Macromol. Symp. ***139**, 125–135 (1999)*

Modification of the Polycarbonate/Poly(vinylidene Fluoride) Interface by Poly(methyl Methacrylate). Effect on the Interfacial Adhesion and Interfacial Tension

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Abstract: Polycarbonate (PC) and poly(vinylidene fluoride) (PVDF) are two immiscible polymers which form two-phase blends with weak interfacial adhesion and high interfacial tension. This situation may be changed by the addition of poly(methyl methacrylate) (PMMA), which concentrates preferably in the PVDF-rich phase, but also at the PVDF/PC interface. The interfacial activity of PMMA was estimated by the measurement of the interfacial adhesion and interfacial tension in relation to the PMMA content in the PVDF/PC blends. The interfacial adhesion between PC and homogeneous PVDF/PMMA blends of various compositions was measured by the dual cantilever beam technique. The imbedded fiber retraction method was used for the measurement of the interfacial tension. A very beneficial effect was observed when PVDF was premixed with PMMA amounts increasing up to ca. 35 wt.-%. Beyond that content, the improvement tends to level off.

INTRODUCTION

Addition of properly designed block or graft copolymers to immiscible polymer blends is a well-known strategy to improve the phase dispersion, to stabilize the phase morphology and to improve the interfacial adhesion (Refs. 1,2). However, the cost of preformed block or graft copolymers and the limitation of reactive processing in the *in situ* formation of block copolymers (Refs. 3-5) are incentives to consider new compatibilization strategies. This problem is still more acute in the case of polycarbonate (PC) and poly(vinylidene fluoride) (PVDF) blends since no parent block or graft copolymers can be made whatever the synthetic approach is. In this work, poly(methyl methacrylate) (PMMA) has been considered as a potential compatibilizer for PC/PVDF polyblends, since PMMA is known to be miscible with PVDF (Refs. 6-8) and compatible with PC (Refs. 9-11). In the extreme, PMMA might behave as a common "solvent" for PC and PVDF in the melt. Before testing the ability of PMMA to improve the PC/PVDF interfacial adhesion and to decrease the PC/PVDF interfacial tension, it is worth noting that PC has been toughened by core-shell rubber particles with a PMMA

CCC 1022-1360/99/$ 17.50+.50/0

shell. The compatibility of this PMMA shell with PC was proposed to provide an interfacial adhesion strong enough for the rubber particles to cavitate rather than to be debonded (Ref. 12). Another valuable observation was reported by Hobbs et al. (Ref. 13), who showed by transmission electron microscopy that PC envelopes PMMA domains in a ternary PC/PMMA/PBT blend, in agreement with the spreading coefficients calculated from interfacial tension data.

For PMMA to have an interfacial activity, it has to be located at the interface of the two immiscible polymers. Although experimental techniques for the surface analysis, such as forward recoil spectroscopy, secondary ion mass spectroscopy and neutron reflectrometry, can be used, they require a preliminary separation of the phases and, for some of these techniques, a labeling of one polymeric component. It might thus be more straightforward and convenient to measure properties in a direct connection with the real interface, i.e., the interfacial tension by the imbedded fiber retraction (IFR) method (Refs. 14-16), and the interfacial adhesion by the dual cantilever beam test (Ref. 17). The purpose of this work is thus to investigate how the PC/PVDF interfacial tension and adhesion are improved by premixing PVDF with increasing amounts of PMMA.

EXPERIMENTAL

Materials

Table 1 lists the source, molecular weight, polydispersity and glass transition of the polymers used in this study.

Table 1 Main characteristics of the investigated polymers

Polymer	**Trade name**	**Source**	**M_w x 10^{-3}**	**M_w/M_n**	**T_g [a] °C**
Polycarbonate (PC)	Makrolon 3103	Bayer	58 [b]	1.7 [b]	150
Poly(methyl methacrylate) (PMMA)	Diakon	ICI	60 [b]	1.6 [b]	118
Poly(vinylidene fluoride) (PVDF)	Solef x10N	Solvay	125	1.8	-45
Poly(vinylidene fluoride) (PVDF)	Solef 1008	Solvay	110	1.8	-45

[a] By dynamic mechanical analysis at 1 Hz; [b] by GPC in THF using polystyrene standards.

