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ATR-FTIR spectroscopy as a tool for studies of polymer-polymer miscibility

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SUMMARY

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy is a useful technique for studies on specific interactions between polymers in miscible blends. The application of ATR-FTIR spectroscopy is demonstrated for blends of chlorine containing vinylpolymers of varying chlorine content with different polycarbonates. The miscibility is correlated to specific interactions between polar groups, leading to shifts of the infrared absorption bands.

INTRODUCTION

FTIR spectroscopy has proved to be a potential tool for studies of intermolecular interactions in polymer blends. Such interactions between polar groups of two miscible polymers leed to small frequency shifts of absorption bands of the involved groups.

A number of FTIR studies on polymer blends with polyesters has been reviewed by Coleman et al. (1). They, as well as others (2,3), recorded transmission spectra of samples prepared by film casting. This preparation method exhibits two major drawbacks. First, the polymer polymer miscibility is influenced by the choice of a common solvent and it is often difficult to remove the solvent quantitatively. Second, many polymers tend to crystallize during film casting. These effects leed to shifts of the absorption bands in the same order of magnitude as those produced by specific interactions between miscible polymers (1).

IR-spectra of bulky polymer samples can be obtained by using the attenuated total reflection (ATR) method. With this technique it is possible to record spectra of polymers of any thickness, not being restricted to polymer films. To the author's knowledge there are so far only very few publications on studies of polymer blend miscibility by ATR-FTIR spectroscopy (4,5).

This paper is concerned with the detection of polar interactions in blends of chlorine containing polymers with carbonyl containing polymers by ATR-FTIR spectroscopy.

EXPERIMENTAL

The polymers used were PVC (Hüls), chlorinated PVC (CPVC) (Dynamit Nobel), vinyl chloride/vinylidene chloride copolymer (IXAN) (Solvay), poly-(bisphenol A carbonate) (PC), poly(3,3',5,5'-tetramethyl bisphenol A carbonate) (TMPC) and a polycarbonate of 30% w/w 3,3',5,5'-tetra- methylbis-(4-hydroxyphenyl)-sulphone and 70% w/w bisphenol A (TMSPC) (Bayer). The characteristic data of these polymers are given in Table 1. The molecular weights were measured by g.p.c. relative to PS standards.

The blends were prepared by spraying a solution (about 2% w/w) of two polymers into a 15-fold excess of a vigorously stirred non-solvent to

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Table 1
Characteristic data of polymers used

Polymer	chlorine content (% w/w)	$\overline{M}_n$ (x10^{-3})	$\overline{M}_w$ (x10^{-3})	T_g (°C)	n
PVC	56.7	16	41	88	1.545
CPVC	60.0	64	130	109	1.543
IXAN	71.3	25	48	16	1.592
PC	/	23	58	150	1.586
TMPC	/	15	43	200	1.546
TMSPC	/	33	63	182	

ensure fast and quantitative removal of the solvent. The samples were dried in vacuo at 50°C until they were free of solvent and non-solvent (thermal analysis). This preparation method yields well mixed blends. For FTIR measurements the samples were pressed to thin plates at temperatures above their glass transition temperatures (T_g).

Differential scanning calorimetry (DSC) measurements were conducted with a Perkin Elmer DSC4 with a TADS microcomputer. The glass transition temperatures were determined during the second scan at a heating rate of 20 K/min. A blend was defined to be miscible when it showed only one single T_g intermediate between the T_gs of the pure polymers.

Infrared spectra were obtained on a Nicolet 60SX FTIR spectrometer using a Spectra Tech micro-ATR accessory with a Ge (n=4.0) internal reflection element (IRE). The effective angle of incidence was 48.7°. 100 scans at a resolution of 2 cm^{-1} were signal averaged.

