Hydrogen bonding in PMMA–fluorinated polymer blends: *FT*i.r. investigations using ester model molecules*

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The sensitivity of the carbonyl stretching vibration of methyl acetate to interactions with the surroundings is re-examined through *FT*i.r. analyses and Fourier self deconvolution. The relevant conclusions permit a study of the mixtures of methyl acetate and methyl pivalate with various fluorinated polymers. Evidence is given for the existence of hydrogen bonding between poly(vinylidene fluoride) and these model compounds of poly(methylmethacrylate). Arguments are put forward in favour of a similar behaviour in poly(vinylidene fluoride)/poly(methylmethacrylate) blends.

(Keywords: Fourier transform infra-red spectroscopy; molecular interactions; fluorinated polymers; poly(methylmethacrylate) model compounds; poly(vinylidene fluoride)/poly(methylmethylacrylate) blends)

INTRODUCTION

Blends of poly(vinylidene fluoride) (PVF_2) and poly(methylmethacrylate) (PMMA) have been the subject of several studies since the compatibility of these two polymers was reported[1,2]. Paul *et al.*[3] emphasized the role of the carbonyl group in the miscibility of various oxygen containing polymers with PVF_2. The interaction parameters for these systems were related to the dipole moments of the polymers: it was suggested that compatibility arises from strong dipolar interactions. Coleman *et al.*[4] and Roerdink and Challa[5] have further shown, through i.r. analyses, that the C=O group is perturbed by its local environment in PVF_2/PMMA blends.

The aim of this work is to perform an *FT*i.r. study of the interactions occurring between PVF_2 (or other fluoropolymers) and model compounds of PMMA, in an attempt to pinpoint the nature of the interactions and their dependence on the chemical structure of the fluoropolymers.

EXPERIMENTAL

Materials

PVF_2, PMMA and PVF_2/PMMA blends were supplied by Solvay, and are similar to those used in a previous study[6]. The other fluoropolymers were obtained from PCUK [poly(vinyl fluoride) (PVF), poly (trifluoroethylene) (PVF_3) and poly(vinylidene fluoride–chlorotrifluoroethylene) ($P(VF_2–ClVF_3)$)], Penwalt [poly(vinylidene fluoride–tetrafluoroethylene) ($P(VF_2–TFE)$)] and SIREM [polytetrafluoroethylene (PTFE)]. Polyethylene (PE) was supplied by CDF-Chimie.

Methyl acetate (MA) and methyl pivalate (MP: $(CH_3)_3CCOOCH_3$) were used as model compounds of PMMA. MA is the simplest model for the ester function; MP reflects the chemical structure of PMMA in a better fashion. They were purchased from EGA. Deuterated methyl acetate was prepared from d_4-methanol and an excess of d_6-acetic anhydride. The ester was then carefully distilled.

Sample preparation

Polymer/polymer blends were cast from *N,N*-dimethylacetamide solutions onto potassium bromide pellets. The films were dried in a vacuum oven to remove the solvent completely; they were sufficiently thin to be within the absorbance range where the Beer–Lambert law is usually assumed to be obeyed (absorbance less than 0.8).

Films of pure semi-crystalline polymers (PVF_2, $P(VF_2–TFE)$, PVF, PVF_3) used in polymer/model compounds studies, were compression moulded above the melting point and quenched in an ice water bath in order to ensure the maximum extent of the amorphous phase. PE was used as supplied and PTFE was made partially amorphous by heat treatment at high temperature.

Film swelling with MA (or MP)

In order to ensure the maximum extent of interaction and to avoid self association, it is essential that the concentration of model compounds in the films is low and approximately uniform. Thus, the film thicknesses and the swelling conditions were chosen so that MA concentration was ~ 1 vol%. Thick samples were swollen at room temperature either in liquid or in gaseous MA, depending on the affinity of MA for the various polymers. MA was then allowed to diffuse in order to equilibrate in the amorphous phase. The absence of self-associated MA band was checked for all the samples under study. Preliminary investigations on 1% solution of MA in hexane, using a variable pathlength i.r. cell, enable one to determine that the Beer–Lambert law applies to the $\nu_{C=O}$ vibration when its absorbance is less than ~ 1.25. Absorbance measurements relative to this band were used to evaluate the final amount of MA in the films.

I.r. technique

I.r. spectra were recorded on a Nicolet 7199 FT-IR

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* Dedicated to Dr P. Thirion on the occasion of his retirement in 1985

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spectrometer at 1 and 2 cm^{-1} resolution. From 100 to 1300 interferograms were co-added and averaged, in order to improve the signal to noise ratio.

In the case of extensively overlapped bands, second and fourth derivatives were used as a classical method to determine their number[7-9]. The Fourier self-deconvolution technique[10,11] was also used as an alternative route to obtain information on the structure of overlapped band contours; it permits the computational resolution of lines that cannot be instrumentally resolved due to their intrinsic linewidth.

