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Calorimetric study of fluorinated methacrylic and vinyl polymer blends: part 2: correlation between miscibility, chemical structure and χ_{12} interaction parameter in binary systems

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Abstract

The miscibility of poly(methylmethacrylate) (PMMA) and (trifluoroethyl methacrylic ester–MMA) copolymers (MMA–MATRIFE) with poly(vinylidene fluoride) (PVDF) and VDF copolymers was studied by differential scanning calorimetry (DSC) as a function of the fluorinated copolymer crystallinity and fluoroalkyl methacrylic ester content in the methacrylic copolymer. Miscibility limits were found identical whatever be the blend preparation technique, although solution mixing induced some polymer fractionation, thus giving slightly higher blend glass transition temperature. The miscibility domain widths are reduced when using MMA–MATRIFE copolymers as compared to PMMA-containing blends and miscibility limits are dependent on the MATRIFE content in the methacrylic copolymer. Moreover, PVDF or VDF copolymer melting enthalpy decrease is associated to a partial dissolution of the semi-crystalline polymer in PMMA or MMA–MATRIFE copolymer above the total miscibility limit. The evolution of dynamic moduli as a function of blends composition confirms the miscibility limits determined by DSC. The Flory–Huggins interaction parameters were determined through the melting point depression analysis and compared to correlate the intensity of inter- or intra-molecular interactions between the polymers to the postulated 'acidity' of hydrogen atoms in various VDF-containing polymers. The interaction parameter χ_{12} increases with the fluoroalkyl methacrylic ester content, corresponding to a prevalence of intra-molecular on inter-molecular interactions in these blends. Similarly, PVDF offers higher χ_{12} values as compared to VDF–TFE or particularly to VDF–TrFE copolymers. These results highlight the importance of the nature of fluorinated polymers and of the inter- or intra-molecular character of dipolar interactions on both, copolymer miscibility and interaction parameter values.

Keywords: Fluorinated polymer blends; Miscibility; Interaction parameter

1. Introduction

Miscibility and crystallization behavior of amorphous/crystalline polymers have been extensively studied in the past two decades. Poly(vinylidene difluoride) (PVDF) is known to be miscible with a number of carbonyl-containing polymers, including poly(methyl methacrylate) (PMMA), poly(methyl acrylate) (PMA), poly(ethyl acrylate) (PEA), poly(vinyl acetate) (PVA), poly(vinyl methyl ketone), poly(caprolactone), poly(tetramethylene adipate) (PTMA) and poly (1,4-butylene adipate) [1–13]. Further, PVDF and its copolymers, such as vinylidene fluoride–hexafluoropropene (VDF–HFP) and vinylidene fluoride–trifluoroethylene (VDF–TrFE), are of particular importance because of their piezo and ferroelectric properties [14]. They all give miscible blends with PMMA [15,16] and exhibit interesting applications for plastic optical fibers cladding. In previous papers [17,18], we have studied the miscibility of commercially available fluorinated copolymers with PMMA and some fluorinated methacrylic copolymers, namely methyl methacrylate–trifluoroethyl methacrylate copolymers (MMA–MATRIFE) with various MATRIFE contents. On introducing fluorine-containing alkyl ester groups, miscibility decrease is always observed, attributed to the occurrence of intra-molecular interactions in MMA–MATRIFE copolymers, competing with inter-molecular interactions between methacrylic polymer ester carbonyl groups and VDF-containing copolymer methylene units. On the contrary, blends with VDF copolymers exhibit larger miscibility domains than with PVDF itself, owing to their lowest crystallinity contents.

In the present work, we have completed these miscibility studies with vinylidene fluoride–tetrafluoroethylene (VDF–TFE) copolymer/PMMA blends and some PVDF/(MMA–MATRIFE) copolymer blends, using both differential

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scanning calorimetry (DSC) and dynamic thermomechanical analysis (DMA). As some differences were observed according to the blend preparation mode, some work was done to explain these data. The influence of structural parameters on crystallization of PVDF and VDF copolymers in blends with PMMA and (MMA–MATRIFE) copolymers was investigated using DSC. Specifically, crystallization and melting behavior of fluorinated copolymers were analyzed as a function of both the amorphous copolymer fluoroalkyl methacrylate ester content and the VDF-containing polymer crystallinity. The interaction parameters were determined in these blends through melting point depression analysis and correlated to the prevalence of intra-molecular interactions onto inter-molecular interactions in these blends. The importance of the acidic character of hydrogen atoms in VDF copolymers was also demonstrated.

2. Experimental

2.1. Materials

Fluorinated polymers are commercially samples, available in pellet form: PVDF (SOLEF 1008), VDF–HFP 80/20 (w/w) (SOLEF 21508) and VDF–TrFE 50/50 (w/w) copolymers were obtained from Solvay (Belgium). VDF–TFE 75/25 (w/w) is Kynar SL from Atochem (France). PMMA OF 104S was supplied by Röhm. Fluorinated methacrylic copolymers MAT66 and MAT80 (66 and 80% w/w MATRIFE units, respectively) were obtained by free-radical suspension polymerization as described earlier [17]. Chemical structures are shown in Fig. 1.

