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Specific interactions in binary and ternary blends of poly(vinyl chloride) with poly(methyl methacrylate-*co*-acrylic acid) and poly(*n*-butyl methacrylate-*co*-4-vinylpyridine)

O. Iguerb[a], R. Bouyahia[a], F. Bouzouia[a], S. Djadoun[a,*], R. Legras[b]

[a]*Chemistry Institute, USTHB, BP32, El Alia, Algiers, 16111, Algeria*
[b]*Unity of Physics and Chemistry of High Polymers, Catholic University of Louvain, la Neuve Place croix du sud, 1 B1348, Louvain-la Neuve, Belgium*

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Abstract

The miscibility of binary blends of poly(methyl methacrylate-*co*-acrylic acid) (MMAA) with poly(*n*-butyl methacrylate-*co*-4-vinylpyridine) (BM4VP) and of ternary blends of each of these copolymers with poly(vinyl chloride) (PVC) has been studied by Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC). As a result of specific interactions of various strengths, BM4VP-26 (containing 26 mol% of 4-vinylpyridine) was found to be miscible with PVC and with MMAA-22 (containing 22 mol% of acrylic acid), while MMAA copolymers were immiscible in all proportions with PVC. There are two possible BM4VP sites for hydrogen bonding to either MMAA or PVC. This copolymer was then used to solubilize the PVC and MMAA in ternary PVC/MMAA/BM4VP blends. This effect was also studied by FTIR spectroscopy and DSC. The results indicate that ternary blends containing an equal amount of PVC and MMAA-22 and more than 50% by weight of BM4VP-26 are miscible.

1. Introduction

Polymethacrylates are known to be immiscible with each other. Poly(methyl methacrylate) (PMMA) is for instance immiscible with poly (*n*-butyl methacrylate) (PBMA). Several studies using different techniques have been carried out on blends of poly (vinyl chloride) (PVC) with each of these two polymers [1–5]. It has been reported that PVC/PMMA and PVC/PBMA blends are miscible up to 145 and 170°C respectively [3]. The miscibility of these blends is attributed to hydrogen bonding interactions between the carbonyl groups of the polymethacrylates and the acidic hydrogen atoms of PVC. Perrin and Prud'homme [6] showed that PVC is miscible in all proportions with poly(*n*-propyl methacrylate) (PPMA), poly(*n*-butyl methacrylate) and poly(amyl methacrylate) (PAMA). To investigate the possibility of rendering PPMA/PBMA or PPMA/PAMA blends miscible by adding PVC, they studied the ternary PVC/PPMA/PAMA and PVC/PBMA/PAMA blends [6]. PVC was used to solubilize the polymethacrylates in each ternary blend. The introduction within polymers of species capable of developing specific interactions between the two polymers in a blend is known as a method for enhancing miscibility of polymers [7–14]. In this work the miscibility behavior of PMMA/PBMA has been studied with respect to increasing the amount of carboxylic groups and 4-vinylpyridine within the PMMA and PBMA chains re-

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[*] Corresponding author. Fax: +1-213-2 24 73 11z.

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Table 1
Characteristics of polymers

Polymers	Copolymers		$[\eta]$(dl/g)	T_g(°C)
	mol% of AA	mol% of 4VP		
PVC	0	0	0.44[a]	81
BM4VP-10	0	10.6	1.33[a]	40
BM4VP-26	0	26	0.71[a]	46
MMAA-8	7.54	0	1.71[b]	103
MMAA-22	22.6	0	1.21[a]	115

[a] THF.
[b] Chloroform.

spectively, by differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR) spectroscopy. The miscibility of binary blends of PVC with each of these copolymers and of ternary blends of PVC with these two copolymers was then studied.

2. Experimental

Poly(methyl methacrylate), poly(*n*-butyl methacrylate) and copolymers of (1) methyl methacrylate with acrylic acid (MMAA-8 and MMAA-22) containing 8 or 22 mol% of acrylic acid, and (2) *n*-butyl methacrylate with 4-vinylpyridine (BM4VP-10 and BM4VP-26) containing 10 or 26 mol% of 4-vinylpyridine, were prepared by free radical polymerization, using AIBN as the initiator. The 4-vinylpyridine content in BM4VP copolymers was determined by UV spectroscopy and elemental analysis. The acrylic acid in the MMAA copolymers was determined by titration. PVC 4000 M ($M_w = 65{,}400$) used in this study was produced at Skikda, Algeria. Table 1 describes the characteristics of these polymers. Films of these copolymers and of their binary and ternary blends were cast from THF solutions and dried in a vacuum oven at 40°C for several days. The glass transition temperatures of these polymers and of their binary and ternary blends of different ratios were measured by DSC using a Perkin Elmer DSC-7 differential scanning calorimeter at a heating rate of 20 K/min. Intrinsic viscosities of these polymers were obtained using a manual capillary Ubbelohde viscometer. Thin films of polymers and of binary PVC/BM4VP, PVC/MMAA, BM4VP/MMAA or ternary PVC/BM4VP/MMAA blends of different ratios were cast from THF solutions onto KBr discs at room temperature. The solvent was first removed slowly at room temperature, the films were then dried in a vacuum oven. Infrared spectra were recorded at room temperature on a FTIR spectrometer type Philips. 60 scans at a resolution of 2 cm^{-1} were signal averaged for each sample.