Fourier self-deconvolution involves the deconvolution of a lineshape function from the experimental spectrum. The removal of the lineshape reduces the bandwidth and thereby improves the 'apparent' spectral resolution. The upper limit of the spectral resolution in the deconvoluted spectrum is the instrumental resolution. One important feature of deconvolution is that the integrated band areas are not altered by the process. Therefore increased information on the number, positions and the relative intensities of the component bands is gained, at the expense of lineshape information.

In the notations of ref. 10, a spectrum $E(v)$ is the Fourier transform of an interferogram $I(x)$:

$$E(v)=\mathscr{F}(I(x))$$

The self-deconvoluted interferogram, $I'(x)$ is then expressed as:

$$I'(x)=\frac{Dg(x)}{\mathscr{F}^{-1}(E_0(v))}I(x)$$

where $E_0(v)$ is the intrinsic lineshape function and $Dg(x)$ is an apodization function. $\mathscr{F}^{-1}$ is the inverse Fourier transformation. The deconvoluted spectrum $E'(v)$ is then simply obtained by taking the Fourier transform of $I'(x)$. The lineshape function in $E'(v)$ is determined by $\mathscr{F}(Dg(x))$.

Self deconvolution software is routinely available on Nicolet FT-IR. A Lorentzian lineshape is used for the intrinsic lineshape function $E_0(v)$ and a Bessel function for the apodization function $Dg(x)$. Two parameters VF_0 and VF_1 are used in this program and control the spectral resolution. VF_0 is the half bandwidth of the Lorentzian; VF_1 controls the signal to noise ratio in the deconvoluted spectrum.

An optimization procedure is required to determine these parameters. The correct value of VF_0 is determined from a series of spectra resulting from deconvolution with different bandwidths. Underestimation of the bandwidths results in a deconvoluted spectrum which has a lower spectral resolution. On the other hand, a too large a value of VF_0 is indicated by the presence of negative side lobes in the deconvoluted spectrum. They are removed by adjusting VF_0. VF_1 is chosen so that the resolution and signal to noise ratio are optimized.

The values of VF_0 and VF_1 used in the self deconvolution treatment are 10 cm^{-1} and 3 respectively, in the case of solution spectra given in this paper. It may be noted that the half bandwidth of the experimental spectrum is about 13 cm^{-1}.

RESULTS AND DISCUSSION

Studies on methyl acetate

The conformational structure of MA has been studied in detail by various methods and it was found that a single conformer is present both in the liquid and in the crystalline states[12]. Therefore, the change in C=O frequency on passing from the vapour (unassociated) phase to another medium can be attributed to dielectric effects or to localized interaction effects such as dipolar interactions or hydrogen bonding. The sensitivity of the carbonyl band to dielectric effects is evidenced by the frequency shift of 15 cm^{-1} observed in a non-associating solvent such as hexane. However, the Kirkwood–Bauer–Magat relationship is known to fail in predicting the magnitude of the solvent-induced shifts[13].

Decisive evidence that the shifts mainly arise from localized interactions is given by *FT*i.r. studies on 1% solutions of MA in mixed solvents (hexane/benzene or hexane/polar solvent: orthodichlorobenzene (ODB)).

Figure 1 displays the i.r. spectra of these systems in the range 1410 cm^{-1}–1790 cm^{-1}, the second and fourth derivatives and the result of the Fourier self-deconvolution of these spectra. The spectra exhibit only one band but both the derivatives and the Fourier self deconvolution unambiguously show that the carbonyl stretch absorption of MA can be resolved into two components, even in mixtures of non-polar solvents (hexane/benzene). In contrast, we detected only one band, using the same techniques, when MA is dispersed in a pure solvent. The observation of a doublet demonstrates that the C=O frequency shift cannot be related to a bulk property of the medium such as the dielectric constant or the refractive index. Therefore the shift mainly results from localized solute–solvent interactions. In a mixture the interactions are competitive and an equilibrium is set up. The departure from a random distribution of MA in the mixture is due to preferred interactions between MA and one of the solvents: the intensities of the two components of the carbonyl band reflect the relative abilities of the two solvents to associate with the ester.

Figure 2 illustrates this point for MA dissolved in hexane/ODB mixtures of various compositions. It is readily seen that ODB is a strongly interacting solvent. The low frequency absorption, assigned to ODB-associated C=O groups, dominates when the amount of ODB is only 8 vol%.

It must be noted that the two C=O bands do not appear exactly at the frequency characteristic of MA in each solvent. This suggests that the solute–solvent complexes may be surrounded by a mixture of the molecules of the two solvents. The two bands shift with change in the composition of the solvation shell, owing to change of its dielectric constant.

