Miscibility of Poly(vinylidene fluoride) and Atactic Poly(methyl methacrylate)

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ABSTRACT: Different results for the miscibility between poly(vinylidene fluoride) (PVDF) and atactic poly(methyl methacrylate) (at-PMMA) have been reported. In this study, the interaction between PVDF and at-PMMA was confirmed, although such a kind of force was weak. With increasing PVDF weight fraction, the blends exhibited more heterogeneous properties, and the films thus appeared more opaque. The difference spectra after subtraction of PVDF and poly(methyl methacrylate) (PMMA) showed that the interaction between the carbonyl groups of PMMA and the hydrogen atoms of PVDF increased as the stretch vibration of C=O bonds band shifted to a lower frequency with higher PVDF content. From the computer analysis, the sum spectra of the blends could not be obtained by simple addition of the separate spectra of the homopolymers. The contact angle measurement demonstrated that the hydrophobicity against water increased with PVDF content and that contact angles against water were larger than 90° when the PVDF content exceeded 30%, indicating good water repellency. The contact angles against *n*-hexane, however, could not be measured because of the complete wetting of the film by *n*-hexane. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1–5, 2004

Key words: blends; miscibility; compatibility; atactic; FT-IR

INTRODUCTION

The miscibility of poly(vinylidene fluoride) (PVDF) with poly(methyl methacrylate) (PMMA) has been studied extensively since the 1970s. The blends have been found to be completely miscible over the entire composition range above the PVDF melting temperature (T_m) of 170°C and below lower critical solution temperature (LCST). However, PVDF crystallizes in the blend when it is held at any temperature between its glass-transition temperature (T_g) and crystalline T_m if its weight fraction exceeds 0.5;[1,2] however, a completely amorphous phase forms if its weight fraction is under 0.5 according to most studies.

The compatibility of these two polymers has been evaluated by such terms as the transparency of the blend, the solubility parameters, the Flory–Huggins interaction parameter, the transition temperature of the blend, the LCST, and the degree of polarization of the longitudinal Brillouin peaks, which can be measured by thermal analysis,[1–5] dilatometry,[2–5] small-angle X-ray scattering,[6] pulsed ^{13}C-NMR,[7,8] Fourier transform infrared (FTIR) spectroscopy,[9,10] and so on.

One of the commonly used methods that has been used to study the strength of the interaction was the determination of T_m depressions of PVDF crystals by Nishi and Wang[3] for a PVDF–PMMA system and Kwen et al.[11] for a PVDF–poly(ethyl methacrylate) (PEMA) system, in which the T_m depressions of PVDF–PMMA blends, which were larger than those of PVDF–PEMA systems, showed the stronger interaction. It was concluded that the compatibility between PVDF and PMMA was stereoselective, which means the miscibility of PVDF–isotactic poly(methyl methacrylate) (iso-PMMA) was better than that of PVDF–syndiotactic poly(methyl methacrylate) (syn-PMMA). The interaction of PVDF and atactic poly(methyl methacrylate) (at-PMMA), however, was proven rather weak, even when the weight fraction of PVDF was less than 0.5. In recent years, nevertheless, Sasaki et al.[12] showed that PVDF–at-PMMA and PVDF–syn-PMMA systems were miscible, whereas PVDF–iso-PMMA blends were immiscible in contrast to previously reported results obtained by methods of crystallization dynamics. In the authors' opinion, the tacticity difference between at-PMMA and syn-PMMA was not so large that only a slight difference in tacticity influenced the miscibility of the blends.

The height of the LCST was also used as a measurement of interaction strength, in which the higher the LCST was, the stronger the interaction was.[13] The upper critical solution temperature (UCST) was also found to be somewhere above the T_m. Special interactions were weak in blends annealed at a low temperature (<UCST).[14]

As far as the interaction nature is concerned, the interaction between PVDF and carbonyl-containing polymers, that is, between the hydrogen atom of