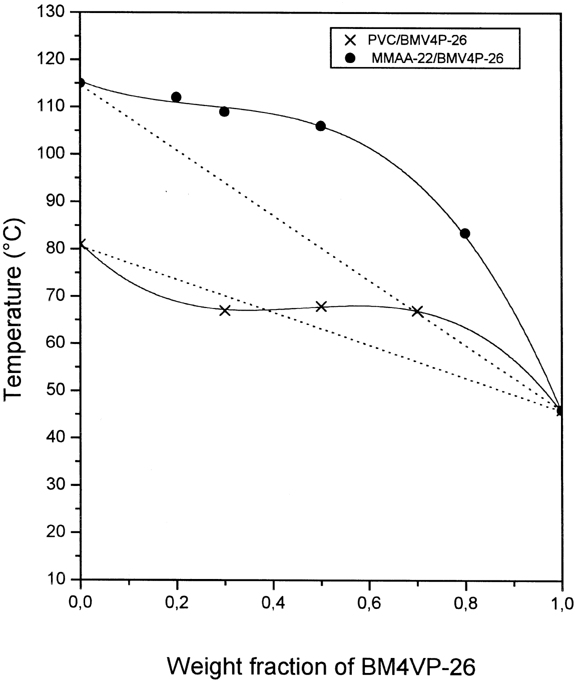

Fig. 1. Glass transition temperature (T_g) of PVC/BM4VP-26 blends and BMV4P-26/MMAA-22 as a function of BM4VP-26 content.

3. Results and discussion

PVC was indeed miscible not only with PBMA as previously reported but also with BM4VP copolymers. The introduction of 4-vinylpyridine within PBMA chains did not affect the miscibility of this latter with PVC. Copolymers of methyl methacrylate with acrylic acid were however immiscible with PVC. The miscibility of the binary BM4VP-26/MMAA-22 is attributed mainly to strong specific interactions that occurred between carboxylic acid and pyridine groups, since MMAA-22 is found to be immiscible with PBMA. MMAA is a self-associating copolymer (intra and intermolecularly), BM4VP is a copolymer that does not self-associate but has two types of sites of different strength that may interassociate with the MMAA copolymer, while PVC is expected to interassociate weakly with each polymethacrylate through the hydrogen-bonding interactions between the ester groups of the polymethacrylate and the acidic hydrogen atoms of PVC. In this study, FTIR and DSC are used to attempt to interpret the miscibility of binary and ternary blends of these polymers.

3.1. PVC/BM4VP blends

In agreement with the qualitative tests, the PVC/BM4VP-26 blends exibit only one T_g as determined by

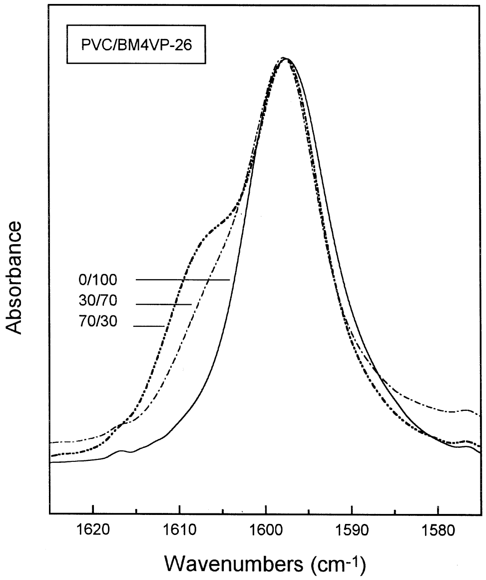

Fig. 2. FTIR spectra of BM4VP-26 and PVC/BM4VP-26 blends in the 1625–1575 cm^{-1} region.

