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

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Abstract

The diffusion coefficient, *D*, of a typical UV-absorbing stabiliser has been measured in a series of poly(ester-*block*-ether) copolymers (PEBEs) with different fractions of the polyether blocks, by using ultra-violet microscopy to monitor the concentration profile of the additive diffused into the edge of a thin film of polymer over a range of temperatures. For all samples, *D* shows an Arrhenius dependence on temperature over the range studied. At a given temperature, *D* increases rapidly with the polyether content, showing a percolation threshold and a marked drop in activation energy at 30 wt% polyether. This is consistent with the view that *D* is higher in the polyether than in the polyester and that there is a change in morphology at the percolation threshold, from isolated particles of the polyether to a co-continuous morphology with percolation paths of polyether. Comparison with data for the same permeant in polypropylene shows differences, which can be accounted for at least qualitatively by a free-volume argument. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyester; Polyether; Diffusion

1. Introduction

Poly(ester-*block*-ether)s (PEBE) 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 an important class of thermoplastic elastomers, well known for their toughness and elasticity at low temperature, but their usefulness is limited by sensitivity to ageing [1–9].

It was shown in the first studies [1,2] of degradation of PEBEs, and confirmed more recently [9] that the two components of the polymer behave differently on ageing. Due to the aromatic chromophores, the polyester is sensitive both to direct photo-degradation and to photo-oxidation and its degradation leads to yellowing [10]. In contrast, the polyether 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, where the polymer is exposed to sunlight, or 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 [11]. Its occurrence and rate depend on both the solubility and the diffusion rate of the additive in the polymer.

Diffusion of stabilising additives in polymers is important both scientifically and practically. The possibility of additive migration is a concern where plastics are used in contact with food, and in health-care applications [12–14]. In other cases, the effect of additive loss on stability and service life of the polymer becomes an issue. The rates of loss of additives from polymers by blooming, or by leaching into contacting liquids, are both controlled by the rate of additive diffusion in the polymer. Understanding diffusion is also intimately linked with a proper interpretation of accelerated ageing tests. Despite their importance, there are very few studies of diffusion of additives in multi-phase polymers, especially the polar polymers.

Any biphasic system, at either extreme of the composition range, can be observed as a dispersed phase surrounded by a continuous one. Under these conditions, the disperse phase is present as discrete particles. As the fraction of

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Table 1
Characteristics of the polymers studied

Polymer	A1	A2	A3
Polyether content[a] (%w/w)	55	30	10
ΔH^f (J g^{-1})	19.3	33.1	50.3
Crystallinity (%w/w)	13	23	34
Density (g cm^{-3})	1.16	1.23	1.28
Polyether content[b] (%w/w)	63	39	15

[a] Without correction for crystallinity.

[b] Expressed as a fraction of the total amorphous material.

disperse phase is increased, there comes a point where the system changes to a structure in which both phases are continuous throughout the matrix. The points of inversion are called the percolation thresholds [15].

In this kind of system, diffusion is governed by the transport of the additive either in the continuous phase or in whichever of the co-continuous phases allows higher mobility. The effective diffusion coefficient can be explained in terms of a qualitative description of the morphology [16–18]. Two reviews have been presented by Ottino et al. [19,20]. Migration of gases in polystyrene–polybutadiene blends has been successfully treated by the percolation concept [21,22]. Csernica et al. [23] preferred to model their results in similar systems with a third 'interfacial' variable. On the other hand, Willett [24] noted that percolation theories could not describe the migration of water in starch–polyolefin blends. This was partly accounted for by the sorption of water by the polysaccharide.

Zielinski et al. [25,26] reported a forced Rayleigh scattering study on the diffusion of dye molecules in poly(styrene-*b*-isoprene). No attempt was made to link these results with the percolation theory. However, these two reports are the only ones we are aware of dealing with the migration of large molecules in a multi-phase polymer.