RESULTS

In the discussion of polymer-polymer miscibility an interesting aspect is the occurance of specific interactions between polar groups of the mixed components. Such interactions can be studied by ATR-FTIR spectroscopy. The principle of the ATR technique is illustrated in Figure 1. The IR beam goes through the IRE and is reflected at the IRE/sample interface. The evanescent field of the radiation penetrates the sample and decays exponentially with distance from the surface. In this upper layer of a few µm thickness the spectrum is produced (6).

Although it is possible to record spectra of polymers of high quality with the ATR technique by use of an FTIR spectrometer, certain rules have to be observed for correct interpretation of the measured frequency shifts.

ATR spectra show enhanced absorption intensities on the small wavenumber side and diminished intensities at larger wavenumbers compared to transmission spectra. This difference arises, because the penetration depth of the IR-radiation into the sample increases with decreasing wavenumber. Harrick (7) defined the penetration depth as the distance required for the electric field amplitude to fall to exp(-1) of its value at the surface. The value of the penetration depth (d_p) is given by eq.(1):

$$d_p = \frac{\lambda}{n2\pi\,[\sin^2\theta_e - (n_s/n)^2]^{1/2}} \qquad (1)$$

where λ is the wavelength, n and n_s are the refractive indices of the IRE and the sample, and θ_e is the effective angle of incidence. Apart from this distortion absorption bands may be broadened and shifted in frequency by dispersion effects.

As the refractive index of the sample shows dispersion in the wavenumber region of an absorption, the penetration depth and the amplitude of the evanescent field are changed to produce a shift of the absorption band to smaller wavenumbers. This shift simulates a concentration dependence of the wavenumber as it decreases with dilution of the absorbing group in polymer mixtures.

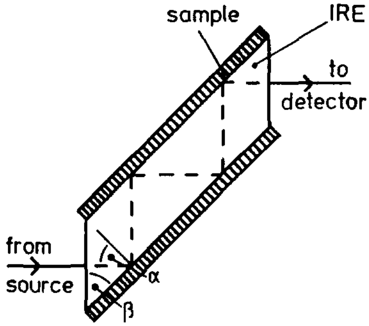

Figure 1. Principle of the ATR technique.

There are two ways to avoid this error. The first possibility is to use an IRE with high refractive index, e.g. Germanium, and a high angle of incidence. The effective angle of incidence

$$\theta_e = \beta - \sin^{-1}\left(\frac{\sin[\beta-\alpha]}{n}\right) \qquad (2)$$

should be substantially higher than the critical angle $\theta_c = \sin^{-1}(n_s/n)$.

The second way is to record a transmission spectrum of a melt film or a microtomed specimen and an ATR spectrum of the pure polymer A containing the group under investigation. The difference between the wavenumber of the absorption maxima in these two spectra gives the artificial shift for pure polymer A. This value has to be weighted by the fraction of polymer A in the blend and subtracted from the observed ATR-values. For better understanding an example is given in Figure 2. These two possibilities can be combined to obtain most reliable results.

Some further points should be observed:

- Intimate contact between sample and IRE
- Complete covering of the IRE
- Clean and polished surface of the IRE
- Resolution 2 cm^{-1} or smaller
- No other absorption bands overlapping
- Approximately symmetrical absorption bands

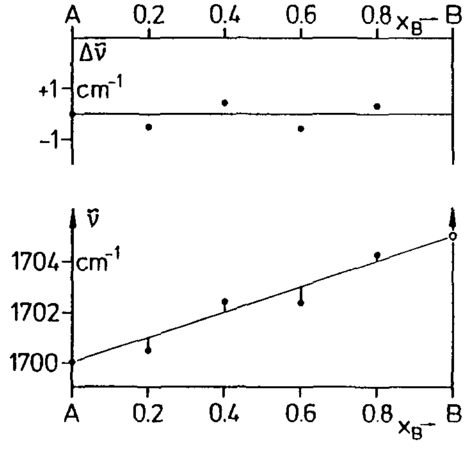

Figure 2. Fictitious example for use of the correction method; (●)ATR, (o)transmission spectrum.