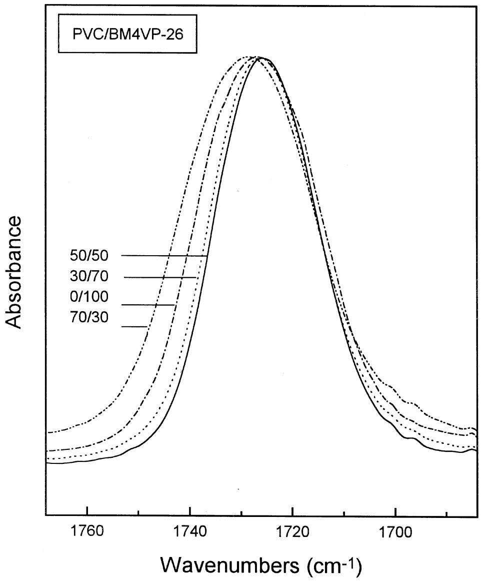

Fig. 3. FTIR spectra of BM4VP-26 and PVC/BM4VP-26 blends in the 1780–1660 cm^{-1}.

DSC. As shown in Fig. 1 the T_g-composition confirms the miscibility of these blends. A positive deviation is observed with a composition lower than 60% by weight of PVC. The miscibility of these blends is characterized by interactions that occurred between the acidic hydrogen atom of PVC and both pyridine and carbonyl groups of BM4VP copolymers as analyzed by FTIR spectroscopy. The FTIR spectra of BM4VP and PVC/BM4VP blends showed that the most affected bands are those concerned with the stretching modes of pyridine in the 1625–1550 cm^{-1} region and of carbonyl in 1780–1660 cm^{-1} region. PVC is transparent in both regions. Fig. 2 displays the scale-expanded infrared spectra of BM4VP-26 and PVC/BM4VP-26 blends, in the former region. The 1597 cm^{-1} band characteristic of free pyridine shifts to higher wavenumbers. An important shoulder, attributed to acidic-pyridine specific interactions, is observed at 1607 cm^{-1} as the content of PVC in the blend increased. We have used a curve fitting procedure for these bands. These

Table 2
Curve fitting results of pyridine ring bands in PVC/BM4VP-26 blends

PVC/BM4VP-26 (wt%)	Non-associated pyridine ring band			Associated pyridine ring band			F_f^N
	Wave number (cm^{-1})	Width (cm^{-1})	Relative area (%)	Wave number (cm^{-1})	Width (cm^{-1})	Relative area (%)	
0/100	1597	11	100				1.00
30/70	1597	09	86.0	1605	08	14	0.86
50/50	1597	11	88.7	1606	11	11.2	0.88
70/30	1597	10	76.7	1607	10	23	0.76
PVC/BM4VP-26 (wt%)	Non-associated carbonyl band			Associated carbonyl band			$F_F^{C=O}$
	Wave number (cm^{-1})	Width (cm^{-1})	Relative area (%)	Wave number (cm^{-1})	Width (cm^{-1})	Relative area (%)	
0/100	1725	28	97				
30/70	1726	23	85.2	1708	42.5	14.7	0.90
50/50	1726	22	87.1	1711	32	12.9	0.91
70/30	1729	30	94				

bands fit to curves essentially gaussian in character. The obtained results are summarized in Table 2.

The fraction of free pyridine groups was calculated from

$$F_{\mathrm{f}}^{\mathrm{N}} = \frac{A_{1597}}{A_{1597} + A_{1607}\dfrac{a_{1597}}{a_{1607}}} \tag{1}$$

where A_{1597} and A_{1607} are the areas of the bands at 1597 and 1607 cm^{-1}, respectively, and a_{1607} and a_{1597} are the absorptivities of the two bands, assuming an absorptivity ratio of unity as previously reported [12]. It is also expected that PVC interacts with the carbonyl groups of BM4VP. Fig. 3 shows the scale-expanded FTIR in the 1780–1660 cm^{-1} region. The band at 1726 cm^{-1} assigned to carbonyl group of BM4VP-26 shifts to 1729 cm^{-1}. A new band appearing at 1710 cm^{-1}, attributed to hydrogen bonded carbonyl groups, was observed with blends containing an excess of BM4VP-26.

The fraction of free carbonyl groups is determined from the expression below:

$$F_{\mathrm{F}}^{\mathrm{C=O}} = \frac{A_{\mathrm{F}}}{A_{\mathrm{F}} + \dfrac{a_{\mathrm{F}}}{a_{\mathrm{H}}}A_{\mathrm{H}}} \tag{2}$$

where A_{F} and A_{H} are the areas of free and hydrogen-bonded carbonyl, respectively, and a_{H} and a_{F} are the absorptivities of the two bands. The ratio of molar absorption coefficient of both bands is taken as 1.6 [15].

