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Concentration-way profiles and interdiffusion coefficients of contacting compatible polymers by scanning FT-IR microscopy

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Abstract

Results of investigations by scanning FT-IR microscopy carried out to estimate the interdiffusion coefficients across the interface boundary of contacting compatible polymers are reported. It is shown that the methods can be used to provide evidence for the evolution of concentration-way profiles along interphases developed during interdiffusion of miscible components of contacting polymers. The data obtained for the contacting polymer pairs assembled of poly(styrene-*b*-methylmethacrylate) diblock-copolymer with poly(2,6-dimethyl-1,4-phenylene ether) and poly(styrene-*co*-acrylonitrile), respectively, are presented. In the former contacting polymer pair, PPE is compatible with the PS block, whereas in the second pair, the PSAN copolymer is compatible with the PMMA block of the block copolymer. Almost symmetrical concentration-way profiles across the interface point at constancy of the interdiffusion coefficients, which are of the order of 10^{-12} cm^2/s. The data obtained suggest additionally that the interdiffusion coefficients are dependent on molecular weight. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer/polymer interfaces; Concentration-way profiles by scanning FT-IR microscopy; Interdiffusion coefficients

1. Introduction

The manufacture of polymer blends is one of the technological preferred ways to tailor new polymeric materials. The extent of adhesion at polymeric interfaces and the interfacial thickness between the polymer blend components are dependent on the thermodynamic condition of miscibility (quantified by the Florry–Huggins interaction parameter') and control both the stability and the mechanical properties of the blend. Different physical properties, such as morphology, glass transition, transparency, rheology, etc., are usually studied to provide evidence for polymer compatibility.

Taking account of the reduced probability of polymer miscibility, predicted by thermodynamics, we find that efficient phase adhesion between immiscible blend components is the crucial problem for the realization of stable multiphase polymer blends due to the minor contributions of combinatorial mixing entropy [1]. It is well known that the use of compatibilizers [2] is responsible not only for the stabilization of morphological structures in multiphase polymer blends, but also for the assurance of substantial improved mechanical properties. One of the possibilities of compatibilization of immiscible polymers is the use of diblock-copolymers supporting blocks either identical to (adhesion realized by entropic entangling) [3] or miscible (adhesion by enthalpic interaction) with the components of the polymer blend [4]. It has been shown that the use of diblock compatiblizers increases the degree of dispersion in immiscible polymer blends contributing additionally to both the stabilization of the blend morphology and improved mechanical properties. It seems, however, that both dispersion and stabilizing effects of block copolymers composed of enthalpic interacting components overcome those of block copolymers built up of identical, entropic interacting components [5], the latter being efficient only if the blocks overcome by far the critical entanglement of molecular weight. For enthalpic interacting block-copolymers, the size of molecular weight is not conditional.

Recently, it has been shown that the use of poly(styrene-*b*-methylmethacrylate) diblock copolymers improves both the dispersion degree and the stability of the incompatible poly(phenylene ether)/poly(styrene-*co*-acrylonitrile) (PPE/PSAN) blends [6,7]. Nevertheless, for a positive characterization of the efficiency of phase adhesion and phase stability, any morphological study has to be accompanied at least by a mechanical, dynamic investigation [8].

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Table 1
Characteristics of the polymers used for FT-IR studies

Polymer	M_w (g/mol)	M_n (g/mol)	M_w/M_n	M_n (PS) (g/mol)	MMA (w/w%)	T_g (K)[a]
PPE[b] 15	15,000[c]	8000	1.88	–	–	463.2
PPE 35	35,800	13,100	2.73	–	–	473.2
PSbM[d] 43	97,000		1.06	43,000	52.0	375.2/403.2
PSbM 78	169,000		1.10	78,000	53.0	380.2/403.2
SAN[e] 20	157,000	86,700	1.81	–	~ 19% AN	380.2

[a] By DSC, second heating scan hr = 15 K/min on the Perkin–Elmer DSC 7.
[b] Poly(2,6-dimethyl-1,4-phenylene ether) by courtesy of BASF.
[c] M_w, M_n by GPC using $CHCl_3$ as solvent and PS standards.
[d] Poly(styrene-block-methylmethacrylate), by courtesy of Auschra, M_w/M_n mean value of the individual blocks.
[e] Poly(styrene-*co*-acrylnitrile) (PscoAN) by courtesy of BASF.

