Compatibility effect on moisture diffusion in polyimide blends

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Blends of rod-like PMDA–B (pyromellitic dianhydride–benzidine) and semi-flexible 6FDA–PDA (6F-dianhydride–phenylenediamine) polyimides with several different compositions were prepared. According to the results from X-ray diffractometry and *FT*i.r. spectrometry, these two polyimides are incompatible when mixed at room temperature for 20 min. When mixed at 50°C for 40 h, the polymers, thermodynamically incompatible, become compatible owing to exchange reactions. Bending beam diffusion experiments show that the diffusion of moisture in these films belongs to case I. The diffusion constant D is 0.10×10^{-9} cm^2 s^{-1} in PMDA–B and 1.65×10^{-9} cm^2 s^{-1} in 6FDA–PDA. In the blends, D increases with increasing content of 6FDA–PDA. The slow diffusion in PMDA–B can be attributed to its highly crystalline structure and relatively small interchain spacing. The diffusion of moisture is faster in the compatible films. Regardless of compatibility, diffusion in all the blends is much slower than in pure 6FDA–PDA. This can be attributed to the comparatively small average interchain spacings of the blends.

(Keywords: polyimide blend; compatibility; case I diffusion; X-ray diffractometry; *FT*i.r.)

INTRODUCTION

Polyimides have many important applications in microelectronic packaging[1–4]. They have several excellent properties, such as a low dielectric constant. However, in order to retain or improve the dielectric property, moisture uptake in imide films should be minimized, otherwise the dielectric constants and the level of dielectric loss will increase[5–7]. Moisture uptake may also have other undesired effects, mechanically as well as electrically[8–10]. Therefore there is a need to understand the diffusion behaviour of moisture in polyimides.

Diffusion of water in polyimide films has been studied for some years[11–19]. However, only Numata *et al.*[11] and Jou *et al.*[12] have attempted to correlate the diffusion characteristics with the structure of polyimide films. The former group examined the dependence of the diffusion constants of moisture on the film packing coefficient in various polyimide films. The latter group investigated the effects of the morphologies and chemical structures of several different polyimide films on water diffusion. In that study, the diffusion of water in two different blends were also studied. However, the two blends were both compatible. Hence the main purpose of the present study was to investigate the effect of compatibility on the diffusion of moisture in the blends of rigid PMDA–B (pyromellitic dianhydride–benzidine) and semi-flexible 6FDA–PDA (6F-dianhydride–phenylenediamine) polyimides. To determine the diffusion behaviour and diffusion constants of moisture in the two polyimides and their blends, a bending beam technique was used. Theoretical details concerning the formulae for the bending beam diffusion measurement are presented in a separate paper[20]. This technique enabled the diffusion mechanism as well as the diffusion constants to be determined.

EXPERIMENTAL

Reagents

The dianhydrides used were pyromellitic dianhydride (PMDA) and hexafluoroisopropylidene-2,2-bis(phthalic acid anhydride) (6FDA). The diamines were *p*-phenylenediamine (PDA) and benzidine (B). The solvent was *N*-methylpyrrolidone (NMP). These reagents were used as received.

Polycondensation of polyamic acids

6FDA–PDA and PMDA–B polyamic acids were prepared as follows[21]. In a four-neck round-bottom flask equipped with a stirrer and a tube for introducing nitrogen, the diamine (PDA or B) was dissolved in the NMP. When the diamine had been completely dissolved, an equimolar amount of dianhydride (PMDA) was gradually added. After dissolution of the dianhydride, the reaction was continued for 5 h with stirring. The entire process was conducted under nitrogen. The resulting solution had a solid content of 14 wt%. The molecular structures of the resulting polyamic acids after curing to solid imides are shown in *Figure 1.*

Polyblends

Blends of 6FDA–PDA and PMDA–B with various compositions were obtained by mixing the two polyamic acids at room temperature for 20 min under nitrogen. Another batch was prepared in the same way, but heated at 50°C for 40 h. The resulting mixtures were kept frozen before use.

