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The influence of aging on the effectiveness of an organophosphite in suppressing transesterification in polymer blends

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SUMMARY

Organophophites are being used with varying degree of effectiveness to suppress transesterification in polyester blends. Using solid state ^{31}P NMR it was discovered that for bis(2,4-di-t-butylphenyl)pentaerythritol diphosphite a conversion of the phosphite group to a phosphonate moiety, probably via hydrolysis, is a prerequisite for an effective inhibition of transesterification. This conversion occurs readily during melt compounding if the polymers are not completely dry. However, if rigorous drying is employed and phosphite conversion does not occur, then transesterification is not arrested. It was also found that over a long period of time the conversion of the phosphite to a phosphonate takes place at room temperature as well. Thus, after aging for about a year, the originally ineffective compound, has become a very effective inhibitor of transesterification in blends containing polyethylene terephthalate, polybutylene terephthalate, polycarbonate, and polyarylate.

INTRODUCTION

The use of polymer blends in the performance-demanding automotive and electronics markets has been growing rapidly. This growth is due largely to the unique combination of properties which is sometimes achieved by blending two or more polymers. Many commercial blends contain crystalline polyesters, such as polyethylene terephthalate (PET) or polybutylene terephthalate (PBT), and amorphous polymers, e.g. polycarbonate (PC). It is well known that polyester blends may undergo three types of exchange reactions during melt processing: acidolysis, alcoholysis, and direct transesterification (1), which result in the formation of new copolymers and the undesirable characteristic of transient properties. Direct transesterification has been shown by Devaux and his colleagues (1-3) to be the most likely mechanism of interchange reaction in blends of PC with PET or PBT. The following conclusions were reached in these studies (1-3): 1) The rate of transesterification depends on the concentration of residual catalyst, e.g. Ti compounds or SbO_3; 2) The mechanism of transesterification in PC/PET and PC/PBT is probably very similar, and 3) The reaction rate may be controlled by the use of organophosphites. The extent of control is a function of phosphite type and its concentration.

In a previous study of melt stability of polyester blends we have found that the control of transesterification does not appear to be just a function of phosphite type and its concentration (4,5). Our results suggest that to be an effective inhibitor of transesterification, the phosphite group has to be converted first to what was identified as a phosphonate (4,5). This conversion takes place during compounding, probably via hydrolysis at the high processing temperatures. In the case of bis(2,4-di-t-butylphenyl)pentaerythritol diphosphite (commercial trade name: Ultranox 624, Borg Warner Chemicals) it was observed that when the phosphite was not allowed to be hydrolyzed (by rigorously controlling processing conditions, i.e. extra drying, compounding under nitrogen atmosphere) the ensued polymeric blend transesterified readily. Conversely, when some conversion to phosphonate took place, as was verified by solid state ^{31}P NMR, transesterification was suppressed substantially.

Recently, we have found that the conversion of the diphosphite in Ultranox 624 occurs not only during polymer processing but also, over a long period of time, at room temperature and in tightly closed steel containers. Thus, in a period of about one year storage in the steel containers, sufficient conversion of the previously ineffective inhibitor took place to bring about a substantial improvement in the effectiveness of Ultranox 624 in suppressing transesterification reactions in blends of PET and PBT with polycarbonate and polyarylate (PAR). The results and the conclusions of this study are presented here.

EXPERIMENTAL

Materials: Polyarylate (Ardel D-100) was received from Amoco. The polycarbonate was Calibre 300-3 received from Dow Chemical Company. Polyethylene terephthalate (Cleartuf 1006B) was supplied by Goodyear, and polybutylene terephthalate (Valox) was supplied by General Electric. The organophosphite used as an inhibitor for the transesterification was bis(2,4-di-t-butylphenyl)pentaerythritol diphosphite (commercial trade name: Ultranox 624, Borg Warner Chemicals). Trace metal analysis was conducted to determine any residual catalysts in the homopolymers. Approximately 0.2% Ti was found in the PBT, Sb was detected in the PET, and traces of P and Ca were detected in the PAR and PC.