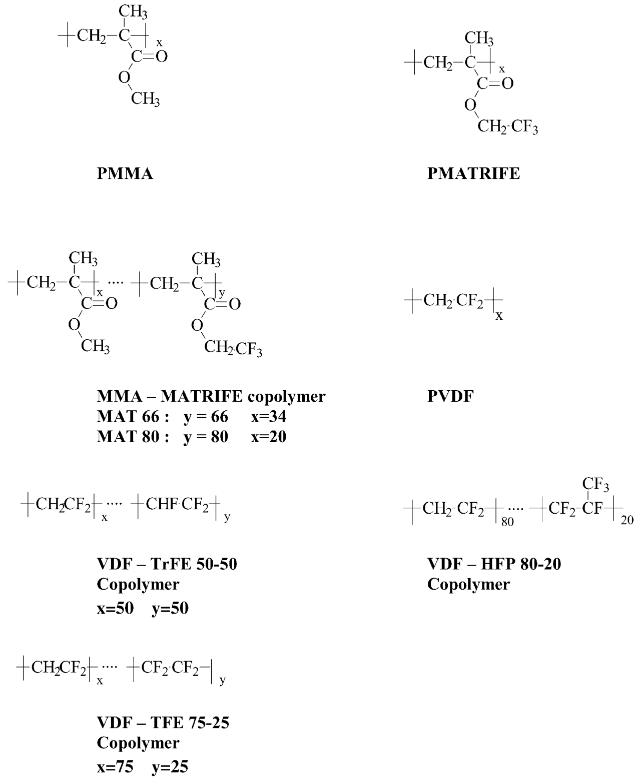


Fig. 1. Chemical structures of polymers.

2.2. Blend preparation

A range of blends covering a wide composition range were prepared by solution mixing and melt mixing.

Solution blending. Blends were obtained by solution mixing followed by fast precipitation. Both polymers were dissolved at room temperature in dry dimethylformamide as 5% (w/w) solutions and aliquots mixed in the required amounts. After 24 h stirring, the blended solutions were poured into a 100-fold excess volume of distilled water under stirring. The blends were filtered off, washed several times with water and dried at 70 °C to constant weight. IR-spectra were recorded to check the absence of any residual solvent.

Melt blending. Blends were prepared at 210 °C using a Brabender Lab-station equipped with a 50 ml mixing unit, at 10 rpm for 18 min. Before use, PMMA and MMA copolymers were dried at 90–100 °C for 2 h, in vacuo.

2.3. Measurements

Differential scanning calorimetry. A Perkin–Elmer differential scanning calorimeter Pyris 1 was used to determine transition temperatures and melting enthalpies under nitrogen atmosphere, using indium and tin calibration standards. All samples were submitted to the same temperature program for anisotherm experiments: first heating from 12 to 210 °C at 20 °C min^{-1}, followed by cooling to 12 °C at 10 °C min^{-1}; the second scan was performed at 10 °C min^{-1}. Non-isothermal crystallization and melting temperatures were determined from peaks extrema, at less than ±0.5 °C.

Dynamic mechanical analysis (DMA). Dynamic mechanical data were obtained on a TA 2980 Dynamic Mechanical Analyzer. Measurements were performed in the tensile mode at a 3 °C min^{-1} scanning rate and 5 μm deformation amplitude at 1 Hz frequency. Thin film samples were prepared by pressing samples (precipitated powder or extrudate) between plates heated at 210 °C.

Size exclusion chromatography (SEC). Average molecular weights and molecular weight distributions were measured by size exclusion chromatography in THF with a laboratory apparatus equipped with G5 PL-gel mixed C 60 cm–5 μm columns (Université du Maine, Le Mans, France), calibrated with polystyrene standard.

3. Results and discussion

3.1. Miscibility in PMMA-fluorinated copolymers blends using DSC and DMA

Miscibility limits were determined from DSC results on

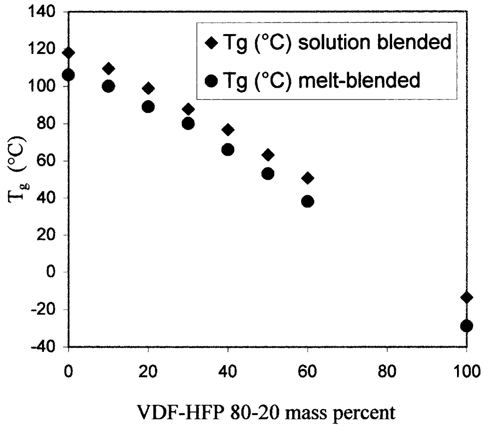


Fig. 2. Influence of mixing modes on DSC results from PMMA/VDF–HFP 80–20 blends.