Additionally it has to be pointed out that the carbonyl band broadens as the interacting ability of the solvent increases, as previously emphasized by various authors[14,15].

The interaction criteria defined above (band shift and broadening, preferred interactions in mixtures) enable us to test if interactions occur between MA and a host fluoropolymer. We have first checked, using self deconvolution, that at a model compound concentration of ~1%, only interactions between the model compounds and the polymer matrices can occur. Only one band is detectable in homopolymers/MA spectra. However its

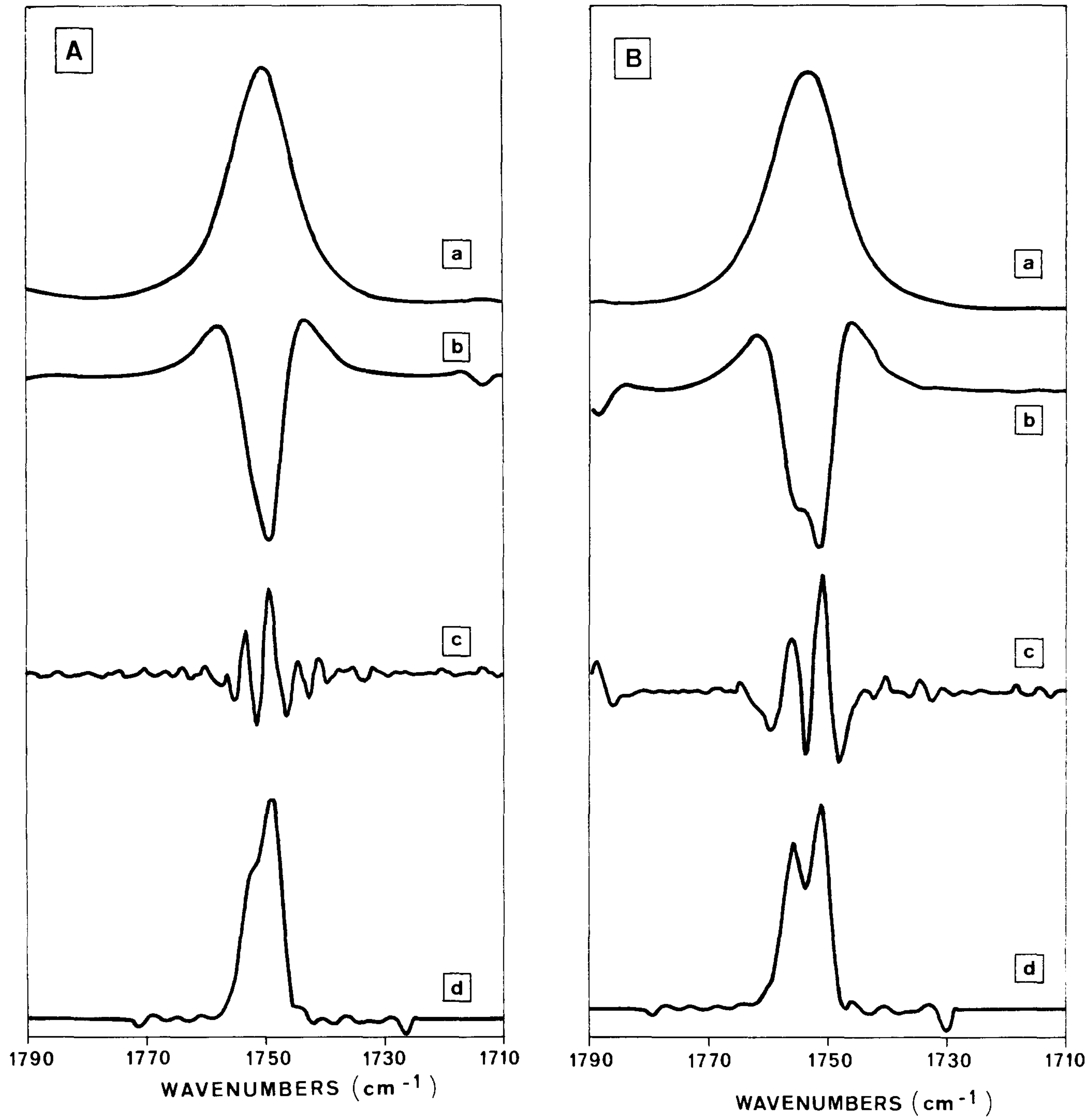

Figure 1 Carbonyl stretching absorption of MA: (A), in a mixture hexane/benzene (50/50 vol%); (B), in a mixture orthodichlorobenzene/hexane (8/92 vol%). (a) *FT*i.r. spectrum; (b) second derivative of the spectrum; (c) fourth derivative; (d) self deconvoluted spectrum