The Ultranox 624 was incorporated in the blend by first preparing a 10% Ultranox concentrate in polycarbonate. The concentrate was compounded in a twin-screw extruder under nitrogen blanket to minimize phosphite exposure to atmospheric oxygen and humidity. The materials were dried over night before compounding. As will be seen later, the NMR spectra showed that the phosphite moiety remained intact during concentrate preparation. The concentrate was stored in steel cans. Polymer blends were prepared in a Haake model 245 mini-extruder. The ratio of the crystalline polymer (PET or PBT) to the amorphous one (PAR or PC) was about 1:1. The blends contained about 0.5% Ultranox 624. Thus, the PAR blends contained 5% polycarbonate from the concentrate. All the materials were dried for at least 16 hr at 125 °C before extrusion.

Phosphorus-31 MAS NMR: Phosphorus-31 MAS NMR spectra were acquired using a Bruker MSL 300 spectrometer (^{31}P resonance at 121.5 MHz) and a Bruker MAS probe. Typical spinning speeds were 3 to 4 KHz. The internal volume of the rotor was approximately 750 mm^3. Sample weight was 400 mg. Acquisition of the MAS-averaged free induction decay was in the presence of high-power proton decoupling (in excess of 80 KHz) following a 1.5 msec ^1H-^{31}P cross polarization contact sequence to enhance the ^{31}P signal (6). Following standard practice, this experiment is referred to as CPMAS. The recycle time was held to 10 sec to insure complete thermal relaxation of the protons. The CPMAS signals were processed using standard Fourier transformation and phasing (7). Chemical shifts are referenced to external 85% phosphoric acid with negative shifts representing upfield resonances. In addition to CPMAS, the total suppression of spinning sidebands (TOSS) experiment was also employed (8). This sequence removes sidebands from the spectrum and is useful when sidebands are potentially overlapping significant spectral features. However, TOSS can lead to erroneous conclusions when quantitative data are desired and so this sequence was not employed throughout. For some spectra, a TOSS protonated phosphorus suppression (TOSS PPS) experiment was employed (9). For this experiment, a delay time with the decoupler switched off is inserted prior to acquisition. The effect of this delay is to remove, or partially reduce, resonances from phosphorus atoms located close to or directly bonded to H (8). TOSS was also employed following use of a single 90 deg pulse for the creation of transverse magnetization. This experiment, referred to as TOSS FID, is sensitive to phosphorus atoms in mobile sites (10). The recycle time for TOSS FID was 1 sec.

Thermal Analysis: The criterion used here to assess the effectiveness of the organophosphite as an inhibitor of transesterification was the retention of crystallinity of PET or PBT in the blend after prolonged exposure to a high temperature, say 300 °C. Progressive transesterification brings about a decrease in crystallinity as a result of formation of mixed copolymers (11, 12). In differential scanning calorimetry (DSC) this is seen as a decrease and, eventually, disappearance of the melting peak, i.e. heat of fusion, as well as a decrease in the melting peak temperature (15). A Mettler TA3000 thermal analysis system with a Mettler TC10A processor was used. An isothermal test was employed as follows: The sample was scanned to 300 °C at 20 °C/min, held at that temperature for 30 minutes, cooled rapidly to 35 °C (about 3 minutes), and then scanned at 5 °C/min to 280 °C.

