Solubility of a UV-stabiliser in some poly(ester-*block*-ether) copolymers

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Abstract

The solubility of a typical UV-absorbing stabiliser has been measured in a series of poly(ester-*block*-ether)s copolymers (PEBE) with different ratios of hard and soft blocks. The solubility is higher in the PEBEs than in polypropylene and increases with the amount of polyether in the PEBE. The composition dependence suggests that the additive is at least ten times more soluble in the soft polyether phase than in the semi-crystalline hard phase. A thermodynamic analysis in terms of regular solution theory shows that increased solubility is due to better compatibility of the additive with the polyether than with PP, mainly due to much more favourable heat of mixing. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ester-*block*-ether)s; Stabilisation; Additive solubility

1. Introduction

Poly(ester-*block*-ether)s (PEBE) are an important class of thermoplastic elastomers. They are multi-block copolymers in which one block (the "hard" block) is a semi-crystalline aromatic polyester, typically poly(butylene terephthalate) (PBT), and the other (the "soft" block) is a flexible, low T_g polymer, typically an aliphatic polyether. They are well known for their toughness and elasticity at low temperature but their usefulness is limited by sensitivity to ageing. There is a reasonable amount of literature on the degradation of typical PEBE [1–7] but very little on their stabilisation [3].

It was shown in the first studies of degradation of PEBE [1,2] and confirmed more recently [3] that the two components of the polymer behave differently on ageing. Due to the aromatic chromophores, the polyester is sensitive both to direct photodegradation and to photo-oxidation and its degradation leads to yellowing [8]. In contrast, the ether part is resistant to direct photo-oxidation but highly sensitive to thermo-oxidation. Thus radicals generated photochemically in the hard block may synergistically induce oxidation of the soft block.

The response to oxidative degradation is to incorporate one or more stabilising additives, typically either a phenolic antioxidant or, where the polymer is exposed to sunlight, a UV-stabiliser. Even in simple polymers, this needs to be

done with care, since concentrations of additive above the saturation solubility can lead to physical loss by crystallisation at the surface of the polymer ("blooming"), leading to a decrease in the efficiency of protection as well as to appearance problems. This phenomenon is well understood for polyolefins [9]. Its occurrence and rate depend on both the solubility and the diffusion rate of the additive in the polymer.

Despite their importance, we are not aware of any published study of either solubility or migration of any stabilising additive in PEBE polymers. Indeed, there is remarkably little literature on the behaviour of stabilisers in any multi-phase polymer. Kulich et al. [10] used scanning electron microscopy with energy dispersive X-ray analysis to show that thiodipropionate and phosphite additives partition preferentially into the rubber phase of ABS to an extent which correlates with their calculated solubility parameters. In a more recent study [11], Kulich et al. used FTIR microscopy to look at partitioning of a hindered amine light stabiliser in a blend of styrene/acrylonitrile copolymer (SAN) with polybutadiene and again showed preferential partitioning into the rubber phase to a degree which could be correlated with solubility parameters. Braun et al. [12], showed that the T_g of PVC is decreased by the plasticising effect of an organo-tin stabiliser at concentrations as low as 0.5 wt%. By measuring the change in T_g of the PVC phase in a PVC/SAN blend they showed that the additive partitions differentially between phases but made no attempt to correlate partitioning with additive solubility. Naito et al. [13], have used T_g measurements to demonstrate partitioning of oils

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Table 1
Characteristics of the polymers studied

Polymer	A_1	A_2	A_3	B_1	B_2	B_{3E}	B_{3B}	PP	A_4
Processing[a]	B	B	E	E	B	E	B	E	–
Polyether content[b] (% w/w)	55	30	10	60	35	10	10	–	100
ΔH^f (J g^{-1})	19.3	33.1	50.3	18.8	29.5	47.4	38.2	–	–
Crystallinity (% w/w)	13	23	34	13	20	33	26	50	–
Density (g cm^{-3})	1.161	1.227	1.279	1.23	1.25	1.38	1.39	0.9	1.06
Polyether content[c] (% w/w)	63	39	15	69	44	15	14	–	–

