

Fourier transform infra-red spectroscopy of nylon-6 blends: binary blends with poly(methyl methacrylate) and ethylene vinyl ester/alcohol copolymer

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Films of blends of nylon-6 with poly(methyl methacrylate), (PMMA) and poly(ethylene-vinyl alcohol) were cast from formic acid solutions and examined by Fourier transform infra-red spectroscopy. At high contents of nylon-6 the vinyl alcohol of the copolymer reacts with formic acid to form vinyl formate. In contrast, the films of 100% copolymer and of the 25/75 and 10/90 blends contained both the alcohol and the ester groups. The FTi.r. results indicate that there are specific interactions between the amide group on nylon-6 and the ester group of PMMA or the copolymer. Data are also presented which show that there are at least two amorphous phases – one miscible containing both the polymers and the other containing almost pure noncrystallizable component. The differences in the specific interactions in the two blend systems are largely due to the inversion of the ester group in the pendant chain.

(Keywords: polyblends; nylon-6; PMMA; ethylene-vinyl formate copolymer; FTi.r. miscibility)

INTRODUCTION

A simple physical mixture of two or more different polymers is generally a heterogeneous multiphase system. This thermodynamic incompatibility is a reflection of an increase in free energy resulting from mixing two or more macromolecular species. A number of miscible two component polymer systems have been investigated, which exhibit a single phase at least in the amorphous region¹⁻⁵. This miscibility is a consequence of an exothermic interaction such as a dipole-dipole or hydrogen bonding, between the functional groups on the component polymers.

The inherent sensitivity and computational facilities of Fourier transform infra-red (FTi.r.) spectroscopy have been particularly valuable in characterizing specific interactions between component polymers in several blend systems⁶⁻¹⁰. If the component polymers are incompatible, the individual polymers do not recognize, in the infra-red sense, the existence of the other polymer in the blend. In such cases it is possible to digitally subtract from the spectrum of the blend the spectrum of one of the pure component polymers using an appropriate weighting factor and the residual spectrum thus obtained should be the same as the spectrum of the other polymer. However, specific interactions in miscible blends may result in band shift, band broadening or intensity change of some of the absorption bands associated with one or both of the component polymers. In such cases, the residual spectrum obtained by digital subtraction of the spectrum of either one of the component polymers will be different from the spectrum of the other. From FTi.r. studies Coleman and coworkers^{6,7}, Wellinghoff *et al.*⁹, and Naiko *et al.*¹⁰ have derived valuable information on the specific interactions in the blends of poly(vinylidene fluoride)-poly(methyl methacrylate), poly(ϵ -caprolactone)-poly(vinyl chloride),

poly(phenylene oxide)-polystyrene and poly(methyl methacrylate)-poly(styrene-co-acrylonitrile). Coleman *et al.*⁸ also showed from FTi.r. studies that the blends of poly(β -propiolactone) with poly(vinyl chloride) are incompatible over the entire range of compositions, in agreement with thermal studies.

In this paper FTi.r. spectroscopy is employed to characterize binary blends cast from formic acid solutions of nylon-6 with poly(methyl methacrylate) (PMMA), and poly(ethylene-co-vinyl alcohol).

EXPERIMENTAL

The polymers employed in this study, Nylon 6, PMMA and poly(ethylene-vinyl alcohol) are described elsewhere¹¹. Thin films of the homopolymers and binary blends with nylon-6 were prepared from dilute solutions in 88% formic acid (about 1% by weight) by casting on Teflon sheets and allowing the formic acid to evaporate. The thin films were mounted on infra-red film holders and dried *in vacuo* for 50°C for 24 h.

Infra-red absorption spectra were recorded on a Nicolet 7199 FTIR spectrometer. Two hundred scans at a resolution of 2 cm⁻¹ were signal averaged and stored on a magnetic disc system. The frequency scale was internally calibrated with a reference helium-neon laser to an accuracy of 0.2 cm⁻¹. The films were sufficiently thin to be within the absorption ranges where the Beer-Lambert law is obeyed. Typical FTi.r. spectra are shown in Figures 1-8.