position and width depend on the host polymer. The i.r. spectrum of MA dispersed in PTFE or PE shows a high frequency band, respectively at 1760 and 1753 cm^{-1} (for comparison the $\nu_{\mathrm{C=O}}$ frequencies of MA in the gaseous and in the liquid (self associated) phases are 1770 and 1746 cm^{-1}). This band is very narrow (7 cm^{-1}). On the other hand, in the PVF_2 host matrix the carbonyl band is shifted to a lower frequency (1739.5 cm^{-1}) and is significantly broader ($\sim$20 cm^{-1}) (*Figure 3*). These experimental findings suggest that the C=O groups do not interact with PTFE and PE but that specific interactions occur between PVF_2 and MA. To add further support to this conclusion we have considered the copolymer (VF_2–TFE) which can be compared to a mixture of two solvents, the TFE units being a non-associating one. If the VF_2 units did not interact with MA, two bands would be expected in the spectrum of the (VF_2–TFE) copolymer swollen with 1% MA; their intensity ratio would be approximately equal to the ratio of the amounts of VF_2 and TFE units (70/30). Only one band at 1739.5 cm^{-1}, corresponding to the carbonyl groups interacting with the VF_2 units, is observed. No band at 1760 cm^{-1} is detectable.

It must be pointed out that this copolymer is highly soluble at room temperature in MA. It is well known that mixture of a random copolymer and a solvent can have a negative heat of mixing simply if the 'repulsion effect' between the comonomers is sufficiently strong. However, another explanation might be in the conformational

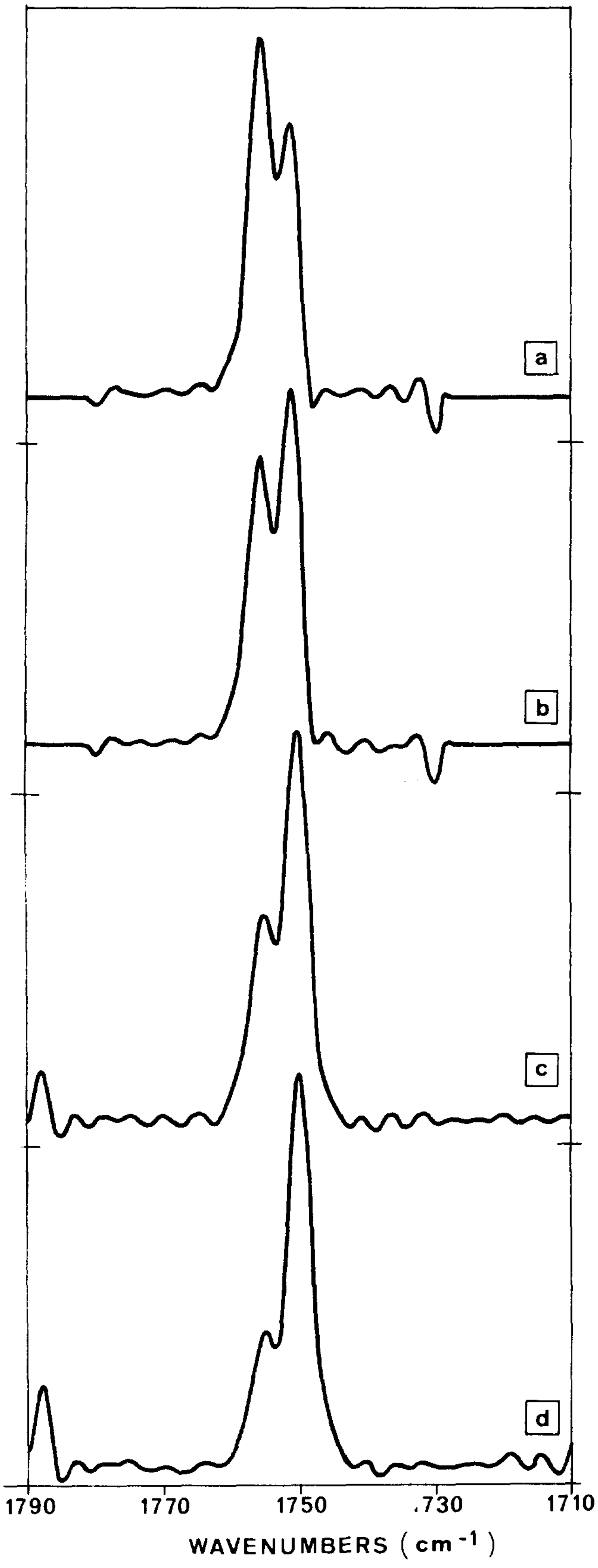

Figure 2 Self deconvoluted spectra of the carbonyl stretching absorption of MA in mixtures orthodichlorobenzene/hexane: (volume %: (a), 5/95; (b), 8/92; (c), 15/85; (d), 20/80)

change of the PVF_2 chains induced by copolymerization with TFE units. Lando[16] has shown that the all-*trans* conformation is the most stable one when the content of TFE units is greater than 12%. Optimum solvation might be attained when PVF_2 has a planar zig-zag conformation.