One of the possibilities to estimate and quantify phase adhesion between polymers is based on the observation of interdiffusion-driven interphase evolution between the compatibilizing agent and the blend components. Jabbari and Peppas [9–11] have shown that among the different techniques recommended in the literature to measure interdiffusion between contacting polymer pairs, infrared spectroscopy is one of the few methods, which does not require additional labelling for diffusion studies. The authors used attenuated total reflection FT-IR to measure interdiffusion in a polystyrene–poly(vinyl methyl ether) compatible pair. von Seggern et al. [12] of our laboratory have shown that scanning FT-IR microscopy can be used to provide evidence for the development of interphase between high and low molecular polystyrene and for the evaluation of the belonging diffusion coefficients.

This latter method has been adopted in our study to evidence and quantify the interpenetration by diffusion of the compatible blocks of the symmetric diblock-copolymer poly(styrene-*b*-methylmethacrylate) (PSbM), into poly(2,6-dimethyl-1,4-phenylene ether) (PPE) and the copolymer poly(styrene-*co*-acrylonitrile) (PScoAN), respectively. The method has been preferred because beside Jabbari and Peppas, High et al. [13] have also emphasized that infrared spectroscopy is in fact one of the very few methods, which does not require additional labelling for interdiffusion studies between contacting polymer pairs. Recently, however, Tomba et al. [14] have shown that in addition, dynamic mechanical analysis may be used without labelling to measure interphase composition profiles for the contacting high molecular–low molecular polystyrene pair.

2. Experimental

The characteristics of the polymers used in this FT-IR study to provide evidence for the interphase evolution by interdiffusion between contacting polymeric pairs are shown in Table 1. The experimental procedure of measuring concentration-way profiles by scanning FT-IR microscopy is sketched in Fig. 1.

The individual polymers were at first press-moulded in vacuum into circular sheets ($\Phi = 24.9$ mm) of 0.5–1 mm thickness. Subsequently, the respective polymer pairs for the following interdiffusion study by contact-pressing circular sheets of the diblock-copolymer PSbM with either PPE or PScoAn were assembled. In the first pair, the PS block of the PSbM copolymer is compatible with PPE, whereas in the second pair, the PMMA block is compatible with the PScoAn copolymer.

The interdiffusion of the respective compatible components through the contacting surfaces of the compressed

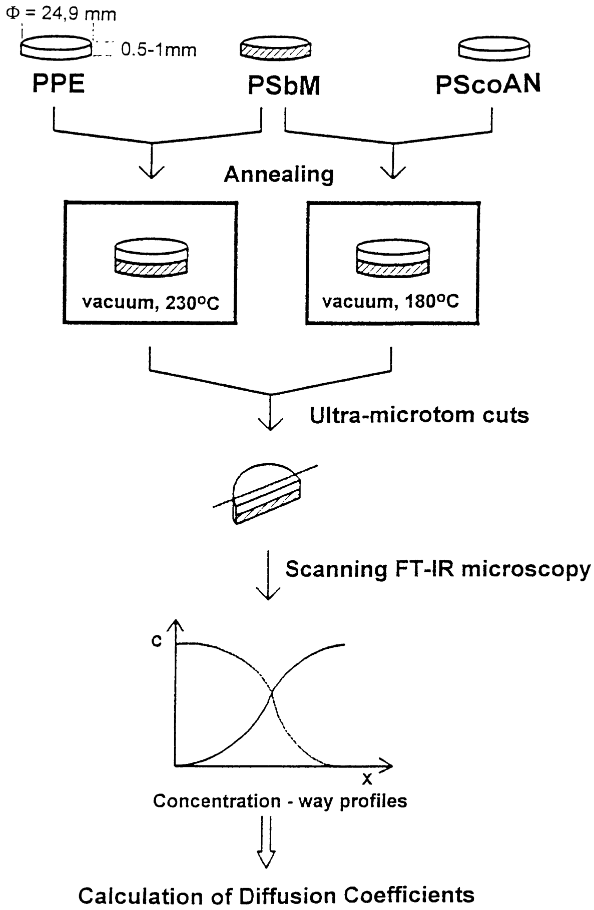

Fig. 1. Sketch of the experimental procedure of measuring concentration-way profiles by scanning FT-IR microscopy.

polymer pairs has been promoted by annealing in vacuum. Subsequently, the set-up of an interphase due to interdiffusion of the miscible components across the contacting surface of the press-moulded pairs, PSbM/PPO and PSbM/PScoAN, respectively, has been evidenced by scanning FT-IR microscopy.