[a] B, Blow moulded film; E, Extruded film.
[b] Without correction for crystallinity.
[c] Expressed as a fraction of the total amorphous material.

and resins between phases in a blend of immiscible elastomers. Most recently, Whiteman et al. [14], used UV-microscopy to show that a UV-absorbing stabiliser partitions preferentially into the rubber phase of a blend of polypropylene with ethylene–propylene rubber and that the rubber phase is increasingly favoured as the temperature increases, so that almost all of the additive is in the rubber phase at typical processing temperatures.

With these considerations in mind, we now report studies of the behaviour of a typical UV-absorbing stabiliser in some PEBE copolymers of different structure and composition.

## 2. Experimental

2.1. Materials

The polymers were supplied by DSM (Netherlands) as two families of PEBE with the same hard phase, PBT. For the group denoted by A, the polyether phase is a PEO/PPO/PEO (20/60/20) block copolymer; for the group denoted by B, it is polytetrahydrofuran (PTHF). The copolymers were supplied as 25 μm films which had been produced by blow moulding or extrusion as indicated in Table 1. All films had been process stabilised with a low concentration of antioxidant, which was assumed not to affect the solubility of the UV absorber. The pure PEO/PPO/PEO copolymer was a viscous liquid at room temperature.

Table 1 shows the compositions and crystallinities of the studied polymers. Heats of fusion were determined by scanning calorimetry with a Mettler Toledo DSC 821, calibrated with indium and tin standards and the crystallinity calculated taking the heat of fusion of crystalline PBT to be 145.5 J g^{-1} [15] and assuming the soft phase to be completely amorphous. Table 1 also shows the soft block content expressed as a fraction of both the total weight of polymer and the weight of amorphous polymer. Densities were measured by helium pycnometry on a Micrometrics Accupyc 1330.

Blown and extruded films of sample B_3 had significantly different heat of fusion and crystallinity. Samples of both

were cooled from the melt at 10°C min^{-1} and then reheated; they showed heats of fusion of 33.5 and 33.7 J g^{-1}, confirming that the initial difference is due to the effect of processing on the crystallinity of the polymers.

The UV absorber was a commercial product, 2-[2-hydroxy-3,5-di-(1,1-dimethylbenzyl)-phenyl]-2H-benzotriazole, **1**, provided by Ciba Specialty Chemicals (Tinuvin 234™). It was used without further purification. Its molecular weight is 448 g mol^{-1}. The melting point and heat of fusion were determined by DSC as 139°C and 39.1 kJ mol^{-1}, respectively.
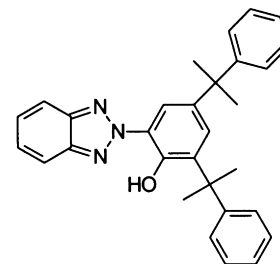
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2.2. Solubility measurements

Solubilities were determined by equilibrating stacks of polymer film with the solid additive and measuring the amount absorbed using UV-spectroscopy of acetone extracts.

In previous work [16] we have used the method of Feldshtein and Kuzminskii [17], which consists of alternating layers of film with layers of additive and studying the build up of the concentration of the additive in the films with time. For the PEBE samples this method was not possible because most of the films were soft enough for the additive crystals to be difficult to remove from the surface. Accordingly, we adapted the method to use multi-film stacks.

