Mechanisms of Antioxidant Action: Photo-antioxidant Activity of Polymer-bound Hindered Amines. Part I—Bismaleate Esters

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ABSTRACT

Bis-(2,2,6,6-tetramethylpiperidin-4-yl) maleate (BPM) has been reacted with polypropylene in the melt to a high level (90%) in the presence of dicumyl peroxide (DCP). Concentrates of polymer bound BPM (BPM-B) were used as masterbatch additives to unstabilised polypropylene and maximal photo-oxidant activity was observed at 70% binding. The photo-antioxidant effectiveness of BPM-B (from the exhaustively extracted masterbatch) was found to be linearly related to its concentration in the polymer up to 70% binding and on a molar basis it is as effective as conventional low molar mass additives. The implication of these results for the theories of antioxidant behaviour in polymers is discussed.

INTRODUCTION

2,2,6,6-Tetramethylpiperidines have become established in recent years as effective light stabilisers for thermoplastic polymers and a great deal of attention has been paid to the mechanism of their action in the polyolefins.[1,2] However, deficiences have become evident in their performance under certain conditions of use, notably in fibres and films where additives can be readily lost by volatilisation and solvent leaching. Oligomeric structures have been developed which are less volatile and hence more persistent in the polymer under aggressive conditions.[3] However, this

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is achieved at the expense of loss of photo-antioxidant activity and, in principle, this approach must be limited by compatibility constraints as the molar mass of the additive is increased.

The attachment of antioxidants and stabilisers to polyolefins by grafting through vinyl monomers has been reviewed by Munteanu.[4] The evidence suggests, however, that the level of binding achievable by this technique (i.e. mass grafted per mass of vinyl monomer) is not generally much more than 20–30% using a variety of acryloyl and methacryloyl compounds.[5,6] This is believed to be due to the formation of homopolymers which are readily removed from the polymer by solvent extraction. Oligomeric antioxidants made in this way are also relatively ineffective as antioxidants due to poor compatibility.[7]

Maleic anhydride and its derivatives are known to be much more resistant to homopolymerisation and it seemed likely to us that higher levels of adduct formation might be achieved by this technique. The bis-maleate, BPM, was synthesised as a 5% concentrate in polypropylene (BPM-B) and its photo-antioxidant activity both in bound and unbound form was studied in polypropylene.

BPM
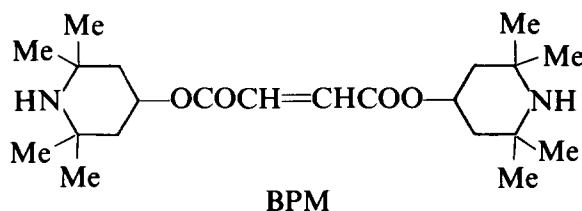
EXPERIMENTAL

Bis-(2,2,6,6-tetramethylpiperidin-4-yl) maleate (BPM) was prepared by transesterification of di-ethyl maleate with sodium piperidinoxide as follows: 4·71 g of 2,2,6,6-tetramethyl-4-hydroxypiperidine (TMP) in 200 cc dry benzene was treated with 0·69 g finely divided sodium metal and warmed at 40°C until H_2 evolution ceased. The warm solution was added to a molar excess of diethyl maleate and excess of TMP in benzene solution. The mixture was refluxed overnight and then filtered hot. After evaporation of the benzene, the product was dissolved in CH_2Cl_2. On cooling, sodium maleate precipitated leaving the product in solution. After removal of the solvent, BPM was obtained as a white solid, Mp 67–69°C. C, H, N analysis; C, 66·0 (calc. 66·8); H, 10·4 (calc. 9·6); N, 6·9 (calc. 7·1). It showed ester C=O, 1720 cm^{-1} and unsaturation, 1640 cm^{-1}.