It should be noted that percolation thresholds predicted by theory are extremely sensitive to the morphology of the polymer, which cannot be predicted exactly. It depends not only on the properties of the different phases but also on the thermal history of the sample and its orientation [21,23].

In a previous study, we showed [27] that a typical UV stabiliser is significantly more soluble in PEBEs than in polypropylene (PP), mainly because of a more favourable heat of solution of the additive in the polar PEBE, but that in the PEBE, the additive is essentially concentrated almost entirely in the soft, polyether phase. In the present paper, we report a study of the migration of the same additive and the effects of polymer composition and temperature.

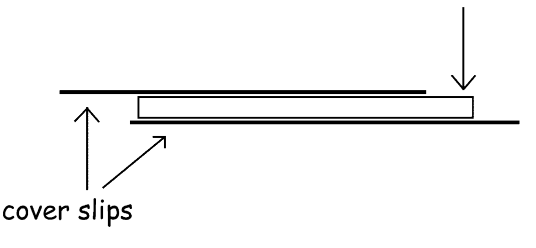


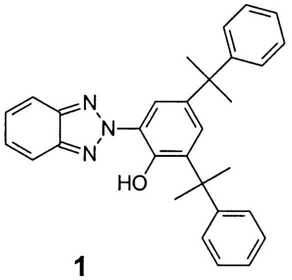
Fig. 1. Schematic preparation of the cover slip experiment for UV microscopy.

2. Experimental

2.1. Materials

Polymers were supplied by DSM (NL) as a family of three materials with PBT as the hard phase, and a PPO-based copolymer as the soft phase. More details of the composition and properties are given in Table 1. These polymers are denoted as series A for comparison with our previous report [27]. They were supplied as 20 μm thick films produced by casting. All films were process stabilised with a low concentration of a phenolic antioxidant, which has no absorption in the UV range used for the diffusion study.

The probe molecule was a typical UV absorbing photostabiliser (UVA), 2-[2-hydroxy-3,5-di-(1,1-dimethylbenzyl)-phenyl]-2H-benzotriazole **1**. It was provided by Ciba Specialty Chemicals (Tinuvin 234™) and 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. UV microscopy

The UVA was chosen for this study partly because it is representative of commercial stabilisation and partly because its strong UV absorption made it a good candidate for study by UV microscopy, a method which has been used very successfully for measurement of diffusion of UVAs in polyolefins [28-30]. In initial work, we attempted to diffuse the UVA into one face of a plaque of polymer, followed by microtoming a thin section perpendicular to the diffusion direction for examination by microscopy, as previously described. This proved unsuccessful because absorption profiles near the edge of the sample were distorted, especially for the samples with high polyether content. This problem was traced to plasticisation of the already soft

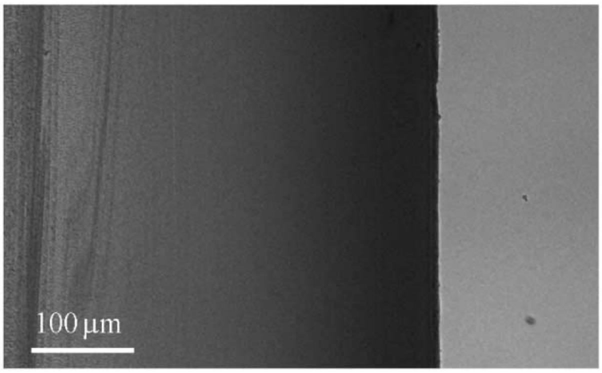

Fig. 2. Typical diffusion profile as observed by UV microscopy.

polymer by the dissolved additive, leading to sample distortion during microtoming, even at low temperatures.

To avoid microtoming, samples were prepared as films between two cover slips (Fig. 1). The cover slips are transparent at the wavelength (350 nm) used for observation. The film was positioned so that part of it was in contact with air. This assembly was rapidly heated to 240°C and kept under gentle pressure for 5 s to fuse the polymer to both cover slips and prevent any capillarity. The whole assembly was then quenched in cold water to produce a transparent film free of interfering spherulites for all grades of polymer. The crystallinity of the polymers was determined by DSC and is presented in Table 1.

