

Miscibility of poly(vinylidene fluoride) and poly(methyl methacrylate-co-zinc polyacrylate) ionomers

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Abstract

A random copolymer of methyl methacrylate and 5.7 mol.% of acrylic acid has been neutralized by zinc cation to different extents in order to study the effect of zinc carboxylate pendant groups on the miscibility of poly(methyl methacrylate) (PMMA) and poly(vinylidene fluoride) (PVDF). The interaction parameter (χ) has been calculated from the experimental depression of the PVDF melting point. χ is minimum at zinc carboxylate content of 2.8 mol.%. The dynamic mechanical analysis of the PVDF–PMMA ionomer binary blends does not agree with the additivity rule of the properties, consistently with the phase morphology that changes with composition. Blends are indeed amorphous as long as the PVDF content does not exceed 40 wt.%, otherwise, semicrystalline PVDF coexists with an amorphous mixed PVDF/copolymer phase. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Poly(methyl methacrylate); Poly(vinylidene fluoride); Ionomers

1. Introduction

The entropy of mixing of macromolecules is usually so small that it cannot overcompensate the unfavorable enthalpic contribution characteristic of most synthetic polymer pairs. Therefore, miscibility is rather an exception observed in case of specific interactions between the constitutive components. Specific interactions actually refer to favorable attractive interactions between homopolymers, but also to repulsive segmental interactions in case of blends of random copolymers and parent homopolymers [1]. Blends of ion-containing polymers have been extensively studied with the purpose to increase miscibility as result of dipole–dipole, ion–dipole, ion pair–ion pair or acid–base interpolymer interactions [2–11].

The most popular example of amorphous one-phase polyblends are the so-called Noryl® polyblends commercialized by General Electric, i.e. polystyrene and poly(2,6-dimethyl-1,4-phenylene oxide) blends [10,11]. Polyvinylidene fluoride (PVDF) and poly(methyl methacrylate) (PMMA) blends are example of miscibility between a semi-crystalline polymer (PVDF) and an amorphous one (PMMA) [12,13]. These blends remain homogeneous, and thus amorphous, even at low temperature (<290°C) [14], provided that the PVDF

content is smaller than ca. 50 wt.% [15]. Otherwise PVDF crystallizes from the melt with formation of two or three phases [15,16]. Some discrepancy in the experimental values of T_g for the PMMA/PVDF blends must be noted, and more likely reflects the effect of the technique used for the sample preparation on the intimate phase morphology [14,15].

One work has recently focused on the “ionomerization” of PMMA by K carboxylate groups and its effect on miscibility with PVDF [17]. Miscibility is increased when PMMA is modified by small amounts of ionic groups (ca. 1–2 mol.%). Indeed, the interaction parameter, χ , calculated from the melting point depression of PVDF, is found to pass through a minimum at ca. 2 mol.% of carboxylate in PMMA. χ increases further with the ionic content in a possible relation to repulsive segmental interactions. This result deserves interest, as it shows that PVDF/PMMA miscibility can be modulated by minor modifications of PMMA. This opportunity has drawn our attention because we have recently observed that the interface between PVDF and polycarbonate (PC) was strengthened by the preblending of PVDF with PMMA [18]. Actually, ca. 35 wt.% PMMA in PVDF is enough to substitute the original PVDF/PC interface by a stronger PMMA/PC one. This situation might however be improved by the “ionomerization” of PMMA. Indeed, a decrease in miscibility with PVDF is expected to favor the migration of PMMA towards

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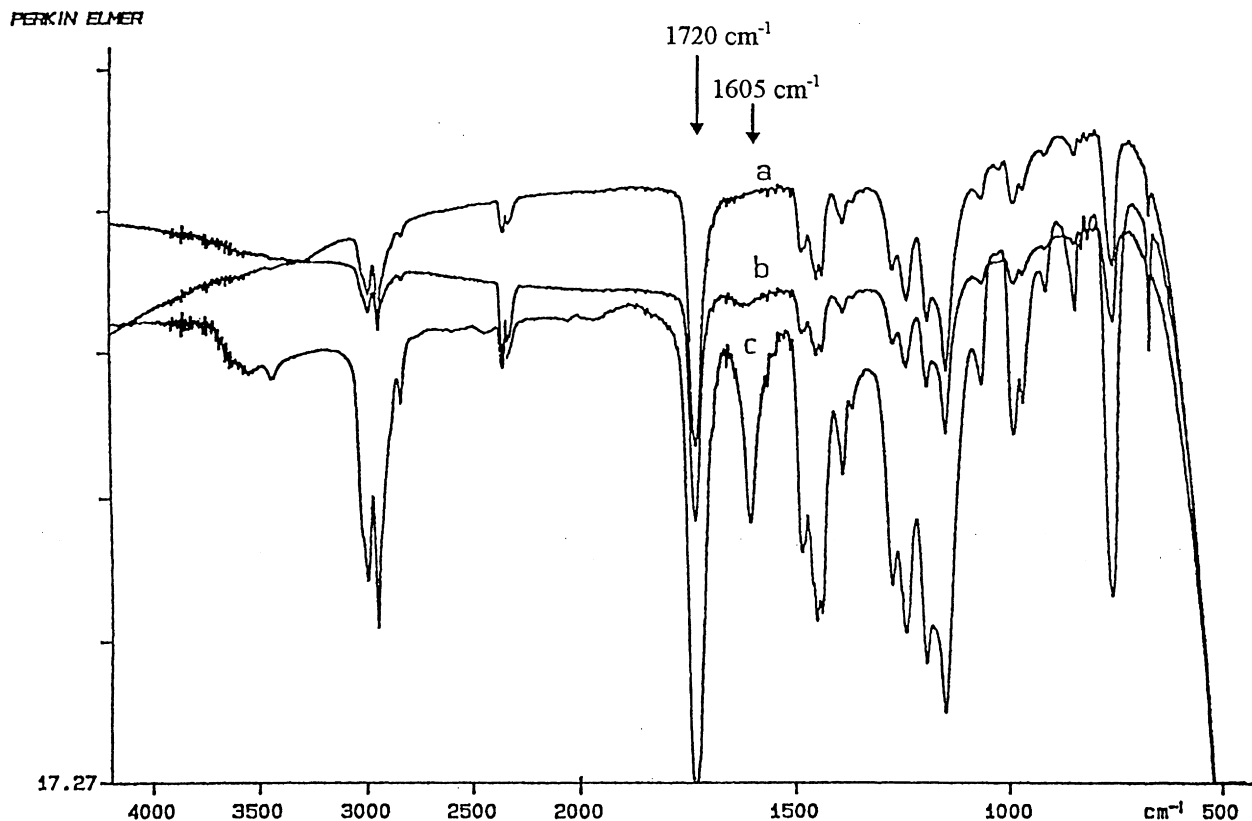