RESULTS AND DISCUSSION

The assignments of various infra-red absorption bands of nylon-6 are well established¹²⁻¹⁴. The spectrum of the

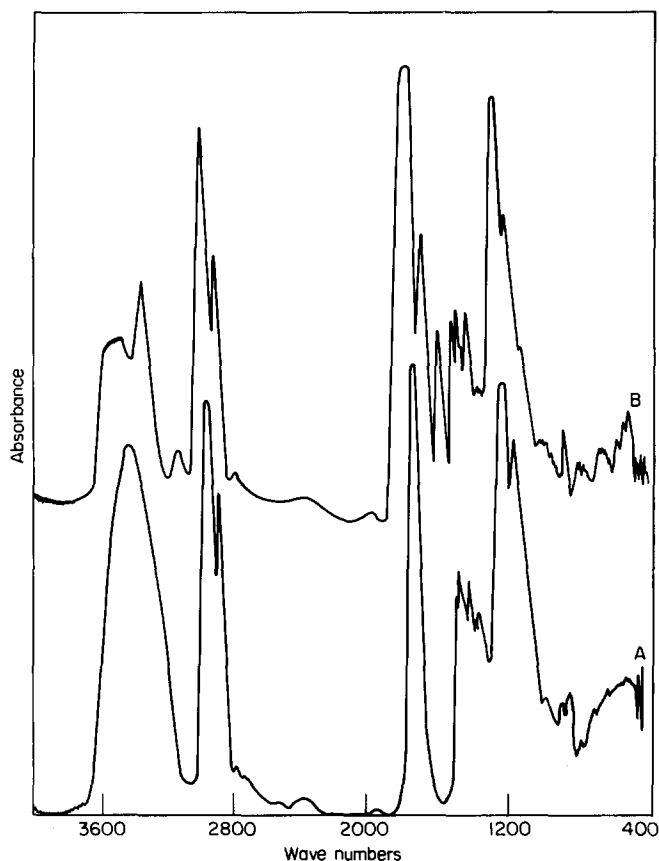


Figure 1 FTi.r. spectra of formic acid cast films. (A) pure copolymer and (B) 25/75 nylon-copolymer blend

solvent-cast nylon-6 has strong absorption bands at 3299 cm^{-1} due to hydrogen bonded NH stretching, at 2943 and 2869 cm^{-1} due to CH stretching of the methylene group, at 1641 cm^{-1} the amide I band (predominantly C=O stretching) and at 1546 cm^{-1} the amide II band (C-N stretching and NH deformation).

The spectrum of the cast film of poly(ethylene-vinyl alcohol) (Figure 1A) shows strong absorption bands at 3450 and 1115 cm^{-1} respectively due to hydroxyl stretching and C-O stretching which are characteristic of the alcohol group, and at 1720 and 1190 cm^{-1} the characteristic frequencies of a formate group^{15,16}. Thus the infrared spectrum of the copolymer suggests that there is partial conversion of the alcohol groups into formate groups. This is perhaps the consequence of the hydrolysis of the ester groups formed when dissolved in formic acid, back to alcohol in the presence of the acid, as suggested earlier by Salyer and Kenyon¹⁷.

NEVF blends

In the 25/75 and 10/90 blends, infra-red spectral features characteristic of both the pure copolymer and nylon-6 are apparent (Figure 1B). In contrast, the spectra of the blends containing 50% or less of the copolymer show very little evidence of the hydroxyl vibrational modes (Figure 2) suggesting that in the presence of equal or excess levels of nylon-6 the alcohol groups are almost fully converted to ester. In spite of these structural