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PVDF and the oxygen atom of carbonyl, was emphasized by Bernstein et al.[15] On the basis of the compatibility of PVDF with poly(vinyl methyl ketone), poly(methyl acrylate), and poly(vinyl acetate) and the incompatibility with the carbonyl-lacking polymer poly(vinyl methyl ether), they suggested that the ether linkage plays a far less important role than the carbonyl group. Spectroscopic techniques, NMR, and IR are useful ways to study this kind of force. ^{13}C-NMR and ^{19}F-NMR[16] showed no any special interaction or complex formation in the PVDF–at-PMMA blends, which meant although the blends were completely miscible in some cases, the interaction was not caused by the hydrogen bonding. Coleman et al.[9] studied the FTIR spectrum and found that as long as PVDF was partly crystalline, such spectra of heterogeneous blends were nearly identical to the sum spectra composed from separate polymers (PMMA wt % < 50%). So the spectra of blends could be synthesized by weighted absorbance additions of partly crystalline PVDF and the amorphous PMMA phase. At higher PMMA contents, the crystallization of PVDF was diminished drastically, which led to homogeneous blends. Roerdink et al.[10] demonstrated that the extinction of the stretch vibration of C=O bonds band (1730 cm^{-1}) in the difference spectrum for iso-PMMA strongly increased in the blends compared with pure PMMA and this band shifted to a lower frequency, which showed a strong interaction between PVDF and it-PMMA, and that the amorphous PMMA phase contained a part of the PVDF molecules rejected from the crystals.

As for the morphology of the blends, mechanical relaxation measurements showed three transitions of the blends, which were at $-40°C$ (at 110 HZ), 70°C, and 90°C. These three kinds of transition temperatures were thought to be the β transition and γ transition of PVDF and the T_g of the amorphous phase of PMMA for heterogeneous blends, respectively.[17]

Kabin and coworkers observed two relaxation regions, one for the T_g of PVDF and the other for the crystalline phase. Ishida et al. found a single relaxation that corresponded to the T_g found by Kabin. Peterlin and (Holbrook) Elwell found the effects of rolling and annealing on the relaxation mechanisms. Yano showed the origins of three such transitions.[18–22]

A two-phase structure was observed by optical microscopy, in which a highly interconnected two-phase morphology with uniform domain size was observed. If the rate of solvent evaporation was fairly high, the modulated structure formed, whereas if the rate was low, a much coarsened and irregular two-phase structure would exist. The PVDF–PMMA–solvent ternary system was a stable homogeneous solution; however, it separated into two phases after solvent evaporation.[14]

Small-angle X-ray scattering showed that PMMA chains resided in the interlamellar region between PVDF crystallites without the formation of any separated PMMA domains.[13]

PURPOSE OF THE MISCIBILITY STUDY

From the previous review on the compatibility of PVDF with PMMA, one can see that the miscibility of these two totally different polymers are possible in certain cases, such as in the molten state. According to most articles, there was good miscibility of PVDF with iso-PMMA–syn-PMMA (PVDF wt % < 50), whereas there was poor miscibility with at-PMMA. However, different results (the miscibility of PVDF with at-PMMA was better than that with iso-PMMA) were obtained by some researchers. Hence, it was necessary to examine the compatibility between them, especially of PVDF with at-PMMA because commercial PMMAs cannot be stereo-regular.

In this study, optical microscopy and FTIR were used as the main methods to study the compatibility between PVDF and at-PMMA. Contact angle measurements were also used to study the hydrophobicity of the PVDF–PMMA blends.

EXPERIMENTAL

PMMA butanone solutions were prepared in the laboratory [typically 30 wt % methyl methacrylates were radically polymerized in butanone solvent with 1 wt % benzoyl peroxides (BPOs) (based on monomer weight) as initiators]. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) were 5.3×10^4 and 10.7×10^4, respectively, as measured by GPC. The tacticities of the PMMAs were measured by NMR, yielding 44% atactic triads, 13% isotactic triads, and 43% syndiotactic triads). PVDF resins were kindly supplied by 3F (Shanghai 3F New Materials Co., Ltd., Shanghai, China). The M_n and M_w were 1.6×10^5 and 3.4×10^5, respectively. Blends of PVDFs with different weight fractions of PMMAs were prepared by the mixture of PMMA 2% butanone solution with PVDF 2% butanone solution. The films were made by the casting of the mixing solutions on glass plates at 110°C. The obtained glass plates were observed directly by optical microscopy at room temperature. FTIR spectra were recorded on a PerkinElmer 1730 FTIR spectrometer (Perkin Elmer, USA). The polymer solutions were cast on KBr pellets. The solvent was allowed to evaporate completely. Four samples (pure PMMA, pure PVDF, PVDF/ PMMA = 7:3, and PVDF/PMMA = 3:7) were scanned, and the difference spectra were made by computerization. Contact angle measurements were performed on a JJC-2 contact angle measurement meter. (Changchun 3rd Optical Instruments Factory, Changchun, Jilin, China).