The pure additive was applied to the unprotected part of the polymer (Fig. 1), and left to diffuse along the film in an air oven. The equilibration of the additive through the film thickness (transverse diffusion) was considered instantaneous compared to its diffusion along the film (longitudinal diffusion). Therefore, the origin of the diffusion profile was taken as the edge of the top cover slip, which allowed precise determination of the edge position.

Of all methods described in the literature to measure diffusion of additives in polymers, this is certainly the one, which offers the quickest thermal equilibration. This advantage is combined with the great resolution typical of microscopy. In our experiments, we have 700 data points per profile which can be compared to a maximum of 7–14 for a conventional stack experiment. Moreover, due to the magnification, a profile can be as little as 50 μm deep for the microscopy technique whereas a film stack needs to be at least 1 mm thick, with a correspondingly much longer diffusion time.

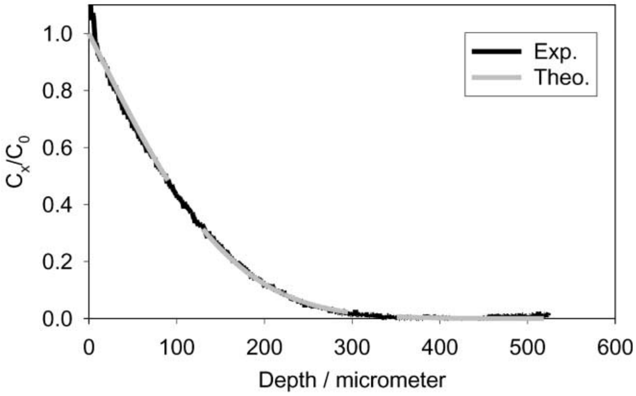

Fig. 3. Typical fit of a diffusion profile with the Fickian equation.

The UV microscope used to observe the diffusion profiles was a Zeiss Universal model with quartz optics [28]. For the present study, it was fitted with a digital camera, which allowed the contrast profile to be detected. Synapse Grabber™ software allowed black and white pictures to be taken from the camera. The profiles obtained with this method were clean, and free of edge effect (Fig. 2). The pictures were digitised using PC Image™ software and the data points were fitted to the Fickan diffusion equation:

$$\frac{C_0 - C}{C_0} = \operatorname{erf} \frac{x}{\sqrt{2Dt}} \tag{1}$$

where C is the concentration at a distance x from the surface at time t, C_0 is the concentration at the surface, equal in this case to the saturation solubility, and D is the diffusion coefficient [31].

Fitting was performed using a least squares method on an Excel™ spreadsheet. A typical fit to some experimental data is shown in Fig. 3.

3. Results and discussion

Diffusion coefficients for the UVA were measured by analysis of the concentration profile of the diffusant by the UV microscopy as described above. In all cases, good fits to the appropriate Fickian diffusion equation were found and D values were determined from at least ten measurements on different parts of the sample, typically giving better than ±10% standard deviation.

Diffusion experiments were performed over a range of temperatures, and the data are presented in Arrhenius coordinates in Fig. 4. Data obtained by Dudler and Muinos, with a similar experimental method, for the same UVA in PP are plotted for comparison [30].

Over the fairly small range of temperatures used, the diffusion in all samples closely follows the Arrhenius law:

$$D = D_0 \exp\left(-\frac{E_D}{RT}\right) \tag{2}$$

where E_D is the activation energy and D_0 is the pre-exponential factor.

