

Reactive compatibilization of PC/PVDF polymer blends by zinc carboxylate containing poly(methylmethacrylate) ionomers

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Abstract

Polycarbonate (PC) has been reacted with a random copolymer of methylmethacrylate and 6 mol% of acrylic acid (poly(MMA-*co*-AA)) and with this copolymer neutralized (totally or not) by Zn cations. When conducted in solution at 240°C, the reaction leads to the grafting of PC onto the copolymer neutralized or not. In the melt at 235°C, the grafting reaction occurs only when the copolymer is at least partly neutralized. Whatever the experimental conditions (solution or bulk), PMMA does not react with PC, which confirms that the acidolysis of PC is at the origin of the grafting reaction.

Poly(vinylidene fluoride) (PVDF) and PC have been melt blended at 235°C in the presence of the poly(MMA-*co*-AA) copolymer totally neutralized or not by Zn cations, the purpose being the reactive formation of PMMA-*g*-PC copolymer that would act as compatibilizer for the PC/PVDF blend. The phase morphology and the mechanical properties of the compatibilized PC/PVDF blends have been compared with the parent non-reactive polyblends. Compared to the modification of PVDF by 20 wt% of PMMA, the use of 20 wt% of the partly neutralized poly(MMA-*co*-AA) copolymer decreases further the average size of the dispersed phase, enhances its adhesion to the matrix, and results in a considerable increase of the elongation at break. The beneficial effect of zinc carboxylate in the PMMA copolymer is explained by the grafting of PC onto PMMA at the interface.

Keywords: Polycarbonate; Poly(vinylidene fluoride); Poly(MMA-*co*-AA) copolymer

1. Introduction

Previous papers [1-3] reported that immiscible PC/PVDF blends could be compatibilized by the addition of PMMA. This polymeric additive has the characteristic feature of being miscible with PVDF and compatible to PC. When PVDF is premixed with 40 wt% PMMA, the interfacial tension with PC is substantially decreased and the interfacial adhesion is increased. Actually the original PVDF/PC interface is replaced by the more favorable PMMA/PC one.

In order to improve this already valuable situation, the required PMMA content in PVDF should be decreased, for instance by enhancing the PMMA/PC interactions. Previous study on the PC/PMMA pair concluded that phenyl rings of PC favorably interact with the carbonyl groups of PMMA [4-5]. Effort was made to strengthen these interactions either by changing the molecular structure of PC [6-7] or by copolymerizing MMA with suitable comonomers [8-9], e.g. acrylic acid.

Another strategy to improve the PVDF/PC compatibility would consist in forming an interfacial agent, e.g. polycarbonate-*g*-poly(methyl methacrylate) copolymer, during the melt blending. In this respect, Rabeony et al. [10], and Kyu et al. [11] observed that PC could react with PMMA as result of transesterification between the ester groups of PMMA and the carbonate groups of PC, as it was also reported for other systems, such as PC and polyesters [12-18].

When PMMA contains acid groups, the carbonate bonds of PC can be acidolyzed [16]. This reaction has been thoroughly studied by Devaux et al. [19] who proposed the following mechanism:



These authors have more recently suggested a two-step mechanism for the reaction between PC and PMMA [20]. The first step, which occurs only in air at 300°C, would lead to formation of acid groups in PMMA as result of the hydrolysis of the ester units by residual water. Formation of these acid groups, and possibly glutaric anhydride, could also be initiated by benzoic acid, which might be released as result of the PC degradation. The

acid groups of PMMA would then be responsible for the acidolysis of PC and formation of graft copolymer through mixed aliphatic–aromatic ester bond (Eq. (2)).



This reaction does not however occur significantly below 240°C, thus at the blending temperature of PC and PVDF (235°C). This situation might be improved by bypassing the first step of the grafting reaction (partial PMMA hydrolysis), which takes place at substantially high temperature (300°C). For this purpose, a random copolymer of methyl methacrylate (MMA) and acrylic acid (AA) could be substituted for PMMA. Further, neutralization of the carboxylic acid groups by metal cation could contribute to the catalysis of the acidolysis reaction. Zinc cation known for coordinative interaction with electron donating heteroatoms (N, O,...) is worth being considered. Therefore, random copolymer of MMA and 6 mol% AA will be synthesized and neutralized by Zn cations to different extents. The reaction of these copolymers with PC will be studied in benzophenone at 240°C and in the melt at 235°C. Under these conditions, no degradation of PC and PMMA occurs [21]. Finally, the question will be addressed to know whether the compatibility between PC and PVDF is improved when the random copolymer of methyl methacrylate and 6 mol% of acrylic acid is used rather than neat PMMA in the blending process. The effect of the (partial) neutralization of the acrylic acid co-units by Zn cations will also be studied, since the formation of the PC-*g*-PMMA copolymer at the interface is expected to be more favorable.

2. Experimental

2.1. Materials

The main characteristics of the commercially available polymers used in this study are listed in Table 1.

Table 1. Main characteristics and origin of the polymers used in this study

Polymers	Abbreviation	Commercial designation	Source	Molecular weight M_w (10^{-3}) ^a	M_w/M_n
Polycarbonate	PC	Makrolon 3103	Bayer	58	1.7
Poly(methyl methacrylate)	PMMA	Diakon	ICI	60	1.6
Poly(vinylidene fluoride)	PVDF	Solef×10N	Solvay	125	1.8

^aDetermined by SEC with polystyrene calibration.

Synthesis of the methyl methacrylate (MMA) and acrylic acid (AA) (6 mol%) random copolymer (poly(MMA-*co*-AA)) and neutralization by Zn cations were reported elsewhere [21]. Apparent molecular weight and molecular weight distribution ($M_n=45,000$ and $M_w/M_n=1.7$) were determined by size exclusion chromatography (SEC) in reference to calibration with polystyrene standards. The molar content of the acid groups was 5.7 mol%, as measured by potentiometric titration by a standard tetramethyl ammonium hydroxide (TMAH) solution in 90/10 (v/v) toluene/methanol mixture.