TABLE I
State of the PVDF–PMMA Film

	PVDF–PMMA									
	0:10	1:9	2:8	3:7	4:6	5:5	6:4	7:3	8:2	9:1	10:0
State	T	T	T	T	T	A little W	Opaque W	W	W	W	W

T = transparent; W = white.

RESULTS AND DISCUSSION

Optical microscopy observations

Nine solutions with different PVDF and PMMA ratios were prepared (PVDF/PMMA = 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, and 9:1) compared with pure polymer solutions. When the PVDF weight fraction was under 60 wt % (PVDF/PMMA = 1:9, 2:8, 3:7, 4:6, or 5:5), the films thus made were much more transparent than those made from higher PVDF content solutions. The lower PVDF content (10–40%) films were almost as transparent as pure PMMA (Table I). Such films were very difficult to be peeled off from the plates. The films made with higher PVDF contents, however, were white opaque and easily peeled off. Such a kind of phenomena showed that the blends with higher PVDF contents separated into two phases because of the crystallization of PVDF in the amorphous PMMA. At lower PVDF contents, however, the blends contained only small amounts of partly crystallized PVDF and the amorphous PVDF and PMMA mixtures, which led to the higher miscibility of PVDF and PMMA.

From optical microscopy, a two-phase structure, with a highly interconnected two-phase morphology with uniform domain size, was observed, which was highly accordant with that reported by Saito et al.[14] Such a kind of morphology was called *modulated structure* by Saito et al., which they believed originated from spinodal decomposition during the solution casting process but not from crystallization. We confirmed that the ternary PVDF–PMMA–butanone system was a stable homogeneous solution; however, it separated into two phases after solvent evaporation at room temperature. This suggests the possibility that the instability of the concentrated solution resulting in spinodal decomposition came from the immiscibility between the two polymers at the casting temperature at around 110°C.

FTIR spectra

From the FTIR records, we hardly observed the difference between the PVDF, PMMA, PVDF–PMMA (7:3), and PVDF–PMMA (3:7) spectra (Fig. 1) because the interaction was so small between PVDF and at-PMMA. However, the difference spectrum (Fig. 2) showed a big difference in the $\nu_{C=O}$ band, with almost 10 cm^{-1} variation. At a lower PMMA weight fraction (0.7), the difference spectrum of the $\nu_{C=O}$ band was at 1718.77 cm^{-1}, and at a higher PMMA weight fraction
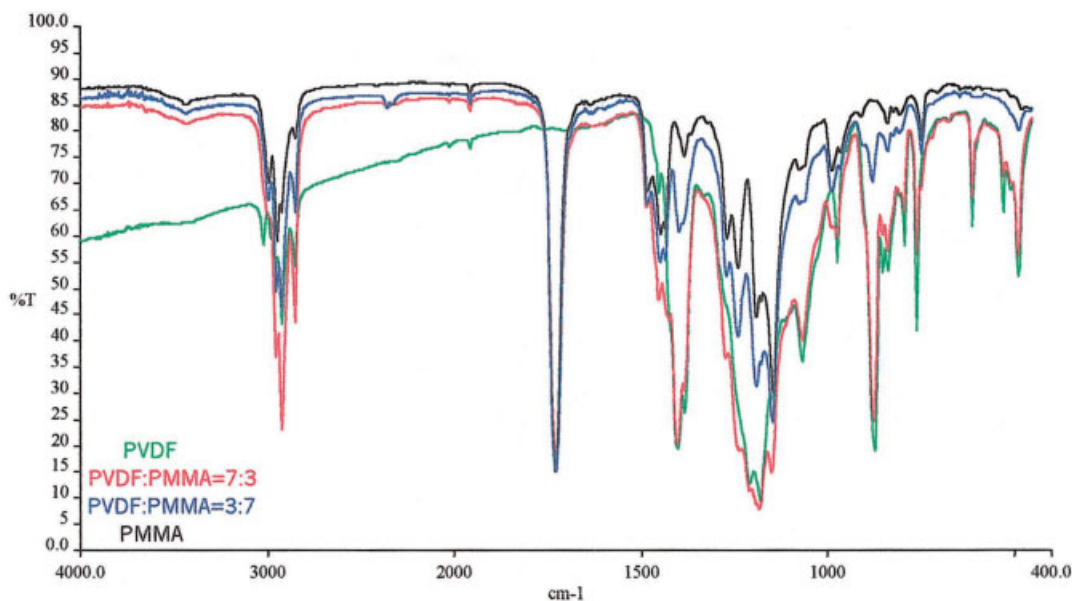