Fig. 1. FTIR spectra of (a) the non-neutralized copolymer: poly(MMA-co-AA); (b) the partially neutralized copolymer (50%); (c) the totally neutralized copolymer.

the interface with PC. Further, the appropriate choice of the metal cation associated with carboxylate groups could also promote stronger interactions of PMMA with PC, and in the extreme to catalyze the formation of PC/PMMA graft copolymer, as it is known that PC can react with PMMA [19]. Zinc cation known for coordination interaction with electron donating heteroatoms (N, O,...) has been considered as catalyst in this study.

A random copolymer of methyl methacrylate (MMA) and acrylic acid (AA) (6 mol.%) has been synthesized and neutralized to different extents by Zn cations. The effect of this PMMA modification on miscibility with PVDF has been studied. The interaction parameter has been estimated from melting point depression data, whereas glass transition temperature has been measured by dynamic mechanical analysis.

2. Experimental

2.1. Synthesis

Methyl methacrylate (MMA) and acrylic acid (AA) were purified by distillation under reduced pressure. A solution of MMA and AA (6 mol.%) in previously distilled ethyl acetate (18 wt.% comonomers) was added with azo-bis-

isobutyronitrile (AIBN; 0.3 mol.%) and degassed by bubbling pure nitrogen for 15 min. Copolymerization was conducted at 60–70°C for 30 h, and the copolymer was precipitated into methanol, redissolved in tetrahydrofuran (THF) and precipitated again. It was finally dried in a vacuum oven at 70°C for 48 h.

The acid groups (50 and 100%) of the MMA/AA random copolymer were neutralized in THF by zinc acetate. The acetic acid formed as reaction byproduct was displaced from the reaction medium by solvent distillation, which was then replaced by toluene. Distillation of the toluene–acetic acid azeotrope was repeated until no acetic acid was detected in the distillate. The copolymer was finally redissolved in THF and precipitated in heptane, washed by methanol, and dried under vacuum at 70°C for 48 h.

2.2. Characterization

The MMA/AA copolymer was analyzed by FTIR (1600 PERKIN–ELMER) before and after neutralization of the acid groups. The absorption band at 1720 cm⁻¹ was characteristic of both the ester and the carboxylic acid groups, whereas the carboxylate group was observed at 1605 cm⁻¹. The IR spectra for the copolymer before (a) and after neutralization of 50% (b) and 100% (c) of the acid functions were recorded (Fig. 1), and the absorption at 1605 cm⁻¹ was

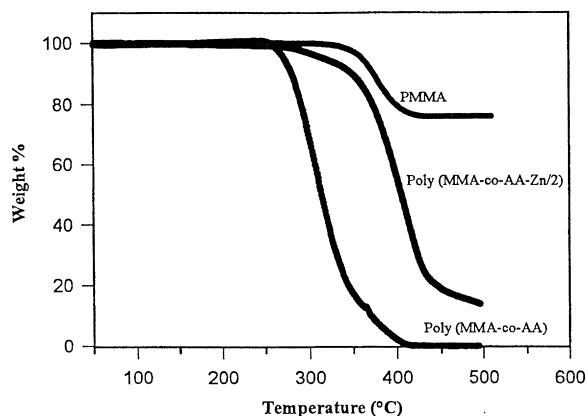


Fig. 2. TGA for PMMA, the poly(MMA-co-AA) copolymer, before and after neutralization to 50% by zinc cations. Scanning rate: 5°C/min, under nitrogen.

observed to increase in intensity with the neutralization degree.

The molar content of the acid groups in the copolymer was measured by potentiometric titration by a standard tetramethyl ammonium hydroxide (TMAH) solution in 90/10 (v/v) toluene/methanol mixture. This molar content was 5.7 mol.%.

Apparent molecular weight and molecular weight distribution were measured by size exclusion chromatography in THF with a Hewlett-Packard 1090 apparatus equipped with linear ultrastayragel columns calibrated with polystyrene standards. The apparent M_n was 45 000 and $M_w/M_n = 1.7$.

Thermal stability of the copolymers was analyzed by thermogravimetric analysis with the Dupont 910 TGA 51. Samples were scanned at 5°C/min under nitrogen, and analyzed at 240°C for 45 min under air atmosphere.

The constitutive polymers were previously dried overnight in a vacuum oven at 70°C and melt blended in a Brabender plasticorder at 200°C and 50 rpm.

Blends were analyzed by DSC with a DuPont 910 calorimeter at a scanning rate of 20°C/min under nitrogen. Blends

were previously heated at 200°C, slowly cooled down to room temperature before the DSC trace was recorded. DSC was calibrated with indium.