For realization of the interdiffusion measurements, samples of the polymer pairs were contact-pressed into a glass fiber-poly(tetrafluoroethylene), PTFE, mould doped with 60% bronze to improve thermal conductivity. Then, the samples were annealed in the Schwabenthan vacuum press-mould Polystat 100 at temperatures situated well above the glass temperature of the respective component with the higher T_g. To prevent, however, any thermal degradation of the less stable PMMA block, the annealing temperature for the first pair, PSbM/PPE, was maintained at 230°C, i.e. at about 40°C above the glass temperature of PPE. The annealing temperature of the second pair, PSbM/PScoAN, was 180°C.

The annealing process was stopped by introducing the PTFE mould containing the respective polymer pair in cold water. A chill of the mould with liquid nitrogen was given up because it has been observed that it is accompanied by the development of cracks within the polymer samples.

Next, the sample-pairs were pulled out from the PTFE mould and cut perpendicular to the contacting surface into ultra-thin slices (3–10 μm) of 1.5 × 5 mm, using the Reichert–Jung ultra-microtome Ultracut FC4. The scanning FT-IR measurements were carried out on the Bruker IFS 88 FT-IR Spectrometer supplied with an IR microscope. A computer-aided *X*/*Y*-slide of the microscope allowed the scanning of the sample in steps of 5 μm along both the *X* and *Y* directions. Due to light inflexions, the spot-sensibility of the slit-objective of the microscope was restricted, however, to only 10 μm.

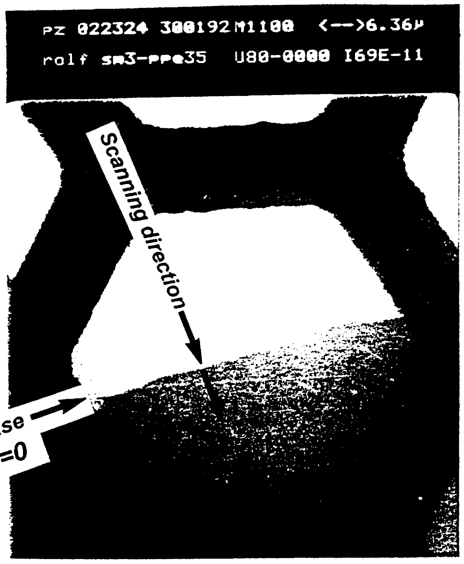

Fig. 2. Interphase boundary of the interdiffusion pair PPE 35/PSbM 43 evidenced by transmission electron microscopy (no staining). Grid-width: 30 μm.

The interphase boundary could be directly recognized without additional staining by transmission electron microscopy (TEM). This is illustrated in Fig. 2 for the polymer pair PPE 35//PSbM 43. The roughness of the interphase boundary was negligible from the point of view of the scanning FT-IR measurements. To improve the sensibility of detection, the spot was maintained at 10 × 30 μm to assure an unequivocal determination of the $X = 0$ reference position representing the contacting interphase.

3. Results and discussion

At first, the spectra of the individual polymers to select IR bands typical for a given component, i.e. those IR bands which possibly are not superposing with outstanding IR bands of the second component of the respective polymer pair used for the interdiffusion study, were scanned. By this procedure, for the diffusion pair PSbM/PScoAN, the carbonyl band at 1734 cm^{-1} for PSbM, the nitrile band at 2237 cm^{-1} for PScoAN were selected (see Fig. 3A). Taking