RESULTS AND DISCUSSION

A 31P CPMAS NMR spectrum of the 10% ultranox 624 concentrate in PC acquired a few weeks after compounding is illustrated in Figure 1a. The 31P spectrum after compounding of a PC/PET/PAR (20/30/50) blend is shown in Figure 1b. Both spectra are characteristic of the ^{31}P spectrum of pure Ultranox 624 with two central transitions (indicative of the chemical structure of the compound) and a manifold of spinning sidebands that results from the application of MAS to narrow the solid state resonance lines. The central transitions are indicated by arrows. The feature at 95 ppm appears to be a low level phosphite impurity and does not appear to have a role in the chemistry discussed in this report. The feature at 115 ppm has been assigned to the single type of ^{31}P in Ultranox 624 (4). No hydrolysis of phosphite is indicated in the spectrum of the concentrate, as indicated by the lack of a new spectral feature at 7 ppm. New spectral features near 7 ppm have been assigned to the hydrolysis products of ultranox 624 (4,13). Following the trend discussed previously, if no conversion is seen in the concentrate, none appears in the blend, again as indicated by the lack of new spectral features. The spectrum from the blend has less signal to noise than that from the concentrate reflecting the lower wt% of phosphite in the blend (0.5%). Contrasting behavior is observed by the concentrate and blend, whose spectra are illustrated in Figure 1c and 1d, respectively. Again, these spectra come from a 10% wt PC concentrate but, in this case, the phosphite in the concentrate was allowed to hydrolyze slightly before blend formulation as is described elsewhere (5). For these spectra, the TOSS sequence was employed to remove the sidebands. The feature resulting from hydrolysis of Ultranox 624 is clearly seen as the broad feature near 7 ppm in Figure 1c. In 1d, the hydrolysis has advanced to the point that the Ultranox 624 is almost completely absent (consider the intensity of the small feature at 115 ppm

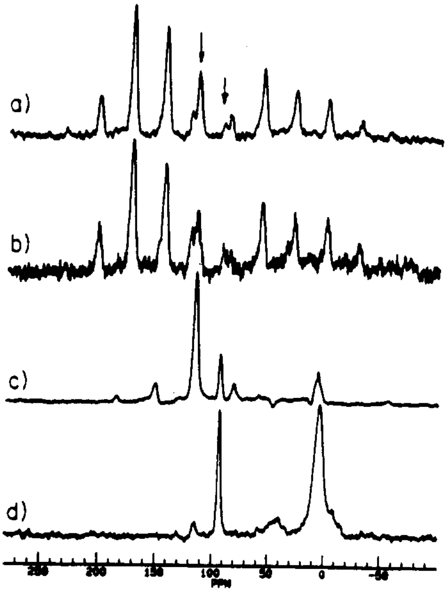

Figure 1: Phosphorus-31 MAS NMR spectra of a) unhydrolyzed concentrate (10% Ultranox in PC; arrows indicate isotropic peaks), b) corresponding blend, c) hydrolyzed concentrate using TOSS, and d) corresponding blend.

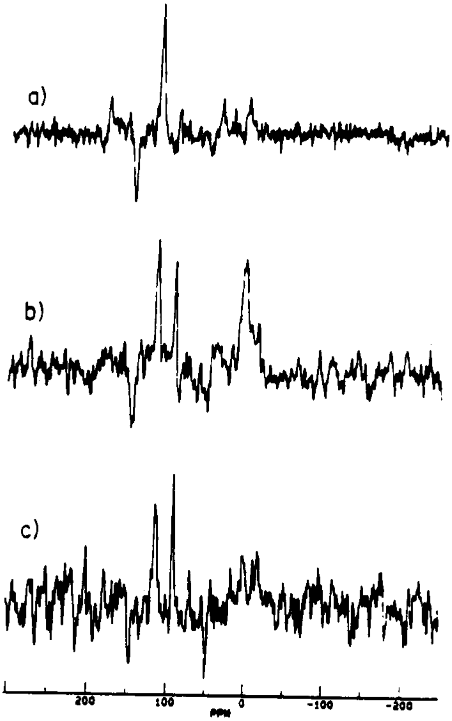

Figure 2: Phosphorus-31 MAS NMR spectra using TOSS of a) aged concentrate (10% Ultranox in PC; ca. 1 year), b) corresponding blend, and c) corresponding blend using TOSS PPS.

compared to the peak at 95 ppm from a compound that does not participate in the hydrolysis chemistry) and the spectrum is dominated by the broad component at 7 ppm. This blend was stable according to the test for stability used in this and the previous reports (4,5).