For each polymer grade and temperature, between 10 and 20 film samples, $(20 \times 40 \text{ mm}^2)$ were stacked. Most of the polymers were soft enough to consolidate easily into a solid stack. The hardest (A_2, A_3, B_2 and B_3) were briefly pressed at 110°C and 0.4 kg cm^{-2} to increase the contact between layers. The outer surfaces of the stack were then put in direct
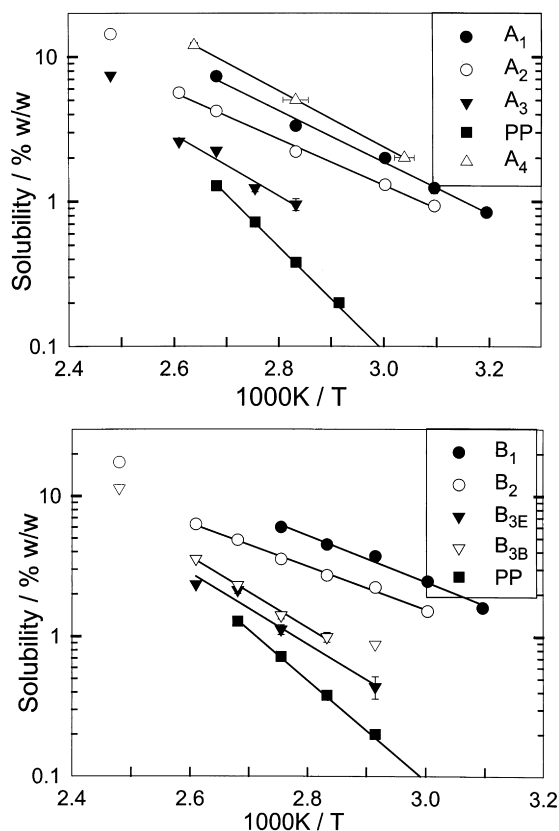
Fig. 1. Solubility of Tinuvin 234 (corrected for crystallinity) in PEBEs, PP and pure polyether. Upper figure: family A; lower figure: family B.

contact with the additive under gentle pressure and the assembly left in an oven to allow the additive to migrate and equilibrate. The advantage of this approach is that there is hardly any contamination, since only one layer of film (which is discarded) is in contact with the pure additive. The drawback is that the experiment is more time consuming and it is not possible (without knowing the diffusion coefficient) to predict when the UV absorber has reached its equilibrium solubility without dismantling and analysing the films. All the data presented in this work were obtained on stacks in which the concentration profile of the additive was flat which proved that the equilibrium had been reached.

After equilibration, the film stacks were peeled apart and the individual films (apart from the two outer ones) were weighed and extracted in acetone at room temperature for two hours, which was shown to be enough to extract at least 98% of the total amount of dissolved additive. The extracts were analysed by UV spectroscopy. The extinction coefficient of the additive was determined to be $15\ 240\ \mathrm{l\ mol^{-1}\ cm^{-1}}$ at 345 nm. Each point plotted on the Van't Hoff plots represents the average of ten measurements on different films, with a maximum of ±5% scatter.

Because the pure polyether, A_4 is a liquid, a different approach was used for solubility measurements. Mixtures of A_4 and known amounts of the pure crystalline additive

were heated at $0.1°\mathrm{C\ min^{-1}}$ in a hot-stage microscope under crossed polars. The temperature at which all of the additive dissolved was taken as the point where the last crystals dissolved, as indicated by disappearance of the light transmitted by the crystalline material. Because temperature is now the variable, the error bars on the data plots are horizontal, along the *T*-axis.

Data for the solubility of Tinuvin 234 in Polypropylene (PP) were kindly supplied by Dr V. Dudler of Ciba Specialty chemicals.

3. Results and discussion

3.1. Solubility and partitioning

The polymers used in this work are exemplars of commercial polymers with a wide range of applications, so that the issue of additive solubility and migration is significant both commercially and as a way of trying to understand solubility in multi-phase polymers. The PEBE materials studied here are effectively triphasic. They contain fractions varying from 10 to 60 wt% of the soft, amorphous, polyether block and a hard, PBT, phase which is roughly 30% crystalline. It is well established [18] that stabilising additives are excluded from the crystallites of a semi-crystalline polymer. Thus it is of interest to ask both how much of a typical additive can be dissolved in the polymers and how it will partition between the hard and soft amorphous phases.

The additive was chosen for two reasons—it is typical of commercial UV-stabilisers and it is easy to detect because of its very high UV-extinction coefficient.