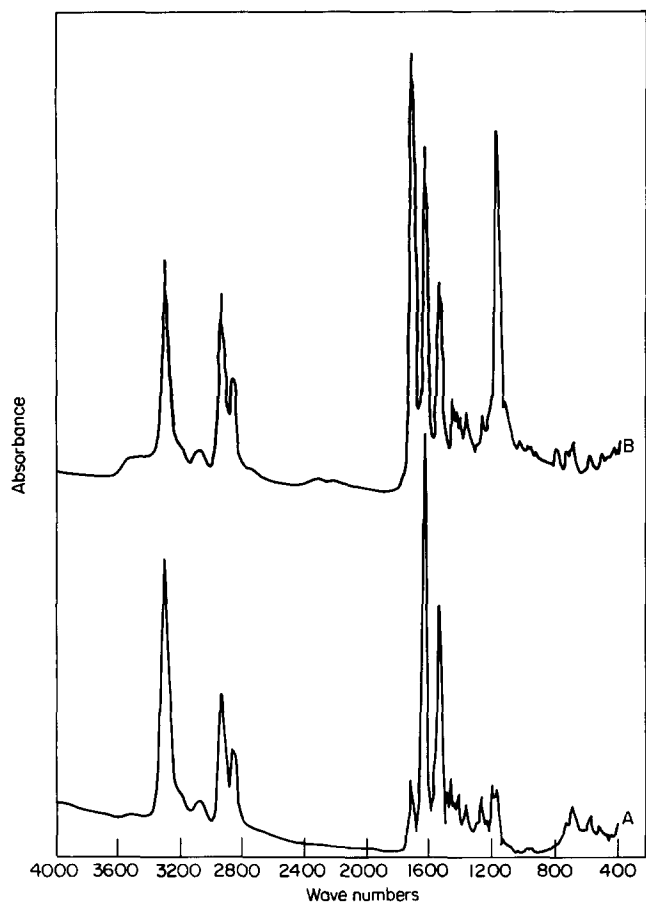


Figure 2 FTi.r. spectra of the NEVF blends. (A) 90/10 and (B) 50/50

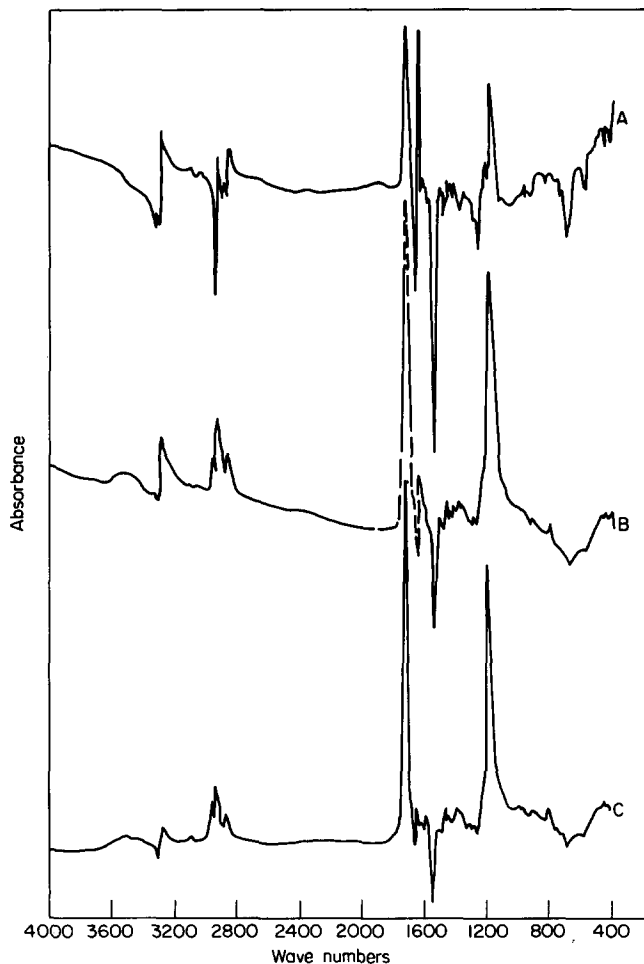


Figure 3 Difference spectra of the NEVF blends. (A) 90/10-nylon 6, (B) 65/35-nylon-6 and (C) 50/50-nylon-6

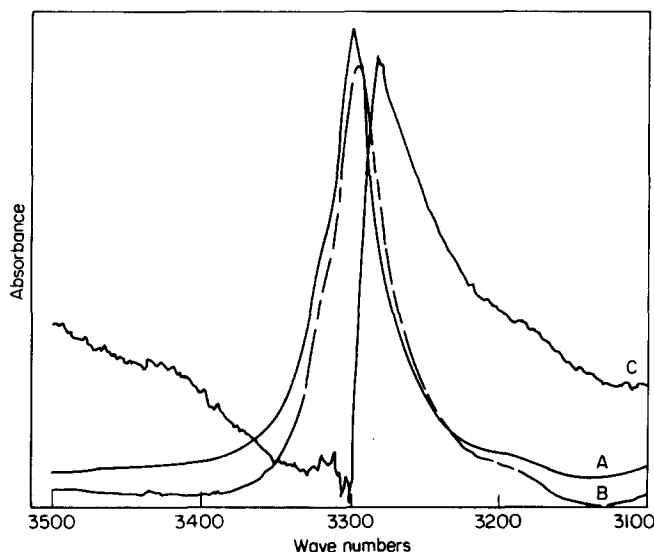


Figure 4 FTi.r. spectra in the 3500–3100 cm^{-1} region (A) nylon-6, (B) NEVF 65/35 and (C) NEVF 65/35–nylon-6