Measurement of the interfacial adhesion

The fracture toughness of the phase boundary, G_c, was measured using the dual cantilever beam method (Ref. 17). Two-mm thick plates of PC and PVDF/PMMA blends were superposed and compression-molded at a desired temperature. After a well defined period of time, the sandwich was cooled down under a small pressure and test samples of 0.9-1 cm width were cut out. A razor blade was inserted between the two constitutive layers, and the length of the crack propagating ahead the razor blade was measured with a travelling microscope after at least 84-h equilibration at room temperature. The toughness of the interface was calculated from Eq. 1 proposed by Creton *et al.* (Ref. 17) in the case where no component of the sandwiched assembly was previously glued on a rigid glass plate.

$$G_c = \frac{3d^2 E_1 h_1^3 E_2 h_2^3}{8l^4\left(E_1 h_1^3 + E_2 h_2^3\right)} \qquad [1]$$

where E and h are the modulus and thickness of the constitutive layers 1 and 2, d is the thickness of the razor blade, and l is the crack length. Since the moduli of the two plates were comparable, the use of a symmetric plate assembly allowed the crack to propagate right along the interface.

The Young modulus was calculated from the initial slope of the stress - strain curves. For this purpose, PVDF/PMMA blends were prepared by melt mixing with a two-roll mill (SCAMIA), at 200 °C for 10 min. 1 mm thick samples of PC and PVDF/PMMA blends were prepared by compression molding at 220 and 200 °C, respectively. Stress - strain curves for the PVDF/PMMA blends were recorded with an Instron universal tensile tester (model DY24) at a tensile rate of 20 mm/min.

Measurement of the interfacial tension

The interfacial tension between melted PC and PVDF/PMMA blends was measured by the IFR technique (Refs. 14-16), based on the measurement of the microscopic tracking of short imbedded fibers. The interfacial tension was calculated from the time dependence of the retraction process, as detailed elsewhere (Refs. 15,16). Briefly, the length and the effective radius (R) of the fiber were measured as functions of time, and the function $f(R/R_0)-f(R_e/R_0)$ was plotted vs. the retraction time t, in agreement with Eq. 2.

$$f(R/R_0) - f(R_e/R_0) = t\gamma_{12}/[((\eta_m+1.7\eta_f)/2.7)R_0] \qquad [2]$$

where γ_{12} is the interfacial tension, R and R_e are the effective radii of the retracting fiber at time t and t=0, respectively. R_0 is the radius of a sphere of the same volume as the fiber, and η_m and η_f are the zero-shear viscosities of the matrix and the fiber, respectively. Equation 3 is the expression of functions $f(R/R_0)$ and of $f(R_e/R_0)$, whose values are available in ref. 15.

$$f(x) = \frac{3}{2}\ln\left[\frac{\sqrt{1+x+x^2}}{1-x}\right] + \frac{3^{3/2}}{2}\tan^{-1}\left[\sqrt{3}\,\frac{x}{2+x}\right] - \frac{x}{2} - \frac{4}{x^2} \qquad [3]$$

where $x = R/R_0$ or R_e/R_0.

PC fibers were prepared by extrusion at 240 °C through the die of an equipment used for the measurement of melt indices. The polymer was previously dried at 120 °C for 24 h under vacuum. The final diameter was 0.1 mm.

The PMMA/PVDF matrices were prepared by melt mixing of PMMA and PVDF with a two-roll mill (SCAMIA) at 200 °C for 5 min. 0.5-mm plates of PMMA, PVDF and PMMA/PVDF blends were prepared by compression molding at 200 °C. The fiber and matrix were annealed at 150 and 100 °C, respectively, under vacuum overnight.