X-ray diffractometry

Solid films of the polyamic acids were prepared by spin-casting the solutions on glass substrates and then

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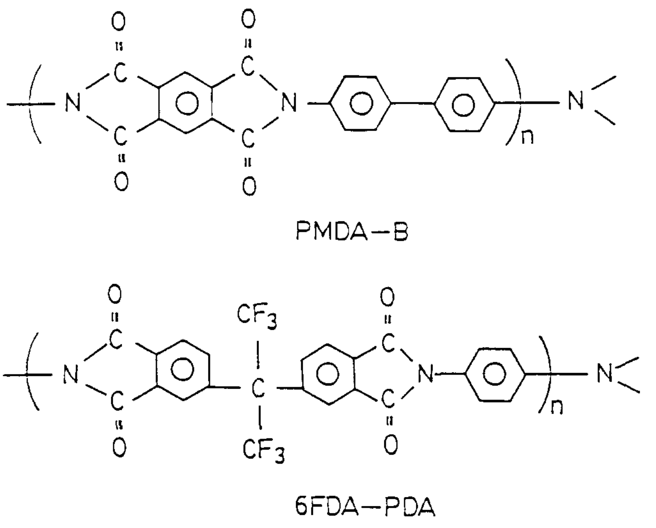

Figure 1 Molecular structures of the polyimides studied

prebaking at 80°C for 30 min. Thermal curing was performed by heating from 80 to 350°C in 3 h. The resulting polyimide films were about 20 μm thick. For X-ray diffraction measurements, several layers of the films were stacked together. In this study, only the out-of-plane structures were determined. Details regarding X-ray and *FT*i.r.-a.t.r. specimen preparation and experiments can be found elsewhere[22].

Bending beam diffusion experiment

For bending beam diffusion experiments, polyimide films were prepared by casting their polyamic acid solutions directly on silicon strips. Details regarding specimen preparation and bending beam diffusion experiments are given elsewhere[12]. Upon uptake of moisture, the polyimide film swelled and the substrate bent accordingly. By measuring the ratio Ω of bending curvature change with respect to diffusion time, the diffusion mechanism can be identified and the diffusion constant D in case I diffusion can be calculated[20]. The ratio Ω is defined as

$$\Omega = \frac{1/R_t - 1/R_0}{1/R_\infty - 1/R_0} \tag{1}$$

where $1/R_0$ is the initial bending curvature, $1/R$ the bending curvature at equilibrium, and $1/R_t$ the bending curvature at a given time t.

Within a relatively short period of diffusion time, D can be calculated according to the following approximate expression[20]:

$$\Omega = 2\left(1 + \frac{K}{2}\right)\left(\frac{Dt}{d_f^2}\right)^{1/2}(\pi^{-1/2}) \tag{2}$$

where D is the diffusion coefficient of moisture in a given polyimide film, t is the diffusion time, d_f is the thickness of the polymer film, and $K = 2d_f/(d_f + d_s)$, where d_s is the substrate thickness.

RESULTS AND DISCUSSION

X-ray diffraction

Figure 2 shows the out-of-plane diffraction patterns of the films of PMDA–B, 6FDA–PDA, and their blends. As compared, the film of PMDA–B is relatively crystalline, while that of 6FDA–PDA is amorphous. Since these two polyimide films have very different diffraction patterns, one can distinguish whether the blends are compatible from their diffraction patterns, according to Jou and Huang[22]. For the blend containing 25% 6FDA–PDA and 75% PMDA–B, mixed at room temperature for 20 min, the diffraction pattern still retains the crystalline characteristics of the PMDA–B film. The diffraction intensity of its main peak is still quite high and is nearly proportional to the content of PMDA–B, indicating that the blend is incompatible. As mentioned elsewhere[22–24], exchange reactions may occur between the amic acid chains of any two polyimides in the soluble precursor stage. If exchange reactions occur, any thermodynamically incompatible blend will gradually become 'compatible' with time and eventually become a random copolymer, as demonstrated by the X-ray diffraction results of Jou and Huang[22]. Here, when the two polyimides are mixed for a much longer period of time at a higher temperature, i.e. 40 h at 50°C, the blend becomes 'compatible', as indicated by its relatively weak diffraction pattern, *Figure 2(c)*. As seen in *Figure 2*, the reduction in the diffraction intensity from incompatible to 'compatible' can be attributed to the irregular structures resulting from the intermixing of the two different imide chain segments.