As discussed in this report, the concentrate that showed no hydrolysis (and thus gave rise to unstable blends) was reused after sitting for 1 yr, and was then observed to produce stable blends. The ^{31}P MAS NMR spectra of this aged concentrate and its corresponding blend was also acquired using TOSS and are illustrated in Figure 2a and 2b, respectively. TOSS is sensitive and was not complete for these spectra and thus some residual sideband intensity is observed, especially as the negative peak near 205 ppm, which should be neglected for interpretation. Some hydrolysis product is observed in the blend as the low intensity broad feature near 7 ppm. While this feature is small, it stands in sharp contrast to the spectrum of this sample (Figure 1a) in which no indication of the hydrolysis product can be seen. Following blending, as has been observed previously, the concentration of the hydrolysis product increases dramatically, as seen in Figure 2b. To verify that the hydrolysis product is a phosphonate, the TOSS PPS sequence was applied, the results of which are shown in Figure 2c. As is discussed elsewhere (9), this sequence selectively removes peaks from the spectrum associated with phosphorus compounds that contain a direct P-H bond, as is found in phosphonates (14). As can be seen, the feature at 7 ppm is absent and thus can be concluded to be the same compound as has been previously identified in stable blends, which has been shown to be a phosphonate.

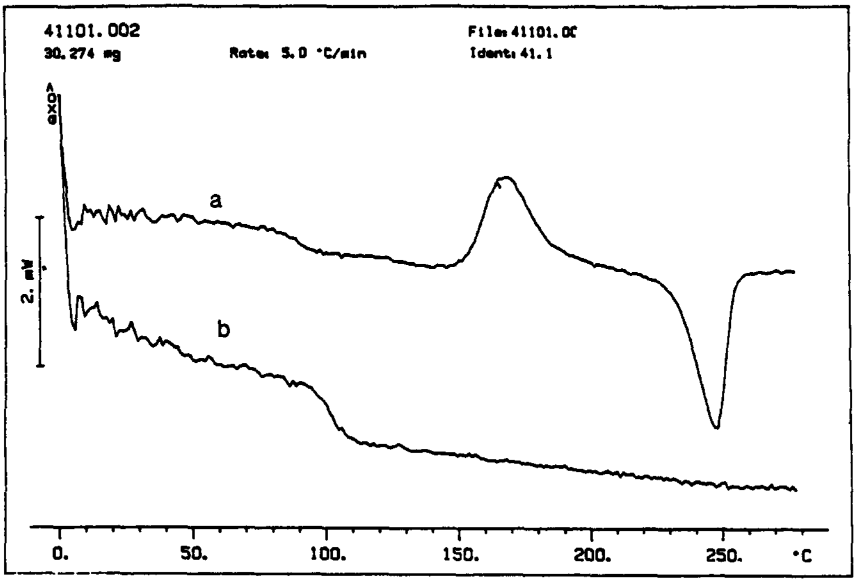

Figure 3: Thermograms of a PET/PAR blend after 30 min. at 300 °C. a) with 0.5% aged Ultranox concentrate; b) with no additives.

Figure 3 shows thermograms of a PAR/PET blend after 30 minutes at 300 °C: 3a is of the blend with 0.5% Ultranox from the aged concentrate; 3b is of the blend with no additives. In Fig. 3a the PET characteristics are well preserved: a crystalline melting peak with a peak temperature at 247 °C and heat of fusion (obtained by integration) of 18 J/g, and glass transition temperature (T_g) at about 85 °C. The T_g of polyarylate is not seen since it is masked by the cold crystallization peak of PET. The same thermogram characteristics were observed also before the thermal history (see Ref. 15, Fig. 3a). This indicates that after 30 minutes at 300 °C there was little transesterification in this blend. On the other hand, in the thermograms of the blend with no stabilizer the characteristic features of crystalline PET are no longer seen. What is observed is a single broad glass transition around 110 °C suggesting the formation of mixed copolymers. In these cases transesterification after 30 minutes at 300 °C was apparently quite advanced. When a blend similar to that of Fig. 3a was tested, except that at the time when it was prepared the Ultranox concentrate was relatively fresh (ca. 3 weeks), the PET characteristics were lost (see Ref. 5, Figure 11).