Acid groups (25, 50 and 100%) of the poly(MMA-*co*-AA) copolymer were neutralized by zinc acetate, and the copolymers were designated as PZn25, PZn50 and PZn100, respectively (the zinc carboxylate content being then 0.7, 1.4 and 2.8 mol%).

2.2. Reaction of poly(MMA-*co*-AA) and neutralized version with PC

The reaction was conducted in the melt by mixing the polymeric components in a Brabender mixing chamber (Plasti-corder) at 235°C, for 8 min, the rotation speed being 50 rpm. PC was first added and melted for 3 min, followed by the addition of PMMA (or the copolymer). The polymers were previously dried overnight in a vacuum oven at 120°C for PC and 70°C for PMMA and copolymers. Polyblends prepared in the melt were dissolved in chloroform, and the reaction product was extracted by acetone.

The reaction was also conducted in 10 wt% solution in benzophenone at ca. 240°C, the reaction time ranging from 0 to 6 h. PC and PMMA copolymers were used in 1/1 (w/w) ratio. The reaction product was precipitated and washed in methanol (solvent for benzophenone), redissolved in chloroform and extracted by acetone.

Films were cast on NaCl windows from chloroform solution and analyzed by FTIR. Size exclusion chromatography was performed in THF with a Hewlett–Packard 1090 apparatus, equipped with linear

ultrastyrigel columns calibrated with polystyrene standards and with RI (refractive index) and UV (ultraviolet, $\lambda=254\text{ nm}$) detectors.

2.3. Preparation and characterization of ternary blends

Blends were prepared by mixing the polymers in a Brabender mixing chamber (Plasti-corder) at 235°C, for 8 min, the rotation speed being 50 rpm. The polymers were previously dried overnight in a vacuum oven at 120°C for PC and 70°C for the random copolymer and PMMA. PC was first added and melted under mixing for 3 min, followed by the addition of PMMA (or the random copolymer) and PVDF. Samples of PC, PVDF/copolymer (or PMMA) binary blends and PC/copolymer (or PMMA)/PVDF ternary blends were prepared by compression molding at 220°C for 5 min and then quenched at room temperature under pressure.

Samples for tensile testing were cut out from these 2 mm thick plates. Stress-strain curves were recorded with an Instron Universal Tensile Tester (model DY 24) at a tensile rate of 20 mm/min for at least five samples.

A Jeol JSM-840A Scanning Electron Microscope (SEM) was used to observe cryofracture surfaces prepared at the liquid nitrogen temperature.

Image analysis was carried out using a Sun Sparc 10 working station equipped with a Visilog Noenis Software (France). The number average diameter of the particles, d_n , was calculated from scanning electron micrographs as the average value over 400–800 particles.

3. Results and discussion

3.1. Reactive blending of polycarbonate and poly(methylmethacrylate-*co*-zinc polyacrylate) ionomers

The FTIR analysis of the PC/PMMA binary blend before and after heating at high temperature cannot provide useful information on the occurrence of an interfacial reaction or not. Therefore, the experimental approach previously reported by Rabeony et al. [10] has been used. It consist in dissolving one component in a selective solvent, e.g. PMMA or poly(MMA-*co*-AA) in acetone. If PMMA or the random copolymer with AA has reacted with PC, then at least part of the reaction product is expected to be in solution. Indeed, PMMA-*g*-PC copolymer of minor PC content will dissolve in acetone, in contrast to rich in PC copolymer that will be unextractable by acetone. The extracted polymer has then to be analyzed by FTIR in order to detect the presence of PC. Although the carbonyl absorption at 1780 cm^{-1} is typical of carbonate and easily observed [10-11], possible overlap with the absorption of the ester group of PMMA at 1730 cm^{-1} might be a problem to detect small amounts of PC. It is therefore more appropriate to consider the vibration of the *para*-disubstituted benzene ring at ca. 1017 cm^{-1} which is observed independently of the PMMA or poly(MMA-*co*-AA) absorption.

3.1.1. Model reactions in solution

Fig. 1A shows the FTIR spectra for the polymer extracted by acetone from the PC/PMMA blend before and after 3 h reaction in benzophenone at 240°C. No significant modification at the wave numbers characteristic of PC, thus 1017 cm^{-1} for the aromatic ring and 1780 cm^{-1} for the carbonate, is observed so that PC and PMMA remain essentially unreacted at this temperature. The situation might however change if PMMA contains some acrylic acid units, since the hydrolysis of the ester groups of PMMA, which is prerequisite for the PC/PMMA reaction, would then be catalyzed by the acid groups [19]. Therefore poly(MMA-*co*-AA) has been heated in the presence of PC under the same experimental conditions as before.

