Mechanisms of Antioxidant Action: Effects of Sulfur Compounds on the Melt Stability of Polypropylene

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Synopsis

The effects of a number of sulfur compounds on the melt stability of polypropylene milled at 165°C have been studied. Dilaurylthiodipropionate (DLTP), Mercapto-benzimidazole (MBI), and Mercaptobenzthiazole (MBT) are all antioxidants in a polymer lightly stabilized with a phenolic antioxidant although the last two are initially pro-oxidants.   2,2'-Dibenzoylaminodiphenyldisulfide (22BDD) is a pro-oxidant under the conditions studied.

In the absence of a phenolic antioxidant the effectiveness of DLTP is reduced in the early stages of oxidation, with increasing concentration although its over all antioxidant activity increases.   The results are consistent with the view that both radical and non-radical processes occur concomitantly.

Introduction

It has been recognized for many years that a wide variety of sulfur compounds can function as antioxidants in technological media.*   In a high proportion of the reported examples, the oxidation kinetics show auto-retarding characteristics[1] suggesting that the sulfur compounds themselves are not the effective agents.   Detailed mechanistic studies have been carried out for several important classes of sulfur antioxidants[1-4] and in each case sulfur dioxide has been identified as the effective antioxidant. This agent functions by catalytically decomposing hydroperoxides in a reaction which does not involve the formation of free radicals.

Recent work has shown[3] that thiodipropionate ester (I) and their derived sulphoxides (II)

$$ROCOCH_2CH_2SCH_2CH_2COOR \qquad ROCOCH_2CH_2SOCH_2CH_2COOR$$
$$I \qquad\qquad\qquad\qquad II$$
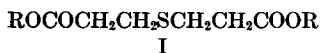
are not only initially ineffective as antioxidants but, at specific ratios of sulfur compound to hydroperoxide, both classes are pro-oxidants.

It was of interest, therefore, to compare the effect of dilaurylthiodipropionate (DLTP), a commercially important member of this class, with other sulfur compounds known to have chemical plasticizing activity under cer-

* See Reference 1. Chaps. 7-9.

tain conditions in polymers but to be antioxidants under different conditions. The medium chosen was polypropylene since many sulfur compounds have been examined empirically in this polymer. To eliminate the complication caused by the presence of unknown commercial stabilizers, unstabilized polypropylene was used throughout this work.

Experimental

Milling of Polypropylene

It was found that unstabilized polypropylene (I.C.I. grade AWR587/7/100) could not be milled on a 10″-mill (roll diameter 6″; roll speed 21 rpm) at 165°C without rapid degradation occurring during the time taken to add the polymer. In a control experiment involving only 100 g of polymer, it was found that the melt flow index had increased during six minutes on the mill at 165°C from the initial 0.19 to 6.5. The addition of 0.2% (0.001 moles/100 g) of tert-butyl-p-cresol (TBC) gave a reproducible induction period before the onset of rapid increase in melt flow index of 50 min.

400 g of polypropylene were added to the mill so that the amount removed for melt flow index measurement during the course of the milling would not seriously affect the milling characteristics. The nip setting was increased from 0.010 in. at the start of the addition of polypropylene to the mill to 0.035 in. at the end of the addition (15 min). 6 g samples of polymer were removed at intervals during the course of the milling and were stored in a thermos flask containing "Drikold" to prevent further oxidation.

Determination of Melt Flow Index (MFI)

The apparatus used was as described in the British Standard method for determination of melt flow index of polyethylene.[5] Determinations were made at a temperature of 230°C and using a load of 2.16 kg. The operational procedure was essentially that described in the manufacturers' handbook[6] except that the die of internal diameter 0.0465 in. was used throughout. The polymer was allowed to extrude for 1 min before sampling commenced. Sample "cut-offs" were taken every 30 sec. The average weight of five consecutive samples was determined and the melt flow index expressed as weight of polymer (in grams) extruded in 10 min. It was found that the results obtained by this technique were quite reproducible for a single sample of polymer compounded and processed in the same way.