Similarly, in the blends of 6FDA–PDA and PMDA–B with compositions of 50:50 and 75:25, the diffraction patterns vary with the mixing time and temperature, as shown in *Figure 3*. The blends mixed at room temperature for 20 min, which are presumed incompatible, do indeed exhibit a stronger diffraction intensity than those mixed at 50°C for 40 h, which are presumed compatible. These blends contain less PMDA–B than does the 25:75 blend, so all their diffraction intensities are much weaker, regardless of compatibility. Consequently the difference between the diffraction patterns of the differently mixed samples with the same composition becomes less prominent, as can be seen. Though the difference is not very marked, it does originate from the difference in the compatibilities of the differently prepared samples. This was confirmed by polarized light microscopy: the blend with the slightly stronger diffraction intensity clearly exhibited a two-phase structure and can be identified as

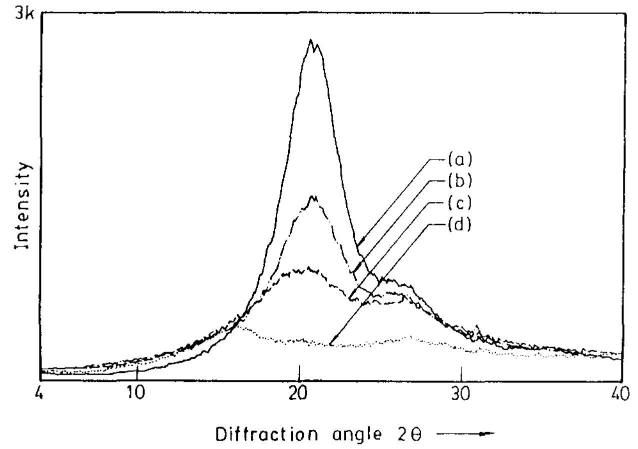

Figure 2 X-ray diffraction patterns of polyimide films of (a) PMDA–B, (b) a presumed incompatible blend (25% 6FDA–PDA and 75% PMDA–B, mixed at room temperature for 20 min), (c) a presumed compatible blend (25% 6FDA–PDA and 75% PMDA–B, mixed at 50°C for 40 h), and (d) 6FDA–PDA

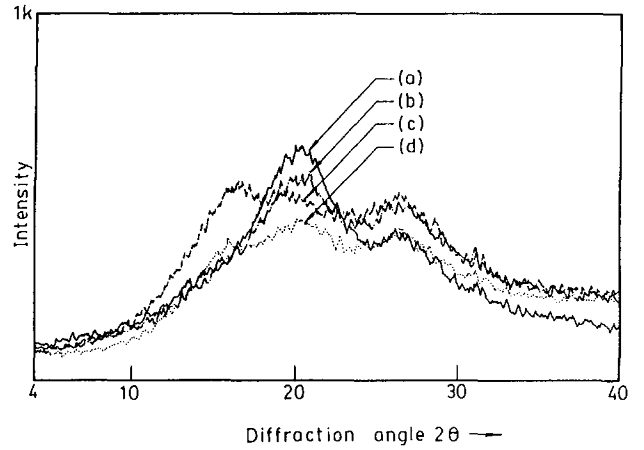

Figure 3 X-ray diffraction patterns of polyimide films of (a) a presumed incompatible blend (50% 6FDA-PDA and 50% PMDA-B, mixed at room temperature for 20 min), (b) a presumed compatible blend (50% 6FDA-PDA and 50% PMDA-B, mixed at 50°C for 40 h), (c) a presumed incompatible blend (75% 6FDA-PDA and 25% PMDA-B, mixed at room temperature for 20 min), and (d) a presumed compatible blend (75% 6FDA-PDA and 25% PMDA-B, mixed at 50°C for 40 h)

incompatible, while that with the weaker diffraction intensity exhibited a uniform phase and can be identified as compatible.