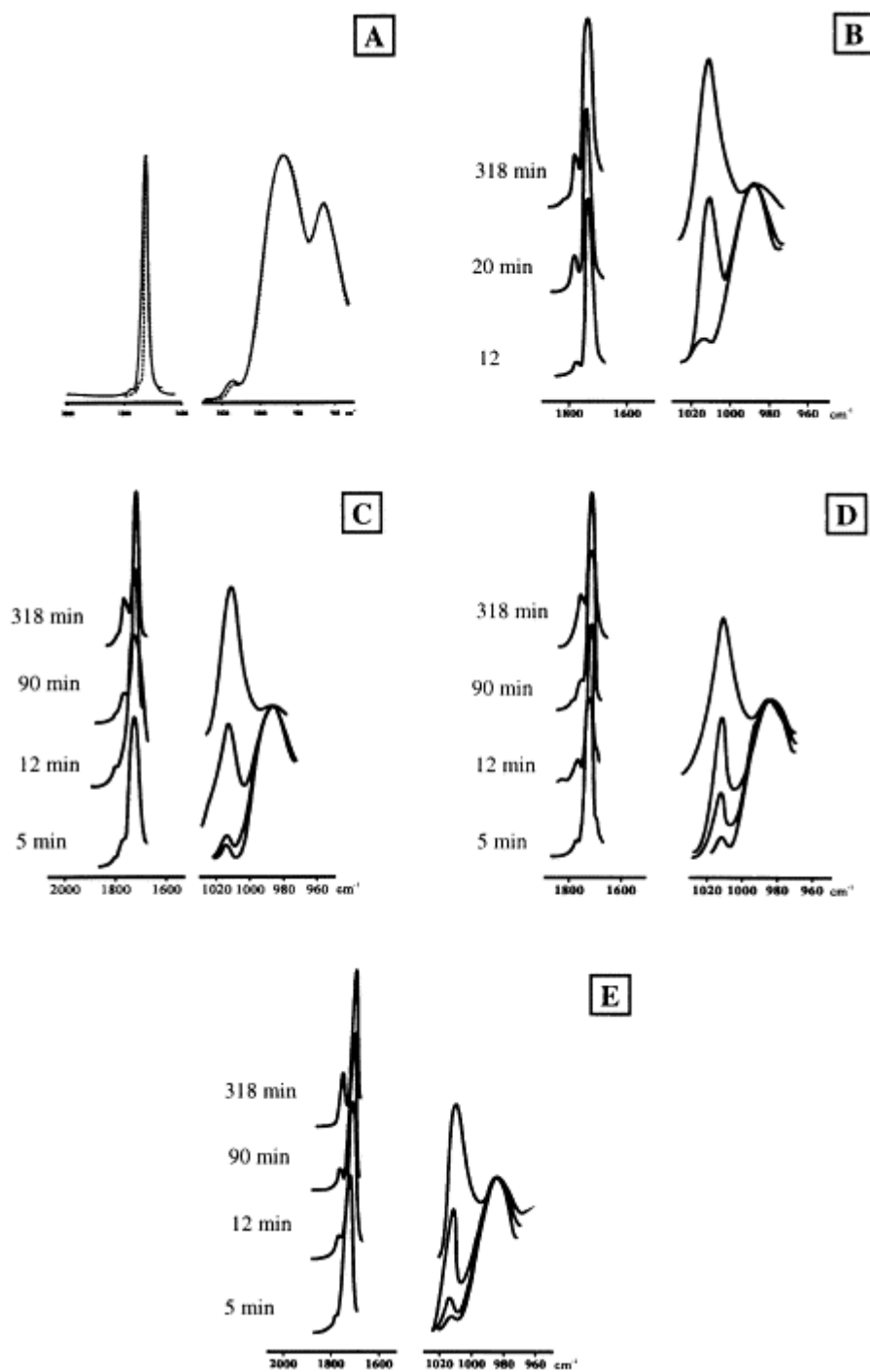


Fig. 1. FTIR spectra of the product extracted by acetone from the PC/PMMA (copolymer) (50/50) blend in benzophenone at 240°C. (A) PC/PMMA before (---) and after (—) reaction. (B) PC/poly(MMA-co-AA), (C) PC/PZn25, (D) PC/PZn50, (E) PC/PZn100.

Fig. 1B–E compare the FTIR spectra of the products extracted by acetone from the PC/poly(MMA-co-AA), PC/PZn25, PC/PZn50, PC/PZn100 blends, respectively, when heated in benzophenone at 240°C for increasing periods of time. The FTIR analysis of the extracted product allows to compare the relative absorption of the carbonate (1780 cm^{-1}) with respect to the ester (1730 cm^{-1}) and to follow the absorption of the aromatic ring at 1017 cm^{-1} at increasing reaction times. Clearly, more PC is found in the acetone solution, consistently with the progress of the PC/PMMA reaction with time. PC is thought to dissolve not only as grafts attached to PMMA but also as short length ω -hydroxyl PC formed as result of the PC acidolysis (Eq. (2)). At least qualitatively, no substantial difference is observed in the time dependence of the FTIR spectra when the poly(MMA-co-AA) copolymer is neutralized at 25, 50 and 100% by zinc cations. This conclusion is confirmed by Fig. 2 which

compares the time dependence of the relative absorption of the carbonate groups with respect to the ester ones. No significant information on the effect of the neutralization of the acrylic acid groups on the progress of the reaction can actually be drawn from this figure, that however shows a substantial progress for the first 20 min. In addition to FTIR analysis, the blends could also be advantageously analyzed by SEC [11 ; 20 ; 22].

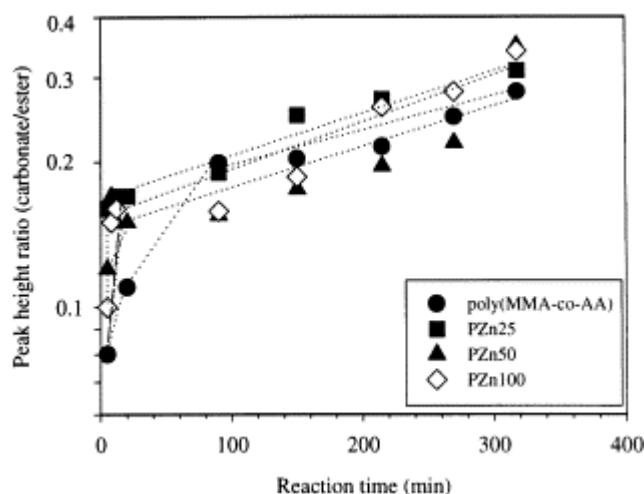


Fig. 2. Time dependence of the relative absorption of the carbonate and ester groups for PC/PMMA (copolymer) blends reacted in bezophenone at 240°C.