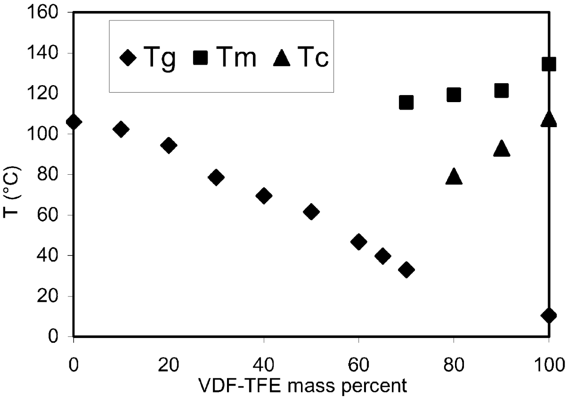


Fig. 3. DSC results from PMMA/VDF–TFE 75–25 blends.

unblended copolymers and blends. For blends noted metastable, crystallization occurred above the glass transition temperature during the second heating step.

PMMA/PVDF blends and PMMA/VDF–HFP 80–20 blends were prepared by both methods (solution and melt blending). Results shown in Fig. 2 for PMMA/VDF–HFP blend are compared. Complete miscibility is observed in PMMA up to, respectively, 40% PVDF and 70% VDF–HFP. Miscibility limits are the same whatever may be the preparation mode. However, an increase in glass transition temperatures (T_g) is observed for blends prepared from polymer solutions. For pure PMMA, the observed T_g is 118 °C after dissolution–precipitation instead of 106 °C for the melt sample. A probable explanation was that, some fractionation occurs during the dissolution–precipitation process, resulting in the elimination of the smallest polymer chains, thus inducing an increase in T_g. M_n and M_w were determined by SEC for the two PMMA samples. M_n and M_w values are, respectively, 63,000 and 136,000 g mol^{-1} for the melt sample and 67,000 and 135,000 g mol^{-1} for the precipitated one. Polydispersity indexes are, respectively, 2.16 against 2.01. These results give evidence of an increase of PMMA number-average molecular weight M_n, corresponding to the elimination of the polymer smallest molecules through dissolution–precipitation.

Miscibility in PMMA-fluorinated copolymers blends is evaluated by both DSC and DMA measurements.

Figs. 2 and 3 show the glass transition and melting temperatures of PMMA/VDF–HFP and PMMA/VDF–TFE blends prepared by melt mixing. From 0 to 65% VDF–TFE copolymer in the blends, they exhibit a single T_g (without any melting or crystallization peaks) slightly decreasing with increasing VDF–TFE content, indicating complete amorphous blends. For blend containing 70% VDF–TFE, crystallization occurs above T_g during the second heating step, before a further melting step. In blends containing 80% or more VDF–TFE, VDF copolymer normal melting and crystallization are observed although the corresponding temperatures decrease on increasing PMMA content. These blends are obviously biphasic. In the same way, PMMA/VDF–HFP (80/20) blends are amorphous up to 70% (w/w) VDF–HFP content.

Such enlargements of miscibility domains, compared to the well known PMMA–PVDF system, miscible only up to 40% PVDF, are closely related to the crystallinity decrease in VDF copolymers as compared to PVDF itself. These results are consistent with previous ones obtained on other blends of fluorinated methacrylic copolymers with fluorinated vinylic copolymers, all prepared by solution blending [17].

To confirm our results, dynamic relaxation spectra of these blends have been determined. Fig. 4(a) shows the plots of the loss modulus E'' versus temperature observed at 1 Hz for PMMA and PMMA/VDF–HFP blends with fluorinated vinyl copolymer mass fraction $\Phi_w < 0.75$.

We can observe that the temperature at which a peak in log E'' appears shifts from PMMA transition temperature (at 122 °C) to lower values as VDF–HFP content increases (down to 38.5 °C for 70% VDF–HFP). This temperature corresponds to the main transition of the amorphous blend, T_g^β; in this composition domain, blends are homogeneous, the two polymers being miscible in the melt as in the solid phase. We also notice in Fig. 4(a), a secondary transition with a loss modulus peak near 20–40 °C, much broader, which could probably be attributed to PMMA side groups rotation in amorphous blends. This transition becomes no longer detectable when PMMA weight content in the blends is <40%. We can suppose that, in this composition range, either PMMA content is too weak to give detectable transition or PMMA side group movements are hindered by association to VDF–HFP chains. As these blends are able to crystallize, the amorphous phase is saturated in VDF–HFP copolymer and interactions with PMMA monomer unit reach their maximum.