It is interesting to observe that diffusion coefficients in PEBEs span the range of values for PP. It is also clear that the more PBT the PEBE matrix contains, the smaller is the diffusion coefficient. Values of E_D and D_0 calculated from the data in Fig. 4 are presented in Table 2, and have a standard deviation of approximately ±10%, except for A2 where slight curvature did not allow better than ±15%. The origin of this small curvature is not clear. It may result from

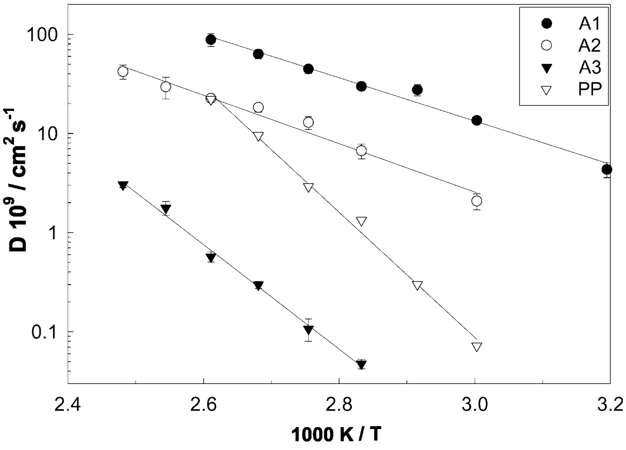

Fig. 4. Diffusion of Tinuvin 234 in PEBE and PP [30] as a function of temperature, expressed in Arrhenius coordinates.

a small concentration dependence of diffusion, from different degrees of annealing of the polymer during the experiments at different temperatures, or from a WLF contribution to the temperature dependence. Whatever its origin, it is small enough to have no effect on our conclusions.

The values of D extrapolated to room temperature can be useful in practical terms when dealing with the storage of material. Although such extrapolation requires caution, Table 2 shows that in the PEBE range, there is up to four orders of magnitude difference and, while A1 and A2 are comparable, A3 is closer to PP than to the rest of the PEBE grades.

The activation energy and pre-exponential factor are very close for A1 and A2, implying a similar diffusion mechanism for both the polymers. This, in turn, suggests that the difference in D, half an order of magnitude, is due mainly to the amount of soft phase. In contrast, A3 shows not only a drop in diffusion coefficient, but also a dramatic increase of activation energy and pre-exponential factor. This is attributed to a different diffusion mechanism. At 80°C, diffusion is three orders of magnitude slower in A3 than in A1. Diffusion is obviously much faster in the polyether phase than in PBT.

Fig. 5 shows the diffusion values measured for the PEBE, plotted on a linear scale as a function of the weight fraction of the soft block in the total amorphous content of the polymer. It is clear that, whatever the temperature, the diffusion coefficient increases with the amount of soft phase, revealing a percolation threshold at 0.3 independent of the temperature. Considering the different densities of both pure phases, 0.30 weight fraction is equivalent to 0.34 volume fraction.

Table 2
Pre-exponential factor, activation energy and extrapolation to room temperature of the diffusion coefficient of Tinuvin 234 in PEBE and PP

Polymer	D_0 (cm^2 s^{-1})	E_a (kJ mol^{-1})	D at 25°C (cm^2 s^{-1})
A1	5×10^{-2}	42	2×10^{-9}
A2	6×10^{-2}	47	3×10^{-10}
A3	$4\times10^{+4}$	101	8×10^{-14}
PP	$8\times10^{+8}$	121	5×10^{-13}

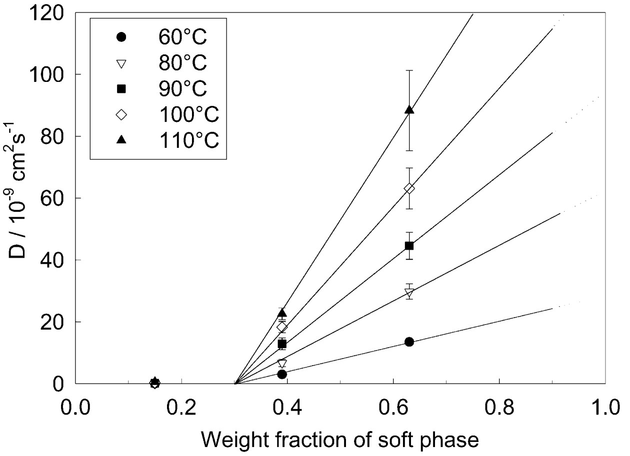

Fig. 5. Diffusion of Tinuvin 234 in PEBE versus the amount of soft phase corrected for crystallinity; plotted on linear scale.