The SEC chromatograms have been recorded with both the ultraviolet ($\lambda=250$ nm) and the refractive index detectors. SEC chromatograms of the original copolymers are shown in Fig. 3. Fig. 4A–D show the analysis of the product extracted from the PC/poly(MMA-co-AA), PC/PZn25, PC/PZn50, and PC/PZn100 blends after reaction (320 min) in benzophenone at 240°C. The UV trace (dotted curve) is characteristic of PC. Each chromatogram is bimodal, these two major fractions becoming better resolved as the neutralization degree of the poly(MMA-co-AA) copolymer is increased. Whatever the PMMA copolymer used, PC is predominantly observed as low M_w component supposed to be short fragments of PC chains released by the acidolysis of PC in agreement with Eq. (2). This low M_w fraction was not observed for the original copolymers. PC detected at smaller elution volumes has to be part of graft copolymer.

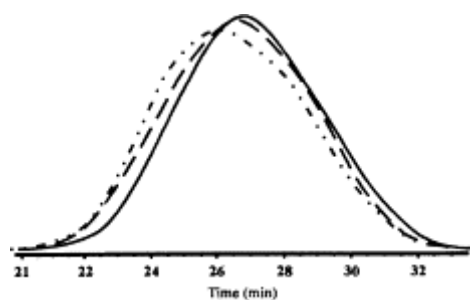


Fig. 3. SEC chromatograms of the: (—) poly(MMA-co-AA), (---) PZn50 and (-·-·) PZn100.

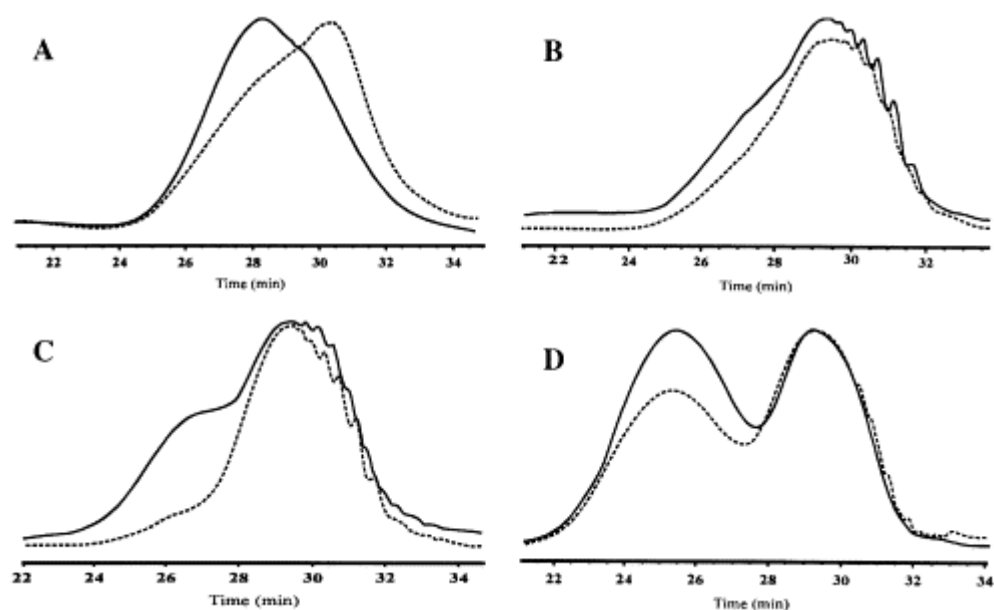


Fig. 4. SEC chromatograms of the product extracted by acetone from PC/copolymer (50/50) blends after reaction in benzophenone at 240°C: RI (—) and UV (---) detections. (A) PC/poly(MMA-co-AA), (B) PC/PZn25, (C) PC/PZn50, (D) PC/PZn100.

3.1.2. Melt mixing

Since poly(MMA-co-AA) neutralized or not react with PC in solution at high temperature, the same polymer blends have been studied in the bulk at 235°C, i.e. the melt processing temperature. A series of 50/50 (w/w) PC/PMMA, PC/poly(MMA-co-AA), PC/PZn25, PC/PZn50, PC/PZn100 blends have been mixed at 235°C for 8 min in the Brabender mixer. After reaction, the samples have been dissolved in chloroform and then precipitated in acetone, so as to extract the original copolymer of MMA and the in situ formed graft copolymer in solution, PC being insoluble. It must be noted that some part of the PC/PZn100 blend remains insoluble in chloroform after melt mixing.

The FTIR spectra of the extracted fractions in case of the PC/poly(MMA-co-AA), blend (Fig. 5A) show the absence of the typical PC absorption (1780 cm^{-1} and 1117 cm^{-1}) after melt mixing at 235°C. Although not shown in Fig. 5, the same conclusion holds when PMMA and PC are melt blended under the same conditions.