changes in the copolymer, no abrupt changes in the behaviour of the blends have been noted, either in the morphology or in thermal properties¹¹. Hence further discussion is restricted to the blends containing 50% or more of nylon-6. These blends are designated NEVF for brevity.

As the copolymer content increases, the intensity of the absorption bands assignable to nylon-6 decreases while the intensity of those bands assignable to the copolymer increases (Figure 2). No change in the position of the ester or amide bands is apparent. Figure 3 shows the residual infra-red spectra of the blends obtained by digitally subtracting the spectrum of nylon-6 with appropriate weighting factors from the spectra of the blends. In selecting the weighting factors, care was taken to compensate for the nylon-6 absorptions in the blends as fully as possible without distorting the band shapes or the baseline. In all the blends the shift of the NH stretching band to lower frequencies is obvious. This shift is much more clearly seen in Figure 4 which shows the NH stretching band of nylon-6 and the 65/35 blend on an expanded scale together with the derivative type residual peak obtained by subtraction. The positive lobe of the residual peak represents approximately 13% of the intensity of the NH stretching band. This suggests that the residual peak in the NH stretching region is not a consequence, as we shall discuss in detail later, of dispersion effects resulting from variations in refractive index¹⁸.

It is interesting to note that there is considerable drop in intensity with minor shifts of the CH stretching vibrations in the 2800–3000 cm^{-1} region. The strong interaction between the component polymers of the blend is also reflected in the amide I and II bands (Figure 5). The amide I band is shifted slightly to lower frequencies giving rise to a residual peak in the difference spectrum. However, there is a significant drop in intensity of the amide II band at 1546 cm^{-1} with no shift. The intensity of the residual peak increases marginally with the concentration of the copolymer (i.e. in the range of 10–50%) suggesting that an almost constant fraction of the amorphous phases of the two polymers is miscible (compare especially Figure 5B with 5E). This

observation is supported by the thermal behaviour which demonstrated that there are two amorphous phases in the blends containing 35% or more of the copolymer—one phase containing almost pure copolymer and the other containing both the polymers¹¹.