Blends were characterized by dynamic mechanical analysis using a Rheometrics RMS 800. Measurements were performed in the rectangular torsion mode at a frequency of 1 Hz and a scanning rate of 5°C/min.

3. Results and discussion

3.1. Thermal stability and glass transition of the poly(MMA-co-AA) before and after neutralization

The MMA/AA copolymer shows a weight loss above 240°C (Fig. 2) as result of the unstability of the acid groups. The zinc-neutralized copolymer remains stable at temperatures well above 300°C, and for 40 min at 240°C (Fig. 3), thus at temperatures substantially higher than the blending temperature (200°C).

The DMA curves for the MMA/AA copolymer of different zinc carboxylate contents are shown in Fig. 4, particularly the temperature dependence of $\tan \delta$ (δ being the loss angle). The α transition is expectedly observed far above room temperature. Fig. 5 shows that the glass transition temperature (i.e. temperature at the maximum of the α peak) linearly increases with the Zn carboxylate content, this increase being 5.3°C/carboxylate. Gronowski et al. [20] and Williams et al. [21] reported similar increase in T_g with the ion content of ionomers.

3.2. Blends of PVDF with poly(MMA-co-AA) and parent Zn salts

3.2.1. DSC analysis

Early study on the miscibility of PMMA and PVDF concluded that the melting enthalpy (ΔH_f) and melting temperature (T_m) of PVDF decreased by mixing with PMMA and that the polyblends were completely amorphous at PMMA contents of ca. 50 wt.% and higher [12]. The same behavior was observed when PMMA was modified by ionic groups [22]. The miscibility of the PMMA ionomer with PVDF however decreased with increasing ion content. Thus, the well known tendency of the ion pairs of the ionomers to self associate into multiplet and clusters seems to be unfavorable to the miscibility of PMMA with PVDF. Figs. 6 and 7 show that T_m and degree of crystallinity of PVDF decrease with increasing content of either PMMA or poly(MMA-co-AA) copolymer neutralized or not. Polyblends are completely amorphous when the content of both PMMA and the half neutralized random copolymer exceeds 50 wt.%. This content has to exceed 60 wt.% when PVDF is blended with the completely neutralized random copolymer. Fig. 7 also shows that the loss of PVDF crystallinity is much more important when blended with 50 wt.% PMMA, rather than with 50 wt.%

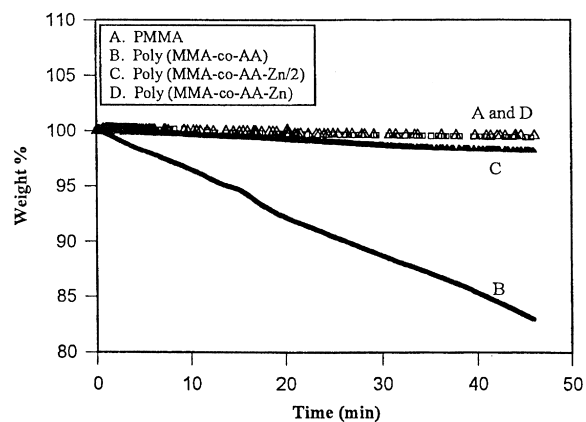


Fig. 3. TGA of PMMA and the poly(MMA-co-AA) copolymer: before and after neutralization to 50% (2.9 mol.% Zn carboxylate) and 100%. Isotherm at 240°C.

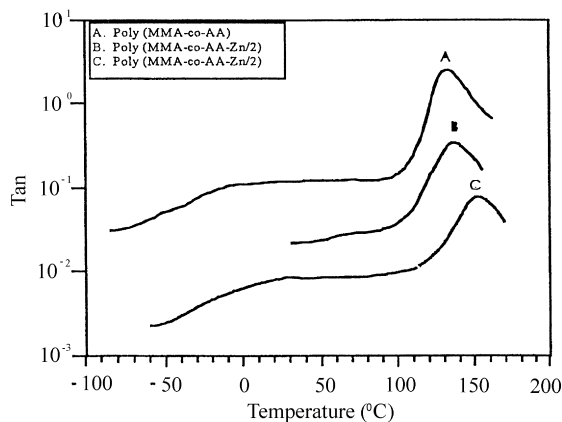


Fig. 4. $\tan \delta$ versus temperature for the poly(MMA-co-AA) copolymer before and after partial (50%) and total neutralization with Zn.

poly(MMA-co-AA). Neutralization of this copolymer has an intermediate depressive effect on T_m .

The Flory–Huggins interaction parameter (χ_{12}) for the PMMA/PVDF pair in the melt has been calculated from Eq. (1) that expresses the melting point depression of a crystalline material added with an amorphous compound [12].

$$1/T_m - 1/T_m^0 = -[(RV_{u,2})/(\Delta H_{u,2}V_{u,1})]\chi_{12}(1 - V_2)^2, \quad (1)$$

where the subscript 1 refers to the amorphous polymer and the subscript 2 to the crystalline one (PVDF), V_u is the volume fraction of the polymer repeating unit, T_m^0 and T_m are the melting temperature of neat PVDF and PVDF in polyblends, respectively, ΔH is the melting enthalpy.

Fig. 8 shows the linear least square fit of Eq. (1) for blends of PVDF with PMMA and random copolymers of MMA and AA, before and after neutralization. χ_{12} has been extracted from the slope of these plots.

