Interdiffusion of free and grafted poly(methylmethacrylate) with polyvinylchloride, studied by infrared spectroscopy

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As a guide for adhesion development between two miscible polymers, interdiffusion of these polymers was studied using external reflection and attenuated total reflection infrared spectroscopy. Using gold substrates coated with a double layer of PMMA and PVC, and s-polarized infrared light, PMMA features in the external reflection spectra increase upon annealing at 150°C as a result of PMMA diffusion away from the gold substrate into regions with a higher electric field intensity. Interdiffusion can also be followed with an external reflection set-up using glass substrates and p-polarized infrared light. Interdiffusion of PVC and PMMA, free or grafted on a glass slide, was observed. Increasing the molecular weight of the PMMA slows down the interdiffusion rate, which might be a consequence of a reduction in the thermodynamic driving force for diffusion or the molecular weight of PMMA. External reflection spectroscopy as well as attenuated total reflection experiments show that interdiffusion of PVC and PMMA grafted on a silicon slide was much slower than that of free PMMA of similar molecular weight.

(Keywords: interdiffusion; miscibility; poly(methylmethacrylate); poly(vinylchloride); grafting; infrared spectroscopy; external reflection; attenuated total reflection)

INTRODUCTION

Interdiffusion of two chemically different polymers as a result of a favourable thermodynamic interaction might lead to a complete mixed state after an appropriate annealing time. However, compared to low molecular species interdiffusion of polymer molecules into each other is rather slow and moreover a full theoretical description of the process is not yet possible[1–4]. Interdiffusion at the interface of two polymers will start at temperatures where the molecules become mobile enough, probably in the neighbourhood of the lowest T_g. As a result of this interdiffusion a continuously changing concentration profile will develop and the measurement of this concentration profile is of great importance for the experimental verification of the theory and also for applications where interdiffusion is an important phenomenon. An example of the latter could be the adhesion between glass fibres and a thermoplastic matrix in a composite material. Grafting of an entangled polymer network onto the fibres and interdiffusion of the matrix polymer into this layer might lead to perfect adhesion between the phases[5–11].

Commonly used techniques to measure the concentration profiles involve different scattering methods like s.a.x.s.[12], s.a.n.s.[13], r.b.s.[2] or s.i.m.s.[14], neutron reflectometry[15] or i.r. microdensitometry[16]. As a qualitative measurement of the interdiffusion process i.r.-a.t.r. was used[17]. However, we believe that the possibilities of i.r. spectroscopy have not yet been fully utilized.

In a previous publication[18] we demonstrated that, using external reflection i.r. spectroscopy with polarized light on gold and glass substrates, interdiffusion of poly(methylmethacrylate) (PMMA) and polyvinylchloride (PVC) could be followed. For gold this experimental set-up utilizes the physical phenomenon of interference of incoming and reflecting i.r. radiation near the surface. This results in a standing wave on the surface and consequently the intensity of the i.r. radiation depends, amongst others, on the distance from the surface. Therefore the absorption of a species near the surface depends on the distance from the surface. This effect can be used to measure interdiffusion of PMMA and PVC, as was shown before[18].

For glass the optical situation is more complex and the measured spectra are a result of interference, reflection and absorption of radiation.

Besides measuring the spectra as a function of interdiffusion time, spectra can also be calculated accurately for this set-up, using the matrix approach[19] for optical waves in layered media provided that the optical constants of the polymers are known. This method is further extended in this paper using PMMA samples of different molecular weights and also PMMA which was grafted onto the surface of a silicon wafer.

Similar calculations were carried out for the a.t.r. set-up and it is shown that this technique can also give valuable information on the interdiffusion of two dissimilar polymers.

