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Ability of PMMA To Improve the PC/PVDF Interfacial Adhesion

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Introduction. It is well-known that the addition of properly designed block or graft copolymers to immiscible polymer blends is an efficient way to improve the phase dispersion, to stabilize the phase morphology, and to improve the interfacial adhesion.[1]

The cost of preformed block copolymers and limitation of reactive processing in the *in situ* formation of block copolymers[2] are incentives to consider new compatibilization strategies. This problem is particularly acute in the case of polycarbonate (PC) and poly(vinylidene fluoride) (PVDF) blends since no parent block or graft copolymer can be made available whatever the synthetic approach. 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[3] and compatible with PC.[4] In the extreme, PMMA might behave as a common "solvent" for PC and PVDF in the melt.

In a preliminary approach, the ability of PMMA to improve the PC/PVDF interfacial adhesion has been investigated. Although PMMA is not expected to compete with tailored block or graft copolymers as interfacial agent,[5] it is worth mentioning that PC has been toughened by core−shell rubber particles, with a PMMA shell. Compatibility of this PMMA shell with PC has been proposed to provide an interfacial adhesion strong enough for the rubber particles to cavitate rather than to be debonded.[6]

The purpose of this work is to investigate whether the PC/PVDF interfacial adhesion can be improved by the premixing of PVDF with PMMA.

Experimental Section. PC was MAKROLON 3103 from Bayer, PMMA was DIAKON from ICI, and PVDF was Solef X10N from Solvay. PVDF/PMMA blends were prepared by melt mixing with a two-roll mill (SCAMIA), at 200 °C for 10 min. Samples (1 mm thick) of PC and PVDF/PMMA blends were prepared by compression molding at 220 and 200 °C, respectively.

Stress−strain curves were recorded with an Instron universal tensile tester (model DY24) at a tensile rate of 20 mm/min. Young's modulus was calculated from the initial slope of these curves.

The interfacial fracture stress was measured with the dual cantilever geometry.[7] Plates (2 mm thick) of PC and PVDF/PMMA blends were superposed and compression molded at the desired temperature. After a well-defined period of time, the sandwich was cooled 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 of the razor blade was measured with a traveling microscope after at least 84 h of equilibration at room temperature. The toughness of the interface can be calculated from eq 1 proposed by Creton et al.,[7] in the case where no component of the sandwich assembly is previously glued on a rigid glass plate.

$$G = \frac{3d^2E_1{h_1}^3E_2{h_2}^3}{8l^4(E_1{h_1}^3 + E_2{h_2}^3)} \tag{1}$$

where E_i and h_i are the modulus and thickness of each component i, d is the thickness of the razor blade, and l is the crack length.

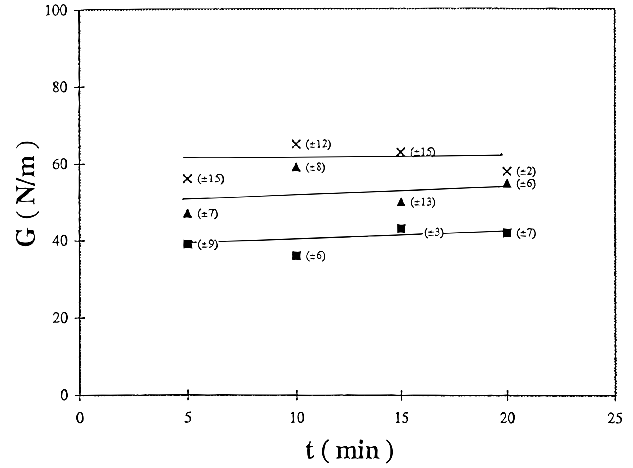

Figure 1. Time dependence of the interfacial toughness (*G*) for the PC/50 PVDF-50 PMMA assembly prepared under different temperatures: (■) 180 °C; (▲) 200 °C; (×) 220 °C. The full line is a guide to the eye. The number in parentheses is the error in the experimental measurement.

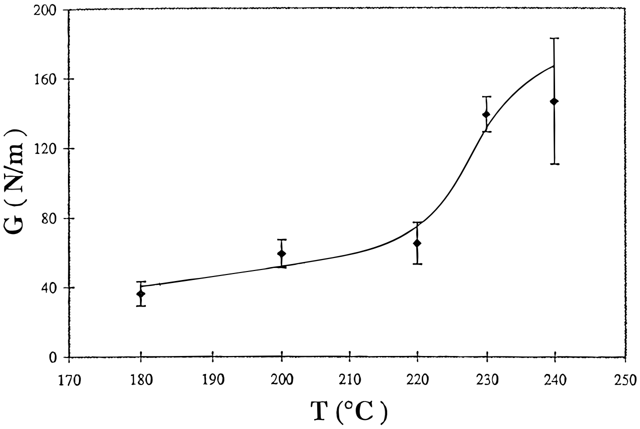

Figure 2. Temperature dependence of the interfacial toughness (*G*) for the PC/50 PVDF-50 PMMA assembly. A pressure of 0.6 MPa was applied for 10 min. The full line is a guide to the eye.