Short-section fibers (ca. 0.5 mm) were sandwiched between two plates of the same PVDF/PMMA blend, and this sandwich was placed between preheated glass slides. The samples were then transferred to an Orthoplan microscope equipped with a Mettler FP-5 hot stage and annealed at 150 °C for 30 min in order to allow PMMA to migrate to the interface. The fiber retraction was then measured at 220 °C.

The melt viscosity vs. frequency curves for all the PC, PVDF, PMMA and PVDF/PMMA blends were measured using a Bohlin constant-stress rheometer at 220 °C. Measurements were performed using the plate - plate configuration and a gap of approximately 1 mm, in the frequency range of 10^{-2}-10^{2} Hz.

RESULTS AND DISCUSSION

Figures 1 and 2 show the frequency dependence of the melt viscosity of PC, PVDF, PMMA and PVDF/PMMA blends of various compositions at 220 °C. The zero-shear viscosity (η_0) has been calculated from Eq. 4 based on the Yasuda model (Ref. 18).

$$\eta = \eta_0\left[1+\left(\alpha\dot{\gamma}\right)^{a}\right]^{(n-1)/a} \qquad [4]$$

where α is a molecular constant (Ref. 19) equal to $12\eta_0/\pi^2 \nu kT$, ν is the number of molecules per unit volume, kT is the usual product of the absolute temperature and the Boltzmann constant, n and a are the constant parameters of this model, which have to be optimized for fitting the experiment.

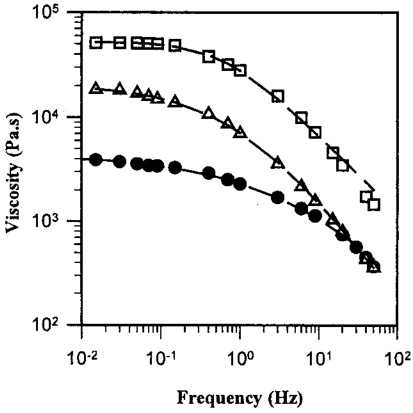

Fig. 1 Viscosity/frequency curves for PC, PVDF, and PMMA at 220 °C. The experimental data are fitted by the Yasuda model (broken line). □ PC, ● PVDF, △ PMMA.

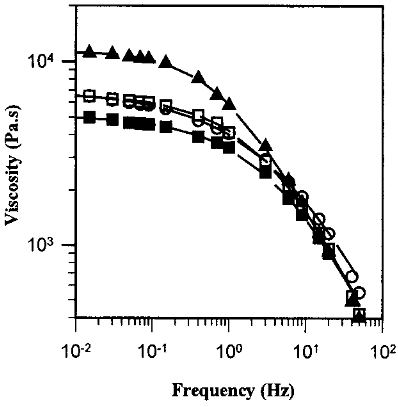

Fig. 2. Viscosity/frequency curves for PVDF/PMMA blends at 220 °C. The experimental data are fitted by the Yasuda model (broken line). ○ 80/20, ■ 60/40, □ 40/60 and ▲ 20/80.

Since the complex viscosity $\eta^*(f)$ should be numerically equal to the viscosity $\eta(\dot{\gamma})$, when the shear rate $\dot{\gamma}$ and frequency f are the same (Cox-Merz rule) (Ref. 20), the values of $\dot{\gamma}$ used in Eq. 4 are numerically equal to the experimental frequency. The values of η_0 are reported in Table 2 and used in Eq. 2 for the calculation of the interfacial tension.

Table 2 Zero-shear viscosity (η_0) of homopolymers and PMMA/PVDF blends

Material	η_0 **at 220 °C (kPa.s)**
PC	51.3
PVDF	4.4
PMMA	20.4
20 PMMA / 80 PVDF	6.9
40 PMMA / 60 PVDF	5.1
60 PMMA / 40 PVDF	6.6
80 PMMA / 20 PVDF	11.3

Plots of the function F= $f(R/R_0) - f(R_e/R_0)$ vs. the retraction time are shown in Fig. 3 for the systems under investigation. The expected linearity is actually observed, with a slope proportional to the interfacial tension. The experimental values of γ_{12} are listed in Table 3.