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Table 1 Molecular weights of materials studied

Polymer	M_w (10^3 g mol^{-1})	M_n (10^3 g mol^{-1})	M_w/M_n
PVC	55	30	1.8
PMMA-1	100	45	2.2
PMMA-2	420	1100	2.6
PMMA-3	2500	1700	1.5
PMMA-4[a]	1700	1100	1.5
PMMA-5[b]	2500	1700	1.5

[a] PMMA grafted on a glass slide with an average surface area per coil of 1600 Å^2 and a layer thickness of 0.1 μm

[b] PMMA grafted on a silicon wafer with an average surface area per coil of 2000 Å^2 and a layer thickness of 0.12 μm

EXPERIMENTAL

Materials

PVC was obtained from Péchiney et St. Gobain (Lucovyl RB8010), PMMA-1 from ICI (Diakon MO900), and PMMA-2 and PMMA-3 were synthesized by radical polymerization in toluene at 70°C. Their molecular weights, measured by GPC (Waters ALC/GPC-150 with THF or chloroform as eluent and using polystyrene standards) are listed in *Table 1*. Gold substrates were prepared by plasma sputtering gold on cleaned microscope slides with a gold thickness of at least 100 nm. Polymer samples were prepared by spincoating a PVC solution in dichloromethane on a microscope slide, floating the polymer film off onto water and picking it up with a substrate already coated with PMMA. This PMMA layer was spincoated from toluene solutions on the substrates or grafted on glass or silicon substrates by initiation of the MMA polymerization by an immobilized radical initiator[20].

The double layer was dried overnight at 80°C *in vacuo*. For external reflection experiments the samples were used without any further preparation. For the attenuated total reflection experiments they were placed with the PVC side against a germanium crystal. By comparison of the transmission spectra of the polymer double layer on the ATR-crystal before and after the annealing experiment, no indications for degradation of either of the two polymers were found.

Infrared spectroscopy

External reflection i.r. spectra were recorded on a Bruker IFS88 spectrophotometer with a narrow band MCT detector with 4 cm^{-1} resolution at a fixed angle of incidence of 80°. Reflection spectra of gold or bare glass slides were used as reference. The thickness of the polymer films was determined by comparison of experimental spectra with simulated ones, using the optical constants as published[18].

Interdiffusion was studied by heating the double layer at 150°C and measuring the i.r. spectrum at room temperature.

Attenuated total reflection i.r. spectra were recorded on a Mattson i.r. spectrophotometer (Galaxy 6020) with a narrow-band MCT detector with 4 cm^{-1} resolution at an angle of 45°, using a germanium internal reflection element. I.r. spectral simulations were carried out as described in our previous paper[18].

RESULTS AND DISCUSSION

In *Figure 1* we show a schematic view of the set-up used for external reflection spectroscopy. Starting with a situation where the PMMA film is in contact with the mirror and the PVC film on top of the PMMA, upon interdiffusion the PMMA will diffuse further away from the mirror surface whereas PVC will be closer to the surface.

Using the 'normal' set-up for reflection spectroscopy with light polarized parallel to the plane of incidence, only small differences can be observed between the spectrum of the double layer and the spectrum of the homogeneous blend. This was also confirmed by the corresponding spectral simulations. However, using s-polarization (perpendicular to the plane of incidence), the standing wave, resulting from interference between the incoming and the reflected radiation, has a node on the gold surface, causing the electric field intensity to increase as a function of distance from the substrate. Consequently, the PMMA features in the spectrum will be enhanced by interdiffusion, because it enters a region of higher electric field intensity and simultaneously the PVC features will decrease due to movement closer to the surface. *Figure 2* shows the C=O stretching absorption intensity at 1730 cm^{-1} as a function of annealing time at 150°C, a temperature below the LCST[21] for this system and far enough above T_g to allow interdiffusion to take place. In *Figure 3* the calculated intensity of the carbonyl absorption of homogeneous, mixed layers consisting of a fixed amount of PMMA, corresponding to a layer thickness of 0.15 μm and a varying amount of PVC, is calculated as a function of the total layer thickness, illustrating the maximum effects which can be expected when PMMA is allowed to diffuse away from the substrate.