Figure 1 FTIR spectra of PVDF, PVDF–PMMA (7:3 and 3:7), and PMMA (the green line stands for PVDF, the red line stands for PVDF/PMMA = 7:3, the blue line stands for PVDF/PMMA = 3:7, and the black line stands for PMMA).
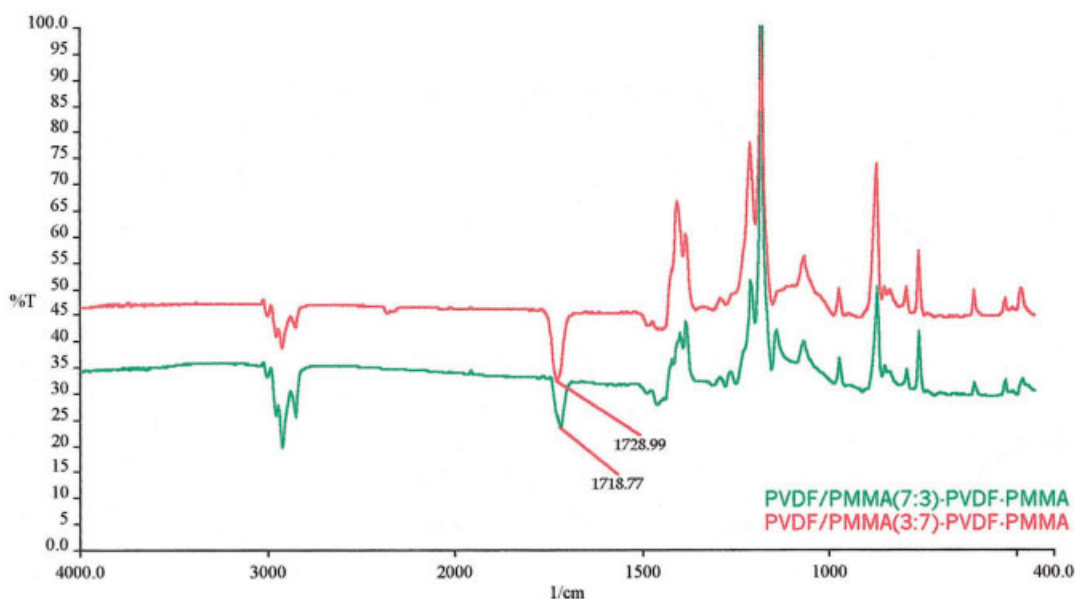
Figure 2 Difference spectrum after subtraction of PVDF and PMMA [the red line stands for PVDF–PMMA (3:7)–PVDF–PMMA, and the green line stands for PVDF–PMMA (7:3)–PVDF–PMMA].

(0.3), the band was at 1728.99 cm^{-1}, which indicated a shift of the $\upsilon_{C=O}$ band to a lower frequency when the blend contained more PVDF compared than pure PMMA (1729.48 cm^{-1}; Table II).