The percolation threshold represents the minimum amount of polyether required to create a continuous path of soft phase throughout the PEBE matrix. This suggests that the morphology of A3, unlike A1 and A2, does not offer a polyether continuum in which the additive can percolate rapidly. Instead, the additive has to diffuse through large volumes of PBT phase between small regions of polyether. This deduction is in agreement with observations of similar PEBEs by SEM and TEM [32]. It was found that PBT blocks crystallise in 100 Å domains forming ‘continuous and highly interconnected’ regions.

This percolation pattern suggests an explanation for the change in activation energy across the composition range. Diffusion in A1 and A2 occurs mostly in the polyether phase (both being above the percolation threshold); its activation energy is near identical in both polymers. In contrast, the limiting factor in the diffusion of the stabiliser in A3 is migration through the amorphous PBT. Obviously these chains, being barely above their glass transition, are very stiff compared to those of the polyether, leading to the much higher activation energy.

We have previously shown that Tinuvin 234 has a very low solubility in the PBT phase in comparison with the soft block [27]. It is reasonable to assume that in A1, any diffusion in the hard blocks is entirely hidden. This is because of the partitioning of the additive and its faster migration in the soft phase. However, in A3, the partitioning of the additive might be offset by the predominance of the hard blocks (9:1). Hence, diffusion in PBT might become detectable. In other words, migration of the additive in the soft blocks is dominant at any given composition, but depending on the composition of the PEBE with respect to the percolation threshold, diffusion in the hard block might not be measurable.

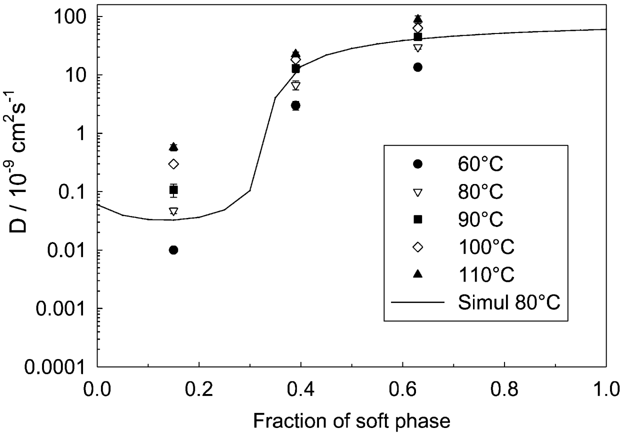

Fig. 6. Diffusion of Tinuvin 234 in PEBE versus the amount of soft phase corrected for crystallinity; plotted on logarithmic scale. Solid line is EMT simulation at 80°C.

The amount of polyether in the PEBE has a direct influence on the quantity of additive present (in saturation conditions) but not on its diffusion rate in the polyether phase. However it also influences tortuosity of the matrix, as well as the constraints applied on polyether chains by crystalline and amorphous PBT. If it did not, we would have a step function at the percolation threshold. Therefore, the changes in tortuosity and constraints are the reasons why, above the percolation threshold, diffusion increases with the fraction of soft phase.

Since we have studied only three compositions of PEBE, one below and two above the percolation threshold, the lines in Fig. 6 are necessarily linear. However, extrapolation of D to high fraction of soft phase (above 0.9) is unlikely to be linear. Indeed prediction of the effect of a few percent of hard block whose glass transition is 50°C in a polyether matrix ($T_g \sim -50$°C) is hazardous. Therefore we will not speculate on those values.