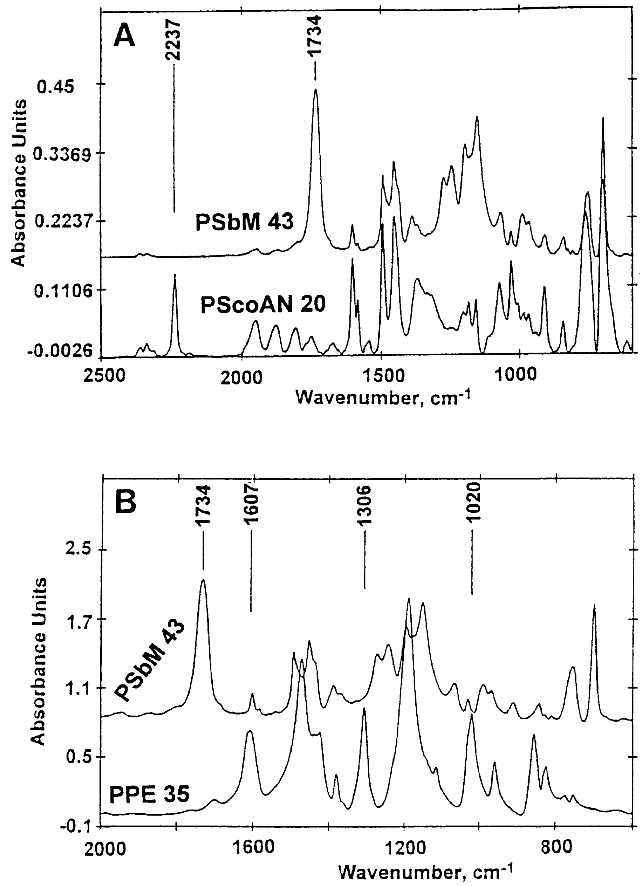

Fig. 3. Comparison of the FT-IR spectra of the individual components of the studied interdiffusion pairs: (A) interdiffusion pair PSbM 43/PScoAN 20; (B) interdiffusion pair PSbM 43/PPE 35.

account of the fact that PScoAN also exhibits weak IR absorption in the 1734 cm^{-1} range (see Fig. 3A), the corresponding constant magnitude of this IR absorption of the pure PScoAN has been considered as the 0% starting level for evaluation of the distribution of the volume concentration of PSbM across the contacting interface. The same carbonyl band at 1734 cm^{-1} was selected for PSbM in the PSbM/PPE pair. PPE exhibits, however, three typical IR bands: the phenyl band at 1603 cm^{-1}, the C–O valence vibration band at 1300 cm^{-1}, and the C–O–C ether band at 1020 cm^{-1} (see Fig. 3B). For calculations, the 1603 cm^{-1} phenyl band has been chosen because in the region of the IR spectrum, the smallest perturbations of the basis line were observed. As PSbM also shows IR absorption in this IR range (see Fig. 3B), the same above-described procedure has been applied to specify the 0% value for the volume concentration of PPE across the contacting interface. Accordingly, the value of the constant IR absorption of PSbM at 1603 cm^{-1} has been considered as the 0% point value for the volume concentration of PPE.

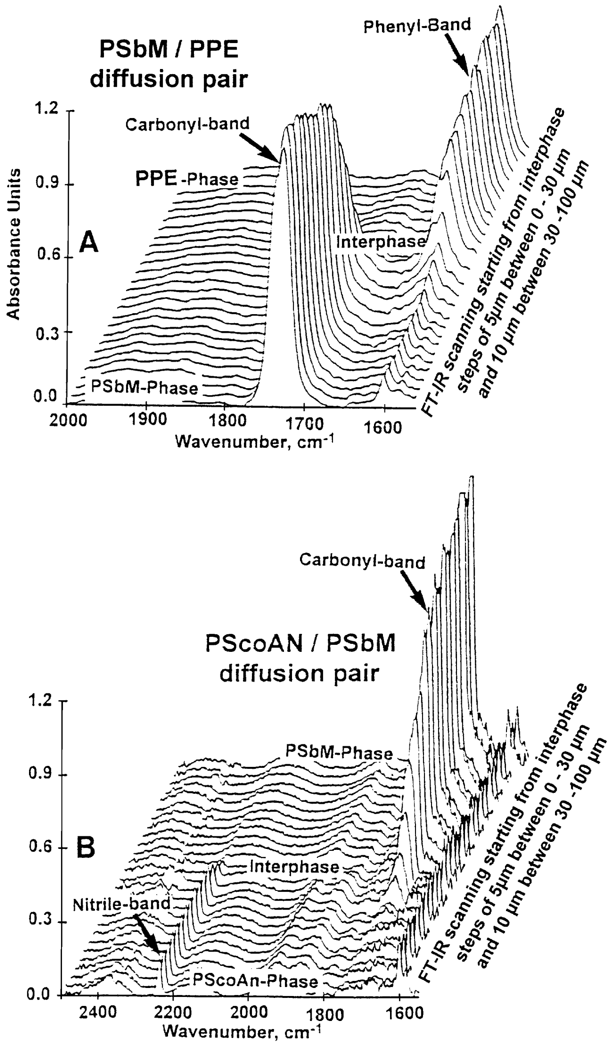

Fig. 4. Evolution of the component specific IR bands across the interphase layer formed by annealing above the glass temperatures: (A) interdiffusion pair PSbM 43/PPE 35; (B) interdiffusion pair PSbM 43/PScoAN 20.