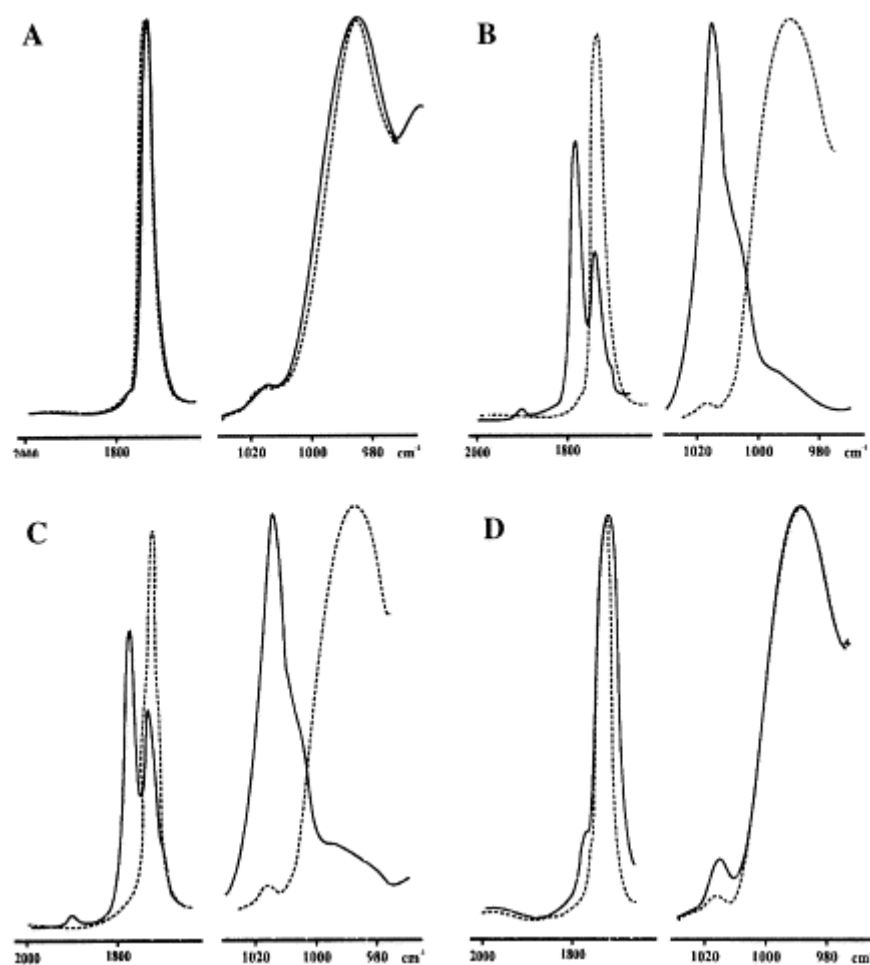


Fig. 5. FTIR spectra of the product extracted by acetone from PC/MMA copolymer (50/50) blends before (---) and after (—) melt mixing at 235°C. (A) PC/poly(MMA-co-AA), (B) PC/PZn25, (C) PC/PZn50, (D) PC/PZn100.

Figs. 5B and C show the FTIR spectrum of the extracted fraction for the PC/PZn25 and PC/PZn50 blends, respectively. The two figures show the typical carbonyl stretching of the ester group (1730 cm^{-1}) and the characteristic PC absorption at 1780 and 1017 cm^{-1} , which indicates that grafting reaction has taken place during the melt mixing.

Conversely, the FTIR spectrum of the fractions extracted from the PC/PZn100 blend after melt mixing (Fig. 5D), does not provide evidence for PC grafting onto the random copolymer of MMA. This observation does not however mean that the grafting reaction has not occurred. Indeed, the major part of the blend (70 wt%) after melt mixing has proved to be insoluble in chloroform, consistently with crosslinking of the polyblend (PC and PZn100 are soluble in chloroform before heating). It might be tentatively proposed that α -, ω -hydroxyl PC chains are favorably formed in the presence of high content of zinc carboxylate and participate to transesterification reactions with the PMMA backbone so leading to crosslinking. Whatever the intimate mechanism of the crosslinking reaction, it must be noted that the grafting of PC onto poly(MMA-co-AA) only occurs when part of the acid groups are neutralized by zinc cations. Coexistence of acid groups and zinc carboxylate seems to be the prerequisite for successful grafting reaction. In the absence of neutralization of the acrylic acid comonomer no reaction with PC occurs, whereas the complete neutralization leads to undesirable crosslinking reaction.

3.2. Reactive compatibilization of PC/PVDF blends

The reactive compatibilization of PC/PVDF blends by the aforementioned copolymers of MMA has been examined in terms of phase morphology and mechanical properties.

3.2.1. Morphology

Surfaces have been prepared by cryofracture and observed by SEM for 20/80 and 80/20 PC/PVDF blends, modified by 20 wt% (with respect to PVDF) of PMMA or poly(MMA-*co*-AA) neutralized or not by Zn cations. PVDF has also been added with 40 wt% PMMA and 40 wt% half-neutralized poly(MMA-*co*-AA). All the blends have a two-phase morphology, the average diameter of the dispersed phase being reported in Fig. 6A and B.

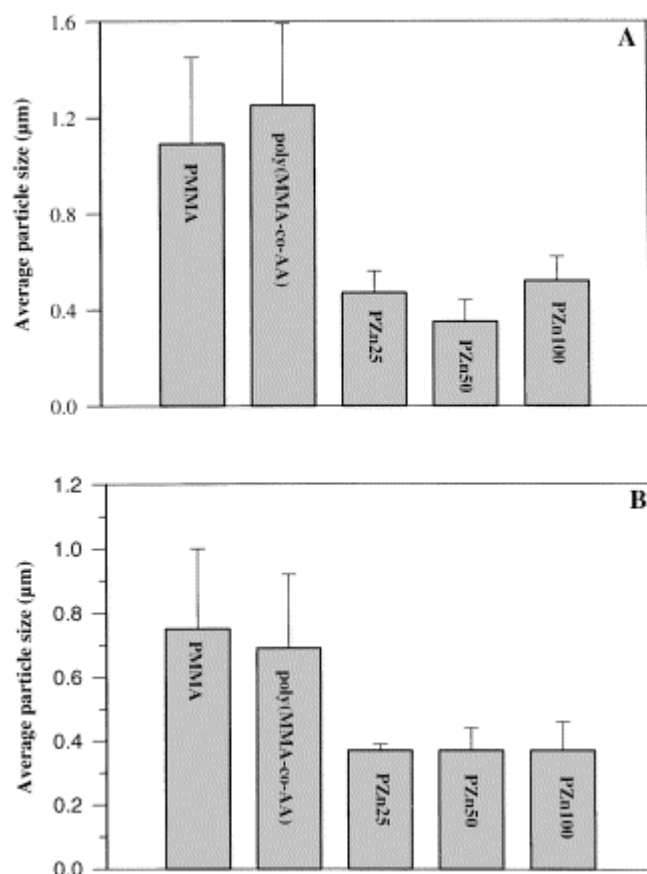


Fig. 6. Average particle size in (A) 20/80 and (B) 80/20 PC/PVDF blends, the PVDF phase being modified by 20 wt% PMMA containing additives.