Results and Discussion. The effect of temperature and time on the experimental adhesion between PC and PVDF/PMMA blends has been first analyzed.

The effect of the annealing time on the interfacial toughness of the PC−PVDF/PMMA (50/50) assembly is shown in Figure 1 at three different temperatures: 180, 200, and 220 °C. It is observed that between 5 and 20 min of compression molding, the time has no significant effect on the experimental interfacial adhesion, which means that time dependence of chain diffusion in the interfacial region can be reasonably ruled out. A compression molding time of 10 min has accordingly been standardized.

Figure 2 shows that the interfacial adhesion depends on the compression molding temperature, particularly above 220 °C. There is indeed a sharp increase between 220 and 230 °C, which might be attributed to a reaction

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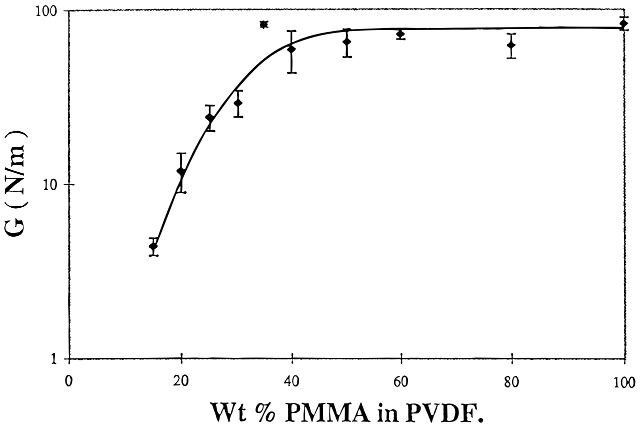

Figure 3. Dependence of the interfacial toughness (*G*) on the PMMA content in PVDF for the PC/PVDF assembly. All samples were prepared at 220 °C under 2.5 MPa for 10 min. The full line is a guide to the eye.

between PC and PMMA, as recently suggested by Legras et al.[8] and Yoon and Han.[9] According to these authors, ester groups of PMMA would be hydrolyzed and the accordingly formed acid units would promote the acidolysis of the carbonate bonds with grafting of PC chains onto the PMMA backbone. If this reaction actually occurs above 220 °C when PMMA is in close contact with PC, it can account for the rapid strengthening of the interface and an interfacial adhesion (*G*) which is much higher (ca. 140 N/m) than the value reported for the PC/PMMA interface at 220 °C (Figure 2). Between 230 and 240 °C, *G* seems to remain unchanged, which might indicate that this reaction does not progress throughout the interface when the temperature is increased, all the other conditions being the same. It must also be mentioned that formation of bubbles is observed in the PVDF/PMMA phase at high temperatures (230−240 °C), which prevents very reliable tests from being performed. It is the reason why the molding temperature will not exceed 230 °C in the forthcoming experiments.

The interfacial adhesion between PC and PVDF containing increasing amounts of PMMA has been measured under standard conditions ($P = 25 \times 10^5$ Pa, time = 10 min, and $T = 220$ °C). Figure 3 shows that as long as the PMMA content in PVDF does not exceed 15 wt %, the fracture energy is too small to be measured accurately. Beyond that PMMA content, the interfacial adhesion increases rapidly to reach a maximum value when ca. 45 wt % PMMA is used. This plateau value is nothing but the interfacial adhesion measured between PC and pure PMMA.

The experimental dependence of the interfacial adhesion on the PMMA content in PVDF clearly shows that PMMA migrates and accumulates at the PC/PVDF interface more rapidly than its nominal concentration in the bulk PVDF. Indeed, a PC/PMMA is completely substituted for the original PC/PVDF interface when only ca. 45 wt % is mixed within 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 compared with the PC/PVDF value, i.e. 0.53 and 3.18 dyn/cm, calculated from the harmonic mean equation[10] at 220 °C. The parameters used in this equation were found in ref 11. A similar behavior has been reported by Hobbs et al.,[12] who have shown by TEM that PC envelopes around PMMA domains in a ternary PC/PMMA/PBT blend. This morphology was in agreement with the spreading coefficients calculated from the interfacial tension data.

It is noteworthy that the shape of figure 3 valid to samples molded at 220 °C is reproduced in the case of samples molded at 200 °C. This is an additional evidence that any measurement carried out at 220 °C is quite reliable. Furthermore, the plateau value of the interfacial adhesion between PC and PMMA/PVDF blends (e.g. 50/50 wt/wt) remains quite constant over long periods of time (16 h) at 200 °C, which indicates that no mutual interdiffusion of PMMA and PC occurs, and this confirms the complete immiscibility of these polymers at 200 °C. Furthermore, and within the limits of these experiments, there is no apparent reaction between PC and PMMA at this temperature. Since PMMA is completely miscible with PVDF, and immiscible with PC at the heating temperature, a very thin layer of PMMA is expected to be formed at the interface. As a piece of information, Yoon and Han[9] have measured a PC/PMMA interfacial thickness of 32.5 and 29.6 Å at 180 and 200 °C, respectively. These values were observed by small angle neutron scattering for a ca. 1000 min heating time. A more detailed study of this system will be reported in the near future.

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