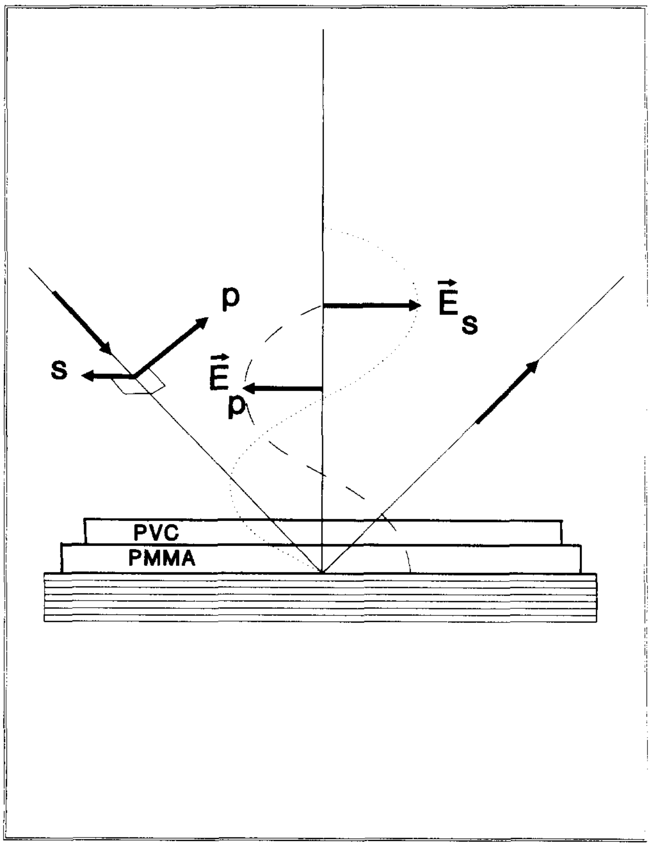

Figure 1 Schematic representation of the set-up for external reflection experiments

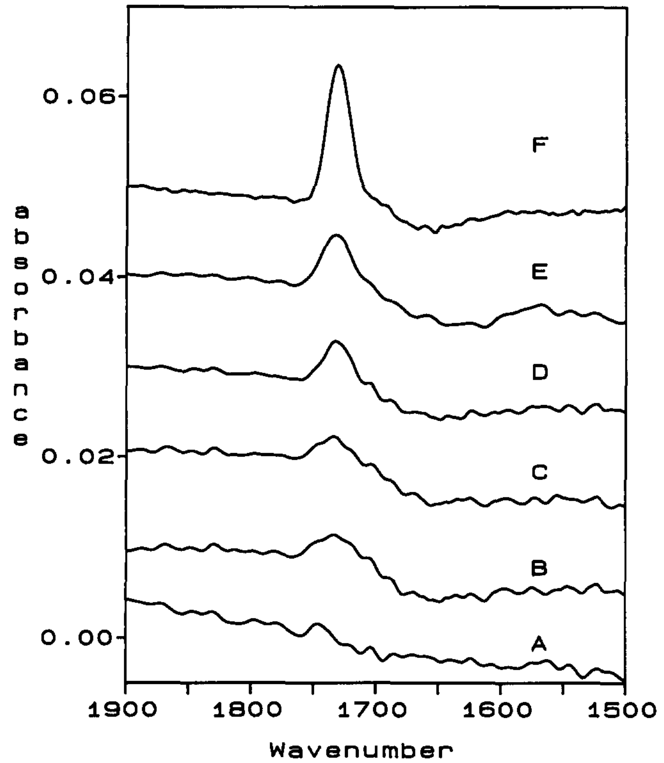

Figure 2 Experimental external reflection i.r. spectra of a double layer PMMA-1/PVC (0.15 μm/0.42 μm) on a gold substrate after: A, 0 h; B, 1/2 h; C: 1 h; D: 2 h; E, 4 h; and F: 29 h annealing at 150°C. The spectra have been *y*-shifted for clarity

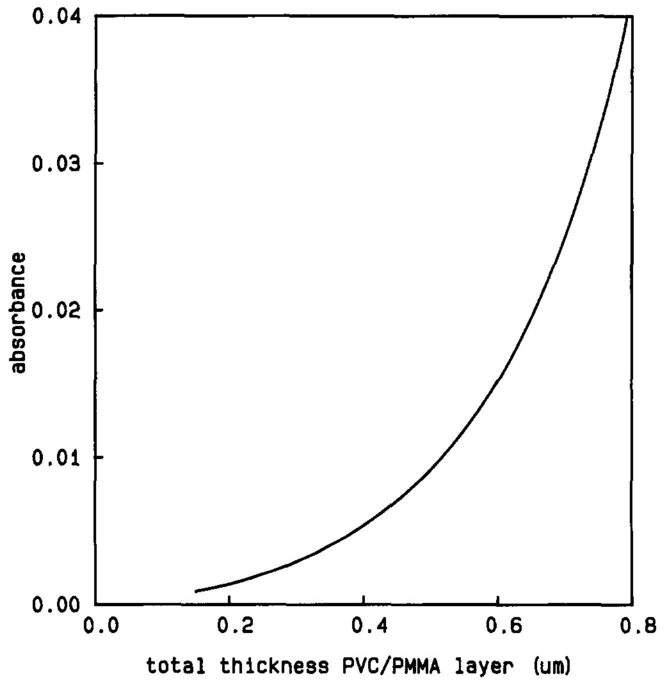

Figure 3 Absolute values of the carbonyl absorption of simulated external reflection i.r. spectra on gold of layers of 0.15 μm PMMA mixed with PVC as a function of total layer thickness