Figure 4 shows a thermogram of a PC/PET blend with 0.5% Ultranox from the aged concentrate. As is seen in Figure 4, the crystalline features of PET are well preserved even after 30 minutes at 300 °C: a crystalline melting peak with peak melting point at 248 °C and heat of fusion of about 18 J/g, and PET's glass transition temperature at around 85 °C. With no stabilizer in the PC/PET blend and after 30 minutes at 300 °C, no crystalline features were noted. The thermogram was similar to that of Fig. 3b. The only distinguishing feature was a single T_g at about 100 °C, the result of mixed copolymer formation. Thus, the addition of the aged Ultranox concentrate, in which the phosphite had converted partially to a phosphonate, suppresses dramatically transesterification in PET/PC as well as in PET/PAR blends.

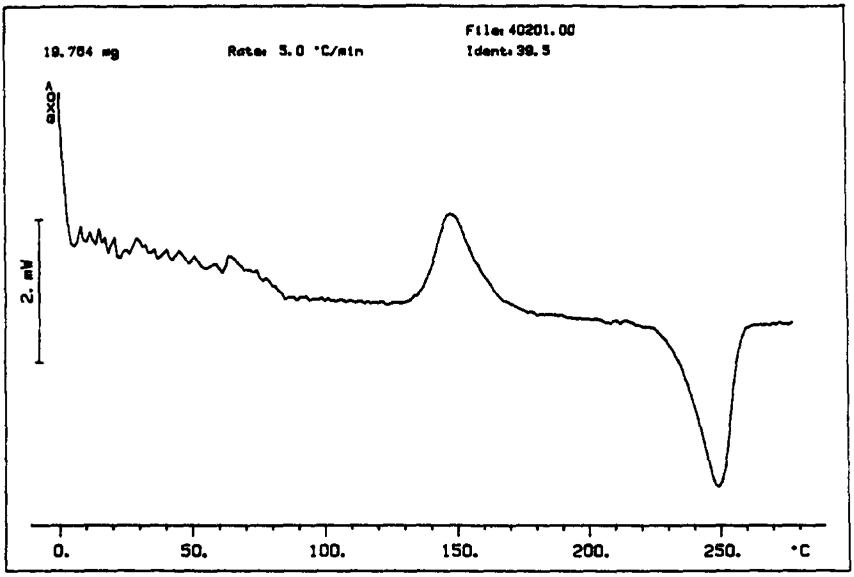

Figure 4: Thermogram of a PET/PC blend with 0.5% aged Ultranox concentrate after 30 min. at 300 °C.

Figure 5 shows thermograms of a PC/PBT blend: Curves 5a and 5b are of the unstabilized blend prior to and after 30 minutes at 300 °C, respectively. Curve 5c is of the blend with 0.5% Ultranox from the aged concentrate after the thermal exposure. As is seen in Fig. 5a the melting peak of PBT has a melt temperature of 222 °C and heat of fusion of 33 J/g.