Results

Two complimentary techniques were used:

(A) The polymer containing TBC was milled for 20 min (which is well short of the induction period: 50 min). After sampling for melt flow index measurement the sulfur compound was added. This method had the advantage that any pro-oxidant effect from the sulfur compound could be studied from the beginning but suffered from the disadvantage that the actual composition of the phenolic antioxidant system was not known since
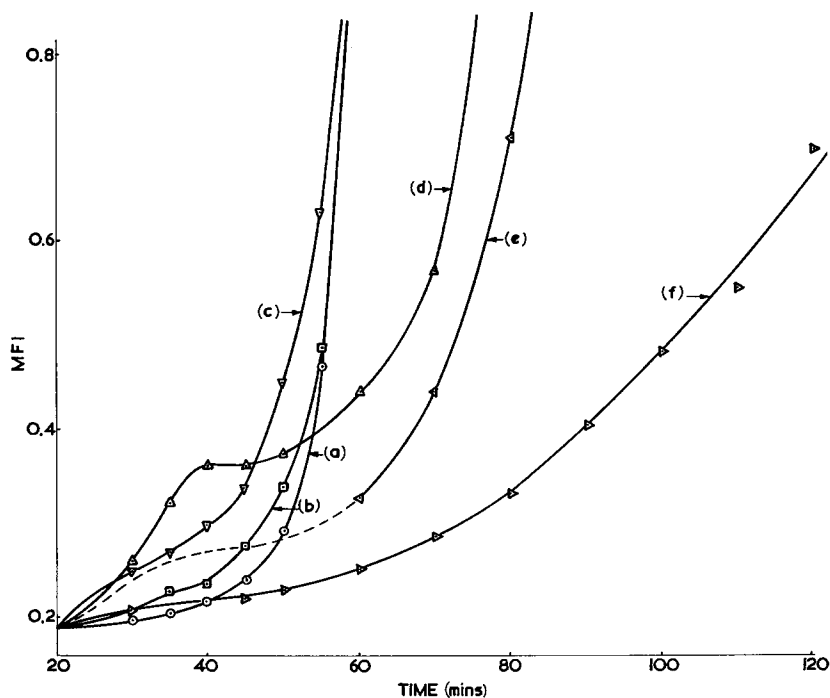
Fig. 1. Effect of milling at 165°C on polypropylene containing 0.001 moles/100 g of TBC and the following additives at 0.002 moles/100 g. (a) no additive; (b) dioctylsebacate (DOS); (c) 2,2'-dibenzoylaminodiphenyldisulphide (22BDD); (d) mercaptobenzthiazole (MBT); (e) mercaptobenzimidazole (MBI); (f) dilaurylthiodipropionate (DLTP).

some of it would have been removed, or changed, during the pre-milling stage.

(B) All additives were tumble mixed with the polymer from the beginning of the experiment. Because it was not possible to sample the polymer during the first 20 min, the shape of the initial pro-oxidant curve (if any) was lost.

In the first series of experiments reported below, technique (A) was used. In the second and third, technique (B).

SERIES 1. *Milling of additives with polypropylene stabilized with TBC by technique (A)*

To polypropylene containing 0.001 moles/100 g of TBC and milled for 20 min was added 0.002 moles/100 g of the following additives which had been purified by crystallisation;

Mercaptobenzimidazole (MBI)
Mercaptobenzthiazole (MBT)
2,2'-dibenzoylaminodiphenyl disulphide (22BDD)
Dilaurylthiodipropionate (DLTP)