Solubilities were determined for the UV absorber in all of the copolymers, by the equilibration method, at a series of temperatures in the range 40–100°C. Fig. 1 shows the resulting data plotted in Van't Hoff co-ordinates for the two series of polymers separately. Also shown for comparison are data for the same additive in PP and in the pure polyether phase A_4. All of the data in Fig. 1 have been corrected for the crystallinity of the sample and represent average solubility in the overall amorphous phase. They give linear plots, from whose gradients the heats of solution can be determined.

At relatively high temperatures (80–90°C), the solubility in the hardest polymer grades (A_3 and B_3) is about twice as high as in PP, whereas there is nearly one order of magnitude difference between PP and the softest grades (A_1 and B_1 and the pure polyether, A_4). This illustrates the wide variation of solubility in the block copolymers with composition and the generally high solubility in the PEBE compared to polyolefins. Increasing the amount of PBT, we decrease the solubility, hence we find bigger differences among the range of PEBE in dealing with the solubility without correction for crystallinity. It is interesting to note that B_{3B} and B_{3E} give

Table 2
Extrapolation to room temperature of the solubility of Tinuvin 234 in PEBE and homopolymers

Polymer	Corrected for crystallinity (% w/w)	Non corrected for crystallinity (% w/w)
A_1	0.45	0.39
A_2	0.37	0.28
A_3	0.07	0.05
B_1	0.77	0.67
B_2	0.49	0.39
B_{3E}	0.06	0.04
B_{3B}	0.05	0.04
PP	5×10^{-3}	3×10^{-3}
A_4	–	0.50

similar results in spite of their different crystallinity (Table 1) proving the validity of the correction for crystallinity.

In a few cases the measurements were extended to 130°C, approaching the melting point of the additive. The Van't Hoff plots then show significant deviation from linearity. Similar behaviour has been seen in polyolefins [14,19]. We believe this failure of near-ideal solution behaviour to be due to the high solubilities of the additive in PEBE.
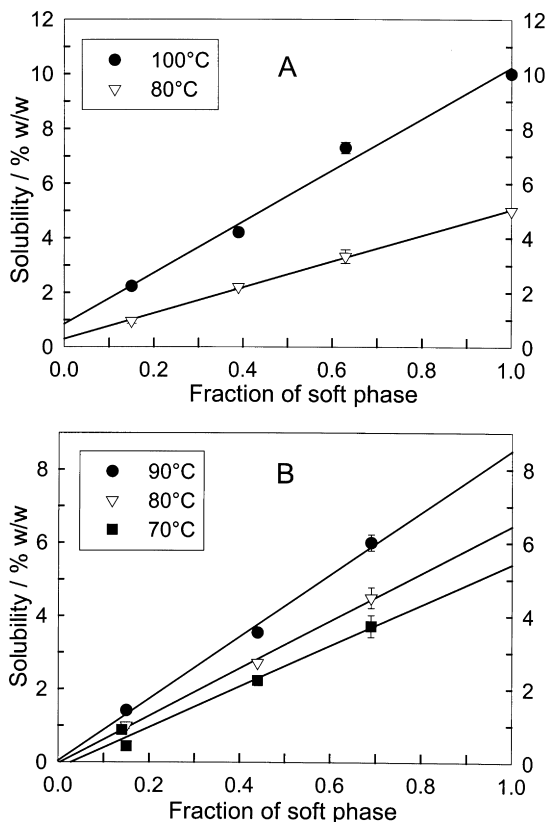

Fig. 2. Solubility of Tinuvin 234 in PEBEs as a function of the composition. Upper figure: family A; lower figure: family B. Solubilities and compositions are corrected for crystallinity.

Indeed, at the highest solubilities, the system is an 85/15 blend of polymer and additive rather than the pure polymer. Since concentrations this high are not technologically relevant, we focus on the lower temperatures.