3.2. PVC/MMAA-22

The introduction of even a small amount of carboxylic groups within the PMMA renders this latter immiscible with PVC in all proportions. Two glass transition temperatures characterizing each of the constituents, observed with these blends confirm their immiscibility.

The FTIR spectra of MMAA and MMAA/PVC recorded in the 1780–1660 cm^{-1} range show practically no changes in this carbonyl region. The intensity of the band at 1708 cm^{-1} characteristic of the carboxyl–ester interactions was not affected by the presence of PVC. Such preferential and stronger carboxyl–ester interactions reduced the PVC carbonyl interactions, evidenced by a very small shift in the 1733–1730 cm^{-1} region which is not sufficient to enhance the miscibility of PVC /PMMA blends.

3.3. BM4VP/MMAA

The immiscibility of PBMA with PMMA or MMAA copolymers, observed qualitatively, can be explained by the non-hydrogen bonding solubility parameter approach [16]. The $\Delta\delta_{\mathrm{nh}}$ value between these polymers is large enough so as not to induce their miscibility. The immiscibility of BM4VP-10/MMAA-8 blends may be explained by very weak interactions between the two components of the blends. The densities of the interacting groups were not sufficient to enhance the miscibility of these blends. As the densities of interacting species within the polymers increase, miscibility, as in the blends of BM4VP-26/MMAA-22 is observed. The glass transition temperature of MMAA-22 is sufficiently far apart from the one of BM4VP-26. The one T_{g}, observed with these latter blends, as shown in Fig. 1, which displays T_{g}–composition, is therefore an indication of their miscibility. The presence of specific intermolecular interactions between these two constituents is evidenced by the positive deviation from linearity as observed in this plot. Fig. 4 displays the scale expanded FTIR spectra of BM4VP-26 and of BM4VP-26/MMAA-22 blends of different ratios in the 1625–1575 cm^{-1} range. MMAA-22 is transparent in this region, while the band of interest of BM4VP-26 and characteristic of free pyridine ring is observed at 1597 cm^{-1}. This facilitates the study of the interactions between these copolymers in this region as compared to the carbonyl 1780–1660 cm^{-1}. Upon mixing BM4VP-26 with MMAA-22, a new band at 1607 cm^{-1}, characteristic of carboxylic acid–pyridine interactions is observed. As the content of MMAA-22 in the blend increases, the intensity of this 1607 cm^{-1} band increases at the expense of the band at 1597 cm^{-1}. The amount of the hydrogen

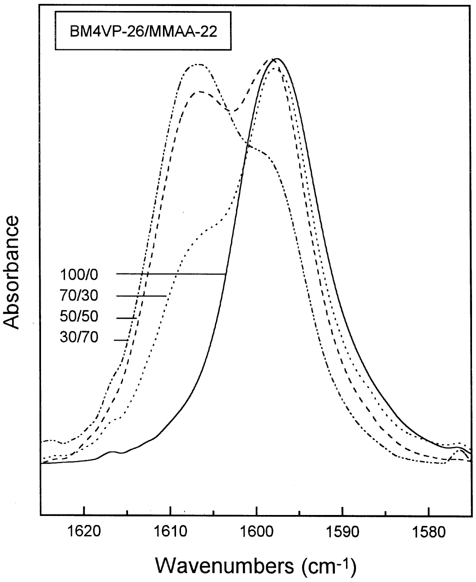

Fig. 4. FTIR spectra of BM4VP-26/MMAA-22 blends in the 1625–1550 cm^{-1} region.

Table 3
Curve fitting results of pyridine ring bands in BM4VP-26/MMAA-22 blends

BM4VP-26/MMAA-22 (wt%)	Non-associated pyridine ring band			Associated pyridine ring band			F_f^N
	Wave number (cm^{-1})	Width (cm^{-1})	Relative area (%)	Wave number (cm^{-1})	Width (cm^{-1})	Relative area (%)	
30/70	1597	09	36.6	1607	11	63.4	0.36
50/50	1597	10	56.2	1607	10	43.7	0.56
70/30	1597	10	76.0	1607	09	24.0	0.75
100/0	1597	11	100				1.00

bonded pyridine increases with an increase of MMAA-22. The fraction of free pyridine of BM4VP-26/MMAA-22 blend compositions is then determined using expression (1) as shown in Table 3.