On the contrary, the self deconvoluted spectrum of poly(VF_2–$ClVF_3$)/MA system has an asymmetric shape, which indicates that both types of monomeric units can interact with MA.

The next logical step of this study is to vary the chemical structure of the polymer and to test if the interaction involving the C=O group is preserved. In PVF and PVF_3 matrices the carbonyl band is observed at 1740.8 and 1738 cm^{-1}, respectively.

The C=O bands are broader in PVF_2 and PVF_3 than in PVF. (PVF_3 is soluble at room temperature in MA.) Assuming that, in these closely related systems, the extent of the $\nu_{C=O}$ shift and band broadening is indicative of the interaction strength, we may rank the polymers in order of increasing interaction with the carbonyl group: $PVF < PVF_2 \leqslant PVF_3$.

A direct comparison of the interacting abilities of PVF_2 and PVF_3 would be useful. Unfortunately, the Fourier self deconvolution of the carbonyl band in the (VF_2–VF_3) copolymers/MA systems leads to only one peak, owing to the strong degree of overlapping of the VF_2/CO and VF_3/CO bands.

Studies on methyl pivalate

Experiments carried out on fluoropolymers/MP systems confirm the above results. The carbonyl band of liquid neat PM is a doublet: a shoulder at low frequency (1724 cm^{-1}) is observed on the broad band at 1737 cm^{-1}. Dybal *et al.*[17] explained this frequency splitting by Fermi

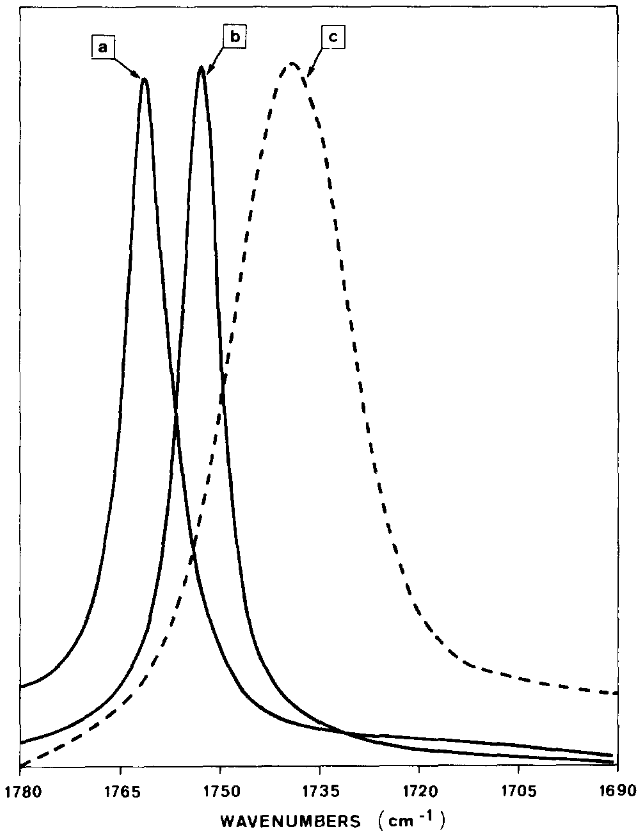

Figure 3 Carbonyl stretching absorption of MA in various polymer host matrices: (a) PTFE; (b) PE; (c) PVF_2

resonance of the carbonyl vibration with the harmonic level of the symmetric CH–O stretching vibration at 863 cm^{-1}. Our results are consistent with this interpretation. In the PTFE or PE non-interacting matrices $\nu_{C=O}$ is shifted to a higher frequency (respectively 1747 and 1740 cm^{-1}). In turn the Fermi resonance vanishes. In the PVF_2 or PVF_3 matrices, $\nu_{C=O}$ is lowered by interactions; as the $\nu_{C=O}$ band moves down toward the overtone, the Fermi resonance is enhanced and the intensity of the overtone grows (*Figure 4*).

Nature of the interactions

The nature of the interaction involving the carbonyl bond remains puzzling. Hydrogen bonding and (or) dipole–dipole interaction may occur. An eventual shift of the CH_2 or CH stretching modes of the polymers, which would be indicative of hydrogen bonding, could not be detected in the systems studied above because of the overlapping of MA and polymer spectra in the 2800–3200 cm^{-1} region. Use of deuterated MA, the spectrum of which is free of absorbances in this frequency range, is therefore required. The experiments are also ruled by a second condition: it is essential that the maximum number of polymer units interact with MA. This implies that the polymer is soluble in MA or that its equilibrium swelling ratio is great. The copolymers (VF_2–TFE) and PVF_3 fulfil this condition but, owing to the sensitivity of the CH and CH_2 modes to crystallinity, direct comparison between spectra of pure (VF_2–TFE) copolymer or PVF_3 and spectra of these polymers dissolved in deuterated MA is not reliable.