Fig. 9 shows that the interaction parameter for the PVDF/PMMA pair (-0.32) is slightly smaller than the value reported by Nishi and Wang (-0.295) [12]. This difference

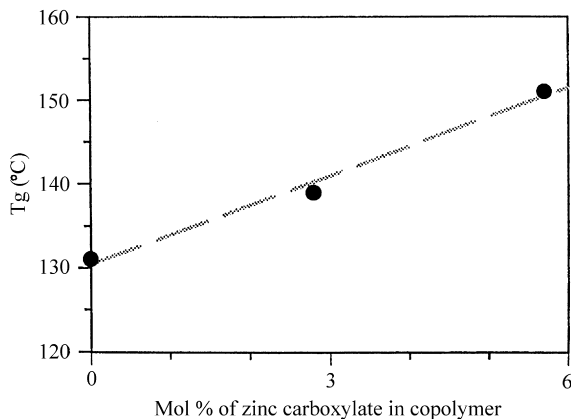


Fig. 5. Glass transition temperature of the poly(MMA-co-AA) copolymer versus zinc carboxylate content.

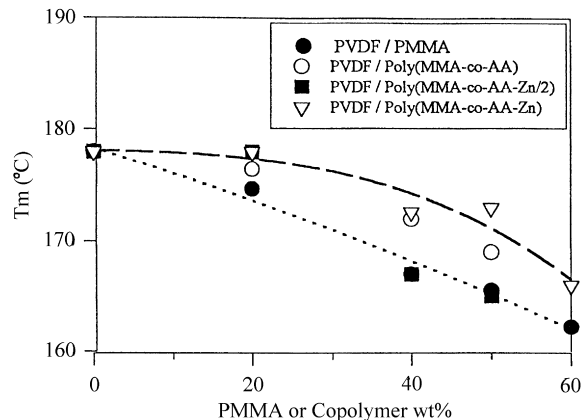


Fig. 6. Dependence of the PVDF melting temperature (T_m) on composition of blends with PMMA or random MMA copolymers.

may be, at least partly, explained by differences in molecular weight and microstructure of the polymers used in the two studies. χ_{12} is definitely smaller when the acrylic acid comonomer (5.7 mol.%) is half neutralized by Zn cations, indicating that the interplay of at least two types of mutual interactions (hydrogen bonding, and ion–dipole interaction) has a favorable effect on the polymer miscibility compared to the situation where only one type of interactions dominate, i.e. hydrogen bonding in case of poly(MMA-co-AA) and ion–dipole interaction when this copolymer is fully neutralized. Further increase in the Zn carboxylate content of the copolymer (5.7 mol.%) results in higher χ_{12} , thus in reduced miscibility, possibly as result of the increased tendency of the ionomer to self organize with formation of multiplets and clusters of Zn carboxylates. Fig. 10 illustrates how the melting temperature of PVDF depends on the Zn carboxylate content of the poly(MMA-co-AA) copolymer in 80/20, 60/40 and 50/50 PVDF/copolymer blends. This melting temperature is essentially independent of the ion content for 80/20 PVDF/copolymer blends. In contrast, when the copolymer content is 40 and 50 wt.%, a minimum in T_m is observed for zinc carboxylate content of 2.8 mol.%.

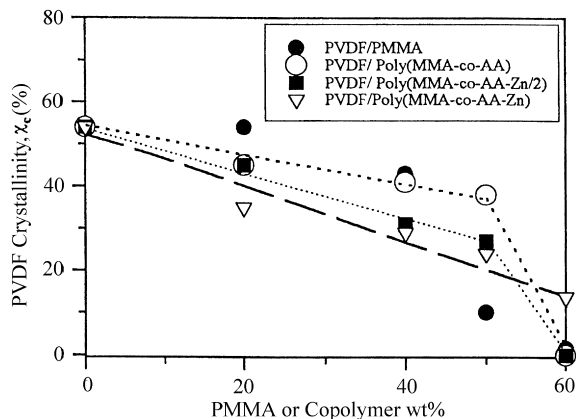


Fig. 7. Degree of crystallinity (χ_c) of PVDF versus composition of blends with PMMA or random MMA copolymer.

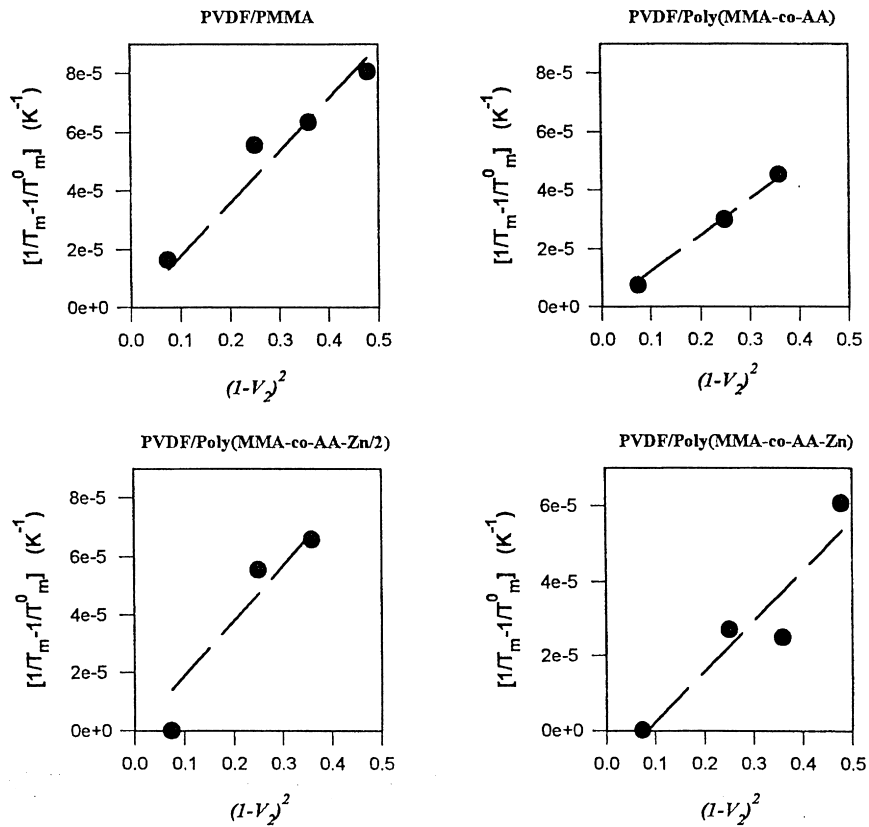


Fig. 8. Melting point depression for PVDF blends with PMMA and random copolymers of MMA with acrylic acid, neutralized or not. The interaction parameter is calculated from the slope.