Sax and Ottino [21] have reported a study on diffusion of gas in the complete composition range of polystyrene–polybutadiene (PS/PB) blends. They attempted to fit their data by the relation $D_{\mathrm{eff}} = \phi_{\mathrm{a}} \ln D_{\mathrm{a}} + \phi_{\mathrm{b}} \ln D_{\mathrm{b}}$, with a and b representing the homopolymers and ϕ_{a}, ϕ_{b}, their respective volume fractions. They found that this logarithmic average rule was inadequate and we confirm this inadequacy for PEBE. Fig. 6 shows our diffusion data in logarithmic coordinates. The relationship is non-linear and the percolation threshold remains clear. This is actually more obvious in the case of PEBE than for PS–PB blends.

Diffusion in a biphasic medium in which the migrating species has different solubility and diffusion rate in both phases is a complex phenomenon [31]. One relatively recent approach is the so-called effective-medium theory, EMT, [17,19], which models diffusion through a three-dimensional structure made up of domains which have some number of plane faces. According to this model, the effective diffusion coefficient in a biphasic medium can be written as:

$$D_{\mathrm{eff}} = \frac{D_{\mathrm{B}}}{S\left(1 + \phi_{\mathrm{B}}\dfrac{(1-S)}{S}\right)}\left[A + \left(A^2 + \frac{2}{z-2}Sx\right)^{1/2}\right] \quad (3)$$

where

$$A = \frac{(Z/2)\phi_{\mathrm{B}} - 1 + Sx((z/2(1-\phi_{\mathrm{B}}) - 1)}{z-2}$$

$S = S_{\mathrm{A}}/S_{\mathrm{B}}$ = solubility ratio

$x = D_{\mathrm{A}}/D_{\mathrm{B}}$ = diffusion coefficient ratio

z = a coordination number

The coordination number in Eq. (3) represents the number of faces per building block of the three-dimensional network. Accurate predictions are said to be made by setting $z = 6$ [19]. Dean and Bird [16] simulated the percolation pattern of a system tessellated with cubes ($z = 6$) and predicted a threshold at 0.32. This value is similar to our experimental value. We have previously measured the solubility of the UVA in the pure polyether at 80°C by hot-stage microscopy and the value for PBT can be extrapolated [27]. Thus the remaining variables in Eq. (3) are the two diffusion coefficients.

The solid line in Fig. 6 represents a prediction of the effective diffusion coefficient at 80°C as calculated by EMT using $z = 6$ and the following values of the variables:

$D(\text{polyether}) = 5 \times 10^{-8}\ \mathrm{cm^2\ s^{-1}}$
$D(\text{PBT}) = 5 \times 10^{-11}\ \mathrm{cm^2\ s^{-1}}$
$S(\text{polyether}) = 5$ wt%
$S(\text{PBT}) = 0.3$ wt%

The simulation is in reasonable agreement with our experimental results, though the fitting is not very sensitive to the parameters used. The simulated percolation threshold is directly linked to value of z and will shift to lower soft phase content with increasing z. This is an ill-defined parameter and there is no particular justification for choosing a value of 6 except that it gives the best fit. The ratio of solubilities (S) mainly influences the curvature of the simulation around the percolation threshold. The ratio of diffusion coefficients (x) influences the change of the diffusion coefficient through the threshold, without modifying either the curvature or the threshold.