We believe that the PVDF–PMMA (3:7) blends were much more homogeneous than PVDF–PMMA (7:3) blends (from the optical observation), indicating a shift of the $\upsilon_{C=O}$ band to a lower frequency when the blends were more heterogeneous. At higher PVDF contents, the crystallization of PVDF perturbed the miscibility of PVDF and PMMA, and the interaction between the carbonyl groups and the hydrogen atom of PVDF was dramatically reduced, thus leading to the shift of the $\upsilon_{C=O}$ band to a lower frequency. However, such a kind of interaction could not be explained as hydrogen bonding because it was not so strong and the peaks of the H atom of PVDF showed no obvious change. From the computer analysis, the sum spectra of the blends could not be obtained by the simple addition of the separate spectra of the homopolymers. All of these showed the existing interaction between PVDF and at-PMMA although it was not so evident.

Contact angle measurement

The contact angles of the PVDF–PMMA films against water and n-hexane were measured on a JJC-2 contact

angle measurement meter. PMMA 2% butane solution, PVDF 2% butane solution, and 2% butane solution with different ratios of PMMA and PVDF (PMMA/PVDF = 2:8, 3:7, 5:5, 7:3, and 8:2) were cast on the glass plate and dried in oven at 110°C. The results are shown in Table III and Figure 3.

As shown in Table III and Figure 3, the contact angles against water increased with PVDF content in the mixture film, which was caused by the PVDF hydrophobicity due to the —CF$_2$ groups of PVDF. We believe that the high electro-negative properties of F atom (4.0), the short atom radius (0.135 nm), the shorter C—F bond, and the high bond energy led to the smaller interactions between the molecules of the fluorine-containing polymers. Such properties exert unique surface properties for fluorine-containing polymers, such as good water and oil repellency, antifouling properties, and good optical properties.[23] The contact angles were larger than 90° when the PVDF content exceeded 30 wt %, which indicated good water repellency. The contact angles against n-hexane, however, could be measured because of the total wetting of the film by n-hexane, which meant that although the CF$_2$ had excellent surface properties, the CH$_2$ groups of PVDF hindered its repellency for oil because PVDF has half the CF$_2$ groups and half the CH$_2$ groups of poly(tetrafluoroethylene) (which has

TABLE II
Comparison of $\upsilon_{C=O}$ Bands of Difference Spectrum and That of PMMA

	Blend		
	PMMA	PMMA:PVDF = 7:3	PMMA:PVDF = 3:7
Location of $\upsilon_{C=O}$ band (cm^{-1})	1729.48	1728.99	1718.77

all of the CF$_2$ groups and a critical surface tension of 18.5 dyn/cm). Thus, the results showed that the hydrophobicity against water increased with PVDF content when PMMA was mixed with PVDF and that the hydrophobicity against oil totally failed.

As shown by optical microscopy and the FTIR spectra, the interaction between PVDF and at-PMMA did exist, which led to the miscibility of these two polymers. The PVDF coating was confirmed with high thermal, chemical, aging, and weather resistances. However, PVDF has various disadvantages: it is often crystalline, it exhibits poor adhesion, and it is not cured or crosslinked easily (a high temperature is necessary). However, acrylate coatings show good adhesion and can be easily cured at room temperature. Therefore, the blends of these two polymers induced disorder of the macromolecule and, thus, reduced or eliminated the high crystallinity of the PVDF while maintaining the advantages of the two polymers, such as good water repellency, as shown by the contact angle measurements.

CONCLUSIONS

According to most studies, good miscibility of PVDF with iso-PMMA–syn-PMMA (PVDF wt % < 50) and poor miscibility with at-PMMA has been observed. However, different results (the miscibility of PVDF with at-PMMA was better than that with iso-PMMA) were obtained by some researchers. The interaction between PVDF and at-PMMA was confirmed in this study, although such a kind of force was weak. With increasing PVDF weight fraction, the blends exhibited more heterogeneous properties, and the films thus appeared more opaque. The difference spectra after subtraction of PVDF and PMMA showed increasing interaction between the carbonyl groups of PMMA and the hydrogen atoms of PVDF as the $v_{C=O}$ band shifted to a lower frequency with higher PVDF content. The contact angle measurement demonstrated that the hydrophobicity against water increased with PVDF content and that the contact angles against water were
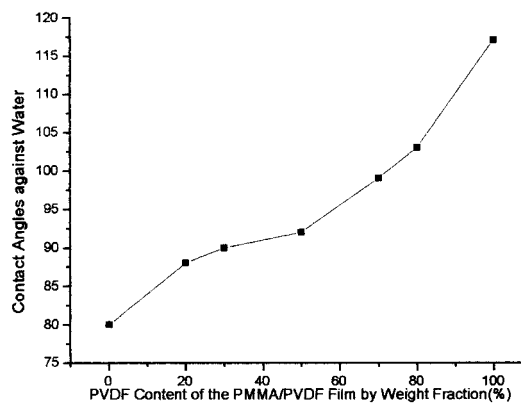