For higher contents of VDF–HFP (≥0.75), we can observe in Fig. 4(b) that the temperature at which log E'' exhibits a peak, corresponding to the blend main transition, shows a less important evolution and remains in the range

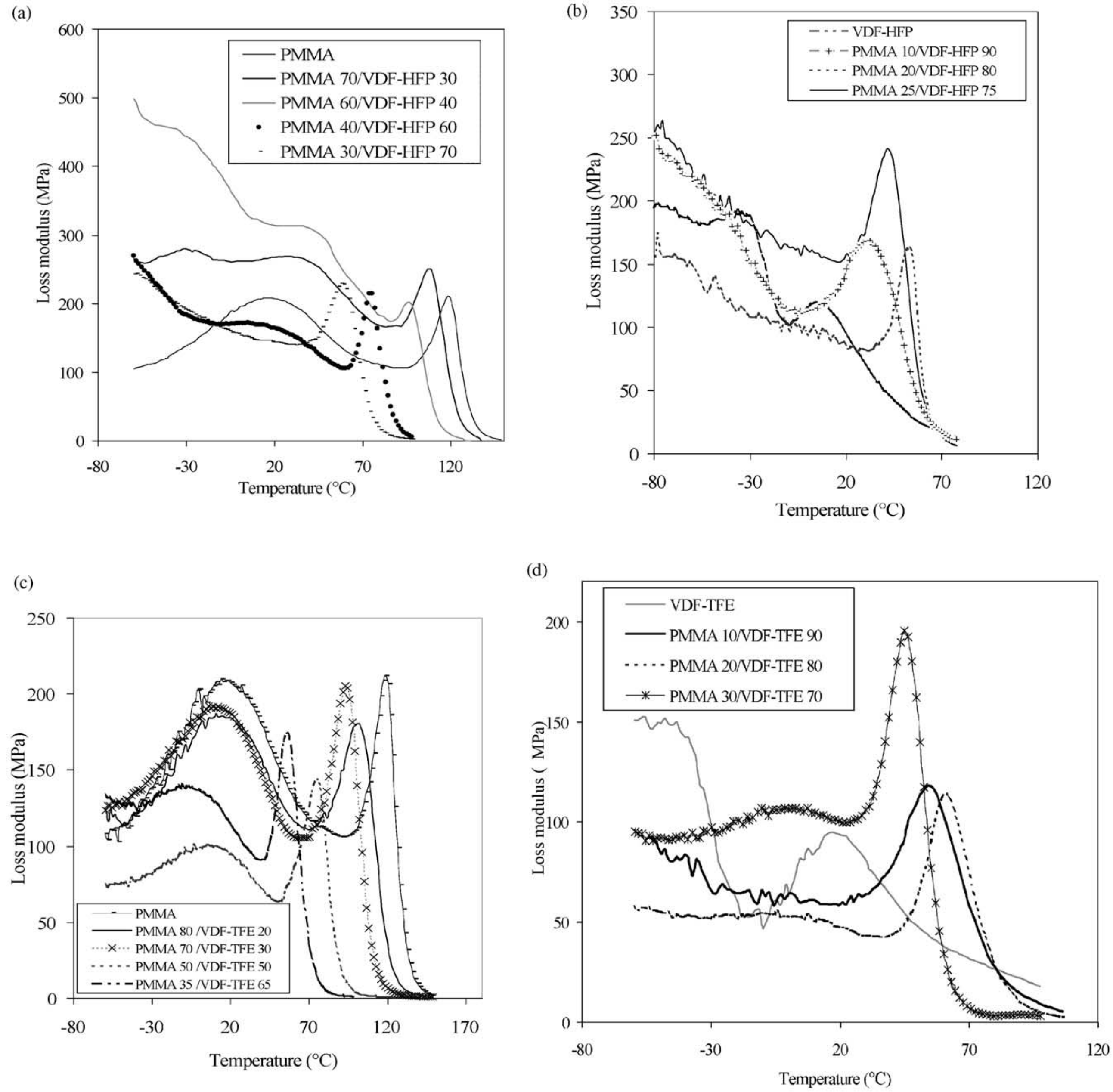


Fig. 4. Temperature dependence of loss moduli from PMMA/VDF–HFP and PMMA/VDF–TFE blends. (a) PMMA/VDF–HFP ($\Phi_w < 0.75$). (b) PMMA/VDF–HFP ($\Phi_w \geq 0.75$). (c) PMMA/VDF–TFE ($\Phi_w < 0.65$). (d) PMMA/VDF–TFE ($\Phi_w \geq 0.65$).

35–50 °C, near to the value observed in the PMMA/VDF–HFP 30–70 blend. This evolution seems directly correlated to the miscibility limit of VDF–HFP in PMMA, as determined by DSC (Fig. 2). The increase in VDF–HFP content above 0.75 no longer contributes to the amorphous phase which is saturated in fluorinated copolymer. We can also notice two transitions for pure VDF–HFP near −30 and 15 °C. The former might be attributed to the amorphous phase relaxation and the latter to a crystalline relaxation of VDF–HFP.