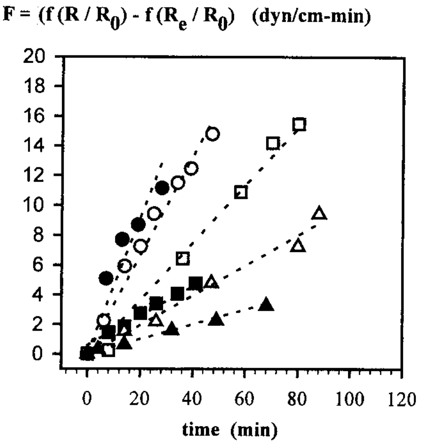

Fig. 3 Typical plot of the function $F=[(f(R/R_0) - f(R_e/R_0)]$ vs. the retraction time for a PC fiber in PVDF, PMMA and PVDF/PMMA blends:
● 100/0, F= 0.46 t; ○ 80/20, F= 0.333 t; ■ 60/40, F= 0.099 t; □ 40/60, F = 0.193 t; △ 20/80, F = 0.101 t; ▲ 0/100, F = 0.05 t.

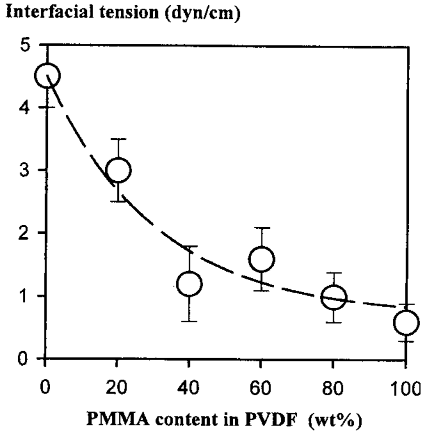

Fig. 4 Plot of the interfacial tension between PC and PVDF/PMMA blends as a function of the weight percentage of PMMA in PVDF (T=220 °C).
O experimental data, – – the fitting curve from Eq. 6.

Table 3 Interfacial tension between PC and PMMA/PVDF blends of different compositions at 220 °C

Matrix	γ_{12} (dyn/cm)
PVDF	4.5 ± 0.6
20 PMMA / 80 PVDF	3.0 ± 0.5
40 PMMA / 60 PVDF	1.2 ± 0.5
60 PMMA / 40 PVDF	1.6 ± 0.5
80 PMMA / 20 PVDF	1.0 ± 0.4
PMMA	0.6 ± 0.3

The PC/PVDF interfacial tension (4.5 ± 0.6 dyn/cm) is much higher than the PC/PMMA interfacial tension (0.6 ± 0.3 dyn/cm), consistently with the complete immiscibility of PC and PVDF and the well-known PC-PMMA compatibility. These experimental data are also in a pretty good agreement with the values predicted by the harmonic mean equation (Ref. 21) on the basis of the surface tension of each constituent polymer (Eq. 5).

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^d \cdot \gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{4\gamma_1^p \cdot \gamma_2^p}{\gamma_1^p + \gamma_2^p} \qquad [5]$$

where the d and p superscripts refer to the dispersive and polar components of the surface tension, respectively. From the values reported in the scientific literature for the surface tension of PC, PMMA and PVDF (Ref. 22,23), $\gamma_{PC/PVDF} = 3.8$ dyn/cm and $\gamma_{PC/PMMA} = 0.5$ dyn/cm at 220 °C have been calculated for the PC/PVDF and PC/PMMA pairs, respectively.

Figure 4 clearly shows that the high interfacial tension of the immiscible PC/PVDF pair at 220 °C decreases rapidly on premixing PVDF with increasing amounts of PMMA. Beyond ca. 40 wt.-% PMMA in PVDF, this effect tends to level off.