Because of its high activation energy, the diffusion coefficient in PP falls within the range of composition of PEBE over the temperature interval studied (Table 2). Analysis of solubility data [27] showed close to zero heat of mixing of Tinuvin 234 in the PEBE matrix, whilst the heat of mixing of the additive and PP was shown to be positive. Thus, we might predict higher activation energy in the case of PEBE, due to the required rupture of these intermolecular forces for the diffusion step to be completed. This should lead to a

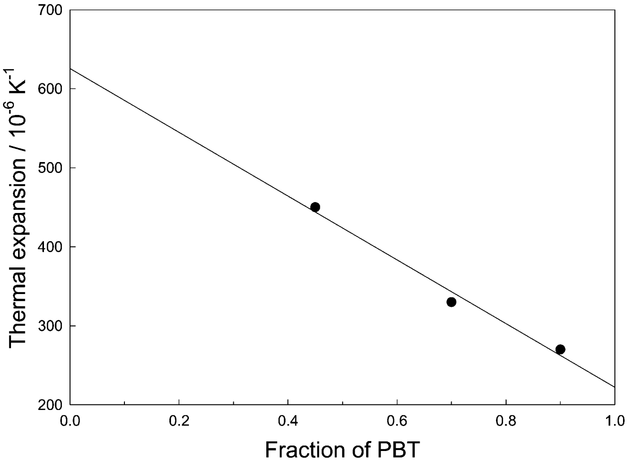

Fig. 7. Coefficient of thermal expansion versus the composition of PEBE.

slower diffusion in PEBE, especially at low temperatures. Moreover, the fact that PEBEs are much denser than PP (Table 1) would also suggest a higher E_a for PEBE than for PP. The fact that diffusion in PEBE is actually faster than that in PP suggests that a free volume interpretation may be more appropriate for the comparison of PEBE with polypropylene, as has already been suggested for other systems [33,34].

PEBEs are complex polymers, containing both crystalline and amorphous material, and with reasonable evidence that the amorphous material is multi-phasic [35]. Complete description of free volume in such a system is difficult and would require rather precise data on the thermal expansion of all the three phases. Since such data are not available, only a simplified discussion is possible, and is based on linear expansion data.

It was demonstrated earlier that in grades A1 and A2, the additive diffuses mostly in the polyether phase while in A3 it must permeate the PBT. Taking into account the complexity of our system, it was decided to compare both pure phases to PP. For this purpose, the following assumptions have been made.

The specific volume and the thermal expansion of the amorphous phase in PP and PBT were approximated to be the same as those of the respective crystalline phases. For the thermal expansion, this was preferred to the alternative of correcting the bulk value for crystallinity. The thermal expansions of both pure phases were extrapolated from measured linear thermal expansion coefficients provided by DSM Research [35] as shown in Fig. 7. It should be noticed that the expansion coefficient thus found for PBT ($2.2\times10^{-4}\ \mathrm{K}^{-1}$) is very close to the value ($2.1\times10^{-4}\ \mathrm{K}^{-1}$) reported by Wagener [36]. The same is true for the difference in glass transition between PBT and A3 which are, respectively, 52 [36] and 46°C. The variables used in our calculations are summarised in Table 3.

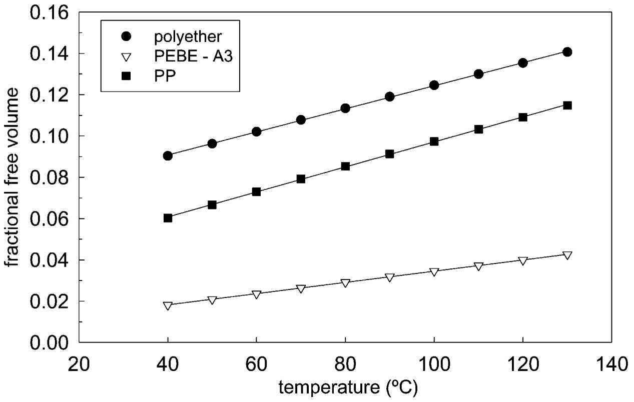

Fig. 8. Fractional free-volume as a function of temperature.

