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Migratory behaviour of a phosphite process stabilizer in polyolefins

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ABSTRACT

The migration of a phosphite process stabilizer tris (2,4-di t-butyl phenol) phosphite from polypropylene and a linear low density polyethylene is examined. At the 0.2% and 0.5% levels, no migration from polypropylene takes place, confirming earlier measurements made at the 10% level of phosphite. In the LLDPE, a slow migration takes place with a diffusion constant of approximately 2×10^{-16} m^2s^{-1}, which is slower than would be expected from single molecules. Migration of aggregates of phosphite molecules through the polymer matrix is suggested as a likely mechanism for this effect.

INTRODUCTION

In a recent paper by two of us (1), the migration of two stabilizing additives from polypropylene was studied at very high concentrations (up to 10 weight-%) by Fourier transform infra red spectroscopy (FTIR). It was found that a phenolic antioxidant that was highly soluble in the polymer (AO1 in figure 1 in the present work) migrated according to Fick's law to a constant concentration. A relatively insoluble phosphite (PS1 in figure 1) did not migrate significantly. The interpretation of the data was that PS1 was immobilized in the polymer matrix probably in the form of a separate glassy phase.

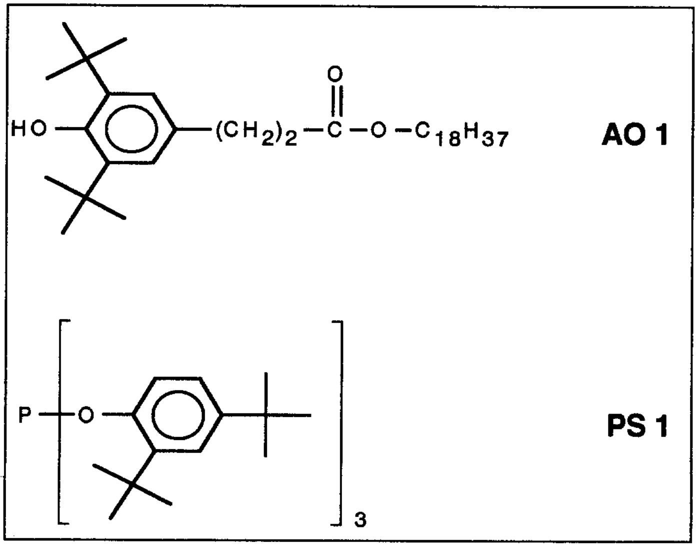

Figure 1: Structures of AO1 and PS1.

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The concentration of PS1 that was used in that work was much higher than is normally used in practice, when <0.2% would be considered sufficient for the molecule to act as a process stabilizer, generally in combination with a hindered phenol such as AO1 (2). We therefore undertook to study the migratory behaviour of PS1 at much lower levels, in this case 0.2% and 0.5%, to see if the immobility of the compound persisted. In addition, we studied migration of PS1 at similar levels in a linear low density polyethylene (LLDPE) of density 0.90. LLDPE's are of interest because their broad molecular weight distribution makes them potentially of more than one phase (3) and a stabilizer such as PS1 may have different interactions with (and hence solubilities in) these phases. In a recent presentation (4), the solubility of PS1 in several LLDPE's was measured and pointed out to be low (< 0.1% at 313 K), so we were interested in whether a similar immobilization of the compound to that in polypropylene takes place.

EXPERIMENTAL

All additives and polymers were used as received from the manufacturers. PS1 and AO1 are commercial products ("Irgafos" 168 and "Irganox" 1076 respectively) and were obtained from Ciba-Geigy Corp. The polypropylene was a "Profax" 6501 powder (nominal melt flow 4.0 g/10 min) from Himont Corp., Wilmington, DE, and the LLDPE (manufacturer not identified here) was received in pellet form. It had been pre-compounded with a small amount (<0.03%) of phenolic stabilizer for storage stability. Compression molded plaques from the LLDPE had a density of 0.903.

The technique used to estimate PS1 levels in thin films was liquid scintillation counting (LSC) on ^{14}C labelled PS1 incorporated into films by extrusion and compression molding. PS1 with a specific activity of either 0.1 or 0.2 microCuries/mg was extruded into polymer on a 9.5mm diameter bench top extruder (Brabender with a standard polyolefin screw) into either the polypropylene or the LLDPE. Polymer was then pressed into films of nominal thickness 127 microns and cut into 25mm x 12.5 mm plaques. The plaques were stored in a capped jar at ambient temperature until use. All samples were prepared and measured in triplicate.