3.2.2. DMA results

Figs. 11–13 show the thermal dependence of $\tan \delta$ for blends of PVDF with the poly(MMA-co-AA) copolymer before and after (partial) neutralization. Two main relaxations are observed for PVDF at -40 and 90°C , respectively (curve F). It was originally proposed by Yano [23], and it is now widely accepted, that the transition at high temperature is related to molecular motions associated with crystalline regions and their defects. The transition at low temperature is related to the main chain motion in the amorphous region,

and thus regarded as T_g . One may anticipate that in blends of high PVDF content, the broad transition characteristic of crystalline PVDF could interfere with the relaxation of the PVDF/copolymer amorphous phase. Indeed pure copolymers (Figs. 11–13, curve A) show a major relaxation in the range of 130°C to 150°C , in agreement with T_g reported in Fig. 5. These copolymers also show a β relaxation at lower temperature, which is thought to originate from rotation of the ester side groups [24].

Fig. 11 shows that the 20/80 (curve B) and 40/60 (curve C) PVDF/poly(MMA-co-AA) blend exhibit a major transition at 117°C and 78°C , respectively, in agreement with a single composition-dependent T_g , intermediate between T_g 's of the neat components. Curve D for the 60/40 PVDF/copolymer blend shows two transitions, at 60°C and between 80 and 120°C , respectively. The lower transition temperature is assigned to the PVDF/copolymer amorphous phase, whereas the higher one, is attributed to the crystalline phase formed by PVDF at this blend composition (Fig. 7). The DMA response of the 80/20 PVDF/copolymer blend (curve E) shows two transitions, at -40°C and 57°C (temperature at the transition maximum). The transition at -40°C is consistent with an amorphous PVDF phase (to be compared with curve F). The transition centered on 57°C is broad and complex, and is assumed to result from the overlap of the α -relaxation of the amorphous PVDF/copolymer phase and

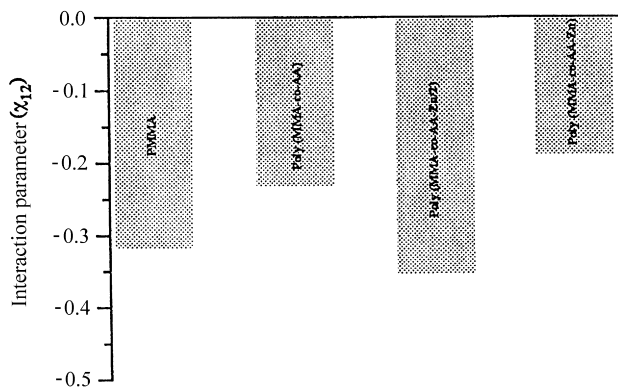


Fig. 9. Interaction parameter for PVDF blends with PMMA and random copolymers of MMA with acrylic acid, neutralized or not.

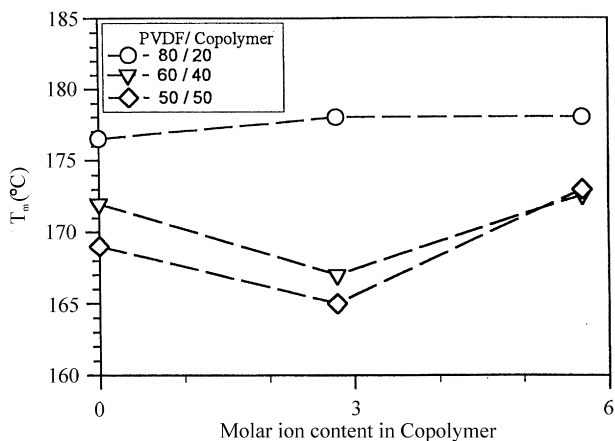


Fig. 10. Dependence of the PVDF melting temperature, T_m , on the zinc carboxylate content of poly(MMA-co-AA-Zn) in 80/20, 60/40 and 50/50 PVDF/copolymer blends.

the relaxation characteristic of the crystalline PVDF phase, as PVDF crystallizes at this blend composition (Fig. 7).

Fig. 12 illustrates the thermal dependence of $\tan \delta$ for the 20/80 and 80/20 blends of PVDF and half neutralized poly(MMA-co-AA). The DMA responses are quite comparable to those ones previously observed for blends with the non-neutralized copolymer (Fig. 11). Indeed, the glass transition of the amorphous PVDF/copolymer phase is observed at 117°C for the 20/80 polyblend (curve B), and at 74°C for the 80/20 composition (curve E) in addition to one relaxation at -40°C , which is the signature of amorphous PVDF.