Table 2 shows the predicted values of solubility at 25°C, obtained by linear regression extrapolation of the data in Fig. 1. The fact that the heat of solution of the additive in PP is much higher than for the copolymers increases the difference between the two types of polymer at room temperature. Indeed, the solubility of the additive in PP is one order of magnitude less than in the hardest grades of PEBE, and two orders of magnitude lower than in the soft grades. Even in the softest grades of PEBE, the solubilities are all well below 1%. Given that UV absorbers are often used at much higher concentrations, this has practical implications.

It is clear from the data in Fig. 1 that the solubility is quite strongly dependent upon the soft phase content of the copolymer. Fig. 2 shows the composition dependence of the solubility in the PEBEs at different temperatures. The additive is clearly very much more soluble in the polyether phase than in the amorphous phase of PBT and extrapolation of the A-series copolymer data to 100% polyether gives intercepts in good agreement with measurements on the pure polyether. Entirely analogous results were obtained for the B-series and the two soft phases thus show similar behaviour. In both series of polymers, there is 10–20 times more additive in the soft phase than in the amorphous part of the hard phase. Thus the additive in this polymer partitions between phases, strongly favouring the polyether phase over the amorphous fraction of the PBT. It is not possible to extract numerical values of the partition coefficients because the experimental errors in the extrapolated low solubilities in the hard block are too large.

In some cases the partitioning can be observed directly by UV-microscopy [20]. Thus Fig. 3 shows visible and UV-images of a cast film sample of B_3, saturated with the UV-absorber. The uneven distribution is clear.

This very low solubility of the additive in the amorphous PBT is also shown by the fact that solubilities are near identical at any given temperature in all the PEBE grades studied, when related to the soft phase fraction (Fig. 4). This graph also shows the clear difference between the PEBE and PP in terms of solubility of this benzotriazole. There is one order of magnitude difference between the amorphous PP and the polyether phase at 100°C and two orders of magnitude at 40°C.

3.2. Thermodynamic analysis of solubility data

Given the very large differences in solvent power between the two phases in the PEBE and between the PEBE and PP, it is of some interest to try to explain these differences in terms of the thermodynamics of solution. Since the additive is effectively insoluble in the PBT
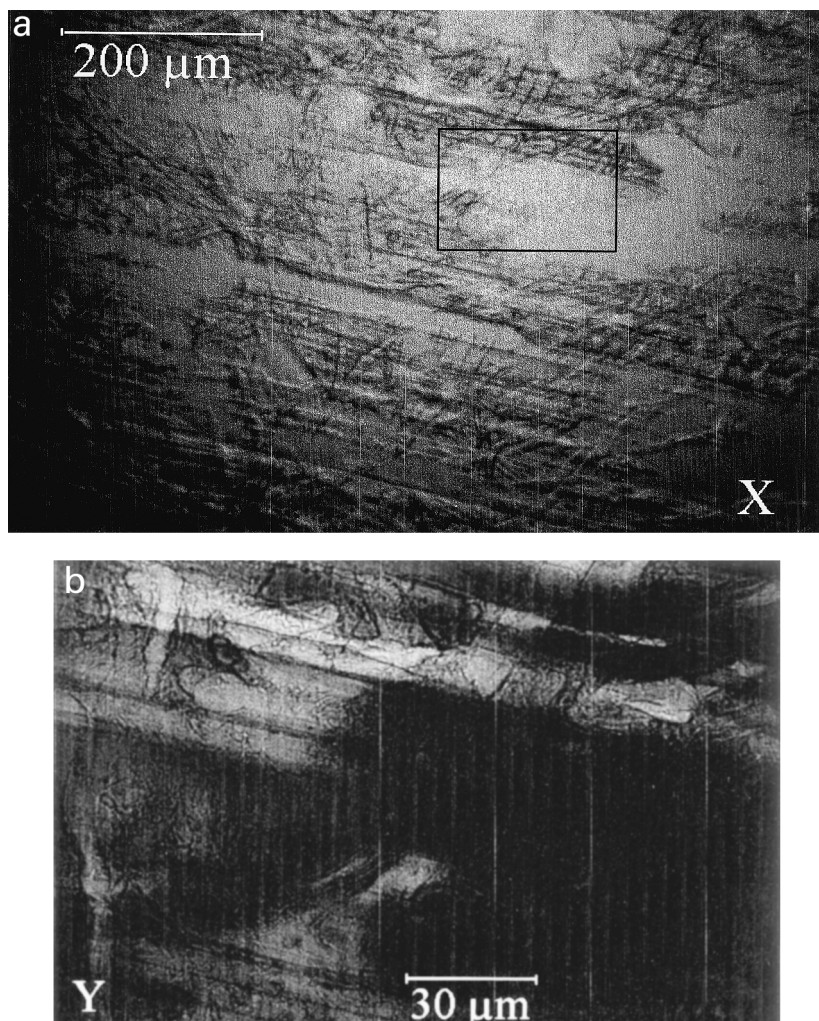
Fig. 3. Photomicrograph of: (X) a 25 µm thick cast film of B_3 saturated with Tinuvin 234 and observed in white light; and (Y) the region of the same sample indicated in (X), observed in UV-light.
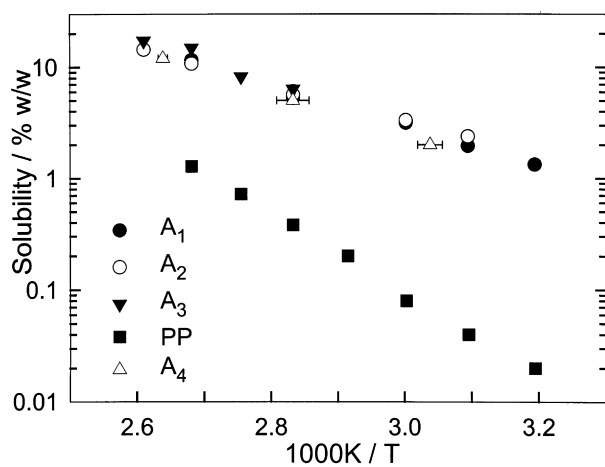