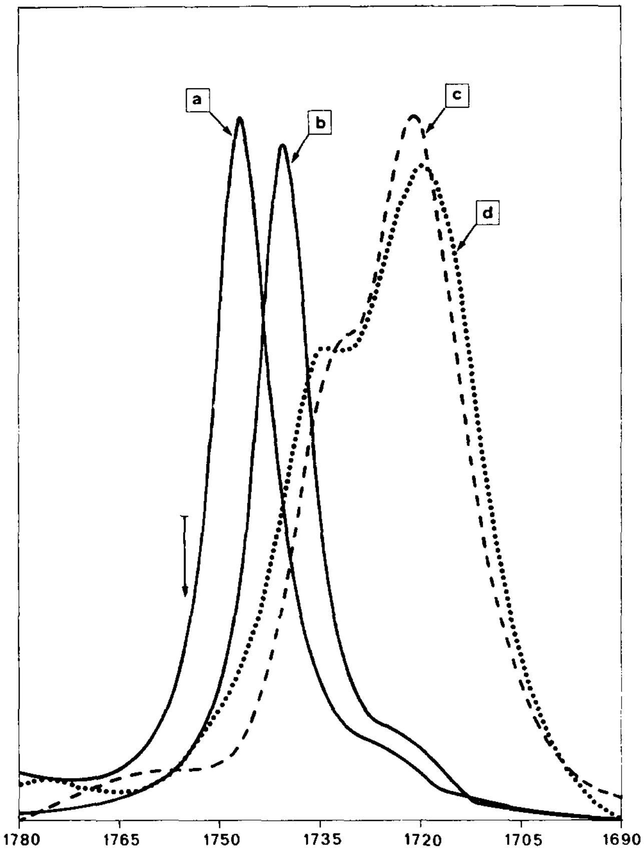

Figure 4 Carbonyl stretching absorption of MP in various polymer host matrices: (a) PTFE; (b) PE; (c) PVF_2; (d) PVF_3. Arrow indicates the position of the MP carbonyl band in the gaseous state

Therefore, we have been led to study the interactions between deuterated MA and the VF_2 units of the (VF_2–$ClVF_3$) copolymer. This copolymer is always amorphous and its swelling ratio is great. *Figure 5* shows the CH_2 stretching region of the spectrum of P(VF_2–$ClVF_3$) swollen by deuterated MA compared to that of neat P(VF_2–$ClVF_3$). We observe that the CH_2 stretching bands are shifted to significantly lower frequencies. We can therefore conclude that hydrogen bonding occurs between the C=O groups and the VF_2 units of the copolymer. In order to get a feeling about the enthalpy of this hydrogen bonding we can tentatively use the frequency shift–enthalpy correlation derived for pyrrole and substituted alcohols and phenols interacting with ethyl acetate[18]. It has been shown that there is a linear relationship between the shift of the X–H frequency and the enthalpy of the bond

$$\Delta H\ (\mathrm{kcal\ mol^{-1}})\ (\pm 0.2) = 0.025\,\Delta\nu_{XH} + 0.6$$

This yields $\Delta H \simeq 1$ kcal mol^{-1}.

If we assume that the CF_2CFCl units do not perturb significantly the CF_2CH_2 units, it is inferred that a type of hydrogen bonding may also occur in PVF_2/MA system. This assumption is reasonable. Indeed, Clark *et al.*[19] have shown, through theoretical and e.s.c.a. studies, that replacing hydrogen by any other atom in polymers has only short range effects. Therefore only CH_2 groups adjacent to a CFCl group can be perturbed. Owing to the chosen composition of the copolymer (70/30) these groups are expected to be few and their contribution to the i.r. spectra weak. Moreover, the e.s.c.a. spectrum of the CH_2 carbons of (PVF_2–$ClVF_3$) exhibits an unresolved peak at