When the poly(MMA-co-AA) copolymer is fully neutralized, Fig. 13 shows a broad transition with a maximum at 145°C for the 20/80 PVDF/copolymer blend (curve B). This observation is in sharp contrast to the symmetric and narrower DMA peak observed for blends of the same composition, in which the copolymer was non- or half-neutralized (Figs. 11 and 12). It clearly indicates that full neutralization of the random copolymer is unfavorable to miscibility with PVDF. In line with this conclusion, a very broad and more symmetric transition

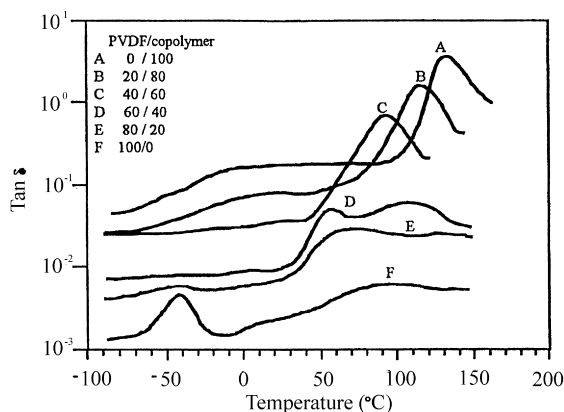


Fig. 11. $\tan \delta$ versus temperature for PVDF/poly(MMA-co-AA) blends of different compositions.

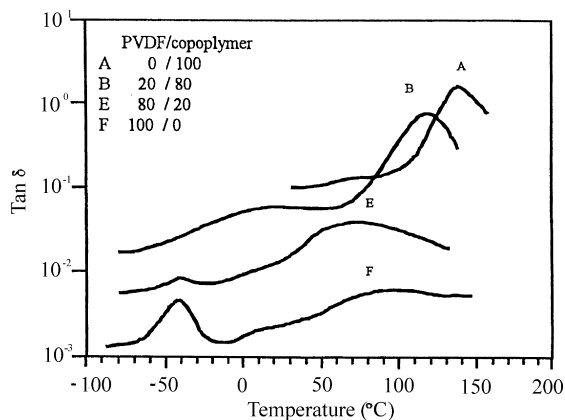


Fig. 12. $\tan \delta$ versus temperature for PVDF/half neutralized poly(MMA-co-AA) blends of different compositions.

is observed between 50 and 120°C for the other compositions (40/60, 60/40 and 80/20; curves C, D and E, respectively). As mentioned before, it more likely results from the overlap of two transitions typical of the PVDF/copolymer amorphous phase and the PVDF crystalline phase, respectively. Fig. 7 confirms the partial crystallization of PVDF at these blend compositions. In addition to this broad transition, the second one, characteristic of amorphous PVDF, is observed at -40°C for the blend containing 80 wt.% PVDF.

It may be concluded from the DMA data that an amorphous PVDF/copolymer phase is systematically formed as supported by a T_g intermediate between T_g 's of the two components. However, when the PVDF content of the blends is increased, signature for PVDF crystallization is reported and T_g of amorphous PVDF is observed at 80 wt.% PVDF. As a rule and in accordance with higher $\chi_{1,2}$, the even full neutralization of the random poly(MMA-co-AA) copolymer has a detrimental effect on miscibility.

Transparency of the films prepared by solvent casting of binary blends is observed at low PVDF contents, in qualitative agreement with DSC and DMA data.

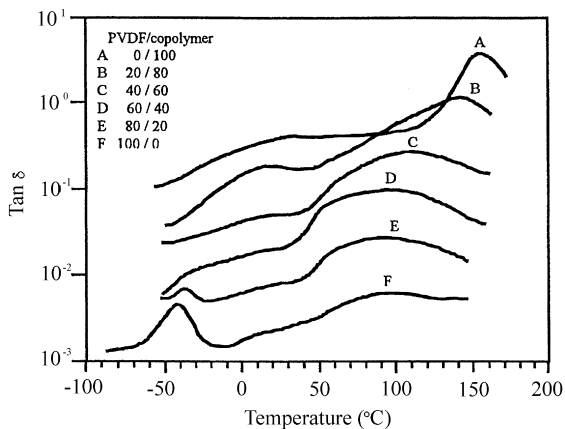


Fig. 13. $\tan \delta$ versus temperature for PVDF/fully neutralized poly(MMA-co-AA) blends of different compositions.

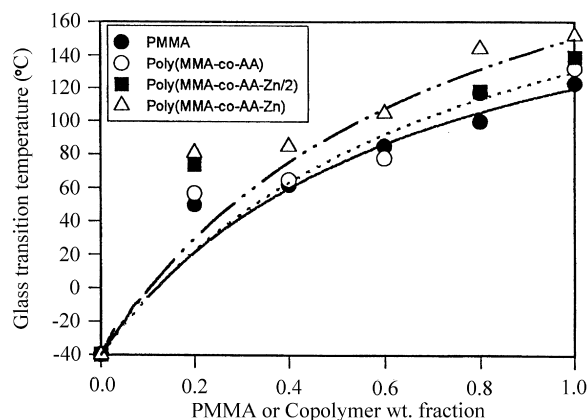


Fig. 14. Glass transition temperature for PVDF blends containing various amounts of PMMA and poly(MMA-co-AA) copolymer neutralized or not. Lines are the Gordon–Taylor predictions.