In this experiment the molecular weight of PMMA is much higher than that of PMMA used before[18], as can be seen from *Table 1*. This leads to a slower rate of interdiffusion as is shown in *Figure 4*, where the absorbance of the C=O band is plotted as a function of annealing time for both molecular weight PMMAs. The limiting value for the carbonyl band intensity of the completely mixed system, which is 0.014 according to the computer simulation, was reached after 2 h annealing in the case of PMMA-1/PVC and only after 29 h for PMMA-3/PVC.

Figure 5 shows the changes in the spectra in the C–H stretching vibrations region only for the unmixed

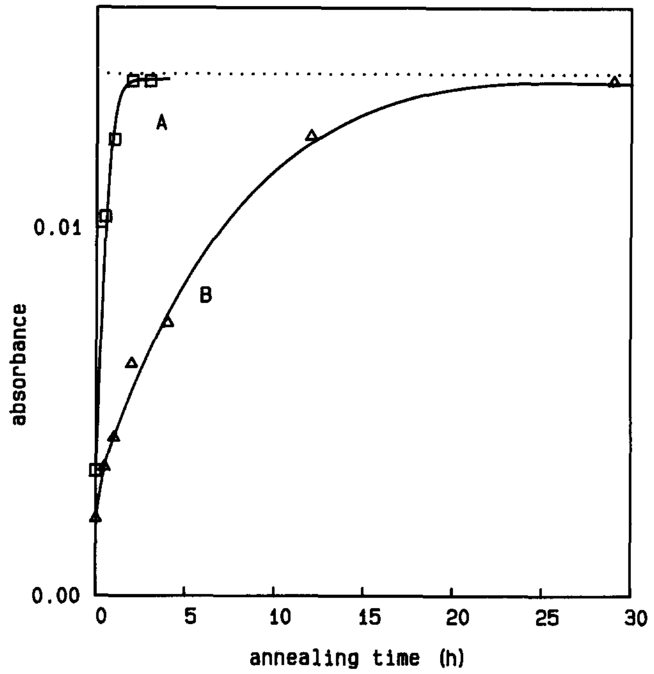

Figure 4 Absolute values of the carbonyl absorption of experimental external reflection i.r. spectra of double layers of: A, PMMA-1/PVC (0.15 μm/0.43 μm); and B, PMMA-3/PVC (0.15 μm/0.42 μm) as a function of annealing time. Spectral simulations reveal that the value of the mixed system is 0.014, indicated by the dotted line