Similar results have been obtained with PMMA/VDF–TFE blends. In Fig. 4(c), we can observe a decrease in the loss modulus main peak when the fluorinated copolymer content increases. This transition temperature, attributed to the amorphous phase relaxation, gradually shifts from 122 °C for pure PMMA to 57 °C for 65% VDF–TFE copolymer blend, this value corresponding to the miscibility limit. For higher VDF–TFE copolymer contents (≥0.70), again this evolution is less important as it appears in Fig. 4(d); the observed transition corresponds to the T_g^β of the amorphous phase saturated in VDF–TFE copolymer. However, we can notice in Fig. 4(b) and (d) that surprisingly, for compositions that correspond to metastable phases, i.e. for blends with 75% VDF–HFP and 70%

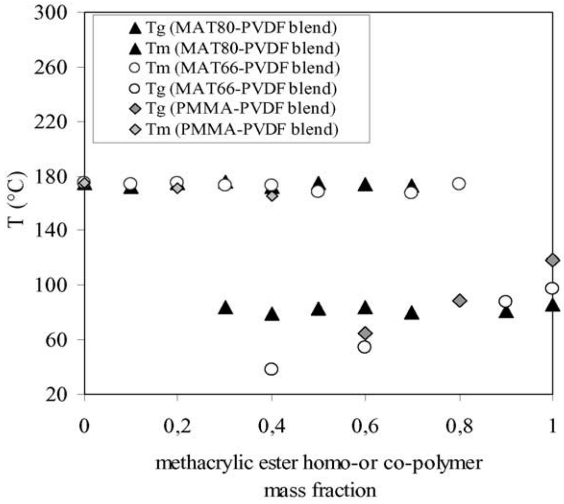


Fig. 5. DSC results from methacrylic fluorinated copolymer/PVDF blends.

VDF–TFE, the transition temperature is located at values lower than that for blends with higher fluorinated copolymer contents. We may postulate in these two systems that the 'metastable' amorphous phase undergoes evolution during the sample analysis. The addition of a few percent of fluorinated copolymer is sufficient to give a stable system with a nearly constant T_g^β.

For pure VDF–TFE copolymer, two peaks are observed in the loss modulus evolution, as for VDF–HFP copolymer, at −40 and 30 °C, transitions that might correspond, respectively, to the amorphous phase glass transition and a crystalline phase relaxation.

3.2. Miscibility in MMA–MATRIFE copolymers/PVDF blends

New results were obtained in blends between MMA–MATRIFE 20–80 copolymer (MAT80) and PVDF. The partial miscibility composition ranges were compared to those obtained with PMMA/PVDF or MAT66/PVDF systems [17]. Glass transition and PVDF melting temperatures in these blends have been determined by DSC and are shown in Fig. 5 versus methacrylic ester copolymer contents. The miscibility domain width is clearly reduced in MAT80/PVDF blend as compared to PMMA/PVDF system: 90% MAT80 are necessary to obtain an amorphous system with a glass transition temperature decreasing from 86.1 °C for pure MAT80 to 80.7 °C (in blend with 10% PVDF). For higher PVDF contents, T_g values remain nearly constant, corresponding to a composition-constant amorphous phase saturated in crystalline polymer. For MAT66/PVDF blends, the unusual decrease of T_g value observed beyond the miscibility limit at 20% PVDF is strongly associated to systems showing an exothermic crystallization peak on heating. In fact, MAT66 and MAT80 give quite similar behavior towards miscibility with PVDF. As previously discussed [17,18], this can be attributed to the influence of fluoroalkyl ester groups in MMA copolymers.

Table 1
T_m^0 values determined from crystallization kinetics

	T_m^0 (°C)
PVDF	178.6
VDF–TrFE 50–50	165.0
VDF–HFP 80–20	168.8
VDF–TFE 75–25	135.9

3.3. Melting and crystallization behavior of PVDF and its copolymers in their blends

The analysis of the melting behavior of a crystalline component in crystalline–amorphous blends is an important tool to evaluate polymer miscibility. In miscible blends, a decrease of the crystalline component melting temperature with respect to the pure polymer is usually observed as a result of thermodynamically favorable interactions. The extent of the melting point depression in such systems allows the determination of the interaction parameter χ_{12} in the Flory–Huggins theory of polymer miscibility [5,6]. We should make use of equilibrium melting point in applying this theory to these data.

The equilibrium melting point of a polymer T_m^0 is generally determined using the Hoffman–Weeks extrapolation method [19]. The Hoffmann–Weeks equation

$$T_m = \eta T_c + (1 - \eta) T_m^0$$

predicts a linear relation between T_m and T_m^0. From isothermally crystallized samples at various T_c, the equilibrium melting point T_m^0 is obtained from the intersection with $T_m = T_c$ line. The slope η of the Hoffmann–Weeks plot may be considered as a measure of crystal stability. A value $\eta = 0$ implies that the crystals are perfectly stable whereas $\eta = 1$ reflects inherently instable crystals [19].

The results concerning various VDF copolymers and their blends with PMMA are summarized in Table 1. The equilibrium melting value of pure PVDF is in good agreement with the previously published values which are in the range 174–180 °C [5,6,12,13].