First of all, it must be noted that a previous study [3] showed that the average particle size was decreased up to four times upon addition of 20 wt% of PMMA to the PVDF phase. Fig. 6 shows that the substitution of poly(MMA-*co*-AA) for MMA has no substantial effect on the phase morphology. However, neutralization (even partial) of the acrylic acid co-units of the MMA copolymer improves further the phase dispersion since the average particle size is decreased by at least a factor of 2. In parallel, the interfacial adhesion appears to be improved, as supported by the cryofractured surfaces that show no particle debonding from the matrix although it was the case when PMMA or the unneutralized random copolymer was used as additive. This improvement is a hint for the reactive interfacial grafting of PC onto the PMMA copolymer when Zn carboxylate groups are available. This conclusion, which relies upon indirect information, is consistent with the previous observation that PC is unable to react at 235°C in the melt with PMMA and with the poly(MMA-*co*-AA) copolymer, at least as long as the acid groups are not neutralized by Zn cations.

The average diameter of the dispersed domains has been compared with predictions based on the Serpe model [23] (Eq. (3)).

$$d_s = \frac{4\gamma_{1,2}(\eta_d/\eta_b)^{\pm 0.64}}{\dot{\gamma}\eta_b(1 - (4\phi_d\phi_m)^{0.8})} \quad (3)$$

with the η_d/η_b exponent $=+0.84$ for $\eta_d/\eta_b > 1$ and -0.84 for $\eta_d/\eta_b < 1$ where, γ is the interfacial tension between components 1 and 2, η_d the viscosity of the dispersed phase, η_b the viscosity of the blend, ϕ_d the volume fraction of the dispersed phase (ϕ_d) and the matrix (ϕ_m), $\dot{\gamma}$ the shear rate.

The agreement between experimental and predicted values is poor when PVDF is modified by 20 wt% of either PMMA or the unneutralized poly(MMA-co-AA) copolymer (Table 2). That the particle diameter is larger than predicted might indicate poor phase stability and particle coalescence when the polyblends are compression molded. The agreement between the experimental and the theoretical data is much better when the copolymer is neutralized (Table 2). It is however assumed that this neutralization does change significantly the interfacial tension between PC and PMMA and the melt viscosity of PMMA. This conclusion is in line with retarded phase coalescence during compression molding, when PMMA is substituted by partly neutralized poly(MMA-co-AA) copolymer. The improved stability of the dispersed phases is an additional, although still indirect, evidence for the reactive formation of a compatibilizer at the interface.

Table 2. Average particle diameter for the 20/80 and 80/20 PC/PVDF blends modified by 20 wt% additives

PC/PVDF	Average particle diameters d_n (μm)					
	Serpe model	PMMA	poly(MMA-co-AA)	PZn25	PZn50	PZn100
20/80	0.56	1.1	1.23	0.47	0.36	0.52
80/20	0.3	0.76	0.7	0.38	0.38	0.38

As recalled in the introduction, when preblended with PVDF, PMMA migrates and accumulates at the interface with PC. Although this modification of the PC/PVDF interface by PMMA has a favorable effect on both the interfacial tension and the interfacial adhesion, further improvement of this situation is expected to result from the interfacial formation of a graft copolymer between PC and PMMA. Block and graft copolymers at polyblend interface are indeed known to improve the interfacial adhesion and to inhibit phase coalescence [24-26].

3.2.2. Mechanical properties

Strong interfacial adhesion is the prerequisite to impart high mechanical properties to immiscible polymer blends, otherwise the stress transfer between the phases is poor and so is the resistance to deformation. The high immiscibility between PC and PVDF results in low interfacial adhesion [3], thus in the absence of chain interpenetration at the interface [27].

Would the hypothesis of reaction of PC with (partly) neutralized poly(MMMA-co-AA) be correct, an interphase consisting of PMMA-g-PC copolymer is expected to bridge the PC and PVDF phases together.

Tensile properties, particularly the elongation at break (ϵ_b), are very sensitive to the strength of the interface and to the phase morphology, which explains why they are routinely measured to evaluate the efficiency of compatibilization strategies [28-29]. Fig. 7 shows the elongation at break of PVDF/PMMA and PVDF/modified PMMA blends. Yield tensile strength and ϵ_b are shown in Fig. 8, Fig. 9, Fig. 10 and Fig. 11 for the 20/80 and 80/20 PC/PVDF blends with dispersed phase morphology, and for the 40/60 and 60/40 co-continuous two-phase PC/PVDF blends.

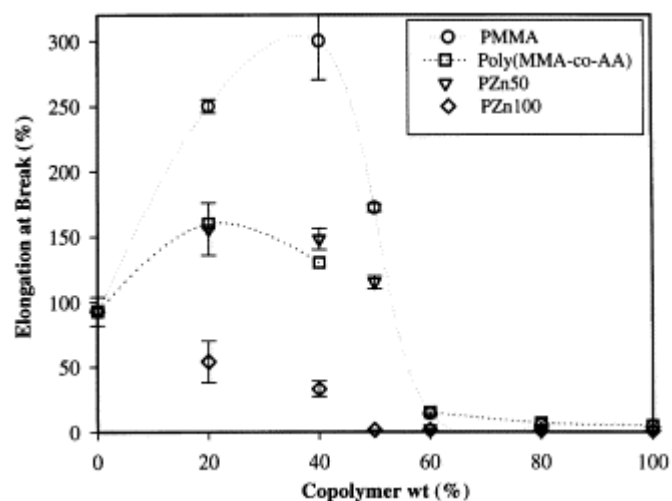


Fig. 7. Dependence of the elongation at break of PVDF/PMMA and PVDF/modified PMMA blends on the PMMA content in PVDF.