FT*i.r.–a.t.r.*

Figure 4 shows the *FT*i.r.–a.t.r. results for the same blend series. Plots (a) and (b) are for the presumed compatible and incompatible samples, respectively. As shown, the crystalline PMDA-B film has a C=O absorption peak at 1714.9 cm^{-1}, while that of the amorphous 6FDA-PDA film occurs at 1724.2 cm^{-1}. According to other work[25,26], a change from crystalline to amorphous shifts the C=O peak from a lower to a higher wavenumber. The results shown here agree with this: the C=O peak wavenumber of the PMDA-B film is lower than that of the 6FDA-PDA film. This again proves that the PMDA-B film is much more crystalline than the 6FDA-PDA film, as shown by X-ray diffractometry. If the blends are compatible, their films will be amorphous as revealed by X-ray diffractometry. Their C=O absorption peaks will therefore shift to higher wavenumbers towards that of the amorphous 6FDA-PDA film, i.e. at 1724.2 cm^{-1}. If they are incompatible, their films will retain the crystalline characteristics of PMDA-B, and their C=O absorption peak positions should shift much less, if at all. As demonstrated by *Figure 4*(*b*), the C=O peaks of the incompatible series appear at comparatively low wavenumbers and are very close to that of the pure PMDA-B. This indicates that these blends are indeed incompatible. In *Figure 4*(*a*), the peak positions shift significantly away from that of the pure PMDA-B and towards that of the pure 6FDA-PDA, showing that the blends are compatible and their structures are more amorphous, if not completely so.

Figure 5 shows the C-N absorption peaks for the two different blend series. The crystalline PMDA-B film has a peak at 1358.4 cm^{-1}, while that of the amorphous 6FDA-PDA film is at 1355.7 cm^{-1}. Contrary to the behaviour of the C=O absorption, on changing from crystalline to amorphous, the C-N peak shifts from a higher to a lower wavenumber[25,26]. Unlike that of the C=O absorption, the difference between the C-N peak wavenumbers of the crystalline PMDA-B and amorphous 6FDA-PDA films is comparatively small. Nevertheless, the C-N peak wavenumbers of the incompatible blends are all higher than those of the compatible ones. For example in the 50:50 blends of 6FDA-PDA and PMDA-B, the C-N peak wavenumber is 1358.0 cm^{-1} for the compatible film and 1360.0 cm^{-1} for the incompatible one. This indicates that the crystallinity of the incompatible blend is higher. Similarly, in the blends of other compositions, the crystallinity of the films is higher in cases of incompatibility.

Moisture diffusion

Figure 6 shows a typical result for moisture diffusion in a polyimide film (pure PMDA-B) measured by the bending beam apparatus. As is seen, the ratio Ω of bending curvature change initially varies linearly with $t^{1/2}$. This means that the diffusion of moisture in the film of PMDA-B belongs to case I, according to equation (2). The diffusion constant calculated is 0.10×10^{-9} cm^2 s^{-1}. The diffusion constant could also be obtained using the model presented by Berry and Pritchet[27]. However, this would require a very complicated numerical computation.