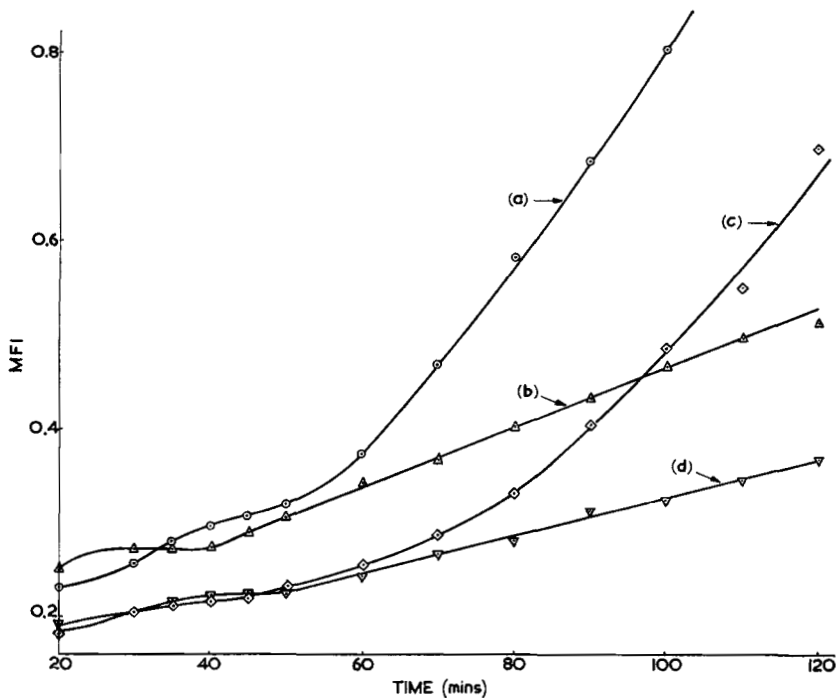Fig. 2. Effect of 2,6-di-tert-butyl-p-cresol (TBC) (0.001 moles/100 g) on the radical generating activity of DLTP. (a) no TBC, 0.002 moles/100 g DLTP; (b) no TBC, 0.004 moles/100 g DLTP; (c) with TBC, 0.002 moles/100 g; DLTP; (d) with TBC, 0.004 moles/100 g DLTP.

Melt flow index on samples taken at intervals is plotted graphically in Figure 1.

It can be seen that under these conditions a variety of behaviors was observed. DLTP, MBI, and MBT were antioxidants but in the last case the antioxidant activity was preceded by a pro-oxidant stage.* 22BDD was a pro-oxidant over the whole course of the milling but the inflexion in the curve suggests that it may have transient antioxidant activity. The results for MBI showed considerable irreproducibility probably due to incompatibility with the polymer during the early stages, but separate experiments confirmed that it acts initially as a pro-oxidant. DLTP appeared to show the least pro-oxidant effect of all the sulfur compounds under these conditions and what effect there was could be due to its lubricating function since dioctyl sebacate (DOS) was shown to have a similar effect at the same concentration.

SERIES 2. *Milling of polypropylene containing DLTP in the presence and absence of TBC*

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* The terms "pro-oxidant" and "antioxidant" are used relatively in this paper since it is becoming increasingly evident that both kinds of activity may be found with the same compound in the same medium. The designations do not necessarily imply similar activity under different conditions.
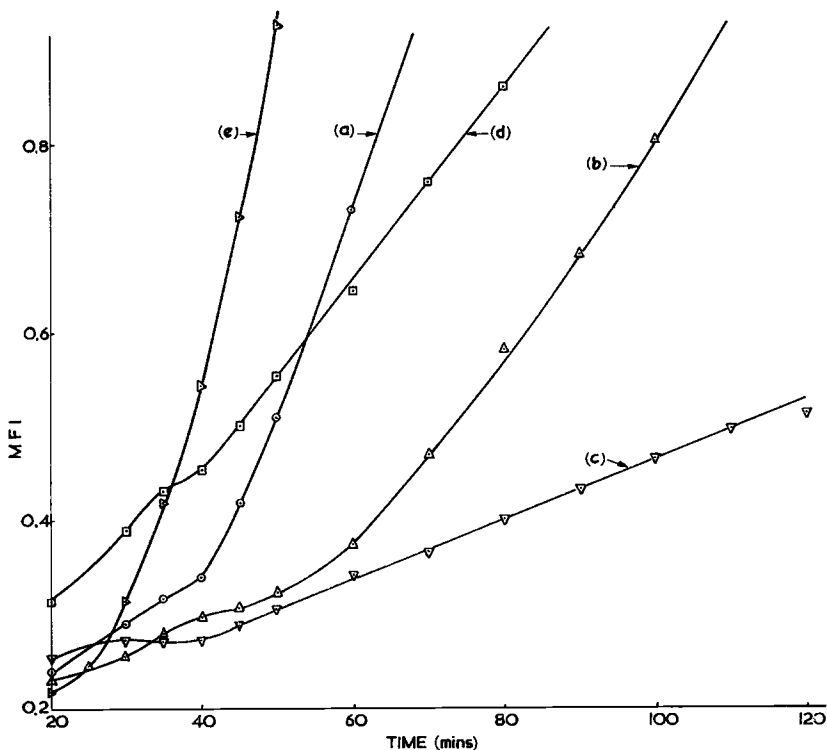
Fig. 3. Effect of DLTP concentration on the melt stability of otherwise unstabilized polypropylene.   (a) 0.001 moles/100 g;   (b) 0.002 moles/100 g;   (c) 0.004 moles/100 g (d) 0.006 moles/100 g;   (e) 0.002 moles/100 g. of dilaurylsulfphinyldipropionate (DLSP).