At each time interval, samples were prepared for analysis by washing each plaque with two 20 mil aliquots of methylene chloride, which is a solvent for PS1. The combined washes were allowed to evaporate to dryness. The evaporated washes were rinsed with 3 x 5 ml aliquots of "Omnifluor" cocktail which were combined in a scintillation vial and measured for PS1 content. A 50 mg sample of each washed plaque was weighed into a scintillation vial and dissolved in 15 mil of cocktail and PS1 content also determined.

Note that the processing of the polymer needed to incorporate the PS1 would have oxidized around 10-20% of the phosphite to the corresponding phosphate, so we present the data here with the caveat that a mixture of PS1 and its phosphate is being studied.

In several plaques co-additives were included to see if they had an effect on the level of migration of PS1 out of the plaques. Of particular interest was AO1, as it is known to form a eutectic in combination with PS1. In order to characterize the interaction of AO1 with PS1, a differential scanning calorimeter (DSC - DuPont instruments) was used to examine the effect of AO1 on PS1 melting and cooling isotherms. The AO1 and PS1 were dissolved in chloroform at weight ratios of 2:1, 1:1 and 1:2 and the solvent evaporated. The resulting mixtures were scanned from room temperature to 473K at 10K/min, and then allowed to cool to around 373 K (below the fusion temperature of PS1 but not of AO1).

In some of the blooming experiments we also included zinc stearate, a common "antacid" co-additive for polyethylene, both with PS1 and with PS1 + AO1 formulations in the LLDPE.

RESULTS AND DISCUSSION

Figure 2 shows the migration of PS1 from polypropylene, and shows that there is none over an 11 day period. For the diffusion rate that would be expected from a molecule the size of PS1 in polypropylene (4), 11 days should be adequate for the level of PS1 to drop to its equilibrium concentration level. Solutions to the diffusion equation that illustrate this fact are shown in figure 3, where the theoretical rate of loss of additive (5) from an initial starting concentration of 0.2% down to a final level of 0.1% is shown. A range of diffusion constants from 10^{-16} to 5×10^{-15} m^2s^{-1} are included, although note

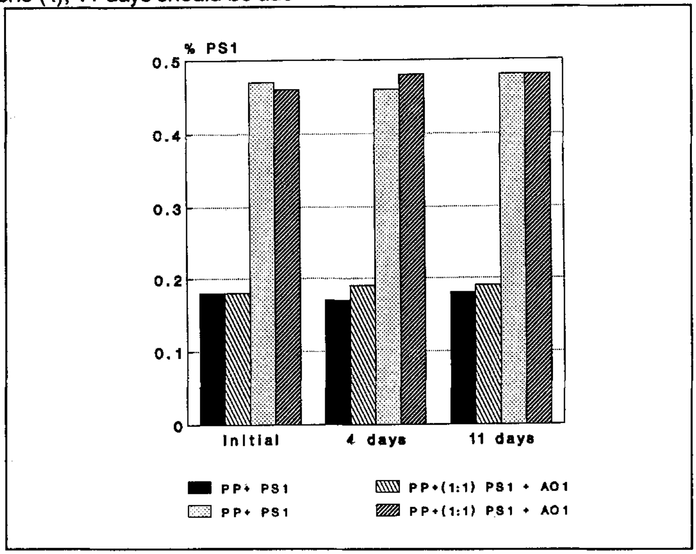

Figure 2: Levels of radiolabelled PS1 left in the polypropylene (PP) plaques initially, and after 4 and 11 days. Two different starting concentrations are shown in each set of blocks, ie. 0.2% and 0.5%. 1:1 combinations with AO1 are also shown.