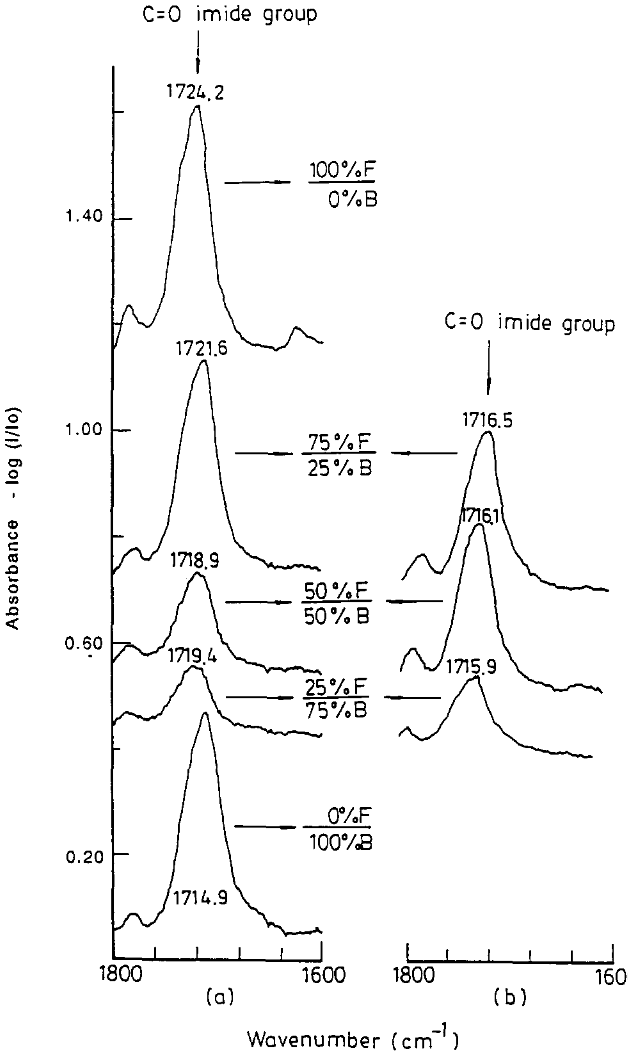

Figure 4 *FT*i.r.–a.t.r spectra of the C=O absorptions of imide films of blends of 6FDA-PDA (F) with PMDA-B (B) with various compositions: (a) compatible series, (b) incompatible series

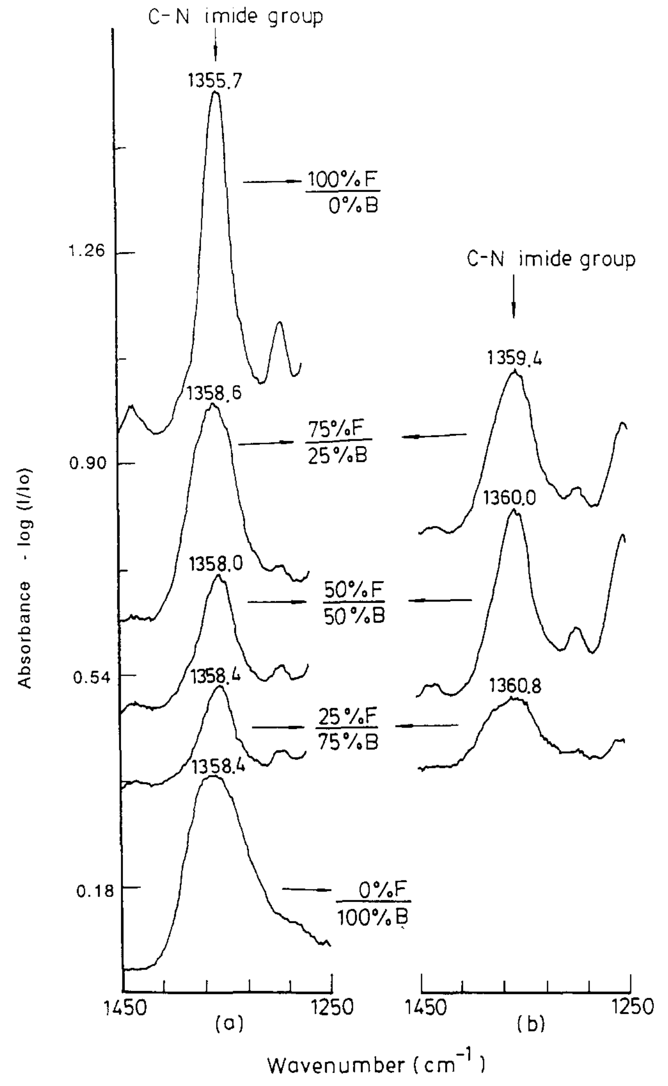

Figure 5 *FT*i.r.-a.t.r. spectra of the C–N absorptions of imide films of blends of 6FDA–PDA (F) with PMDA–B (B) with various compositions: (a) compatible series, (b) incompatible series