The distributions of the above-selected IR bands of the compatible components across the contacting surface are illustrated in Fig. 4 for the two interdiffusion pairs studied, i.e. PSbM/PPE (Fig. 4A) and PScoAN/PSbM (Fig. 4B), respectively.

In these figures, the evolution of the selected specific IR bands of the blend components across the contacting interface, to which the volume concentrations of the respective components of the studied diffusion pair starting from the constant level of the absorbance of the characteristic IR band of the given component of the interdiffusion pair observed in the bulk of the countercomponent to the constant plateau value of the absorbance in the bulk of the component itself are related, is exhibited. The areas of these absorption bands were then used to estimate the distribution of the volume concentration of the components across the contacting interface.

For calculations, the reference volume concentration of 100% has been attributed to the constant plateau value of the absorbance of the corresponding IR absorption band measured in the bulk region of the component, far away from the contacting surface, whereas the value of 0% volume concentration was determined by the magnitude of the same IR band in the bulk region of the countercomponent. In this way, we attempted to quantify the degree of interpenetration by interdiffusion through the contacting surface of the compatible components of the contacting polymer pair. In this way, quantified areas of the selected IR bands were subsequently used for evaluation of the volume concentration-way profiles of the compatible components of the respective polymer pairs across the contacting surface.

In Fig. 5A evaluated concentration-way profiles for the compatible components of the interdiffusion pair PPE 35// PSbM 43 measured after 23 h annealing at 230°C are shown in this way. The presented concentration-way profiles may be considered as a kind of experimentally determined 'mastercurves' (i.e. the exhibited data points represent mean values obtained from at least 36 individual FT-IR spectra, each of them scanned additionally several times for different cuts and positions across the contacting surface). The contact quality between the components of the interdiffusion pair has been proved by applying additional weights. The superposition of the corresponding individual mastercurves for no respective 50 and 100 g additional pressing weights has been considered satisfactory and at the same time, a confirmation of thorough contact realization between the compressed circular sheets of the interdiffusion pair even without application of additional pressing weights.

Starting with the data of these experimentally determined mastercurves of the concentration-way profiles were evaluate the belonging diffusion coefficients according to the second law of Fick [15]. For each of these concentration-way

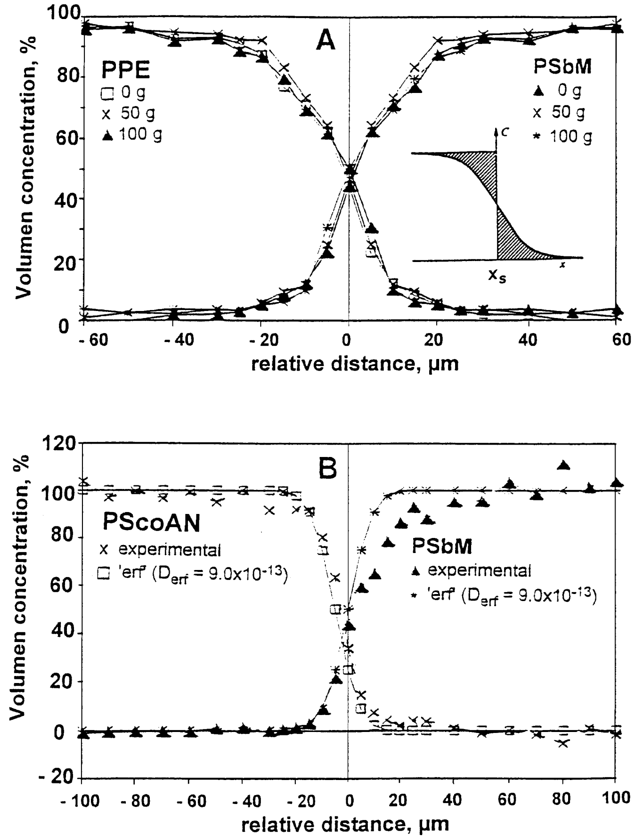

Fig. 5. Concentration-way profiles of interdiffusion pairs: (A) PPE 35/PSbM 43. Concentration-way profiles obtained for different compressing weights during annealing; (B) PSbM 43/PScoAN 20. Comparison between the experimental concentration-way profiles and the profiles computed using the same diffusion coefficient, D_{erf}, for both components (points connected by full line).