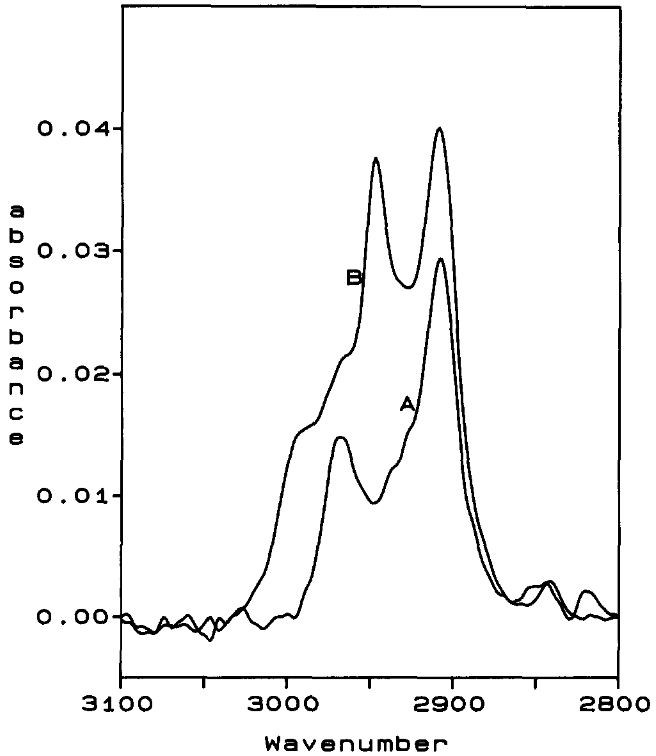

Figure 5 Experimental external reflection i.r. spectra of the C–H stretching region of a double layer PMMA-1/PVC (0.15 μm/ 0.42 μm) on a gold substrate after: A, 0 h; B, 29 h annealing at 150°C. The spectra are baseline corrected

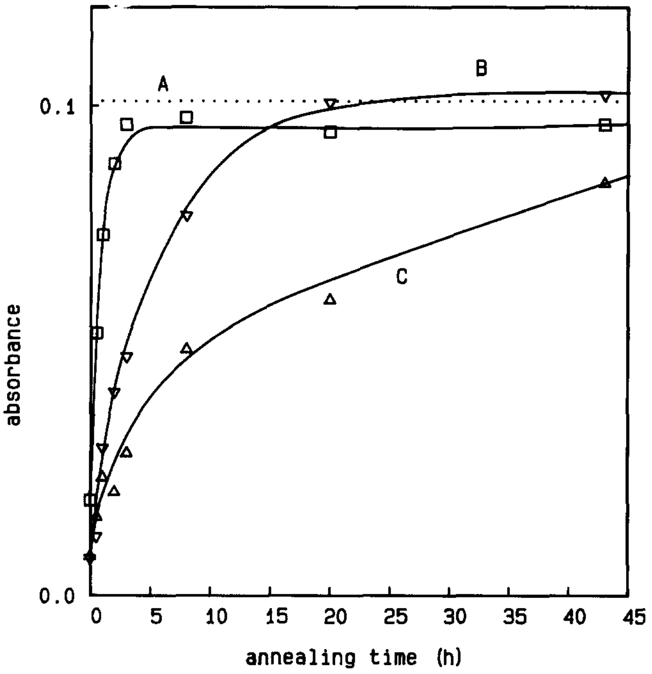

Figure 6 Absolute values of the carbonyl absorption of experimental external reflection i.r. spectra on gold of double layers of: A, PMMA-1/PVC; B, PMMA-2/PVC; and C, PMMA-3/PVC (all 0.2 μm/0.7 μm) as a function of annealing time. Spectral simulations reveal that the value of the mixed system is 0.101, indicated by the dotted line

two-layer system and for the completely mixed system. Clearly bands of PMMA (2947 and 2995 cm^{-1}) appear in the spectrum after annealing.

Increasing the thicknesses of the layers up to 0.2 μm PMMA and 0.7 μm PVC as shown in *Figure 6* still yields similar results, but evidently leads to larger diffusion times for the double layer before complete mixing is attained. Interdiffusion appeared to be complete after 3 h at 150°C for the PMMA-1/PVC system and after 20 h for the PMMA-2/PVC couple, but for PMMA-3/PVC mixing is not complete even after 43 h. The small differences in absorption values at 43 h (*Figure 6* A and B) can arise from very small differences in thickness of the double layer, but do not influence the characteristics discussed below. With increasing molecular weights of PMMA the diffusion rate decreases, which might be due to a shift of the spinodal curve to lower temperatures[21] or to a decrease of the intrinsic diffusion coefficient because of the higher molecular weight. At constant temperature, a shift of the spinodal curve would diminish the driving force for interdiffusion. A similar effect has recently been found for the polymer couple PMMA/SAN[22].