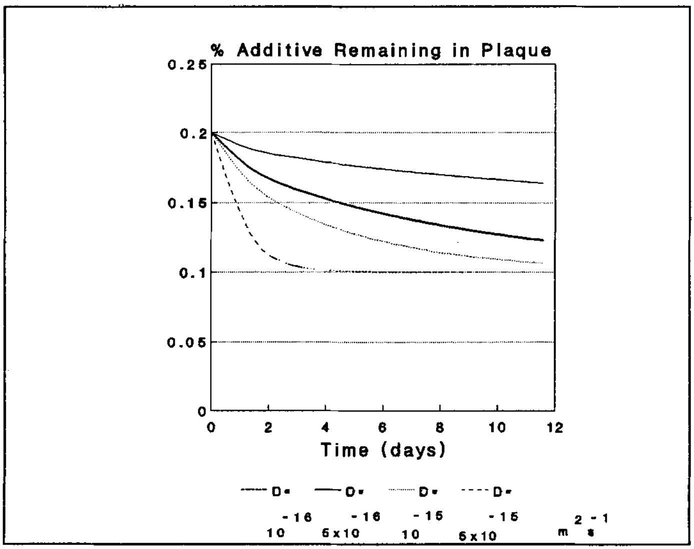

Figure 3: Theoretical diffusion curves for diffusion out of a 125 micron thick plaque of an additive at an initial concentration of 0.2% and a final solubility of 0.1%.

that AO1, for example was found to migrate from polypropylene with a diffusion constant of 1.27 x 10^{-15} m^2s^{-1}(1). We conclude that even at the 0.2% initial level, PS1 undergoes the immobilization in polypropylene that characterized its behaviour at much higher concentrations.

Figures 4 to 6 show the data that were obtained from the LLDPE. First, in figure 4, the level of PS1 is shown from the first series of experiments together with the amount of PS1 found in the wash. The % of PS1 in the plaque drops with time and has not levelled out even after 70 days.

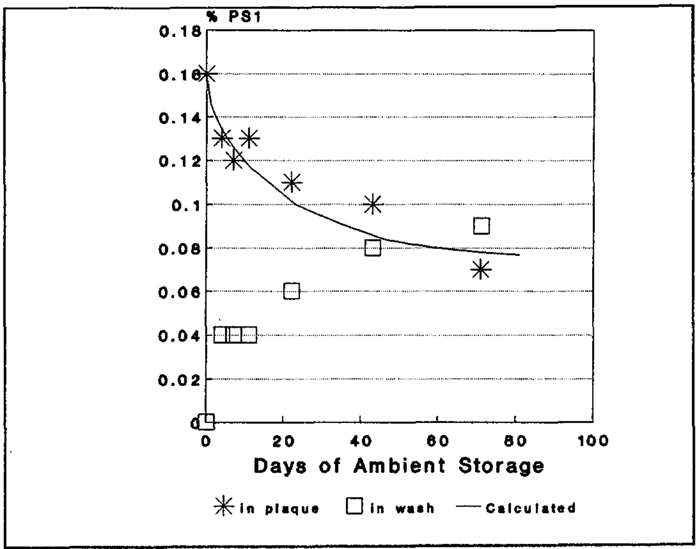

Figure 4: Level of PS1 found left in LLDPE plaques and in the wash as a function of time at ambient temperature (approximately 300 K).

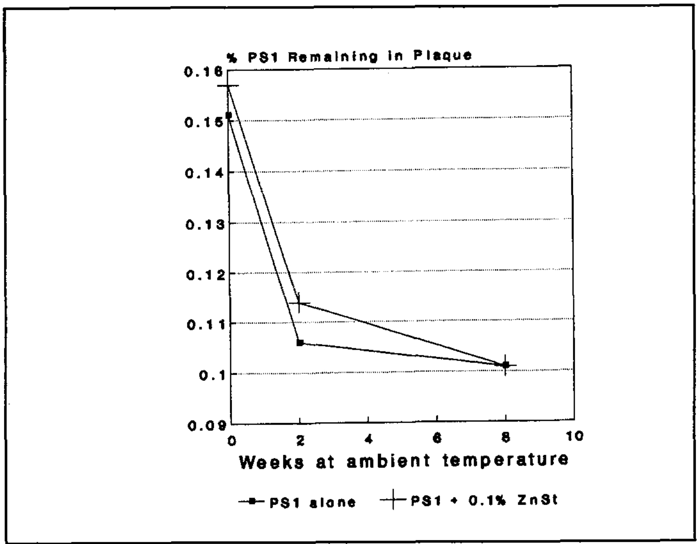

Figure 5: Level of PS1 found in LLDPE plaques as a function of time at ambient temperature in samples with and without 0.1% zinc stearate.

No further sample was available to continue the study so we were unable to ascertain a final solubility for PS1 in the LLDPE. The calculated additive loss curve shown in figure 4 is based on the data given in reference 4, where a solubility of 0.075% w/w at room temperature of PS1 was found in an LLDPE of density 0.906. The diffusion constant of 2 x 10^{-16} m^2 s^{-1} is an estimate based on a best fit by eye of the curve to the data.