Figs. 6 and 7 show the evolution of VDF–TrFE melting enthalpies, respectively, in its blends with PMMA or MAT66 and PVDF melting enthalpies in its blends with PMMA, MAT66 and MAT80. We may notice that the melting enthalpy of the fluorinated copolymer decreases with increasing content of methacrylic ester copolymer. The loss of fluorinated copolymer crystallinity is associated with a partial dissolution of the semi-crystalline copolymer in PMMA or in MAT66. PVDF or VDF–TrFE solubility is less important in MAT66 than in PMMA, as shown in Figs. 6 and 7. In MAT80–PVDF blends, these observations are still more obvious: PVDF melting enthalpy does not show any evolution with increasing MAT80 mass fraction. Moreover,

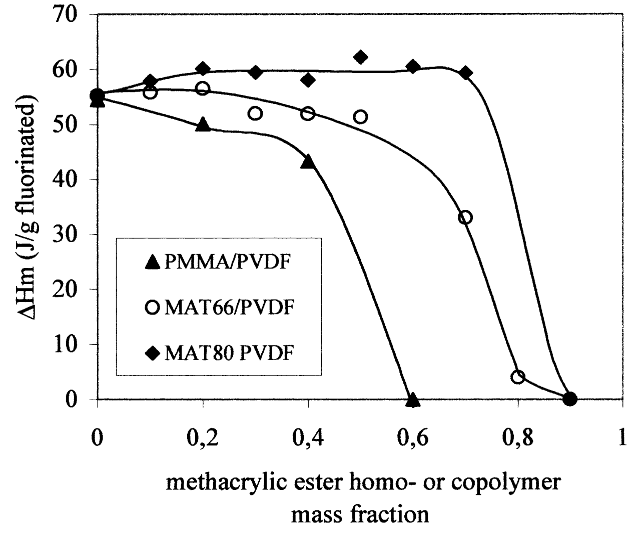


Fig. 6. Melting enthalpies in methacrylic fluorinated copolymer/PVDF blends.

the melting point depression generally observed in partially miscible blends is not very pronounced in MAT80 and MAT66 blends, as compared to PMMA blend where PVDF melting temperature decreases from 174.5 °C in pure PVDF to 163.9 °C at the miscibility limit (50/50 w/w). This can be justified by the existence of intra-molecular interactions in or between MMA and MATRIFE units in MAT66 and MAT80 copolymer. Such intra-molecular interactions are in competition with inter-molecular interactions between MMA and VDF units, as shown in Fig. 8. For entropic reasons, MMA and MATRIFE units interact preferably intra-molecularly in MATRIFE–MMA copolymers, then decreasing the probability of inter-molecular interaction occurrence between the methacrylic copolymer and the fluorinated one. Direct consequences are a loss of miscibility as well as an attenuation of melting point depression in these blends. We can suppose that these specific interactions are consistent with strong dipole–dipole interactions between the carbonyl groups of PMMA and/or MMA–MATRIFE copolymers and the 'acidic' hydrogen atoms in PVDF and/or VDF copolymers.

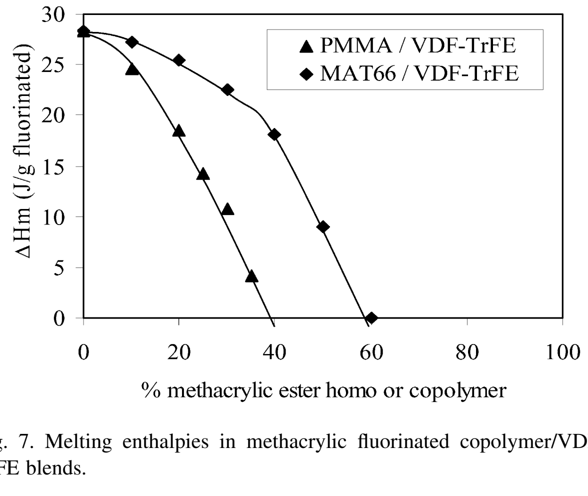


Fig. 7. Melting enthalpies in methacrylic fluorinated copolymer/VDF–TrFE blends.

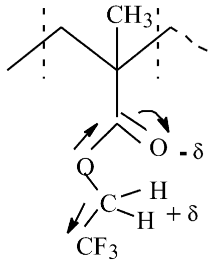
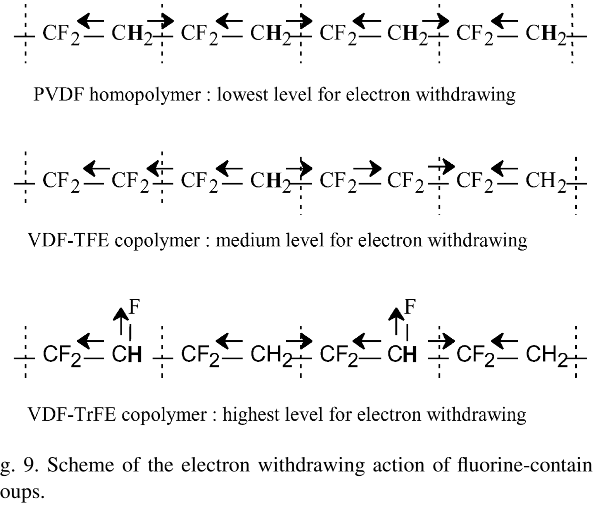


Fig. 8. Example of intra-molecular interaction postulated between carbonyl oxygen atom and hydrogen atoms from the first carbon of the fluoroalkyl ester group in the poly(trifluoroethyl methacrylate) structural unit (only the main group polarizations and more intense electron attractive effects are shown).