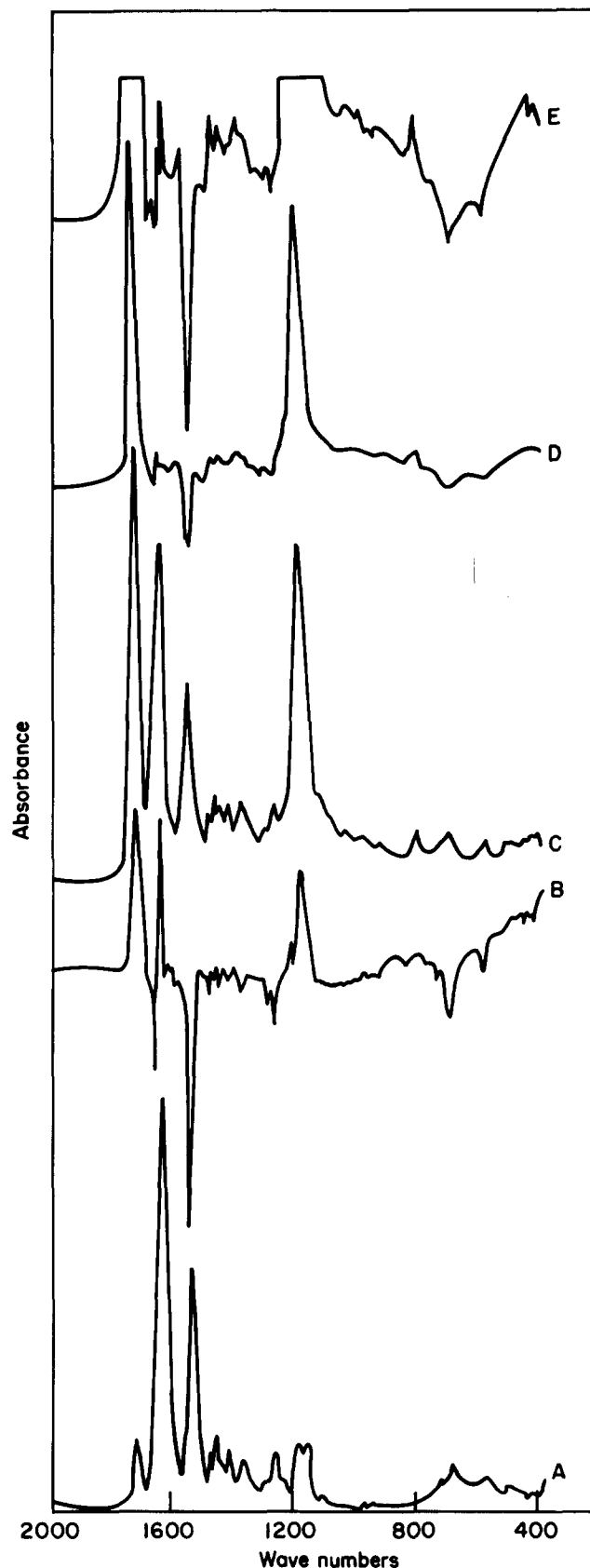


Figure 5 FTi.r. spectra of the NEVF blends. (A) NEVF 90/10, (B) NEVF 90/10–nylon-6, (C) NEVF 50/50, and (D) and (E) NEVF 50/50–nylon-6

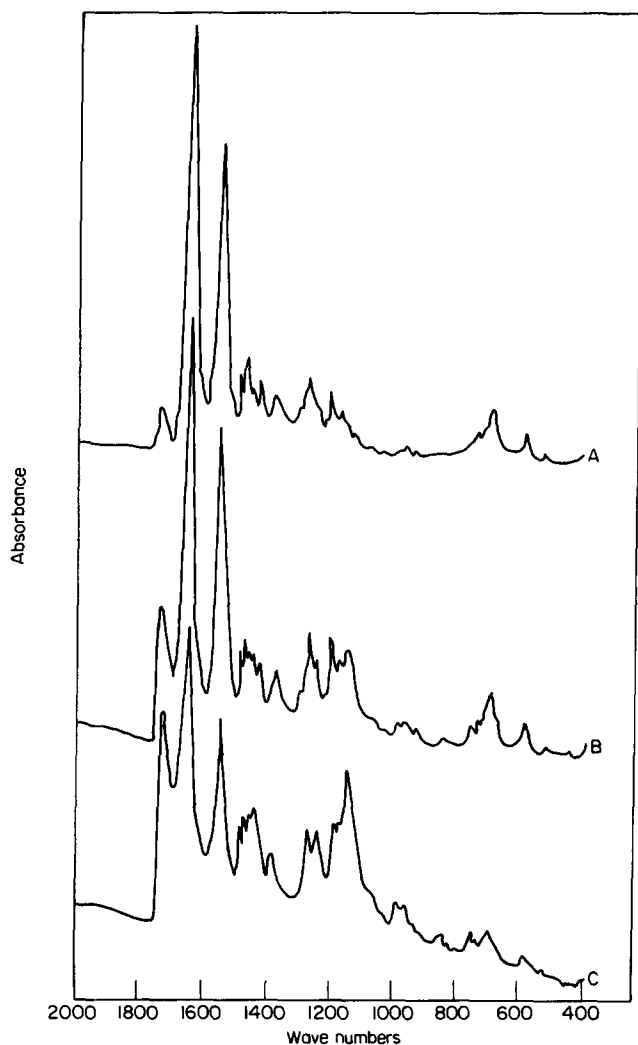


Figure 6 FTi.r. spectra of the NMMA blends, (A) 90/10, (B) 65/35 and (C) 50/50

NMMA blends

The infra-red spectra of PMMA have been investigated by many workers¹⁹⁻²¹. There is broad agreement on the assignments of many of the absorption bands. The bands in the region 2900–3000 cm^{-1} , namely at 2950 and 2993 cm^{-1} , are due to the CH stretching vibrations or the methylene, (C)CH₃ and (O)CH₃ groups which overlap. The carbonyl stretching vibration occurs at 1732 cm^{-1} . The assignments of the bands in the region 1250–1100 cm^{-1} are still debated. According to Willis *et al.*²⁰ and Derhikov and Koenig²¹ all the three bands at 1242, 1192 and 1150 cm^{-1} are associated with different vibrations of the ester groups of PMMA.