T_g 's for the three categories of blends considered in this study are reported in Fig. 14 (T_g was measured at the inflection point of the $\tan \delta$ vs. temperature curves). These data deviate from theoretical predictions based on additivity rules, in agreement with the study of PVDF/PMMA blends by Chuang and Han [25]. As a rule, there is much discrepancy between the values reported in the scientific literature for T_g of PVDF/PMMA blends [12,15,24,26–28], more likely in relation to the non-standard experimental conditions used for the samples preparation [15]. It was reported elsewhere that PMMA/PVDF blends are amorphous for PVDF content smaller than ca. 50 wt.%. Beyond this content, there is phase separation [14–16] into an amorphous PMMA/PVDF phase and crystalline PVDF domains [14]. It was found that T_g for amorphous miscible blends fitted the Gordon–Taylor equation very closely [15].

$$(T_g^{\text{PMMA}} - T_g^{\text{blend}})\phi_{\text{PMMA}} + k(T_g^{\text{PVDF}} - T_g^{\text{blend}})\phi_{\text{PVDF}} = 0, \quad (2)$$

where $k = \Delta\alpha_{\text{PVDF}}/\Delta\alpha_{\text{PMMA}}$ with $\Delta\alpha$ the difference between the thermal expansion coefficients below and above T_g of

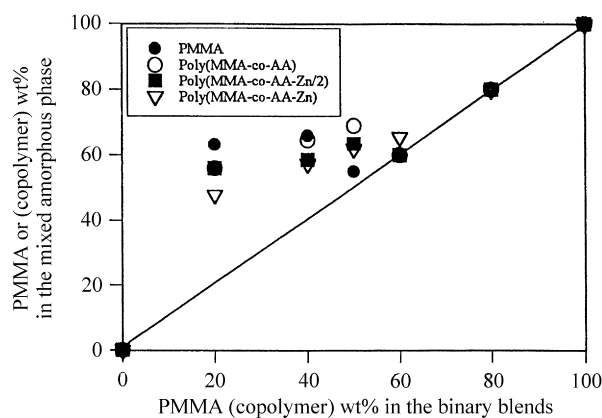


Fig. 15. Composition of the mixed amorphous PVDF/PMMA (copolymer) phase versus the nominal blend composition.

the parent homopolymers [15], ϕ is weight fraction. Fitting data of Fig. 14 to a linear regression yields $k = 0.35$ for the PVDF/PMMA blends and $0.40 \leq k \leq 0.43$ for PVDF/copolymer blends, which is in good agreement with values (0.37–0.4) reported elsewhere [12,29]. The theoretical curves are plotted in Fig. 14 and show deviation from the experimental data at high PVDF content (80 wt.%), whatever the copolymer used. This deviation is easily accounted for by taking the PVDF crystallinity (Fig. 7) into account and calculating accordingly the weight composition of the mixed amorphous PVDF/copolymer blends. T_g calculated by the Gordon–Taylor equation is then in agreement with the experimental values. Fig. 15 shows how the weight composition of the amorphous mixed PVDF/PMMA (copolymer) phase depends on the blend composition. A single amorphous phase containing ca. 60 wt.% PMMA (or copolymer) is formed as far as the nominal PVDF content of the blends exceeds 40 wt.%. At lower PVDF contents, blends are amorphous and of the same composition as the initial one. Although PVDF would be completely miscible with poly(MMA-co-AA) (5.7 mol.% AA) and the half neutralized copolymer until 40 wt.% PVDF, the loss of miscibility appears earlier in case of the fully neutralized copolymer (Fig. 15).

3.2.3. Mechanical properties

Composition dependence of the elongation at break (ϵ_b) and yield strength (σ_y) for PVDF/copolymer blends is illustrated by Figs. 16 and 17, respectively. Blends containing more than 50 wt.% copolymer are typically brittle whatever the copolymer (Fig. 16). There is a synergism in the elongation at break when PVDF is blended with less than 50 wt.% poly(MMA-co-AA) and the half neutralized version. D.R. Paul et al. [30] observed the same results when PVDF is blended with PMMA. In contrast, this property is adversely affected by blending PVDF with the fully neutralized copolymer.

Fig. 17 shows that the yield strength of the PVDF/copolymer blends passes through a minimum versus the blend composition, which is in qualitative agreement with the observations reported for the PMMA/PVDF blends [31]. In order to explain the main characteristic features of Figs. 16 and 17, it must be recalled that the glass transition temperature (T_g) of the blends increases rapidly from ca. -40°C as the copolymer content is increased, and already exceeds the testing temperature when the copolymer content is as low as 20 wt.% (Fig. 14). Therefore, it is not surprising that the yield tensile strength starts to decrease when PVDF is added to the copolymer, as it is the case when a rubbery diluent is added to glassy copolymer. Indeed, when less than 40 wt.% PVDF is mixed with the copolymer, PVDF is amorphous and plasticizes the copolymer. Beyond 40 wt.%, PVDF starts to crystallize which has a strengthening effect on the polyblend, which explains that the property goes through a minimum as the PVDF content is increased.

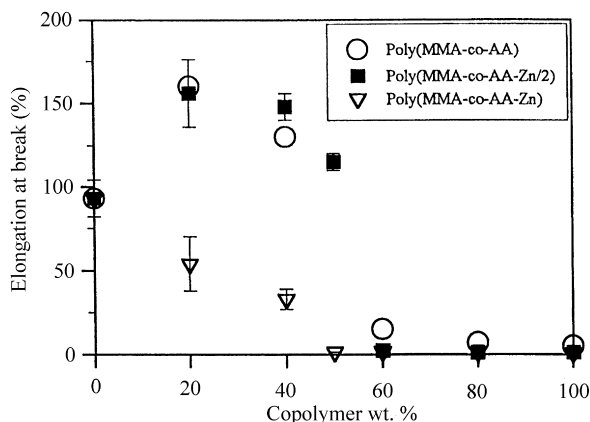


Fig. 16. Dependence of the elongation at break on the copolymer content for PVDF/copolymer blends.

Conversely, the elongation at break increases when the PVDF content exceeds 40 wt.%, thus as the copolymer is plasticized by PVDF. A maximum is then observed between 60 and 80 wt.% of PVDF when it is blended with the acid copolymer or the copolymer containing 2.8 mol.% of zinc carboxylate and then declines as crystallinity becomes a dominant factor. Blends of fully neutralized copolymer and PVDF exhibit however poor elongation properties (ϵ_b) with a negative deviation with respect to the additivity rule, as result of decreased miscibility.