Strong electron withdrawing is usually associated with fluorine-containing alkyl groups: it is possible to postulate an increasing order for the influence of such attractive groups in VDF polymers and copolymers. In respect to PVDF itself, VDF–TFE copolymer contains less methylene groups which are statistically linked to successive difluoromethylene groups instead of isolated ones. More intense polarization is then expected for CH_2 in VDF–TFE copolymers. In VDF–TrFE copolymers (as in PTrFE itself) fluorine atoms are linked directly to the carbon bearing hydrogen and this CHF group is placed between two strongly attracting CF_2: such a structure would probably induce the strongest polarization in C–H bonds available in these polymers (Fig. 9).

3.4. Interaction parameter determinations

The free energy of mixing $\Delta G_m = \Delta H_m - T\Delta S_m$, where ΔH_m and ΔS_m are ,respectively, the mixing enthalpy and entropy, should be negative in a miscible blend. For high molecular weight polymers, ΔS_m is negligibly small and ΔG_m sign is dominated by ΔH_m. In general, ΔH_m is negative



PVDF homopolymer : lowest level for electron withdrawing

VDF-TFE copolymer : medium level for electron withdrawing

VDF-TrFE copolymer : highest level for electron withdrawing

Fig. 9. Scheme of the electron withdrawing action of fluorine-containing groups.

only if there are specific associative interactions between the two polymers.

The mixing enthalpy can be represented by a Van Laar relationship [20]

$$\Delta H_m(T) = \chi_{12} RT \phi_1 \phi_2$$

where ϕ_i is the volumic fraction of component *i*, *R* the gas constant, *T* the temperature and χ_{12} the Flory–Huggins polymer–polymer interaction parameter.

The melting point depression of a crystallizable polymer in a compatible mixture with a non-crystallizable diluent or polymer is expressed, according to the Flory–Huggins theory [5,6], as:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{RV_2}{\Delta H_2 V_1} \chi_{12} \Phi_1^2$$

In this relation, index 1 refers to amorphous polymer and index 2 to crystalline polymer, T_m^0 and T_m are, respectively, the equilibrium melting temperature of the fluorinated polymer in the bulk and the melting temperature of the fluorinated polymer in the mixtures. *R* is the gas constant, ΔH_2 is the melting enthalpy of the crystalline polymer. V_i is the molar volume of the repeating unit and Φ_1 is the volume fraction of the component 1. χ_{12} is calculated from the slope of the plot of $1/T_m - 1/T_m^0$ versus Φ_1^2, equal to:

$$-\frac{RV_2}{\Delta H_2 V_1} \chi_{12}$$

In Table 2, χ_{12} values calculated from preceding results for some binary blends are reported. The negative χ_{12} values are indications that the polymer pairs can form thermodynamically stable mixtures in the molten state.

It appears that all blends are compatible in this respect, with the exception of MAT66/PVDF and MAT80/PVDF blends that offer the highest values, respectively, −0.05 and −0.039, near zero.

A comparison of χ_{12} values between PMMA blends and MAT66 or MAT80 blends shows clearly that absolute χ_{12} values are more important in systems where inter-molecular interactions are predominant. The introduction of MATRIFE units in methacrylic ester copolymer introduces new intra-molecular which are competing with inter-molecular interactions existing between the fluorinated copolymer and PMMA or (MAT66, MAT80). The observed miscibility domain width decrease are coherent with these χ_{12} values. For MAT66–PVDF and MAT80–PVDF systems, χ_{12} values are very near zero, corresponding to nearly immiscible blends where PVDF crystallization is observed even above 80% (w/w) amorphous polymer in the blend.

Table 2
Interaction parameters for different fluorinated polymer–methacrylic polymer pairs

PMMA/PVDF	$\chi_{12} = -0.125$
MAT66/PVDF	$\chi_{12} = -0.050$
MAT80/PVDF	$\chi_{12} = -0.039$
PMMA/VDF–TrFE 50–50	$\chi_{12} = -0.268$
MAT66/VDF–TrFE 50–50	$\chi_{12} = -0.126$
PMMA/VDF–HFP 80–20	$\chi_{12} = -0.126$
PMMA/VDF–TFE 75–25	$\chi_{12} = -0.200$

χ_{12} values can also be compared according to the nature of fluorinated polymer in their blends with PMMA, particularly within the acidity of hydrogen atoms induced by the intense electron withdrawing action of fluorine-containing groups. As discussed earlier, when hydrogen atoms are bonded to a fluorine-bearing carbon atom like in PTrFE units, they are probably more acidic than in methylene groups of VDF homo or copolymers, thus inducing more intense dipolar interactions with PMMA carbonyl groups. This can explain the lowest observed χ_{12} value for PMMA–VDF–TrFE 50/50 system (−0.268), compared to −0.126 for blends of PMMA with VDF–HFP 80/20 or −0.125 for blends with PVDF. PVDF and its HFP copolymer behave quite similarly in respect to χ_{12} values, although miscibility limits are different in relation to their crystallinity rates.