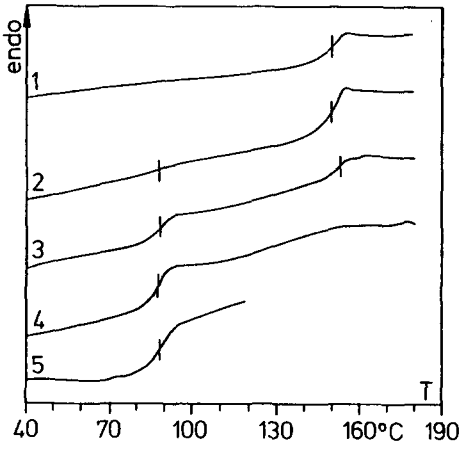

Figure 3. DSC traces of PVC/PC blends; (1) PC, (2) PVC/PC 10/90, (3) 50/50, (4) 90/10, (5) PVC.

Table 2
Shifts of absorption bands in blends

P_1/P_2	$\tilde{\nu}$ (cm^{-1})		$\Delta\tilde{\nu}$ (cm^{-1})		miscibility
	(P_2)	10/90	50/50	90/10 (w/w)	(DSC)
PVC/PC	1773.5	0	+0.5	+1.2	-
CPVC/PC	1773.5	-0.2	-0.2	-0.9	+/-
IXAN/PC	1773.5	-0.4	-1.9	-4.0	+
PVC/TMPC	1774.5	-0.1	-0.2	+0.1	-
CPVC/TMPC	1774.5	-0.3	-0.8	-4.1	+
IXAN/TMPC	1774.5	-0.4	-3.5	-9.1	+
PVC/TMSPC	1774.5	0	-0.2	0	+
PVC/TMSPC	1325.3	-0.2	-1.1	-3.4	+

Some experimental data are chosen to demonstrate the efficiency of the described technique. PVC certainly is the polymer of which the greatest number of miscible blends has been found as yet. PVC forms miscible blends with a series of polyesters, exhibiting specific interactions with the carbonyl group (1).

We studied blend systems of vinyl polymers with varying chlorine content and different polycarbonates. The results are shown in Table 2.

As the transmission spectra of melt films on KBr and ATR spectra of the pure polycarbonates showed no differences in peak positions, a correction of the obtained values was not necessary.

From DSC measurements (Figure 3, Table 3) it was found that PC is miscible over the entire composition range with IXAN, but immiscible with PVC. Blends with CPVC seem to be partially miscible with PC.

Introduction of methyl groups into the polycarbonate enhances the miscibility, so that TMPC is miscible with all investigated chlorinated polymers except PVC.

Miscibility with PVC is found in blends with a polycarbonate containing sulphone groups (TMSPC).

Stretching vibrations are expected to be shifted to lower wavenumbers by polar interactions due to a reduction of the force constant of the bond.

The frequencies of the carbonyl stretching mode show shifts to lower wavenumbers for all miscible blends but the PVC/TMSPC blends, indicating that in those cases the carbonyl group is involved in specific interactions. The reverse shift of 1.2 cm^{-1} in the immiscible PVC/PC blend might arise from the introduction of phase boundaries into the self-interacting polymer.

For the PVC/TMSPC blends the asymmetric SO_2 stretching vibration (8) is shifted to lower wavenumbers. This shows that the interactions leading to miscibility in this case are not located at the carbonyl group but, at the sulphone group (Figure 4).

The attempt to evaluate difference spectra of polymer blends recorded with the ATR technique failed, because absorption intensities and peak shapes depend on the contact between IRE and sample.