The free volume was calculated from Eq. (5), assuming that the free volume at the glass transition is 2.5% of the volume of the amorphous phase [37]. In the equations below, the specific volume of a polymer at temperature T is denoted $\bar{v}_T$, the subscripts g and f refer, respectively, to the glass transition temperature and the free volume at any temperature T. At the glass transition temperature, we have:

$$\bar{v}_f = 0.025\times\bar{v}_g = 0.025(\bar{v}_{25} - \alpha(25 - T_g)) \tag{4}$$

where $\bar{v}_{25}$ is the specific volume measured at 25°C.

At any other temperature T, we then have

$$\bar{v}_f = 0.025(\bar{v}_{25} - \alpha(25 - T_g)) + \alpha(T - T_g) \tag{5}$$

and the fractional free volume is

$$f = \frac{\bar{v}_f}{\bar{v}_T} = \frac{\bar{v}_f}{\bar{v}_g + \alpha(T - T_g)} \tag{6}$$

Fig. 8 shows the fractional free volumes thus calculated as a function of temperature over the range used in our diffusion experiments. These data clearly illustrate the reason for the extremely low diffusion and solubility in A3; the combination of high density and high T_g offers barely any free volume in PBT for any additive to accumulate or to migrate. Moreover, it helps understanding why, despite a much higher density than polypropylene, the migration in the polyether is faster; there is more free volume in the copolyether matrix despite its higher density.

Table 3
Parameters for the free-volume interpretation of diffusion in PEBEs

Polymer	D_{25} (g cm^{-3})	$\bar{v}_{25}$ (cm^3 g^{-1})	T_g (°C)	$\bar{v}_g$ (cm^3 g^{-1})	α (10^{-4} K^{-1})
PPO copolymer	1.06	0.94	− 63	0.89	6.2
PBT	1.27 (A3)	0.79	46	0.79	2.2
PP	0.90	1.11	− 10	1.09	7.45

A high free volume combined with a high density is not inevitably paradoxical since the polyether contains oxygen atoms. Although these conclusions are based on a fairly approximate model, we believe they are valid, since quite unrealistic changes in the basic parameters are needed to alter the fundamental conclusions.

4. Conclusions

The diffusion of a typical UV absorber has been measured in a series of poly(ester-*b*-ether)s with different contents of a soft, polyether phase in a hard polyester. The diffusion in the soft PEBE grades is up to three orders of magnitude faster than in the hard grade. The diffusion shows classic percolation behaviour, with a percolation threshold estimated as 30% by weight of the polyether phase. This suggests a change from a morphology of polyether particles in a continuous PBT matrix to a morphology with a continuous polyether phase. There is a marked change in the activation energy at the percolation threshold. At low polyether content, the additive has to diffuse through PBT domains, which slows the diffusion and increases the activation energy.

With some approximations, EMT was shown to be useful to interpret the kinetics of diffusion of an additive in a biphasic material as a function of the medium composition. This is the first time that this model has been applied to such a large diffusant.

Comparison of the diffusion rates in polyether and PP show that diffusion is faster in the polyether at a given temperature despite the thermodynamically more favourable environment. The fast diffusion of the additive in PEBE can be related to a high free volume in the polyether, despite its high density, due to a low T_g. The low free volume of the PBT matrix, as well as causing an extremely low diffusion rate, contributes to the low solubility of the additive in this matrix.

We have already reported that the solubility of Tinuvin 234 is higher in any PEBE than in PP, thus implying that supersaturation is less likely in these copolymers than in PP [27]. The present results suggest that additive loss by blooming is less likely in A3 than in PP because A3 offers higher solubility and slower diffusion. Similarly, loss by solvent leaching should be slower for A3 than for PP. In contrast, the softer PEBE grades offer solubilities two orders of magnitude higher than PP but any excess with respect to this concentration will be lost 3–4 orders of magnitude faster because of the higher diffusion rate. Similarly, loss by leaching from A1 and A2 is expected to be rapid.

The collected data for solubility and diffusion presented here and in our previous work are sufficient to allow complete modelling of loss by leaching or blooming. The development of such a model and its comparison with experiment will be the subject of a future paper.

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