Bound antioxidant (BPM-B) concentrate was made by processing 35 g of a mixture (5 g BPM/100 g PP) in a Hampden-RAPRA torque rheometer at (180°C/10 min closed mixer/60 rpm). Different molar ratios of dicumyl peroxide (DCP) to BPM were used as indicated in Table 1. The polymer was cooled rapidly by quenching in cold water and was then compression moulded to films (1.8×10^{-2} cm at 180°C) between cellophane sheets at a pressure of 85 kg cm^{-2} for 2 min. The platens were cooled to 40°C before removing the films. It was found that the carbonyl peak in the IR due to conjugated ester originally at 1720 cm^{-1} was shifted to 1772 cm^{-1} (saturated ester) and this remained unchanged when the films were extracted with either acetone or dichloromethane under reflux for 12 h. A peak due to unsaturation (unreacted acrylic ester) at 1640 cm^{-1} was completely removed by this treatment, as was a peak at 1690 cm^{-1} due to acetophenone. The increase in height of the peak at 1772 cm^{-1}, coupled with the decrease in height of the peak at 1720 cm^{-1}, was used to estimate the extent of the reaction. (Film containing BPM processed without peroxide was used as a reference.) The 1720 cm^{-1} peak was removed completely by 12 h extraction with acetone. The extent of binding as a function of [DCP]/[BPM] molar ratio is indicated in Table 1. The masterbatch concentrates were comminuted and added to unstabilised PP to give a concentration based on BPM originally present at the beginning of the masterbatch synthesis of 10^{-3} mol per 100 g. The polymer was processed at 180° per 5 min and compression moulded to films as described above.

TABLE 1

Extent of Binding and Photo-antioxidant Effectiveness of BPM-B in Polypropylene from 5% Masterbatch. (Concentration of BPM before extraction $= 10^{-3}$ mol per 100 g in All Cases.)

| $[DCP]/[BPM]$ molar ratio	% Bound	Embrittlement time (h)	
		U	E
0	0	2 300	90
0·004	8	2 400	250
0·01	20	2 800	650
0·05	60	2 900	1 200
0·1	70	2 850	1 400
0·2	90	2 000	900
Control	—	90	90
Tinuv. 770	0	2 250	90

U, unextracted.

E, extracted 12 h with refluxing acetone.

Photo-oxidation of the PP films was carried out in an S/B accelerated weathering cabinet (symmetrical array of 24 fluorescent Type C Phillips actinic blue lamps (05) and 8 Type A2 Westinghouse sunlamps (FS 20)[8]). The measured average intensity of irradiation falling on the films was calculated[9] to be $4.2 \, W \, m^{-2}$. Embrittlement time was time to fracture of the films on bending through an angle of 180°. Each measurement was carried out in triplicate and the accuracy was $\pm 5\%$.

RESULTS AND DISCUSSION

Bis-piperidinoxyl maleate, BPM, was reacted with polypropylene (5 g per 100 g) in the melt in the presence of dicumyl peroxide (DCP) at various [DCP]/[BPM] molar ratios and the amount bound to the polymer was measured after exhaustive extraction as described in the experimental section. Table 1 shows the extent of binding of BPM with increasing [DCP]/[BPM] molar ratio. It also records the effectiveness of the bound photo-antioxidant when the masterbatch concentrate was added to unstabilised polypropylene to give a concentration (based on the original concentration in the masterbatch) of 10^{-3} per 100 g (i.e. 0.4 g per 100 g). Figure 1 shows that there is a direct relationship between BPM-B concentration after extraction and its photo-antioxidant activity up to 70% binding, corresponding to a molar ratio [DCP]/[BPM] of 0.1. Above this ratio the photo-antioxidant activity of the bound antioxidant falls off sharply.