Fig. 4. Solubilities of Tinuvin 234 in A-series PEBE relative to the poly-ether phase and in PP (corrected for crystallinity).

phase, we can neglect any contribution of the hard phase to solubilisation of the benzotriazole in PEBE.

3.2.1. Theory

The solubility of an additive in a polymer represents the maximum concentration of additive at equilibrium with the polymer and should be amenable to thermodynamic analysis. In previous studies of additive solubility in polyolefins [16,21], we found that a useful approach is the simple regular solution model, first applied to antioxidants by Roe et al. [22].

The solubility of a crystalline additive in an amorphous polymer (treated as a liquid) is determined by the condition that the (positive) free energy of fusion required to convert the solid additive to a liquid at a temperature below its melting point (T_m) is compensated by the free energy of mixing of the liquid additive with the polymer. In the regular solution model, the free-energy of mixing is evaluated from the Flory–Huggins equations for mixing of a small molecule with a polymer [23]. For the case where the

Table 3
Thermodynamic values for solution of Tinuvin 234 in the polyether phase of PEBE and the amorphous phase of PP

Polymer	ΔH^s (kJ mol^{-1})	$\Delta \bar{H}^m$ (kJ mol^{-1})	$\Delta \bar{S}_E^m$ (J mol^{-1}K^{-1})
A_1	34.1 ± 3.1	−4.9 ± 3.1	−13.4 ± 3.4
A_2	30.6 ± 2.3	−8.5 ± 2.3	−22.9 ± 3.1
A_3	40.4 ± 4.3	1.3 ± 4.3	4.7 ± 7.7
B_1	31.8 ± 1.8	−7.3 ± 1.8	−19.9 ± 4.2
B_2	29.5 ± 3.0	−9.6 ± 3.0	−26.0 ± 3.2
B_{3E}	48.4 ± 4.6	9.3 ± 4.6	24.6 ± 13.0
B_{3B}	48.6 ± 3.0	9.5 ± 3.0	28.7 ± 4.0
PP	68.8	29.7	61.5
A_4	37.1 ± 3.0	−2.0 ± 3.0	−6.42 ± 0.05

additive solubility is low, this approach leads to the solubility in the form [22].