The carbonyl stretching vibration is observed at 1733 cm^{-1} in the spectrum of the 90/10 NMMA blend. This absorption band shifts to lower frequencies with increasing PMMA content (Figure 6). Considerable changes are also observed in the regions of NH stretching, CH stretching, amide I, amide II and ester group vibrations (1200–1100 cm^{-1}). These changes are more clearly seen in the difference spectrum obtained by subtracting from the spectrum of the blend the spectra of Nylon 6 and PMMA with appropriate weighting factors. The different spectra are shown in Figures 7 and 8. There is a net decrease in intensity of the NH stretching vibration and the amide II band at 1546 cm^{-1} . Weak multiple

peaks are observed in the amide region. The shifting to lower frequencies of the carbonyl stretching absorption with increasing PMMA content results in the negative peaks on the high frequency side and positive peaks on the low frequency side in the different spectra. A weak band due to CH₂ wagging is observed at 1170 cm^{-1} in the infra-red spectrum of nylon-6. One of the ester group vibrations of PMMA is observed at 1150 cm^{-1} . In the 65/35 blends this vibration is observed at 1147 and 1143 cm^{-1} respectively. The shift of this absorption is obvious from the difference spectrum. These observations suggest strong interaction involving the ester group of PMMA and the amide group of nylon-6.

In the nylon-6/poly(ethylene-vinyl formate) blends mainly the NH stretching vibration and the amide I band are shifted to lower frequencies while in the NMMA blends the carbonyl stretching vibration is the one most affected by blending with nylon-6. These spectral differences suggest that the specific interactions leading to the observed miscibility in these two blend systems are different. For the NEVF blends a hydrogen bonding interaction between the amide groups and the α -hydrogens on the copolymer plays an important role while a dipole-dipole and/or a hydrogen-bonding interaction between the formate and the amide groups is of minor consequence. On the other hand, the poly(methyl