BPM, when used as an additive (without radical generator), has a photo-antioxidant activity similar to the commercial hindered piperidine, Tinuvin 770, at the same molar functional group concentration (see Table 1). However, peroxide treatment significantly improves this activity up to a molar ratio of 0.05. As in the case of the fully bound piperidine, above this ratio activity decreases sharply. The reason for the decrease in activity at high peroxide to vinyl antioxidant ratios is not at present clear and is being investigated further. One possibility is that residual peroxide or thermolysis products sensitise the polymer to photo-oxidation. However, the evidence suggests that this is not the explanation since, in the extracted polymer, the peak due to acetophenone at $1690 \, cm^{-1}$ was completely removed and yet activity still fell away. Similarly, we would expect dicumylperoxide to be removed under these conditions. A second postulate is that the peroxide or derived alkoxyl radicals actually attack the piperidine ring under these conditions. Other studies currently in progress have shown that the piperidine ring is rather unstable in the presence of peroxides at elevated temperatures, giving rise to ring opened products.[10]
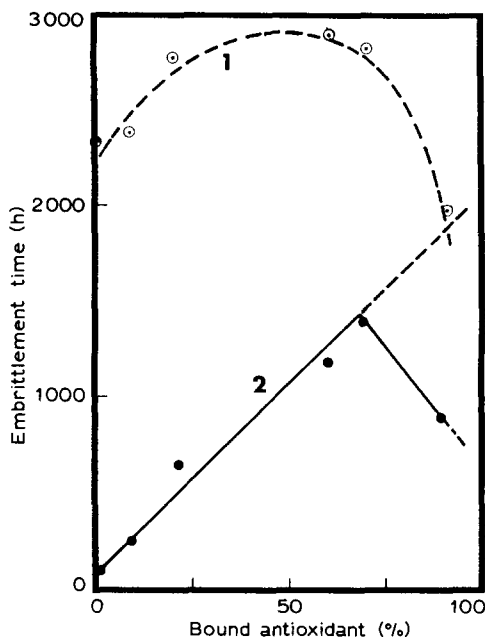
Fig. 1. Time to embrittlement of polypropylene films. 5% concentrates prepared by reactive processing of BPM with dicumyl peroxide at various molar ratios (see Table 1) were diluted to 10^{-3} mol per 100 g in PP. The percentage that has become bound to the polymer is indicated in the abscissa. 1, Without solvent extraction; 2, extracted with acetone for 12 h.

The beneficial effects of peroxide treatment at low [DCP]/[BPM] ratios are unexpected. It is known that the piperidinoxyl is more effective than the piperidine as a photo-antioxidant,[11,12] and the most obvious interpretation is that a proportion of the amine was being converted to nitroxyl, but no evidence was found for this from ESR measurements on the polymer. The alternative explanation that the binding process increases the inherent solubility of the photo-antioxidant in the polymer seems more compelling. Certainly, the photo-antioxidant activity of the bound hindered piperidine is of the same order as that of the unbound additive without peroxide treatment (see Fig. 1).

The high level of photo-antioxidant activity of the polymer-bound hindered piperidine raises some fundamental questions as to how antioxidants trap macroradicals in a polymer matrix. Does the chain carrying species diffuse to the reaction sphere of the antioxidant which is defined by the rotational mobility of the polymer bound antioxidant in the amorphous phase of the semi-crystalline polymer, or does the 'migration' of the chain propagating species (alkyl and alkylperoxyl) occur by chemical reaction along and between chains to arrive at the site of the antioxidant? There are so far no clear answers to these questions but it now seems

probable that physical diffusion of antioxidants is less important than has previously been assumed.

Wiles and Carlsson[13] have adduced evidence to suggest that hindered amines or nitroxyls may be associated with macrohydroperoxides in the solid state. This implies that they are then in a position to scavenge more effectively the radicals resulting from hydroperoxide breakdown. It is difficult to visualise how this process can take place in the solid polymer containing a completely polymer-bound hindered amine other than by the segmental motions that are possible in the rubbery amorphous domains or by 'chemical migration' of hydroperoxide groups associated with the propagation reaction. It seems clear that further work is required to resolve the problem of diffusion of reactive intermediates during polymer oxidation in the solid state.

From a practical point of view, the masterbatch procedure solves one of the major objections to the use of polymer bound antioxidants and stabilisers; namely, the cost involved in modifying the whole polymer substrate during a conventional processing operation. The polymer bound antioxidants, like conventional additives, appear to be essentially in the amorphous region of the polymer where they are required to function and there is no evidence to suggest that the morphology and mechanical properties of the polymer modified in this way are different from polymers made by incorporating additives normally. Further studies are in progress to determine the physical distribution of the modified polymer chains in semi crystalline polymer matrices.

CONCLUSIONS

(1) Treatment of a maleatester (BPM) containing a hindered amine group with dicumyl peroxide (DCP) in the melt leads to polymer-bound antioxidants. However, the most highly bound systems obtained at high molar ratios of peroxide to hindered amine are less effective than those bound to intermediate levels, possibly due to oxidative destruction of the piperidinoxyl.

(2) Polymer-bound hindered piperidines have a similar level of photo-antioxidant activity to a commercial hindered piperidine (Tinuvin 770) used as an additive at the same molar concentration.

(3) DCP treatment of BPM significantly increases photo-antioxidant activity up to a limiting molar ratio. This is probably for physical rather than chemical reasons.

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