$$-\ln \varphi = \frac{\Delta H^f}{R}\left[\frac{1}{T} - \frac{1}{T_m}\right] + (1 - V_1/V_2) + \chi \qquad (1)$$

where φ is the solubility of the additive (expressed as a volume fraction), ΔH^f is its heat of fusion and V_1 and V_2 are the molar volumes of the additive and polymer, respectively. The first term in Eq. (1) is the free energy of fusion of the additive and is independent of the polymer. The second term represents the geometric entropy of mixing, assuming the additive to behave as a hard sphere. χ is the additive-polymer interaction parameter and is the excess free-energy of mixing expressed in units of RT. Note that φ is strictly a *volume* fraction-it is usually reasonable to assume that the density difference between additive and polymer is small enough that we can equate the weight and volume fractions.

In the regular solution model, we assume that V_1 and V_2 are only weakly dependent on T. By differentiating Eq. (1) with respect to $1/T$, it is easy to show that, for a dilute solution:

$$-\frac{\partial \ln \varphi}{\partial(1/T)} = \frac{\Delta H^f}{R} + \frac{\partial \chi}{\partial(1/T)} = \frac{\Delta H^f}{R} + \frac{\Delta \bar{H}^m}{R} = \frac{\Delta H^s}{R} \qquad (2)$$

where ΔH^s is the measured heat of solution and $\Delta \bar{H}^m$ is the heat of mixing. Thus the temperature dependence of φ is
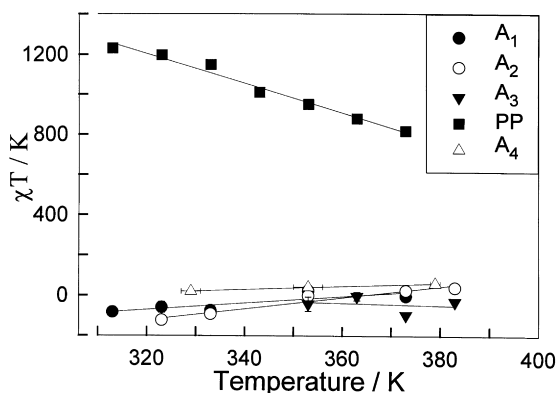

Fig. 5. χT versus T for Tinuvin 234 in the soft phase of A-series PEBE, in pure polyether and in the amorphous phase of PP.

simply the sum of the molar heat of fusion of the additive and its partial molar heat of mixing with the polymer.

In a similar way, it is relatively easy to show that the overall entropy of mixing is given by

$$\Delta \bar{S}^m = \frac{\Delta H^f}{T_m} - R \ln \varphi_1 - R(1 - V_1/V_2) - R\frac{\partial(\chi T)}{\partial T} \qquad (3)$$

In the ideal case, the entropy is made up of the entropy of fusion of the additive and the geometric entropy of mixing, and χ is temperature independent. Thus the first three terms in Eq. (3) represent the ideal case, and we can write:

$$\Delta \bar{S}_E^m = \Delta \bar{S}^m - \Delta \bar{S}_{ideal}^m = -R\frac{\partial(\chi T)}{\partial T} \qquad (4)$$

where $\Delta \bar{S}_E^m$ is the *excess* entropy of mixing and can be derived from the plot of χT against T. Thus from the temperature dependence of solubility and the known heat of fusion and T_m of the additive we can calculate both the enthalpy and the excess entropy of mixing. If $\Delta \bar{H}^m$ is positive, the implication is that the intermolecular forces between additive and polymer are net repulsive and vice versa. Similarly, if $\Delta \bar{S}_E^m$ is positive it implies that the additive gains freedom on dissolution, over and above that allowed by the ideal geometric mixing of hard spheres.