External reflection i.r. spectroscopy to study polymer interdiffusion is not restricted to metallic surfaces as substrates; even silicon or glass slides can be used. These substrates have the advantage that they can be modified chemically more easily than metallic surfaces. In our previous article[18] we have shown that interdiffusion of a double layer of PMMA and PVC on glass can be studied using p-polarized i.r. light in an external reflection experiment. This method appeared to be more sensitive to early stages of interdiffusion: already after 1/2 h annealing the spectrum was identical to the spectrum of the completely mixed system, whereas the same experiment on a gold substrate using s-polarized light exhibited changes up to 2 h. This sensitivity to the early stages of the interdiffusion was confirmed by preliminary spectral simulations using assumed interdiffusion profiles, describing subsequent stages of the interdiffusion process. In *Figure 7a* we present the spectra of PMMA-1/PVC (0.15 μm/0.48 μm), PMMA-3/PVC (0.2 μm/0.7 μm) in *Figure 7b* and (grafted) PMMA-4/PVC (0.1 μm/0.5 μm) in *Figure 7c*, as a function of annealing time. The decrease of the central dip of the carbonyl absorption upon annealing indicates that PMMA and PVC are mixing. It is clear that the interdiffusion is much slower in the experiments in *Figure 7b* than *Figure 7a*. Because the difference in layer thicknesses used in *Figure 7a* and *7b*, cannot account for the large difference in diffusion rate, as can be concluded from *Figure 4A* and *Figure 6A*, it seems reasonable to suppose that the higher molecular weight of PMMA-3 compared to that of PMMA-1 lowers the interdiffusion rate with PVC, as was also observed in the experiments with s-polarized light using gold substrates. *Figure 7b* shows that after 23 h, interdiffusion is not yet complete and only after 44 h are the experimental and simulated spectra for a mixed system identical. This does not necessarily mean that the layers are completely mixed, as can be concluded from the results of *Figure 6C*. Except for different absolute values of absorption, which arise from different thicknesses of both systems, we see similar characteristics in *Figure 7b* and *7c*. This means that the double layer, composed of (grafted) PMMA-4 and PVC is at least partially mixed after annealing for 35 h. Again we cannot conclude whether the end situation, total mixing, has already been

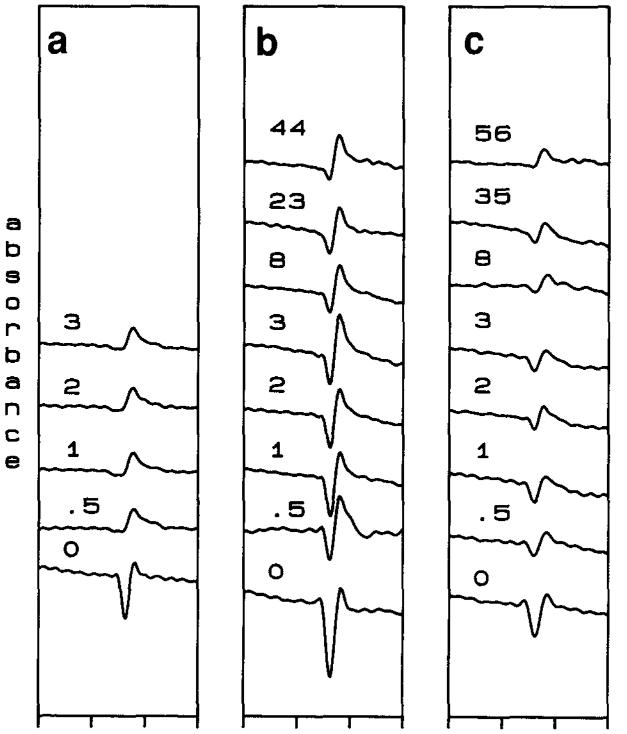

Figure 7 Experimental external reflection i.r. spectra on glass with p-polarization of double layers of: (a) PMMA-1/PVC (0.15 μm/0.48 μm); (b) PMMA-3/PVC (0.2 μm/0.7 μm); and (c) PMMA-4/PVC (0.1 μm/0.5 μm). The annealing times (h) at 150°C are shown. The spectra were y-shifted for clarity

reached, because of the mentioned low sensitivity of this set-up for the last stages of the interdiffusion process. As far as we can deduce the interdiffusion rate from these experiments, we see no major differences between free and grafted high molecular weight PMMA in mixing with PVC.