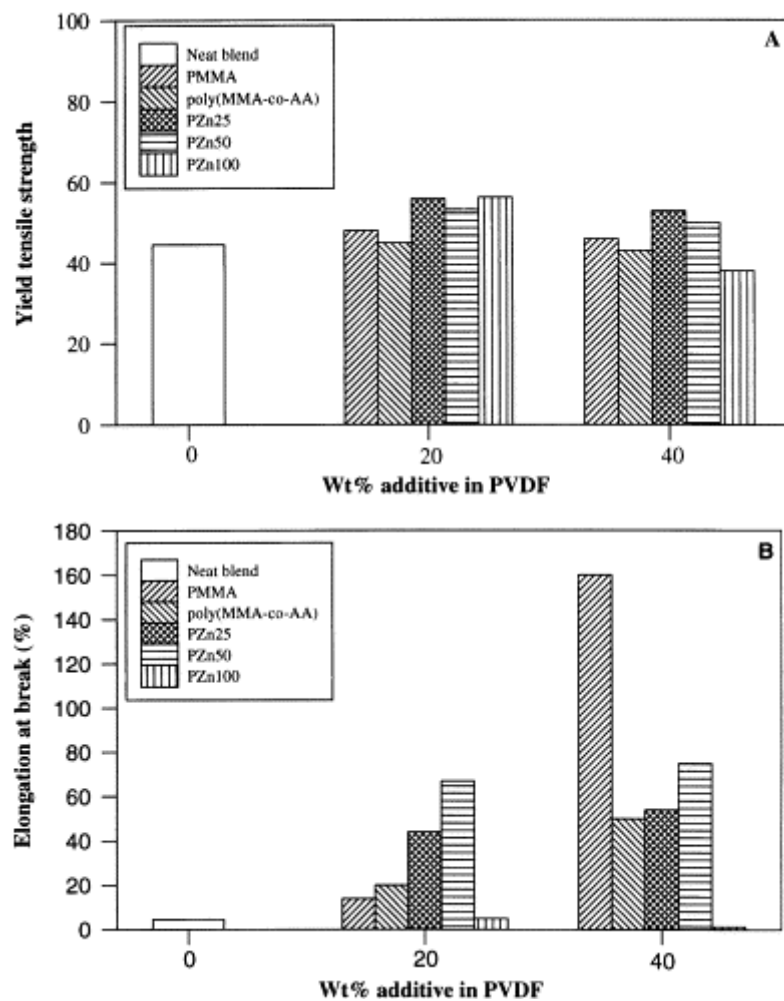


Fig. 8. Dependence of (A) the yield tensile strength and (B) the elongation at break on the type of additive and content in PVDF, for the 20/80 PC/(PVDF-additive) blends.

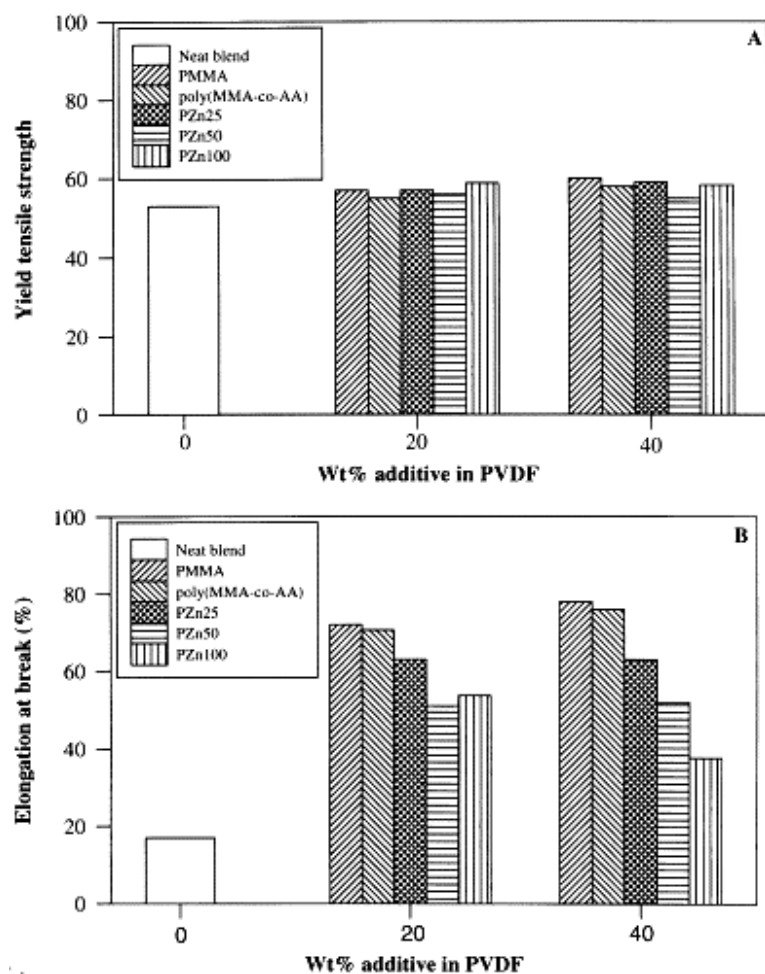


Fig. 9. Dependence of (A) the yield tensile strength and (B) the elongation at break on the type of additive and content in PVDF, for the 80/20 PC/(PVDF-additive) blends.