χ_{12} value for PMMA–PVDF system is different from the value reported by Nishi and Wang (−0.295) [5,6] and Moussaif and Jerome (−0.32) [21] but very similar to the value of Roerdink and Challa (−0.10) [7]. Some parameters have been evidenced to explain these differences: PMMA and PVDF molecular weights, tacticity of PMMA chains [7] or PVDF chain structure, in particular head-to-head defects concentration. This last parameter has been studied in detail by Maiti and Nandi in PVDF/PMMA blends [9].

4. Conclusion

The miscibility of poly(methylmethacrylate) (PMMA) and (fluoroalkyl methacrylic ester–methyl methacrylate) copolymers with poly(vinylidene fluoride) (PVDF) and some VDF copolymers has been studied by DSC as a function of the fluorinated copolymer crystallinity and fluoroalkyl methacrylic ester content in the methacrylic copolymer. Miscibility limits were found identical whatever be the blend preparation technique, although solution mixing induced some polymer fractionation, thus giving slightly higher blend glass transition temperature. The miscibility domain widths are reduced when using MMA–fluoroalkyl methacrylate copolymers as compared to PMMA-containing blends and miscibility limits are dependent on the fluoroalkyl content in the methacrylic copolymer. Moreover, PVDF or VDF copolymer melting enthalpies are associated with a partial dissolution of the semi-crystalline polymer in PMMA or MMA–MATRIFE copolymer above the total miscibility limit. The evolution of dynamic moduli (E'', DMA) as a function of blends composition confirms the miscibility limits determined by calorimetry. The Flory–Huggins interaction parameters were determined from the melting point depression analysis; the interaction parameter χ_{12} evolution allows to correlate the intensity of inter- or intra-molecular interactions between the polymers to the postulated acidity of hydrogen atoms in various VDF-containing polymers. Experimental χ_{12} value increases with the fluoroalkyl methacrylic ester content, corresponding to a prevalence of intra-molecular on inter-molecular interactions in these blends. Similarly PVDF offers higher χ_{12} values as compared to VDF–TFE or particularly to VDF–TrFE copolymers. These results highlight the importance of the nature of fluorinated polymers and of the inter- or intra-molecular character of dipolar interactions on both copolymer miscibility and interaction parameter values.

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References

[1] Bernstein RE, Wahrmund DC, Barlow JW, Paul DR. Polym Engng Sci 1978;18:1220.
[2] Bernstein RE, Cruz CA, Barlow JW, Paul DR. Macromolecules 1977;10:681.
[3] Eshuis A, Roerdink E, Challa G. Polymer 1982;23:735.
[4] Reckinger C, Rault J. Rev Phys Appl 1986;21:11.
[5] Nishi T, Wan TT. Macromolecules 1975;8:909.
[6] Nishi T, Wan TT. Macromolecules 1977;10:421.
[7] Roerdink E, Challa G. Polymer 1978;19:173.
[8] Roerdink E, Challa G. Polymer 1980;21:509.
[9] Maiti P, Nandi AK. Macromolecules 1995;28:8511.
[10] Maiti P, Nandi AK. Macromol Chem Phys 1998;199:1479.
[11] Hirata T, Kotaka T. Polym J 1981;13:273.
[12] Penning JP, Manley RStJ. Macromolecules 1996;29:77.
[13] Morra BS, Stein RS. J Polym Sci, Polym Phys Ed 1982;20:2243.
[14] Scheirs J. Modern fluoropolymers—high performance polymers for diverse applications. New York: Wiley, 1997. Chapter 26.
[15] Faria O, Moreira RL. Polymer 1999;40:4465.
[16] Saito K, Miyata S, Wang TT, Jo YS, Chujo R. Macromolecules 1986;19:2450.
[17] Jouannet D, Pham TN, Pimbert S, Levesque G. Polymer 1997;38:5137.
[18] Pimbert S, Avignon-Poquillon L, Levesque G. Optical polymers: advances in optical fibers and waveguides. Washington, DC: American Chemical Society, 2001.
[19] Hoffman JD, Weeks JJ. J Res Natl Bur Stand A 1962;66:13.
[20] Flory PJ. Principles of polymer chemistry. Ithaca, NY: Cornell University Press, 1953.
[21] Moussaif N, Jerome R. Polymer 1999;40:6831.