Figures 5 and 6 show separate measurements on PS1 plus some other co-additives. The measurement was made out to 8 weeks in this case. A similar result in figure 5 is seen with pure PS1 and with PS1 + zinc stearate as in figure 4. Equilibrium has not been reached. The presence of AO1 with PS1 alone, and in particular with zinc stearate (figure 6) seems to stabilize the concentration of PS1 at a higher level than the 0.075% w/w. Unfortunately our data do not unambiguously allow us to say that an equilibrium has been reached as we would like to have more data points, both within the 8 week period and out further. The DSC data on the interaction of AO1 with PS1 and on the behaviour on cooling from the melt of PS1 are summarized in table 1. The pure PS1 sample, as received from the manufacturer, has a sharp endotherm at 461K on heating, with a heat of fusion of 65.4 J.g^{-1} (average of two determinations). When a ratio of 1:2 AO1 : PS1 is used, this endotherm broadens considerably. The onset of the endotherm is reduced to around 193 K. When the ratio of AO1 to PS1 is raised to 1:1, the endotherm disappears completely. The heat of fusion data suggest that the same fraction of AO1 is removed from the melting endotherm whatever the ratio of AO1 to PS1. In none of the samples (even with no AO1) was there sign of an exotherm on cooling PS1.

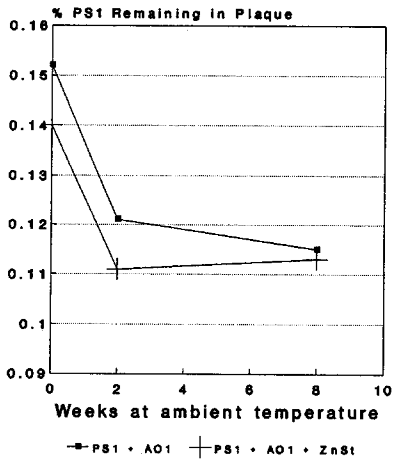

Figure6: As figure 5 with 0.2% AO1.

Table 1: Summary of DSC Data

Composition	Heat of Fusion of AO1	Heat of Fusion of PS1
AO1:PS1	J.g^{-1} of AO1(endotherm)	J.g^{-1} of PS1 (endotherm)
1:0	118.6	not applicable
2:1	94.8	no endotherm
1:1	99.3	too broad to measure
1:2	98.3	ditto
0:1	not applicable	65.4

Note: in no case was an exotherm seen at 461 K (the fusion temperature of PS1) on cooling.

The data are difficult to interpret confidently without more information on the molecular interactions that are taking place in the LLDPE. However, in general terms, the very slow migration of PS1 (and slower than would be expected from a molecule that size in polyethylene (6,7)) from the LLDPE suggests a complexation of that molecule either with itself, or with some component of the LLDPE. In reference 7 a molecule of similar molecular weight to PS1 (Irganox 1010, tetrakis [methylene - 3 - (3' ,5' - di - tert - butyl - 4 - hydroxy -phenyl) proprionate] methane, MW = 1178) in a LDPE of density 0.9175 was studied. If the data in that reference are extrapolated to 298K, a diffusion constant of 10^{-14} m^2s^{-1} results. As density goes down, an increase in diffusion constant would be expected, so the behaviour of PS1 in this study becomes even more unlikely for single molecules. In reference 4, diffusion of PS1 into 150 micron cast LLDPE films was studied. The first data point (28 days at 296 K) showed saturation of the LLDPE with PS1. No further diffusion in of PS1 took place over several weeks. As discussed previously (1), studies of "diffusion in" do not therefore necessarily reflect "diffusion out" behaviour, especially if additive morphology in polymer is a factor in migration behaviour. In view of the result that we obtain with polypropylene, ie. that complete immobilization results from formation of a separate PS1 phase, it seems reasonable to propose that a similar phenomena is taking place here. The diffusion of PS1 is being slowed by microaggregate formation. Note that the lack of crystallization of PS1 in the DSC is evidence for the "microglass" formation that was proposed at high levels of PS1 in polypropylene (1) after that material had been quenched from the melt.

CONCLUSIONS

The immobilization of a phosphite process stabilizer in polypropylene that was seen at the 10% level persists even down to 0.2%. We propose a separate glassy phase of the phosphite is again the cause of this immobilization. In LLDPE, slow migration of phosphite at these low levels takes place, but the diffusion is slower than would be expected from a molecule of that size, and is slower than has been seen in "diffusion in" experiments.

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