mastercurves, three different diffusion coefficients were estimated, which could be defined as

- $D_{(xs)}$, at the coordinate x_s, characterized by the criterion of dividing the areas delimited by the vertical at the coordinate x_s and the mastercurve along the interphase in two identical areas (see insert in Fig. 5A),
- $D_{(x=0)}$, at the optical interphase boundary (i.e. the reference point of all FT-IR scans) and
- D_{med}, a mean value of the diffusion coefficients, D_{xc}, estimated for an interphase range delimited between -20 and $+20$ µm using the expression

$$D_{xc} = -(1/2t)(\mathrm{d}x/\mathrm{d}c)\int_0^{c_1} x\,\mathrm{d}c.$$

The almost symmetrical concentration-way profiles, shown in Fig. 5A, point to satisfactory constancy of the diffusion coefficients. The symmetry is connected with the condition that, assuming a step function the concentration is at $x = 0$ for any step $t > 0$ always $c = 0.5c_0$. Thus, the expression recommended by Crank and Henry [16]

$$c_{(x,t)} = (1/2)c_0\,\mathrm{erf}[1 - (x/2\sqrt{Dt})]$$

can be used to calculate a theoretical concentration-way profile for supposed 'constant' diffusion coefficients, using tabulated values of the 'error-function', erf.

In Fig. 5B, the experimentally determined way-dependent diffusion coefficients of the interdiffusion pair PScoAN 20//PSbM 78 with this 'theoretical' values calculated according to the expression of Crank and Henry and using a constant 'mean' diffusion coefficient are compared. The accordance is satisfactory, the deviations being in the limit of experimental errors, confirming thus the validity of the assumption of constant diffusion coefficients for the interdiffusion of the studied contacting polymer pairs.

The calculated values of the diffusion coefficients are shown in Table 2 for the different studied interdiffusion pairs PPE/PSbM and in Table 3 for the pairs PScoAN/PSbM, respectively.

The data obtained for the different PPE/PSbM pairs certify the general tendency of decreasing diffusion coefficients with increasing molecular weight. This results if, for instance, the values of the diffusion coefficients for the diffusion pairs PPE 15//PSbM 43, PPE 35//PSbM 43 and PPE 35//PSbM 78, respectively are compared (see Table 2).

Table 2
Diffusion coefficients of diffusion pairs PPE/PSbM (influence of molecular weight and compressing weight)

Diffusion pair	T (°C)	Annealing time (h)	Pressing weight (g)	$D_{(xs)} \times 10^{-12}$ (cm^2/s)	$D_{(X=0)} \times 10^{-12}$ (cm^2/s)	$D_{\mathrm{med}} \times 10^{-12}$ (cm^2/s)	$D_{\mathrm{erf}} \times 10^{-12}$ (cm^2/s)
PPE 15/PSbM 43				PPE 49	46	50	
	230	5	100	PSbM 31	31	25	40 ± 8
PPE 35/PSbM 43				PPE 7.5	7.3	6.3	
	230	23	0	PSbM 6.7	6.5	5.9	6.9 ± 1.4
				PPE 8.4	8.4	7.3	
	230	23	50	PSbM 5.6	5.7	5.5	7.1 ± 1.4
				PPE 14	13	11	
	230	23	100	PSbM 6.3	6.5	6.6	9.8 ± 2.0
PPE 35/PSbM 78				PPE 7.5	7.5	9.5	
	230	23	50	PSbM 13	12	14	11.0 ± 2.1

Table 3
Diffusion coefficients of diffusion pairs PScoAN/PSbM (influence of molecular weight)

Diffusion pair	T (°C)	Anneal. time (h)	Pressing weight (g)	$D_{(xs)} \times 10^{-12}$ (cm^2/s)	$D_{(x=0)} \times 10^{-12}$ (cm^2/s)	$D_{\mathrm{med}} \times 10^{-12}$ (cm^2/s)	$D_{\mathrm{erf}} \times 10^{-12}$ (cm^2/s)
SAN 20[a]/PSbM 43				SAN 2.0	0.84	1.3	
	180	77.5	0	PSbM 2.9	2.4	2.8	0.9 ± 0.18
SAN 20/PSbM 78				SAN 0.51	0.71	0.67	
	180	77.5	0	PSbM 1.7	1.4	1.4	1.0 ± 0.2

[a] SAN 20 stays for PscoAN 20.