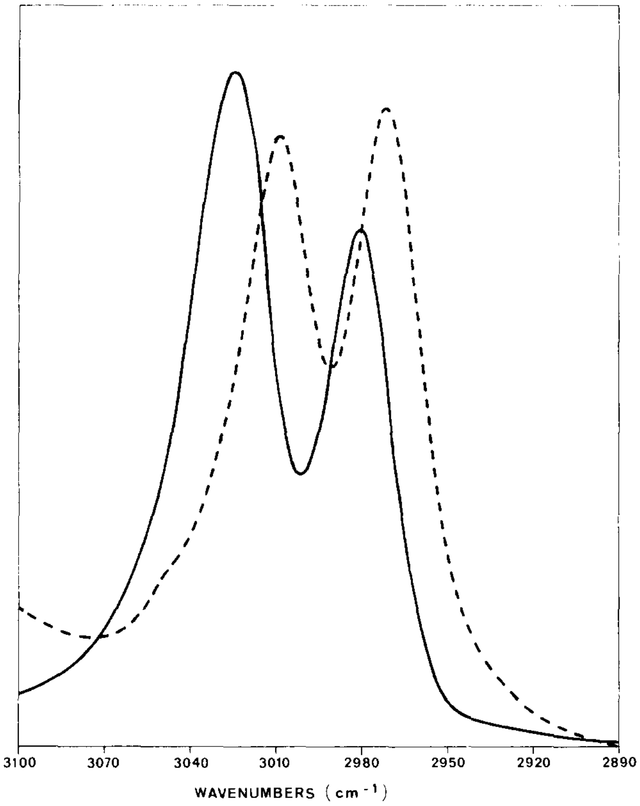

Figure 5 *FT*i.r. spectra of (VF_2–$ClVF_3$) copolymer in the CH_2 region: neat (solid curve); swollen with deuterated MA (broken curve)

an energy close to that of the CH_2 carbons of PVF_2.[19]

As for PVF_3/MA mixture, a type of hydrogen bonding involving the CH group is also feasible but we cannot state that the type of interaction is the same in PVF/MA mixtures.

Indeed, no obvious correlation exists between the relative strength of the interactions with the C=O groups and the respective binding energies of CH_2 carbons in PVF_2 and CHF carbons in PVF. Interactions seem to be weaker in PVF/MA mixture whereas the carbon binding energy of the CHF group is stronger[19].

Studies on polymer/polymer blends

It is expected that, if specific interactions involve a polymer A and low molecular weight model compounds of a second polymer B, the same type of interactions may occur in polymer A/polymer B mixtures. This suggests potential miscibility of the two polymers. However, the extent of association may be lower in the polymer blend than in polymer/model compounds mixtures. For example, Garton *et al.*[14] have shown that the degree of association is less between chloroform and polycaprolactone than between chloroform and low molecular weight esters.

It may be suggested that stiffness, steric constraints or conformations of the macromolecular chains may hinder or even prevent the access of the interacting groups.

The purpose of this section is first to give a deeper insight into the compatible PVF_2/PMMA blend and then to test if PMMA is miscible with PVF_3 and PVF.

The stretching mode $\nu = 1730\,cm^{-1}$ of the carbonyl group of PMMA is shifted to lower frequency in PVF_2/PMMA blends (*Figure 6a*). *Figure 6b* shows that the shift depends on the composition of the amorphous phase of the mixture; if the spectrum of a sample quenched from the melt is subtracted from that of the same sample after a long time annealing above the glass transition temperature T_g, a positive absorption at high frequency and a negative absorption at low frequency are evidenced. So, as PMMA content in the amorphous phase of the sample increases owing to crystallization of PVF_2 induced by annealing, the frequency of the C=O band is shifted toward that observed in pure PMMA.

The previous studies on PVF_2/low molecular weight esters systems suggest that the observed frequency shift is indicative of specific interactions between PVF_2 and PMMA. In the latter case the two components of the C=O band are not resolved, in such a way that the difference between the C=O stretching frequency of PMMA in the blend and that of pure PMMA depends on the fraction of C=O groups associated with PVF_2. The fraction of carbonyl groups which may interact with PVF_2 grows with increasing PVF_2 concentration, leading to a progressive shift of the $\nu_{C=O}$ band toward lower frequencies.

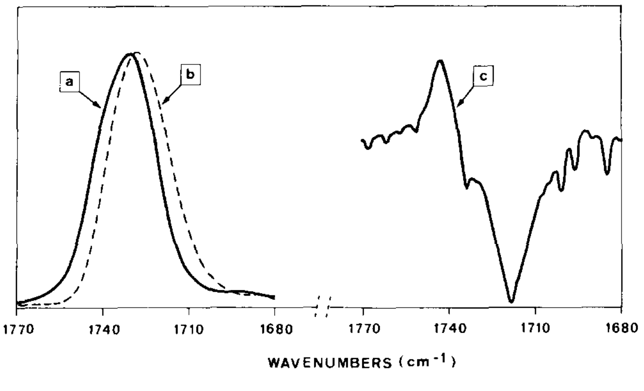

Figure 6 Blending effects on the carbonyl band of PMMA: (a) pure PMMA; (b) blend PVF_2/PMMA (50/50 wt%); (c) difference spectrum of annealed and quenched PMMA/PVF_2 blends (50/50 wt%)