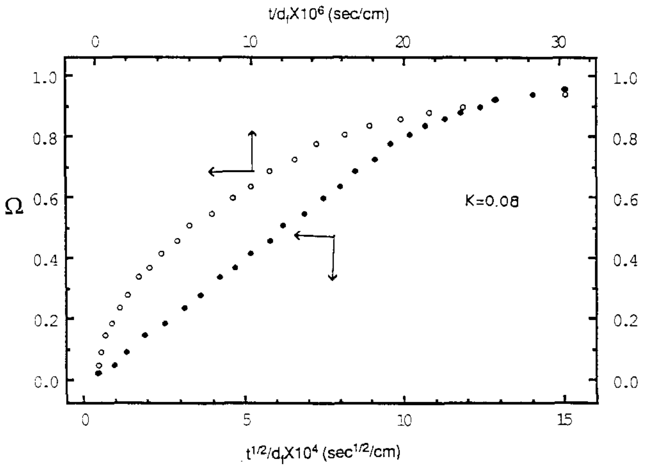

Figure 6 Measured ratio Ω of bending curvature change as a function of diffusion time and its square root for the diffusion of moisture in the imide film of rod-like PMDA–B at room temperature and 55% r.h.

As presented in the study[12] in which Berry's model was applied, the diffusion of water in various polyimides differing from those of the present study invariably belonged to case I.

Compared with that in the PMDA–B film, the diffusion of moisture in the 6FDA–PDA film is much faster. The diffusion constant calculated is 1.65×10^{-9} cm^2 s^{-1}. *Figure 7* shows the bending beam diffusion result. According to the imide structures of these two polyimides, one can at least attribute the faster diffusion in the 6FDA–PDA film to its irregular chain structure. Furthermore, the X-ray diffraction patterns show that the amorphous 6FDA–PDA film has a relatively large interchain spacing, 0.54 nm. That of the crystalline PMDA–B film is 0.43 nm. Since the interchain spacing is a direct measure of the intermolecular interaction of the imide chains, a larger spacing means a weaker intermolecular interaction. As a result, small molecules could penetrate much more easily into such a film. The amorphous structure coupled with a weaker intermolecular interaction means that the diffusion of moisture in the 6FDA–PDA film should be relatively faster, as is observed. On the other hand, the crystalline PMDA–B film has a much smaller interchain spacing, so the diffusion of moisture in it is much slower.

Compatibility effect

The diffusion of moisture in the films of the compatible and incompatible blends is shown in *Figures 8* and *9*,

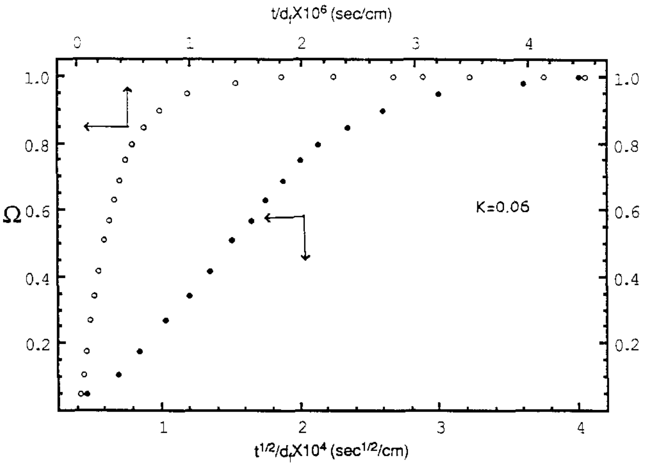

Figure 7 Measured ratio Ω of bending curvature change as a function of diffusion time and its square root for the diffusion of moisture in the imide film of semi-flexible 6FDA–PDA at room temperature and 55% r.h.

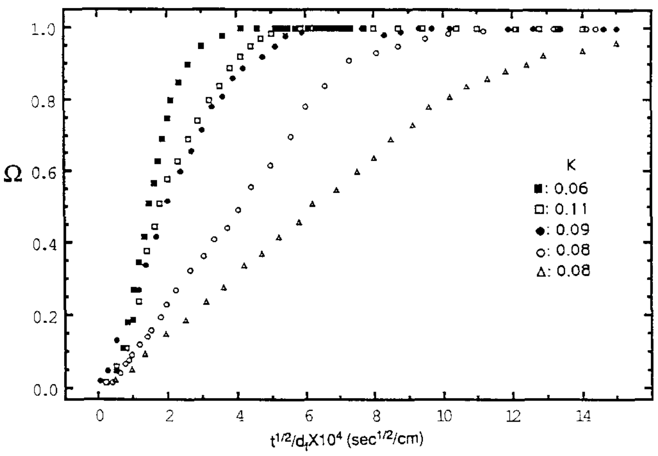

Figure 8 Measured ratio Ω of bending curve change as a function of diffusion time for the diffusion of moisture in compatible blends of 6FDA–PDA with PMDA–B. Mass ratio, 6FDA–PDA:PMDA–B: ■, 100:0; □, 75:25; ○, 50:50; ●, 25:75; △, 0:100