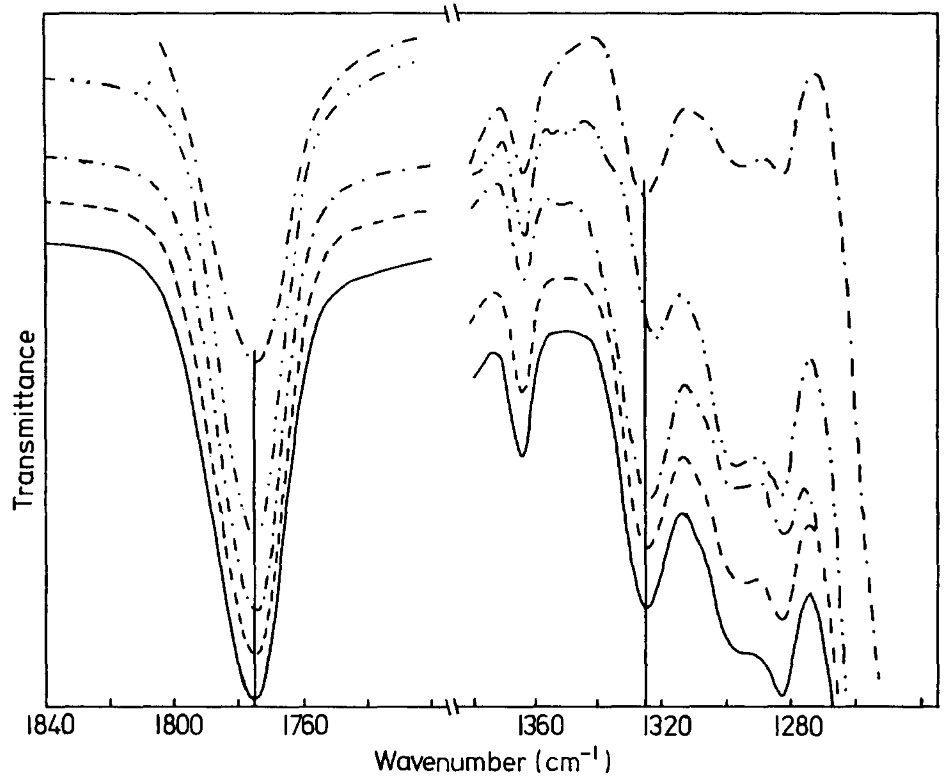

Figure 4. Infrared spectra of PVC/TMSPC blends (C=O and SO_2 regions); —— TMSPC (ATR), --.-- TMSPC (transmission); PVC/TMSPC (w/w): --- 10/90, -.-. 50/50, -..- 90/10.

Table 3
Glass transition temperatures

P_1/P_2	10/90	50/50	90/10
PVC/PC	88/150	88/150	88/150
CPVC/PC	-/136	111/137	107/-
IXAN/PC	139	73	14
PVC/TMPC	88/200	87/200	88/200
CPVC/TMPC	156	145	117
IXAN/TMPC	164	126	51
PVC/TMSPC	178	104	92

CONCLUSIONS

ATR-FTIR spectroscopy is a suitable tool for the qualitative determination of specific interactions in miscible polymer blends. It allows to investigate any specimen, regardless of the preparation method used. Nevertheless care has to be taken not to misinterpret artificial effects.

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REFERENCES

1. Coleman, M.M., Painter, P.C., Appl. Spectrosc. Rev. 20, 255 (1984).
2. Léonard, C., Halary, J.L.,Monnerie, L., Polymer 26, 150 (1985).
3. Garcia, D., in "Current Topics in Polymer Science, Vol.I," ed. by R.M. Ottenbrite, L.A. Utracki, S. Inoue, Carl Hanser Verlag München, Wien, New York, 187 (1987).
4. Könnecke, K., Makromol. Chem. 186, 2061 (1985).
5. Fowkes, F.M., Tischler, D.O., Wolfe, J.A., Lannigan, L.A., Ademu-John, C.M., Halliwell, M.J., J. Polym. Sci., Polym. Chem. Ed. 22, 547 (1984).
6. Mirabella, F.M., Appl. Spectrosc. Rev. 21, 45 (1985).
7. Harrick, N.J., "Internal Reflection Spectroscopy," Harrick Scientific Corporation New York, 30 (1987).
8. Bellamy, L.J., Williams, R.L., J. Chem. Soc., 863 (1957).

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