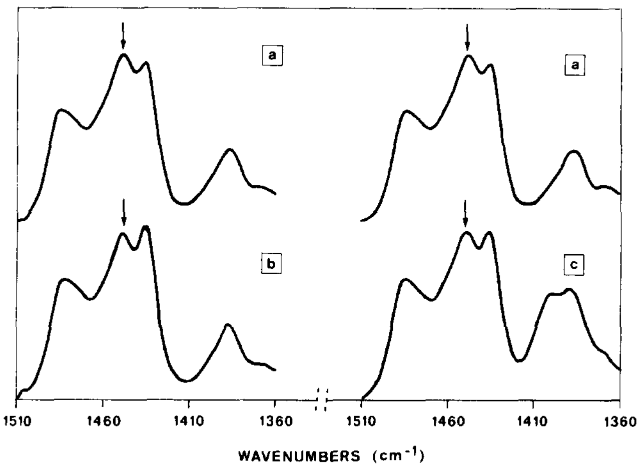

Figure 7 Comparison of temperature and blending effects on the (O)–CH_3 band of PMMA (marked by an arrow): (a) pure PMMA at room temperature; (b) pure PMMA at 115°C; (c) blend PVF_2/PMMA (15/85 wt%) at room temperature

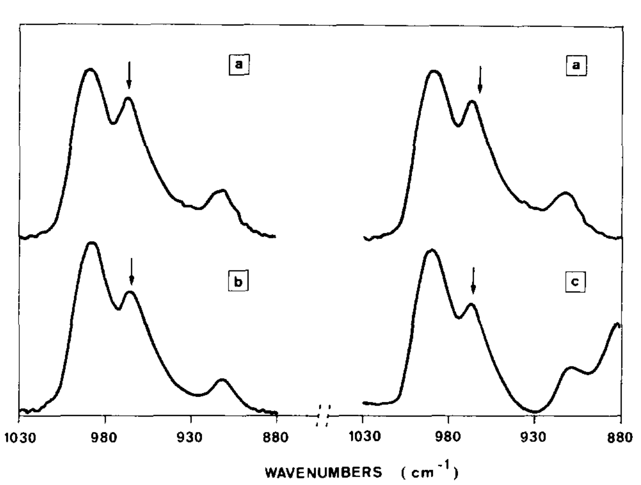

Figure 8 Comparison of temperature and blending effects on the α-CH_3 band of PMMA (marked by an arrow): (a) pure PMMA at room temperature; (b) pure PMMA at 115°C; (c) blend PVF_2/PMMA (15/85 wt%) at room temperature

Two other groups in PMMA are affected by the presence of PVF_2, namely the (O)–CH_3 and the α-CH_3 groups. *Figure 7* shows that the intensity of the vibration at 1450 cm^{-1} (ester methyl group antisymmetric bending) is lowered when PVF is added to PMMA. Schmidt *et al.*[20] evidenced that this band undergoes similar change in pure PMMA when viscosity in the vicinity of the (O)–CH_3 group is decreased owing to the increase in temperature or to the swelling with a solvent. They have shown that the changes of absorbance are accompanied by changes of linewidths so that the integrated intensities remain roughly unchanged. They demonstrated that the intensity and width of the (O)CH_3 antisymmetric bending vibration are mainly sensitive to the dynamics of this group. The dependence of this band intensity on PVF_2/PMMA blend composition may be related to changes in the mobility of the CH_3 group around the O–CH_3 bond as a function of PVF_2 content. The increase in the ester methyl group mobility in the blends is further indication of the intimate mixing of PVF_2 and PMMA.

The α-methyl rocking vibration at 968 cm^{-1} is also sensitive to mixing with PVF_2. A decrease of the intensity of this band is observed in PVF_2/PMMA blends (*Figure 8*). The same trend is observed in pure PMMA when the temperature is raised (*Figure 8*).

Changes in intensity with temperature may be caused by intermolecular interactions, changes in conformational populations or by the dynamics of molecular groups. Therefore further experiments would be necessary to determine unambiguously the origin of the observed intensity lowering in PVF_2/PMMA blends.

As for PVF_2, all the changes induced by PMMA in the PVF_2 spectrum may be ascribed to a lowering or a loss of the crystallinity or to a change of the crystal phase[6].

Rapid investigations by i.r. and d.s.c. on PVF/PMMA, P(VF_2–TFE)/PMMA, PVF_3/PMMA and P(VF_2–VF_3)/PMMA show that these systems are compatible.

CONCLUSION

Use of ester model molecules have been proven to be a suitable and simple tool to investigate molecular interactions in compatible PVF_2/PMMA blends. This approach enables us to show that hydrogen bonding occurs between PVF_2 and the carbonyl groups.

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