4. Conclusions

Modification of PMMA by 5.7 mol.% AA (random copolymer) has a deleterious effect on miscibility with PVDF. Neutralization of half the AA comonomer units by Zn cations changes the situation completely, as χ_{12} decreases significantly becoming even smaller than χ_{12} for the original PVDF/PMMA pair. Nevertheless, the complete neutralization is very unfavorable to miscibility, which may be explained by the tendency of the Zn carboxylate groups

to self associate into multiplets and/or clusters (which is the typical behavior of ionomers) rather than to contribute to specific interactions with PVDF.

It is clear from DMA that PVDF and the random copolymer (neutralized or not) are miscible, at least until the PVDF content does not exceed 40 wt.%. Beyond this composition, an amorphous mixed PVDF/copolymer phase of a nearly constant composition coexists with semi-crystalline PVDF. There is however evidence that the fully neutralized copolymer is less miscible with PVDF than the unneutralized and the 50% neutralized copolymer.

The mechanical properties of the PVDF/copolymer blends are consistent with glassy monophase blends at low PVDF content, whereas they are dominated by the PVDF phase separation from an amorphous PVDF/copolymer phase when PVDF is the major component. Some synergism in elongation at break must be noted when less than 50 wt.% copolymer (non-neutralized and 50% neutralized) is blended with PVDF. Once again the fully neutralized copolymer has a detrimental effect on this ultimate mechanical property.

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References

- [1] Brinke GT, Karasz FE, Macknight WJ. *Macromolecules* 1983;16:1827.
- [2] Smith P, Eisenberg A. *J Polym Sci Lett* 1983;21:223.
- [3] Hara M, Eisenberg A. *Macromolecules* 1984;17:1335.
- [4] Molnar A, Eisenberg A. *Macromolecules* 1992;25:5774.
- [5] Rutkowska M, Eisenberg A. *Macromolecules* 1984;17:821.
- [6] Sakurai K, Douglas E, Macknight WJ. *Macromolecules* 1993;26:208.
- [7] Lu X, Weiss RA. *Macromolecules* 1993;26:3615.
- [8] Lu X, Weiss RA. *Macromolecules* 1992;25:6185.
- [9] Pilar J, Sikora A, Labsky J, Schlick S. *Macromolecules* 1993;26:137.
- [10] Register RA, Bell TR. *J Polym Sci-Phys B* 1992;30:569.
- [11] Tomita H, Register RA. *Macromolecules* 1993;26:2796.
- [12] Nishi T, Wang TT. *Macromolecules* 1975;8:909.
- [13] Lu S, Weiss RA. *Macromolecules* 1992;25:3242.
- [14] Hahn BR, Herrmann-Schonherr O, Wendorff JH. *Polymer* 1987;28:201.
- [15] Hirata Y, Kotaka T. *Polymer J* 1981;13:273.
- [16] Wang TT, Nishi T. *Macromolecules* 1977;10:421.
- [17] Leung LM, Lo KKC. *Polymer International* 1995;36:339.
- [18] Moussaif N, Maréchal Ph, Jérôme R. *Macromolecules* 1997;30:658.
- [19] Debier D, Devaux J, Legras R. *J Polym Sci Part A Polym Chem* 1995;33:407.

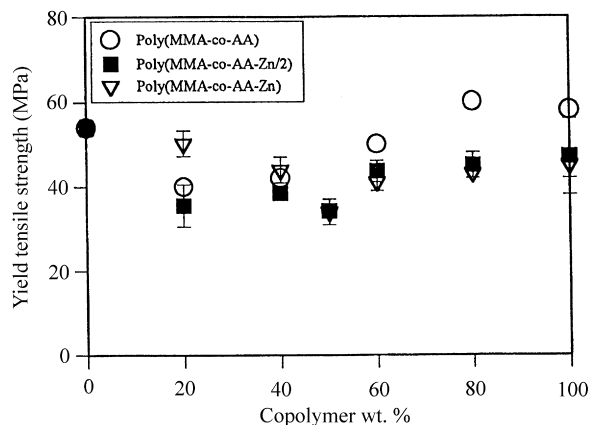


Fig. 17. Dependence of the yield tensile strength on the copolymer content of PVDF/copolymer blends.

- [20] Gronow skin AA, Jiang M, Yeager HL, Wu G, Eisenberg A. *J Membr Sci* 1993;82:83.
- [21] Williams MW. *J Polym Sci Symp* 1974;45:129.
- [22] Eisenberg A, King M. *Ion-containing polymers*. New York: Academic press, 1977.
- [23] Yano S. *J Polym Sci Part A-2* 1970;8:1057.
- [24] Paul DR, Altamirano JO. *Copolymers, polyblends, and composites* Chapter 32. *Advances in Chemistry Series 142*. Washington, DC: American Chemical Society, 1975. p. 371.
- [25] Chuang H, Han CD. *J Appl Polym Sci* 1984;29:2205.
- [26] Wahrmund DC, Bernstein RE, Barlow JW, Paul DR. *Polym Eng Sci* 1978;18:677.
- [27] Wu S. *J Polym Sci Polym Phys* 1987;25:2511.
- [28] Martinez-Salazar J, Camara JC, Calleja FJ. *J Mater Sci* 1991;26:2579.
- [29] Garcia JL, Koelling KW, Seghi RR. *Polymer* 1998;39:1559.
- [30] Murff SR, Barlow JW, Paul DR. *Multicomponent polymer materials* *Advances in Chemistry Series No. 211*. Washington, DC: American Chemical Society, 1986. p. 313–324.
- [31] Moussaif N, Jérôme R. *Polymer* 1999.