Anastasiadis et al. (Ref. 24) have studied the compatibilizing effect of a diblock polystyrene-*block*-1,2-polybutadiene in polystyrene/1,2-polybutadiene blends. They have observed that the interfacial tension was decreasing as the concentration of the diblock copolymer was increased according to a relationship quite similar to that one reported in Fig. 4. On the basis of the experimental data for the polystyrene/1,2-polybutadiene blends, Tang and Huang (Ref. 25) have proposed a theoretical equation accounting for the dependence of the interfacial tension (γ) on the content of the compatibilizer (Eq. 6).

$$\gamma = (\gamma_0 - \gamma_s) \cdot e^{-KC} + \gamma_s \qquad [6]$$

where K is the rate constant for the change in the interfacial tension with the concentration of the compatibilizer (C) and γ_0, γ, γ_S are the interfacial tension in the absence of the compatibilizer, in its presence, and for the completely saturated interface, respectively.

Equation 6 fits very well the experimental data reported in this study for the PC/PVDF system, where a homopolymer (PMMA) is responsible for the compatibilization effect rather than a traditional diblock (or graft) copolymer (Fig. 4). Equation 7 is the expression of Eq. 6 in the particular case of the PC/PVDF two-phase system modified by PMMA.

$$\gamma = 3.8\, e^{-0.0328c} + 0.7 \qquad [7]$$

It thus appears that Eq. 6 might be of a general applicability.

From Fig. 4, it might be qualitatively concluded that as soon as premixed with PVDF, PMMA basically migrates to the interface and decreases very efficiently the interfacial tension. When enough PMMA is premixed with PVDF to saturate the interface, hence for substituting a PMMA/PC interface for a PVDF/PC interface, the effect tends to level off. In an essentially empirical way, the tangents at each origin of the curve fitting Eq. 6 intersect at a PMMA content in the PVDF/PMMA blend of ca. 35 wt.-%. This value might be considered as the concentration of the compatibilizer required for the saturation of the interface.

The interfacial adhesion between PC and PVDF containing increasing amounts of PMMA has also been measured under standard conditions (Ref. 26) (time = 10 min, T = 200 and 220 °C). Figure 5 shows that as long as the PMMA content in PVDF does not exceed 15 wt.-%, the fracture toughness is too small to be measured accurately. Beyond that PMMA content, the interfacial adhesion increases rapidly reaching a plateau value, which is nothing but the interfacial adhesion measured between PC and neat PMMA. Once again the intersection of the tangents at the two extremities of the experimental curve defines an initial PMMA content in PVDF of ca. 35.-wt % in a close agreement with the value extracted from the interfacial tension data.

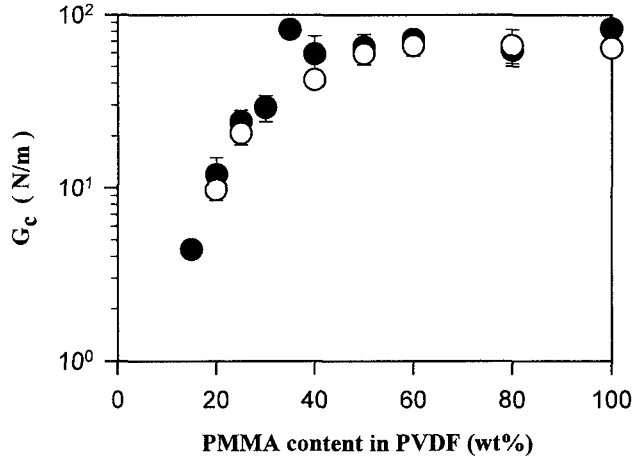

Fig. 5 Dependence of the fracture toughness (G_C) on the PMMA content in PVDF for the PC/PVDF assembly (● T = 220 °C, o T = 200 °C).