Figure 3 Contact angles of PVDF–PMMA films against water.

larger than 90°when the PVDF content exceeded 30%, which indicated good water repellency. The contact angles against *n*-hexane, however, could not be measured because of the complete wetting of the film by *n*-hexane. The blends of these two polymers induced disorder of the macromolecule and, thus, reduced or eliminated the high crystallinity of the PVDF while maintaining the advantages of the two polymers, such as good water repellency, as shown by the contact angle measurements.

References

1. Noland, J. S.; Hsu, N. N.-C.; Saxon, R.; Schmitt, J. M. Adv Chem Ser 1971, 99, 15.
2. Paul, D. R.; Altamirano, J. O. Polym Prepr 1974, 15, 409.
3. Nishi, T.; Wang, T. T. Macromolecules 1975, 8, 909.
4. Roerdink, E.; Challa, G. Polymer 1978, 19, 173.
5. Hirata, Y.; Kotaka, T. Polym J 1981, 13, 273.
6. Wendorrff, J. H. J Polym Sci Polym Lett Ed 1980, 18, 439.
7. Douglass, D. C.; Mcbrierty, V. J. Macromolecules 1978, 11, 766.
8. Ward, T. C.; Lin, T. S. Adv Chem Ser 1984, 206, 59.
9. Coleman, M. M.; Zarian, J.; Varnell, D. F.; Painter, P. C. J Polym Sci Polym Lett Ed 1977, 15, 745.
10. Roerdink, E.; Challa, G. Polymer 1980, 21, 509.
11. Kwei, T. K.; Patterson, G. W.; Wang, T. T. Macromolecules 1976, 9, 780.
12. Sasaki, H.; Bala, P. K.; Yoshida, H.; Ito, E. Polymer 1995, 36, 4805.
13. Paul, D. R.; Barlow, J. W.; Berstein, R. E.; Wahrmund, D. C. Polym Eng Sci 1978, 18, 1225.
14. Saito, H.; Fujita, Y.; Inoue, T Polym J 1987, 19, 405.
15. Bernstein, R. E.; Wahrmund, D. C.; Barlow, J. W.; Paul, D. R. Polym Eng Sci 1978, 18, 1220.
16. Hahn, B.; Wendorff, J. Macromolecules 1985, 18, 718.
17. Bovey, F. A.; Schilling, F. C.; Kwei, T. K.; Frisch, H. L. Polym Prepr 1977, 18, 704.
18. Kabin, S. P.; Malkevich, S. G.; Mikhailov, G. P.; Sazhin, B. I.; Smolyanskii, A. L.; Chereshkevich, L. V. Vysokomol Soedin 1961, 58, 137.
19. Ishida, Y.; Watanabe, M.; Yamafuji, K. Kolloid Z 1964, 200, 48.
20. Peterlin, A.; (Holbrook) Elwell, J. J Mater Sci 1967, 2, 1.
21. Yano, S. J Polym Sci Part A-2: Polym Phys 1970, 8, 1057.
22. Peterlin, A.; Holbrook, J. D. Kolloid Z 1965, 203, 68.
23. Holloway, J. H. Surf Coat Int 1995, 78 (2), 50.

TABLE III
Contact Angle of the PMMA–PVDF Films Against Water and *n*-Hexane

Film (PVDF:PMMA)	Contact angle (°)	
	Against water	Against *n*-hexane
0:10	80	Totally wetted
2:8	88	Totally wetted
3:7	90	Totally wetted
5:5	92	Totally wetted
7:3	99	Totally wetted
8:2	103	Totally wetted
10:0	117	Totally wetted