3.4. PVC/BMVP-26/MMAA-22 blends

The binary blend study showed that BM4VP-26 interacts more strongly with MMAA-22 than with PVC and that the miscibility of its blends with either polymer is mainly due to hydrogen bonding interactions. It is expected that BM4VP-26 copolymer acts as a compatibilizer. Several ternary blends of PVC/BM4VP-26/MMAA-22 were studied. Fig. 5 shows as an example DSC curve of some ternary PVC/BM4VP-26/MMAA-22 blends. As can be seen, blends containing low contents of BM4VP-26 are immiscible and exhibit two T_gs. Ternary blends containing an equal amount of PVC and MMAA-22 and 50% or more of BM4VP-26 are miscible since only one glass transition temperature is obtained. Moreover, these T_gs are higher than the one of BM4VP-26/MMAA-22 or BM4VP-26/PVC binary blends. It is observed that PVC/MMAA-8 and BM4VP-10/MMAA-8 are immiscible. We have similarly determined the glass transition temperatures of PVC/BM4VP-10/MMAA-8 blends. The FTIR study showed that an important amount of free pyridine is observed with each of these BM4VP-26/MMAA-22 binary blends. It is expected that the introduction of PVC will increase the amount of associated pyridine. This was found to depend however on the ratio of BM4VP-26 and MMAA-22. Fig. 6 shows FTIR spectra of some of these ternary blends in 1625–1575 cm^{-1} region in which both PVC and MMAA-22 are transparent. The fraction of free pyridine calculated using expression (1) is shown in Table 4. As can be seen, the fraction of free pyridine versus the fraction of PVC in ternary PVC/BM4VP-26/MMAA-22 blends containing equal amounts of

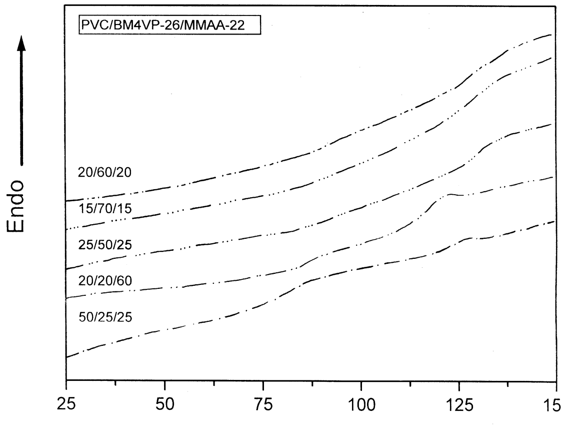

Fig. 5. DSC traces of PVC/BM4VP-26/MMAA-22 blends.

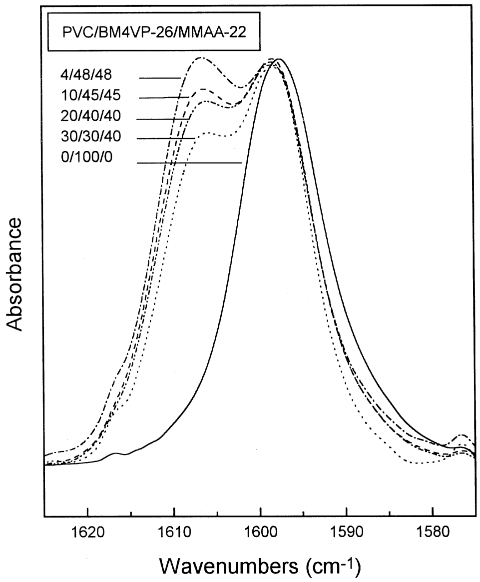

Fig. 6. FTIR spectra of BM4VP-26 and PVC/BM4VP-26/MMAA-22 blends in the 1625–1575 cm^{-1} region.

Table 4
Curve fitting results of pyridine ring bands in PVC/BM4VP-26/MMAA-22 blends

PVC/BM4VP-26/MMAA-22 (wt%)	Non-associated pyridine ring band			Associated pyridine ring band			F_f^N
	Wave number (cm^{-1})	Width (cm^{-1})	Relative area (%)	Wave number (cm^{-1})	Width (cm^{-1})	Relative area (%)	
00/50/50	1597	10	56.2	1607	10	43.7	0.56
04/48/48	1597	10	53.4	1607	11	46.6	0.54
10/45/45	1597	10	55.7	1607	11	44.3	0.55
20/40/40	1597	10	57.9	1607	11	42.2	0.58
50/25/25	1597	10	61.3	1606	11	38.6	0.61
70/15/15	1597	09	40.6	1606	12	59.4	0.40
10/35/55	1597	09	41.8	1607	11	58.1	0.42
20/60/20	1597	10	78.5	1607	10	21.4	0.78
25/50/25	1597	09	77.3	1607	09	22.6	0.77
30/30/40	1597	09	53.8	1607	10	46.1	0.53

BM4VP-26 and MMAA-22 indeed decreases for blends containing high PVC content.

Acknowledgements

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