To test the theory that the phenolic antioxidant was scavenging free radicals produced from the sulfide and hence eliminating a possible pro-oxidant effect,[3] the last series of experiments was repeated at two concentrations both in the presence and absence of TBC.   Results are shown in Figure 2.   It is clear that the phenol is exerting its effect mainly during the first 20 min.   The crossing of the curves both in the presence and absence of TBC and the more pronounced auto-retardation in the case of the higher sulfide concentration is consistent with the view[3] that free radicals are initially formed from the sulfide.   This concentration effect was studied in more detail in the next series of experiments.

SERIES 3.   *Effect of DLTP concentration on the melt stability of polypropylene*

Polypropylene of initial melt flow index 0.190 was tumble-mixed with DLTP at concentrations ranging from 0.001–0.006 moles/100 g and milled in the usual way.   Sampling commenced at 20 min from the time of commencement of milling.   The results are graphed in Figure 3.   It is clear from Figure 3 that the antioxidant activity during the initial stages of the degradation decreased with increasing concentration of the antioxidant. The auto-retarding activity and ultimate antioxidant activity also increased

in the same order except for the highest concentration which did not become an effective antioxidant in the period of the experiment.

Dilaurylsulfinyldipropionate (DLSP) was also included in this series for comparison since it has been argued that sulfoxides are the effective antioxidants formed from sulfides by interaction with hydroperoxides.[7] Although this material showed an initial antioxidant effect it was considerably less effective under these conditions than TBC or DLTP at the same concentration and unlike the latter it did not become auto-retarding in the period of the experiment. This could be due to the extreme instability of the sulfoxide under the conditions of the experiment.[8]

Discussion

It is clear that all the sulfur compounds studied with the exception of the sulfoxide, have certain features in common. The first is that they are all ineffective antioxidants initially, although in the case of DLTP the initial inefficient stage can be removed by a relatively small amount of a phenolic antioxidant. This accords with the fact that it is the most widely used commercial stabilizer for polypropylene and is almost always used in conjunction with a phenolic antioxidant. However, optimum performance is achieved with a relatively small proportion of phenolic antioxidant.[9]