3.2.2. Application to PEBE copolymers

The heats of solution of the UV absorber in PEBE and PP are easily derived from the Van't Hoff plots (Fig. 1) and, knowing the heat of fusion of the pure additive, the heat of mixing with the polymer is easily derived from Eq. (2). The results are presented in Table 3.

The major difference is that the heats of mixing are very small for PEBE samples and significantly positive for PP. Thus mixing of the additive with PEBE is close to thermo-neutral whilst mixing with PP is strongly endothermic. This shows that the intermolecular forces in polypropylene are net repulsive, which may be expected for the interactions of a polar additive with a non-polar polymer. The large positive heat of mixing is the main reason for the low solubility in PP.

Within the PEBE series the heats of mixing are all close to zero, especially considering the standard deviations. The very low heat of mixing is clearly because the additive is much more compatible with the polar polyether than with the non-polar PP. Although the values are negative for the soft grades, they become slightly positive for the hard grades (A_3 and B_3). This probably reflects the contribution of the PBT phase. Although the solubility in PBT is very low, it is not zero and 85% of the weight of the amorphous phase in these two materials is PBT. It is not possible to separate the two phases with any precision, but these data suggest that the heat of mixing has a small negative value in the polyether and a small positive value in the amorphous PBT.

It should be noted that the heats of mixing are not influenced by any correction for crystallinity or composition,

since such corrections act as multipliers of φ and simply shift ln φ without altering the gradient of the Van't Hoff plot.

From the solubility data we can also extract values of χ, by using Eq. (1). Fig. 5 shows the resulting plots of χT against T. As expected, the χ values for PP are all positive, leading to low solubility, whereas χ values for the poly-ethers are close to zero, accounting for the high solubility observed in PEBE.

The gradients of the lines in Fig. 5 can be used to compute the excess entropy of mixing via Eq. (4) and the results are collected in Table 3. The standard deviations are significant because of the accumulation of errors throughout the calculations. Unlike the heats of mixing, the calculated excess entropies depend upon the corrections used for crystallinity and composition.

The excess entropy of mixing is strongly positive for PP implying that the additive gains freedom on dissolution in the PP matrix over and above that due to geometrical entropy. This is presumably associated with the availability of free volume in the PP. In contrast, the PEBE is a much denser material and the softest grades show small, negative excess entropy of mixing. The materials with only 10% polyether (A_3, B_{3B} and B_{3E}) have small positive values for the excess entropy, presumably due to the contribution of the large fraction of amorphous PBT.

4. Conclusions

The overall solubility of a typical benzotriazole in the series of PEBE copolymers studied here is found to be up to one order of magnitude higher than in PP. This is due to the high solubility in the polyether soft phase into which the UV stabiliser partitions significantly at the expense of the PBT phase. The different soft phases (PTHF and PPO/PEO) studied gave similar results which could be predicted from their near identical structures.

Thermodynamic analysis suggests that the high solubility of the additive in the PEBE is because the similar polarities of the additive and the polyether phase lead to a near-zero heat of mixing. This is only slightly offset by a small negative excess entropy of mixing, which can be linked to the high density of the PEBE. The opposite is true for PP, in which the additive is slightly soluble due to a high excess entropy of mixing opposed by net-repulsive intermolecular forces which lead to a positive heat of mixing.

Solubilities extrapolated to room temperature are between one and two orders of magnitude higher in PEBE than in PP. This means that more additive can be used in the PEBE without risk of blooming in the range of temperatures of everyday use. However, the saturation solubilities are still low compared to possible use concentrations and a kinetic study is required to determine how fast any excess of additive will migrate to the surface since it is the other crucial issue in the physical loss of additive. Studies of diffusion are in progress and will be reported later.

At present it is not clear whether the heterogeneity of distribution of the UV-stabiliser in these copolymers influences their ability to stabilise the polymer. It is clear that the additive is mostly present in the phase, which is least UV sensitive. This is a complex issue since it will depend on the relative contributions of UV absorption and antioxidant action of the additive to polymer stabilisation, upon the distribution of the two phases, and upon the ability of the additive to migrate between phases in response to its consumption.

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