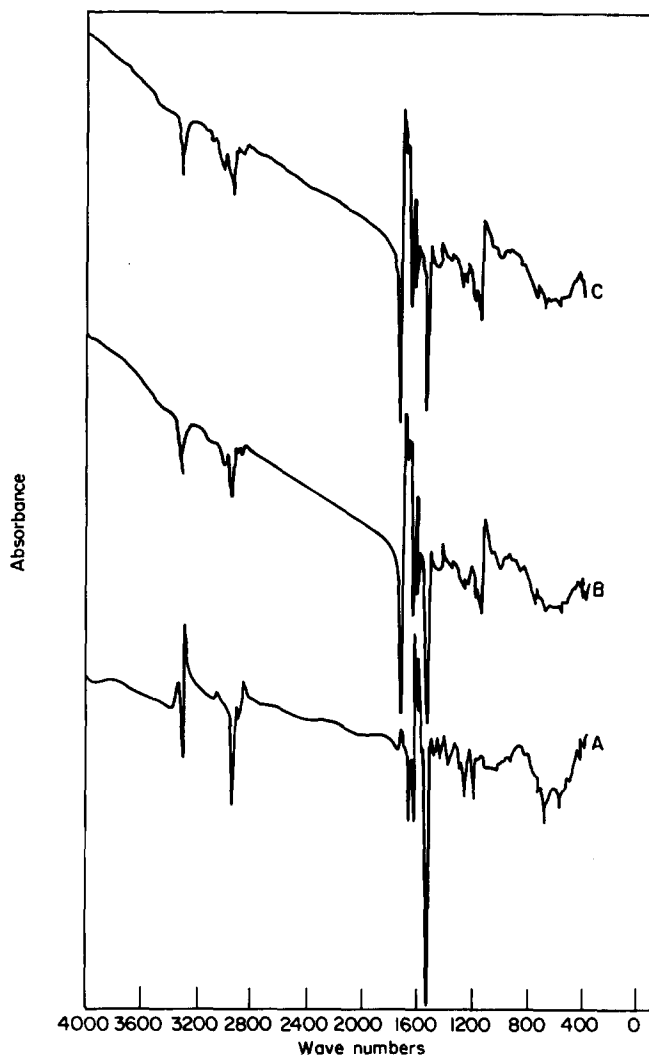


Figure 7 Difference spectra of the NMMA blends. (A) 90/10 – nylon-6-PMMA, (B) 65/35–nylon-6-PMMA and (C) 50/50–nylon-6-PMMA

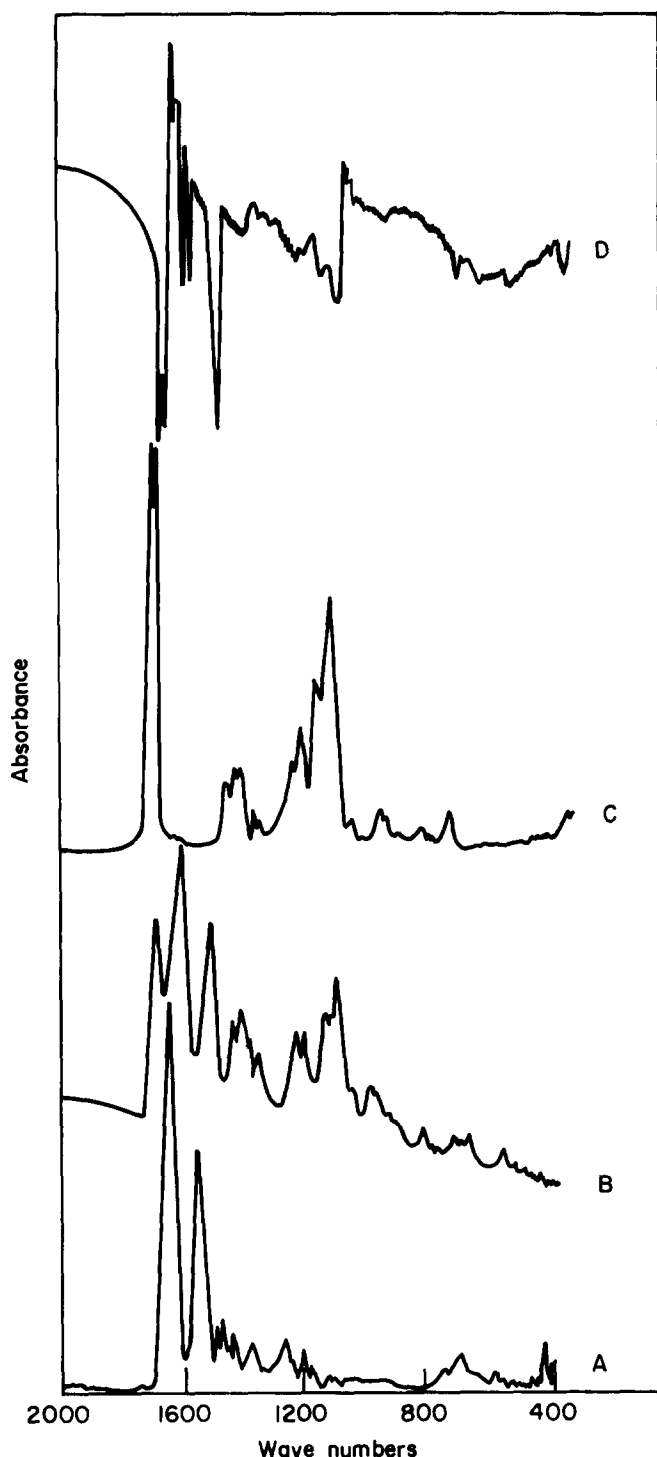


Figure 8 FTi.r. spectra of the NMMA blends. (A) nylon-6, (B) 50/50, (C) PMMA and (D) 50/50-nylon-6-PMMA

methacrylate) contains no α -hydrogens. However, the methacrylate group is more favourably oriented for a stronger dipole-dipole and possibly a hydrogen-bonding interaction between the methacrylate groups and the amide groups, leading to the observed miscibility in the NMMA blends.