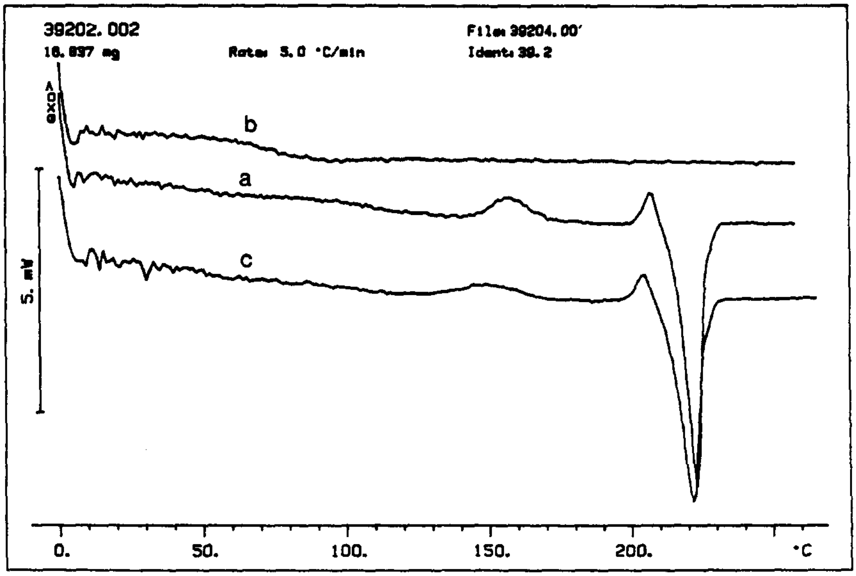

Figure 5: Thermograms of a PBT/PC blend. a) no additives, prior to thermal treatment; b) no additives, after 30 min. at 300 °C; c) with 0.5% aged Ultranox concentrate after 30 min. at 300 °C.

The peak melt temperature and heat of fusion in Fig. 5c are 223 °C and 33 J/g, respectively. Both thermograms are almost identical indicating that the aged Ultranox is an effective inhibitor of transesterification. It is obvious from Fig. 5b that with no stabilizer PC and PBT transesterify readily to form mixed copolymers with a single T_g around 70 °C, which is between the T_g's of PBT and PC.

In the above examples a common observation is that the aged Ultranox has become an effective inhibitor of transesterification and the fresh Ultranox, as was found in a prior study (5), is not. From the NMR results it is seen that the aging brought about chemical changes in the Ultranox. Specifically, it is noted that some phosphite has been converted during a period of about one year to a phosphonate. The extent of this conversion was not quantified but it seems that a little conversion is sufficient for effective inhibition since, once started, it appears to increase during blend compounding, as is seen, for example, in the NMR spectra of the PC/PBT blends (Figure 2).

It has been suggested that transesterification is catalyzed by residual trace metal polymerization catalysts, e.g. Ti and Sb, and that phosphites complex them and thus quench their catalytic effect (1-3). In the case of PET, which contains SbO_3, we have sometimes observed that the addition of small quantities of Ultranox (0.25-1%) causes the development of grey color, presumably due to complex formation. Indeed, the appearance of grey color in PET blends was found to be a reliable indicator of the blend stability. It is interesting to note here that the appearance of grey color in PET blends was not seen when the fresh Ultranox concentrate was used. It was observed only when the phosphite group in the Ultranox has partially converted to a phosphonate. This suggests that the complexing may be between the latter rather than the former, or that the presence of the latter facilitates complexing of the phosphite and SbO_3. In blends of PBT, which contains about 0.2% Ti residual catalyst, color differences were not observed. All the blends were opaque-cream, regardless of the state of phosphite conversion.

CONCLUSIONS

For Ultranox 624 conversion of the diphosphite to a phosphonate group appears to be a prerequisite for effective inhibition of transesterification reactions in blends of PET/PC, PET/PAR, PBT/PC, as well as a ternary blend of PET/PC/PAR (5). The extent of conversion necessary to bring about effective inhibition was not quantified. The NMR data show that once some conversion took place prior to incorporation in the blend, additional conversion would continue readily during subsequent processing, e.g. extrusion and injection molding, resulting in a stable material. On the other hand, if no prior conversion took place there would not be appreciable change in the diphosphite during subsequent processing to render the material stable. It follows that the evaluation of Ultranox 624 as an inhibitor to transesterification reactions in polyester blends may lead to erratic results depending on the state of its conversion. Aging of this diphosphite was found to change its performance from an originally ineffective stabilizer to a very effective one. And this was shown to be the result of the chemical transformation of the diphosphite to a phosphonate. It is important to note that this chemical change occurred in an air conditioned laboratory maintained at about 23 °C and in closed steel containers.

To what extent are the above observations valid to other organo-phosphites used as inhibitors in similar applications is not known. The patent and technical literature related to phosphites does not address this issue. But if true, at least in some other phosphites, then studying the effectiveness of a given phosphite compound in various polymer blends, or conducting a comparative evaluation of phosphites in order to rank their effectiveness may lead to inconsistent and sometimes wrong results.

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