Taking account of the results shown in Table 2 for the PPE35/PSbM43 pair, it may be supposed that the use of additional pressing weights is not noticeably influencing the diffusion of the contacting polymers. The small differences observed between the values of the diffusion coefficients for different pressing weights may be attributed to the fact that in our calculations, possible volume changes, within the interdiffusion region which may influence diffusion, were neglected. It is worth mentioning that the diffusion coefficients reported in Tables 2 and 3 are of the order of magnitude of the values reported in the literature.

So, it is interesting to notice that for the pair PSAN (i.e. PScoAN) 25/PMMA, Yukioka et al. [17] have measured by ellipsometry for the temperature range of 115–130°C interdiffusion coefficients of the order $D = 10^{-15}$–10^{-16} cm^2/s. Taking account of the diffusion coefficients of the order of 10^{-12} cm^2/s, reported in Table 3 for the compatible pair PSbM/PScoAN 20 for 180°C, it may be supposed that the respective values are consistent. The difference between the values may be explained by both the WLF-like temperature behaviour of diffusion coefficients [14] and the fact that Yukioka et al. have analysed the interdiffusion between the higher molecular PSAN 25 and PMMA homopolymer, whereas we have studied the interdiffusion between the lower molecular PScoAN 20 and the compatible PMMA block of the PSbM 43 block copolymer.

Generally, values of diffusion coefficients reported in the literature for polymers oscillate between 10^{-12} and 10^{-16} cm^2/s [18]. Thus, for instance, Kramer et al. [19] indicate for the tracer diffusion of PS ($M_w = 110,000$), at 50°C, a value of $D^* \sim 3.0 \times 10^{-13}$ cm^2/s, whereas Straub et al. [20] report for modified poly(arylethersulphone)s diffusion coefficients of the order of 10^{-14}–10^{-15} cm^2/s at 195°C. For the compatible PMMA/PVF (i.e. poly(vinylidene fluoride)) pair Wu et al. [21] indicate for PMMA ($M_w = 150,000$) an interdiffusion coefficient of $D_{\mathrm{PMMA}} = 4.0 \times 10^{-11}$ cm^2/s measured at 150°C, whereas Maas et al. [22] report for the same pair at 190°C values of $D_{\mathrm{PMMA}} = 7.10^{-11}$ cm^2/s ($M_w = 100{,}000$) and of $D_{\mathrm{PVF2}} = 15.10^{-11}$ cm^2/s ($M_w = 500{,}000$), respectively.

The diffusion coefficients presented in Tables 2 and 3 show generally a mean error of 25% for the $x = 0$ reference position (i.e. the optically evaluated interphase boundary). The errors are generally larger and called by us 'negative' range, defined as the range of interpenetration by diffusion of the miscible polymer component from the own bulk phase through the interphase into the bulk phase of the countercomponent of the polymer pair. In the own phase, i.e. the 'positive' range, the errors are below 5%.

The D_{erf} values, which were evaluated using a mean value, D_{med}, of the individual diffusion coefficients evaluated for the ± 15 μm interphase range, show a maximum error of 20%. These errors are due mainly to deviations of the experimentally measured individual profiles from the mean concentration-way 'masterprofiles' i.e. they correspond to the scatter of the experimental data around the mean value. A comparison of the experimental concentration-way profiles with the profiles computed using the constant diffusion coefficient, D_{erf}, evidenced in Fig. 5B for the compressed polymer pair PSbM 43/PScoAN 20, confirms larger errors of D_{erf} coefficients. Additional measurements have provided evidence to the fact that the main source of errors is related mainly to the unsatisfactory reproductibility of the computer-aided displacement across the contacting interface of the *X*/*Y*-slide of the microscope attached to the FT-IR instrument.

In conclusion, scanning FT-IR measurements can be used both to confirm the development of interphases between contacting compatible polymer pairs and to evaluate interdiffusion coefficients. The inherent errors of the method can be reduced, mainly by improving the movement of the *XY*-slide of the microscope attached to the FT-IR instrument. The decisive condition for sensible diffusion measurements is, however, the presence of specific, well-defined IR bands of the individual components of the interdiffusion pair studied.

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