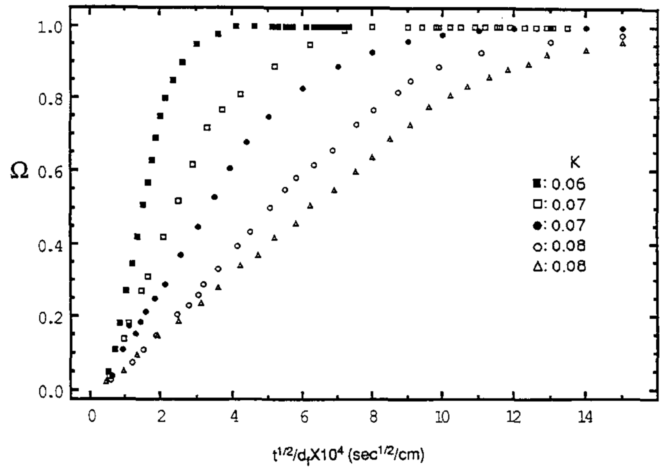

Figure 9 Measured ratio Ω of bending curve change as a function of diffusion time for the diffusion of moisture in incompatible blends of 6FDA-PDA with PMDA-B. Symbols as in *Figure 8*

Table 1 Diffusion constants of moisture in films of blends of 6FDA-PDA and PMDA-B

Mass ratio, 6FDA-PDA:PMDA-B	Diffusion coefficient ($\times 10^{-9}$ cm^2 s^{-1})
100:0	1.65
0:100	0.10
75:25[a]	0.37
50:50[a]	0.30
25:75[a]	0.14
75:25[b]	0.61
50:50[b]	0.49
25:75[b]	0.19

[a] Incompatible series
[b] Compatible series

respectively. They both clearly show that the diffusion constant increases with increasing content of 6FDA-PDA, regardless of compatibility. This result is what is expected, since it is much easier to diffuse into a film with a higher content of amorphous structures. The diffusion constants are listed in *Table 1*. However, in the compatible series, the diffusion constants are all much higher than those in the incompatible series. Apparently the diffusion of water in these polyimide films was affected by the blend compatibility. This may be attributed to the action of the segregated domains of crystalline PMDA-B in the films as diffusion barriers, since water as a non-solvent could not possibly penetrate any crystalline structure. In the case of incompatibility, the presence of the segregated crystalline domains could inhibit and hence retard water diffusion. In the case of compatibility, the crystalline domains no longer exist, so the diffusion of water molecules would be enhanced. However, the diffusion constants for the blends are relatively small, compared with that for the pure 6FDA-PDA. Although the crystalline structures of the PMDA-B imides can be greatly destroyed by introducing irregular 6FDA-PDA imides into the films, especially when the films are compatible, even for the compatible blend with 75% 6FDA-PDA, the diffusion constant is less than half that of the pure 6FDA-PDA. Obviously, besides compatibility there must be other factors which affect the diffusion of water in these films. As described elsewhere[12], one of the possible factors is the chemical nature of the imide. The large hydrophobic benzidine units in the PMDA-B imide chains might also act as a water diffusion barrier. Furthermore, as revealed above, the interchain spacing of 6FDA-PDA is much larger than that of PMDA-B. On mixing with the PMDA-B imide chains, the mean interchain spacing of the blends became much smaller than that of the pure 6FDA-PDA film. This can be inferred from the various diffraction positions of the blends in *Figures 2* and *3*. Therefore one may also attribute the slow diffusion of water in the films of the blends to their larger intermolecular interaction forces compared with those of the pure 6FDA-PDA film.

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