Another way to study interdiffusion of polymers is a.t.r. spectroscopy. We used this technique on a sample of PMMA grafted upon a silicon wafer (PMMA-5, 0.12 μm), which was coated with a PVC film (0.5 μm) and brought into contact with the a.t.r. crystal (*Figure 8*). The fact that contact between sample and crystal cannot be expected to be perfect, affects firstly the absolute intensity of the spectra, causing lower intensities than the simulated spectra for which perfect contact was assumed. Secondly the relative absorptions might be affected, because the penetration depth of the electric field, the so-called evanescent field, is dependent on the wavelength[23]. To account for this problem, we used the 1430 cm^{-1} band of PVC as an internal standard, for scaling of the PMMA carbonyl band at 1730 cm^{-1}. Because of the proximity of these two bands we can neglect in a first approximation the effect of the different penetration depth of the evanescent field as a function of the wavelength. When doing so, we observe that the carbonyl band grows relative to the 1430 cm^{-1} band upon annealing (*Figure 8*). After 5 days' annealing at 150°C the ratio of the intensities of the 1730 and the 1430 cm^{-1} bands (*Figure 8* D) is still smaller than that of the simulated spectrum for a completely mixed system (*Figure 8* F). This ratio is only reached after 11 days of annealing, which is much longer than the 29 h given in *Figures 2* and *4* for (free) PMMA-3/PVC interdiffusion, in which the same molecular weights and comparable film thicknesses were used.

Although the shapes of the electrical field intensities of the external and internal reflection set-ups are very different, spectral simulations, comparing both techniques using the same layer thicknesses and hypothetical interdiffusion profiles, revealed that the time scale of the increase of the carbonyl absorption will not exhibit major differences. This means that the increase of the carbonyl band upon annealing of the bilayer described above (0.12 μm PMMA/0.5 μm PVC), measured with external or internal reflection spectroscopy, is very similar. This allows us to compare the results of both techniques, showing that grafting of PMMA greatly slows down its interdiffusion rate. The fact that all PMMA chains are linked to the silicon wall might imply that swelling of the PMMA layer, resulting from penetration of PVC, can only be achieved by stretching of the PMMA chains, which is opposed by elastic forces resulting in slower diffusion than for unlinked PMMA chains.

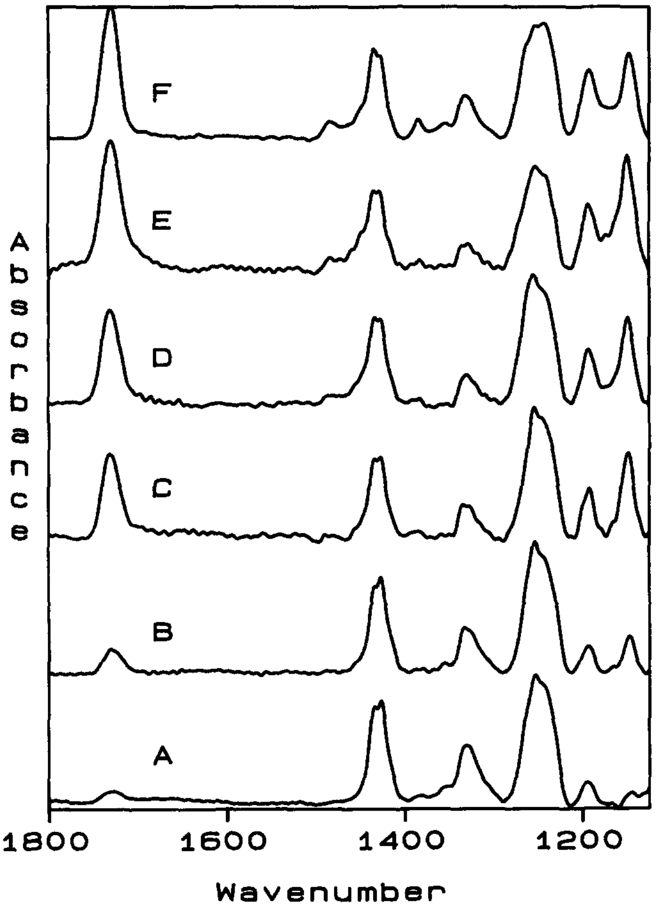

Figure 8 Experimental attenuated total reflection i.r. spectra of silicon slide grafted PMMA and PVC double layers after: A, 0 h; B, 1.5 h; C, 4 days; D, 5 days and E, 11 days annealing at 150°C. F is the simulated spectrum of the completely mixed system. All spectra were scaled on the largest band, because the absolute intensities were not the same in all cases due to differences in contact between PVC and crystal. The PVC side of the double layer was placed against the germanium crystal

CONCLUSIONS

We studied interdiffusion of two miscible polymers, *viz.* PMMA and PVC, using external reflection and attenuated total reflection i.r. spectrometry. On a gold substrate with respectively a PMMA and PVC layer and s-polarized i.r. light, we observe increasing PMMA features in the spectra upon annealing at 150°C, indicating interdiffusion of the polymers. On glass substrates, using p-polarized light, differences between mixed and unmixed layers could also be clearly distinguished.

