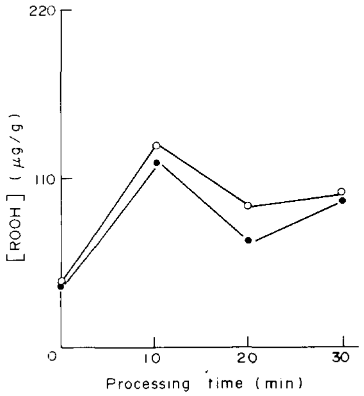

Fig. 2. Development of hydroperoxide in DP polypropylene during processing samples: (○) DP(D); (●) DP(F) polymers.

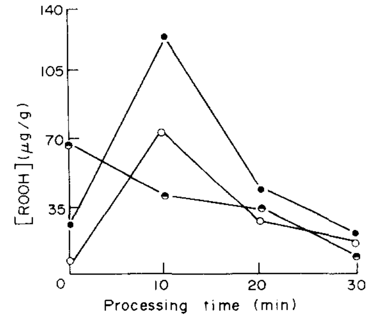

Fig. 3. Development of hydroperoxide in GP polypropylene during processing samples: (○) GP(A); (●) GP(J); (◓) GP(D) polymers.

Table 4. Effect of processing history at 200° on the photooxidative stabilities (*T* 0.06) of polypropylene films

Polymer		Processing times (min)			
Type	Sample	0	10	20	30
GP	A	120	45	40	50
	D	126	90	85	50
	J	115	67	73	70
DP	D	160	39	46	52
	F	170	50	70	90

Table 5. Effect of SO_2 treatment on the photooxidative stabilities (*T* 0.06) of polypropylene films before and after oven-ageing for $\frac{1}{2}$ hr at 130°

Polymer		Oven-ageing	U.V. embrittlement times (*T* 0.06)/hr	
Type	Sample		Untreated	Treated-SO_2
DP	A	No	140	220
	D	Yes	90	240
GP	J	No	100	70
	D	Yes	65	65

cessing for up to 30 min. One of the GP polymers (D) showed a totally different pattern of behaviour and exhibited a marked reduction in hydroperoxide concentration on processing, indicating the involvement of mechanisms such as (1) and (2).

The photostabilities of all the films examined are compared in Table 4. For the DP polymers, light stability correlates roughly with hydroperoxide concentration up to 20 min processing, whereas for GP polymers the rate of decomposition of hydroperoxides exceeds their rate of production due to the presence of higher catalyst residues; it must be remembered that hydroperoxide formation and decomposition are competing and concurrent reactions.

The key role of hydroperoxides in initiating the photooxidation of DP polymer compared to the negative effect in GP polymer is demonstrated by the final section of results dealing with the effect of sulphur dioxide treatment.

Effect of sulphur dioxide treatment

The effects of sulphur dioxide treatment on the photoxidative stabilities of unheated and heated ($\frac{1}{2}$ hr at 130°) polymer films made by both processes are compared in Table 5. There is a dramatic difference between the two types of polymer. For DP polymer, prior sulphur dioxide treatment substantially improves photostability and, as reported earlier [9], both unheated and heated polymer films have virtually the same light stability after sulphur dioxide treatment. In the case of GP polymer, sulphur dioxide treatment had little effect on light stability; in fact, whereas the heated polymer remained virtually unaffected by sulphur dioxide treatment, the unheated polymer was destabilised.

It is probable that, where stabilisation is achieved, SO_2 destroys hydroperoxides by a reaction similar to that investigated for polyethylene [9, 23]:

$$\mathrm{ROOH} + \mathrm{SO_2} \rightarrow [\mathrm{ROSO_2OH}] \rightarrow \text{further products} \quad (3)$$

In the latter case, it is almost certain that the high catalyst levels interfere with reaction (3).

CONCLUSIONS

Catalyst residues, especially titanium, play an important role in controlling the thermal and photochemical stability of polypropylene. High concentrations of catalyst residues can ionically decompose hydroperoxides (e.g. to give carbonyl groups) thus substantially affecting the rate of oxidation. Finally, the results clearly demonstrate the key role of hydroperoxides as photoinitiators as well as their interaction with catalyst residues.

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