Recently, Allara¹⁸ has theoretically investigated the effects of the refractive index of the component polymers on i.r. band shapes associated with strong absorbing groups. Residual peaks, both positive and negative, shifted from the absorption peak centre and, with varying intensity, can arise purely from optical dispersion effects. A typical calculation shows that for a 10/90 blend of two

polymers, A (with strong absorption band) and B, with refractive indices of say 1.5 and 1.4 respectively, a large positive peak of intensity about 4% of that of the main blend peak occurs shifted down by 12 cm^{-1} . The residual peaks are smaller, the higher the concentration of A in the blend or the smaller the refractive index differences. In the present case the residual peaks are much stronger (more than 10% of the blend peak intensity). Also, it is the absorption bands of the major component, namely nylon-6, which showed residual peaks in the NEVF blends. In the NMMA blends stronger residual peaks are observed for the blends with compositions of 65:35 and 50:50. Furthermore, the carbonyl stretching frequency shifts are evident in the normal spectra of the blends. Thus it is clear that the observed spectral features reflect mostly the true intermolecular interaction between the component polymers.

CONCLUSIONS

FTi.r. studies of the NEVF and NMMA blends have shown that there are significant band shifts and intensity changes in the spectra of the blends suggestive of strong intermolecular interactions. These specific interactions could be responsible for the partial miscibility observed in their thermal properties.

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REFERENCES

- 1 Manson, J. A. and Sperling, L. H. 'Polymer Blends and Composites', Academic Press, New York, 1976
- 2 Klemmner, D. and Frisch, K. D. (Eds.) 'Polymer Alloys: Blends, Blocks, Grafts and Interpenetrating Networks', Plenum Press, New York, 1977
- 3 Paul, D. R. and Newman, S. (Eds.) 'Polymer Blends', Vol. I and II, Academic Press, New York, 1978
- 4 Olabisi, O., Robeson, L. M. and Shaw, M. T. 'Polymer-Polymer Miscibility', Academic Press, New York, 1979
- 5 Klemmner, D. and Frisch, K. C. (Eds.) 'Polymer Alloys II', Plenum Press, New York, 1980
- 6 Coleman, M. M., Zarian, J., Varnell, D. F. and Painter, P. C. *J. Polym. Sci. Polym. Lett. Edn.* 1977, **15**, 745
- 7 Coleman, M. M. and Zarian, J. *J. Polym. Sci. Polym. Phys. Edn.* 1979, **17**, 837
- 8 Coleman, M. M. and Varnell, D. F. *J. Polym. Sci. Polym. Phys. Edn.* 1980, **18**, 1403
- 9 Wellinghoff, S. T., Koenig, J. L. and Baer, E. *J. Polym. Sci. Polym. Phys. Edn.* 1977, **15**, 1913
- 10 Naito, K., Johnson, G. E., Allara, D. L. and Kwei, T. K. *Macromolecules* 1978, **11**, 1260
- 11 Venkatesh, G. M., Fornes, R. E. and Gilbert, R. D. *Polymer* (communicated)
- 12 Schmidt, P. and Schneider, B. *Collect. Czechoslov. Chem. Commun.* 1963, **28**, 2685
- 13 Miyake, A. *J. Polym. Sci.* 1960, **44**, 223
- 14 Tadokoro, H., Kobayashi, M., Yoshidome, H., Tai, K. and Makino, D. *J. Chem. Phys.* 1968, **49**, 3359
- 15 Haken, J. K. and Werner, R. L. *Spectrochim. Acta* 1971, **27A**, 343
- 16 Socrates, G. 'Infrared Characteristic Group Frequencies', J. Wiley and Sons, New York, 1980
- 17 Salyer, I. O. and Kenyon, A. S. *J. Polym. Sci. A-1* 1971, **9**, 3083
- 18 Allara, D. L. *Appl. Spectrosci.* 1979, **33**, 358
- 19 Nagai, H., *J. Appl. Polym. Sci.* 1963, **7**, 1697
- 20 Willis, H., Zichy, V. and Hendra, P. *Polymer* 1969, **10**, 737
- 21 Derlikov, S. and Koenig, J. L. *Appl. Spectrosc.* 1979, **33**, 551 and 555