Increasing the molecular weight of PMMA results in a lower rate of interdiffusion. This may be explained by a shift of the spinodal curve to lower temperatures, as reported in the literature[21], which, at a constant annealing temperature, will lower the driving force for interdiffusion. Infrared spectroscopy on glass substrates using the external reflection set-up is very useful, allowing us to study the interdiffusion of e.g. grafted polymers with non-grafted polymers, which might be an interesting possibility for studying the processes occurring in the fabrication of glass-fibre reinforced thermoplastics.

Attenuated total reflection was also used to study interdiffusion of PVC and PMMA grafted on silicon slides.

With both experimental set-ups we observed that PMMA, grafted on a glass or silicon slide, is still miscible with PVC, but has a low interdiffusion rate compared to free PMMA/PVC interdiffusion.

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REFERENCES

1 Brochard, F., Jouffroy, J. and Levinson, P. *Macromolecules* 1983, **16**, 1638

2 Kramer, J., Green, P. and Palmstrom, J. *Polymer* 1984, **25**, 473

3 Sillescu, H. *Makromol. Chem., Rapid Commun.* 1984, **5**, 523

4 Kausch, H. H. and Tirell, M. *Ann. Rev. Mater. Sci.* 1989, **19**, 341

5 Vidal, A. and Donnet, J.-B. *Bull. Soc. Chim. France*, 1985, 1088

6 Taubman, A. B., Yanova, L. P. Blyskosch, G. S., Ryachikova, G. G. and Glasunov, P. Y. *J. Pol. Sci., A-1* 1972, **10**, 2085

7 Hasjimoto, K., Fujisawa, T., Kobayashi, M. and Yosomiya, R. *J. Appl. Pol. Sci.* 1982, **27**, 4529

8 Abate, G. F. and Heikens, D. *Polym. Commun.* 1983, **24**, 137; *ibid* 342

9 Eastmond, G. C. and Mucciariello, G. *Polymer* 1982, **23**, 164

10 Popov, V. A., Grishin, A. N., Zvereva, Yu. A., Palayeva, T. V., Fomin, V. A. and Ivanchev, S. S. *Vysokomol. soyed* 1983, **A23**, 760 (*Polym. Sci. USSR* 1983, **25**, 883)

11 Trachenko, V. I., Zil'berman, Ye. N., Shatskaya, T. F. and Pomerantseva, E. G. *Vysokomol. soyed.* 1986, **A28**, 580 (*Polym. Sci. USSR* 1986, **28**, 646)

12 Garbella, R. W. and Wendorff, J. H. *Makromol. Chem.* 1988, **189**, 2459

13 Finerman, T. and Crist, B. *Polym. Prepr.* 1987, **28**, 375

14 Whitlow, S. J. and Wool, R. P. *Macromolecules* 1989, **22**, 2648

15 Fernandez, M. L., Higgins, J. S., Penfold, J., Ward, R. C., Shackelton, C. and Walsh, D. J. *Polymer* 1988, **29**, 1923

16 Klein, J. and Briscoe, B. J. *Polymer* 1976, **17**, 48

17 Vorenkamp, E. J., van Ruiten, J., Kroesen, F. A., Meyer, J. G., Hoekstra, J. and Challa, G. *Polym. Commun.* 1989, **30**, 116

18 Boven, G., Brinkhuis, R. H. G., Vorenkamp, E. J. and Schouten, A. J. *Macromolecules* 1991, **24**, 967

19 Abelès, F. *Ann. de Phys.* 1948, **3**, 504

20 Boven, G., Folkersma, R., Challa, G. and Schouten, A. J. *Polym. Commun.* 1991, **32**, 50

21 Vorenkamp, E. J., ten Brinke, G., Meijer, J. G., Jager, H. and Challa, G. *Polymer* 1985, **26**, 1725

22 Yukioka, S. and Takashi, I. *Polym. Commun.* 1991, **32**, 17

23 Harrick, N. J. 'Internal Reflection Spectroscopy', Wiley-Intersicnece, New York, 1967