The second is that all the divalent sulfur compounds show an auto-retarding stage to a greater or lesser degree. This is most marked again with DLTP even in the absence of a phenolic but is evident even with 2,2'-dibenzoylaminodiphenyldisulfide (22BDD) which is used industrially as a chemical plasticiser for rubber (Pepton 22). It has also been reported to be an effective prodegradant for polypropylene during spinning to fiber which nevertheless gives good oxidation stability of the spun fiber.[9,10] Mercaptobenzthiazole (MBT)[1e,11] and mercaptobenzimidazole[11] (MBI) have been used as synergistic stabilizers for polypropylene. The latter is also an antioxidant for rubber[12] but the former does not appear to be so. Levin and his co-worker[11] have shown that the synergistic combination of MBT and a chain-breaking antioxidant requires a much higher ratio of phenol to sulfur compound than does MBI with the same antioxidant. Moreover the optimum activity of the latter is much higher than the former. This is explicable on the basis of the present work which shows that MBT is a more powerful pro-oxidant during the early stages of its action than is MBI. It has been suggested earlier[2] that the antioxidant activity associated with this class of compound is due to oxidation by hydroperoxide to give SO_2;
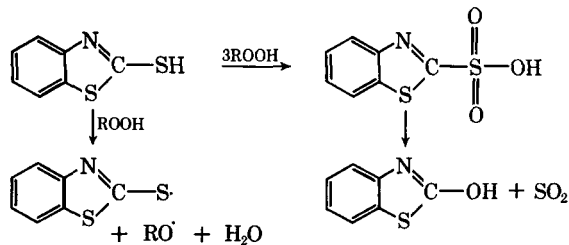
Pro-oxidant activity results from the redox reactions they, and possibly their oxygenated derivatives, can undergo both with alkylperoxy radicals and hydroperoxides.[1b,13]

In the absence of a phenolic antioxidant DLTP was found to be an effective antioxidant in the later stages of oxidation up to concentrations in the region of 2%. The auto-retarding effect was evident at each concentration (see Figure 3) and the fact that the initial antioxidant activity is inversely related to concentration is consistent with the idea that free radicals are initially generated in this case too. At higher concentrations the antioxidant activity is suppressed for practical purposes. The effect of a phenolic antioxidant was both to reduce the initial radical generating activity and to displace the induction period (see Fig. 2). The effect on the subsequent rate of polymer degradation was not very great but did nevertheless, contribute to the over-all synergistic effect observed. It can be seen that 0.002 moles/100g of DLTP combined with 0.001 moles/100 g of TBC approximately doubled the time taken to a similar degree of degradation to that given by 0.004 moles/100 g of sulfide alone. The position was reversed, however, in the late stages of the oxidation when the sulfide alone was the more effective antioxidant.

These results are consistent with the mechanism that has been proposed previously to account for the complex pro-oxidant-antioxidant behavior of the thiodipropionate esters.[3] Studies in tetralin at 50°C have shown a maximum pro-oxidant activity at the sulfide/hydroperoxide mole ratio of 1:1. This has been explained on the basis of parallel radical and nonradical breakdown of the derived sulfoxides. The nonradical reactions lead ultimately to the formation of the antioxidant, sulfurous acid.

References

1. G. Scott, *Atmospheric Oxidation and Antioxidants*, Elsevier, 1965, (a) 77,189 et seq.; (b) 392; (c) 292.

2. J. D. Holdsworth, G. Scott, and D. Williams, *J. Chem. Soc.*, **1964**, 4962.

3. G. Scott, *Chem. Comm.*, 1572 (1968).

4. W. G. Hawkins and (Mrs.) H. Sautter, *Chem. & Ind.*, 1825 (1962). *J. Poly. Sci. A*, 3499 (1963).

5. British Standard 2782, 105 c. Part I (1965).

6. Operating Instructions for Melt Indexer, Serial No. 985, Davenport (London) Ltd.

7. L. Bateman, M. Cain, T. Colclough, and J. I. Cunneen, *J. Chem. Soc.*, **1962**, 3570. T. Colclough and J. I. Cunneen, *J. Chem. Soc.*, **1964**, 4790.

8. C. Armstrong and G. Scott., unpublished work.

9. G. Scott, Lecture to the International Conference on Chemical Transformations of Polymers, Bratislava, 1968, *European Polym. J.*, in press.

10. F. J. L. Roberts, G. Scott, and E. Walker, U.S. 3,143,584/64.

11. M. S. Khloplyankina, A. F. Lukownikov, and P. I. Levin, *Vysokomolekul. Soedin.* **5**, 195 (1963).

12. J. R. Shelton and W. L. Cox, *Ind. Eng. Chem.*, **43**, 456 (1951).

13. C. E. Kendall, *Ind. Eng. Chem.*, **43**, 452 (1951).