The experimental dependence of both the interfacial tension and the interfacial adhesion on the PMMA content in the PVDF/PMMA blends clearly shows that PMMA migrates and accumulates at the PC/PVDF interface more rapidly than its nominal concentration in PVDF would suggest. Indeed, a PC/PMMA interface is completely substituted for the original PC/PVDF interface when ca. 35 wt.-% PMMA is mixed with PVDF. The thermodynamic driving force for the preferential localization of PMMA at the interface has to be found in the smaller PC/PMMA interfacial tension (0.6 dyn/cm, Table 3) compared with the PC/PVDF value (4.5 dyn/cm, Table 3).

Although some intermolecular reactions might be suspected to occur between PC and PMMA at 220 °C (Ref. 27), the experimental data in Fig. 5 remain unchanged when the samples are molded and tested at 200 °C. This observation indicates that the measurements carried out at 220 °C are quite reliable. Furthermore, the plateau value for the interfacial adhesion between PC and the 50/50 PMMA/PVDF blend remains quite constant over long periods of time (16 h) at 200 °C, which agrees with a good thermal stability and the absence of PMMA and PC interdiffusion at this temperature.

In order to confirm that the substitution of a PMMA/PC interface for the original PVDF/PC interface is responsible for the improved interfacial adhesion, this property has been measured at 220 °C for a trilayer PC/PMMA/PVDF assembly prepared by spinning preliminarily PMMA onto PVDF and molding the final assembly for 10 min at 220 °C. In this case, the fracture toughness is 9 ± 1 N/m, hence as low as for the system prepared by premixing 20 wt.-% PMMA in PVDF (Fig. 5). This observation proves that the trilayered PC/PMMA/PVDF system is so far from a thermodynamic equilibrium that PMMA rapidly diffuses into PVDF and leaves the PVDF/PC interface only partly covered. This diffusion is no longer observed when the 60/40 (wt/wt) PVDF/PMMA is similarly spin-coated with PMMA before assembling with PC. After molding at 220 °C for 10 min, the interfacial toughness (98 ± 6 N/m) is very close to the value reported in Fig. 5 for the same system without the intermediate layer of PMMA. Since the spin-coated PMMA layer maintains the interfacial adhesion, it has to interconnect PVDF and PC more likely as a result of interdiffusion in the PVDF/PMMA phase. At this stage of the research, no conclusion can be drawn about the concentration of PMMA chains in the PC matrix, although this would be the expected way for creating good adhesion (Refs. 28-30). It is, however, worth pointing out that Yoon and Han (Ref. 31) have measured a PC/PMMA interfacial thickness of 32.5 and 29.6 Å at 180 °C and 200 °C, respectively, by small-angle neutron scattering for a ca. 1000-min annealing time.

CONCLUSIONS

The interfacial tensions between PC and PVDF as well as PMMA and a series of PVDF/PMMA blends have been measured by the imbedded fiber retraction method. The high interfacial tension between PC and PVDF rapidly decreased by premixing ca. 35 wt.-% PMMA with PVDF. In parallel, the PC/PVDF interfacial adhesion increased as rapidly as the interfacial tension decreased in relation to the PMMA content in the PVDF/PMMA blends. These observations are consistent with the interfacial activity of PMMA at the PVDF/PC interphase, as confirmed by the validity of the model proposed by Tang and Huang, accounting for the interfacial activity of a diblock copolymer in two-phase polymer blends. The best reinforcing effects appear to take place when the PMMA/PC interface is completely substituted for the original PVDF/PC interface.

ACKNOWLEDGMENT

The authors are very grateful to the *Services Fédéraux des Affaires Scientifiques, Techniques et Culturelles* in the framework of the "Pôles d'Attraction Interuniversitaires: Chimie et Catalyse Supramoléculaire". N. M. is indebted to the *Ministère de l'Enseignement Superieur, de la Formation des Cadres et de la Recherche Scientifique du Maroc* for a fellowship. He wishes to thank Mr. C. Pagnoulle and Dr. P. Maréchal for fruitful discussions, and Mr. R. Pirard for help in using the Bohlin rheometer.

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