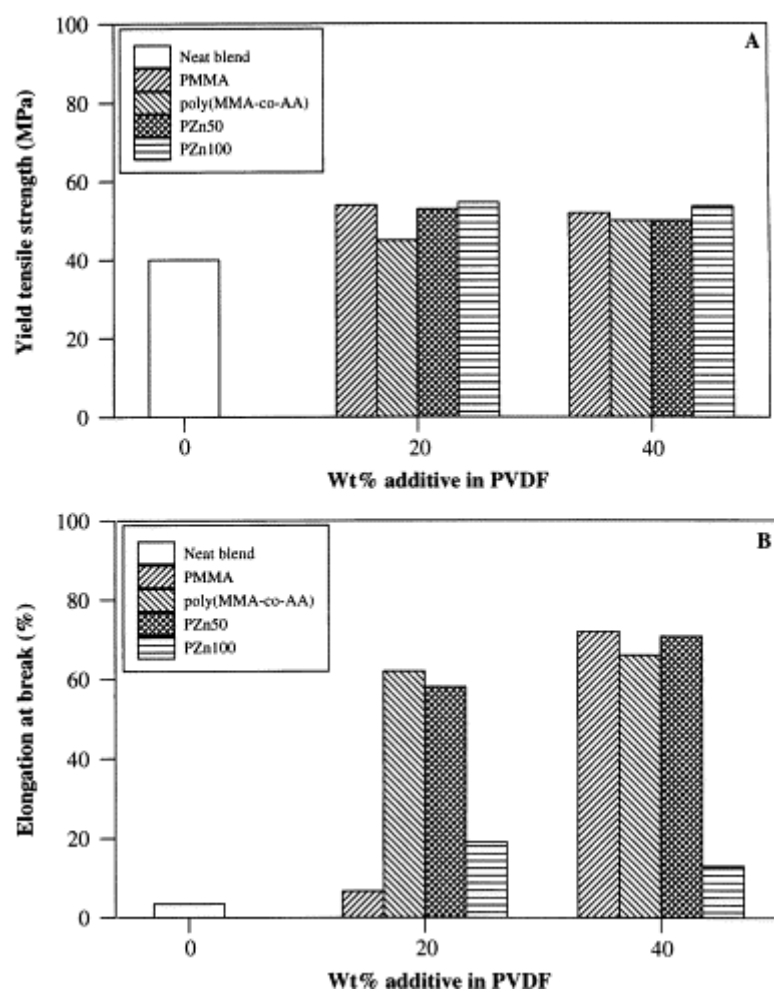


Fig. 10. Dependence of (A) the yield tensile strength and (B) the elongation at break on the type of additive and content in PVDF, for the 40/60 PC/(PVDF-additive) blends.

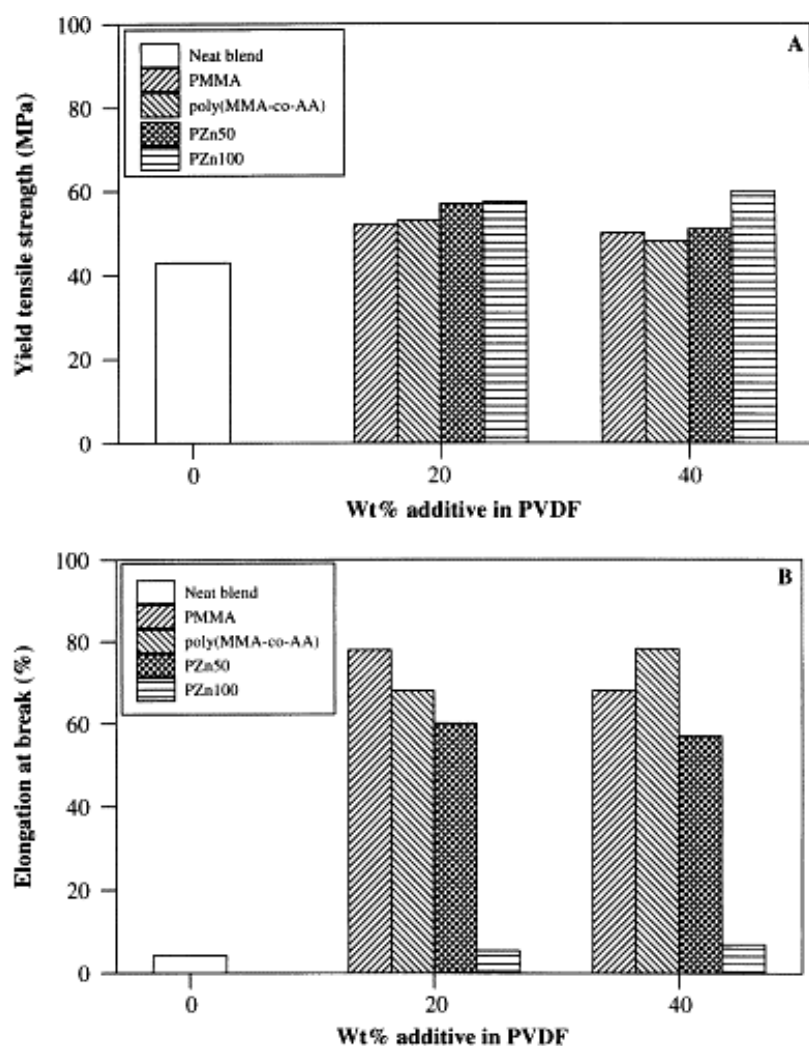


Fig. 11. Dependence of (A) the yield tensile strength and (B) the elongation at break on the type of additive and content in PVDF, for the 60/40 PC/(PVDF-additive) blends.

Fig. 8A and B is a bar chart that shows how the yield tensile strength and the elongation at break of 20/80 PC/(PVDF-additive) blends depend on the structure of the additive and its content in PVDF (0, 20 and 40%). According to Fig. 8A, the yield tensile strength of the neat blend is slightly increased when PVDF is mixed with 20 wt% of PMMA. An additional small increase is observed when the random poly(MMA-co-AA) copolymer is neutralized. The increase of the additive content from 20 to 40 wt% has no beneficial effect, particularly in case of the 100% neutralized random copolymer. From Fig. 8B, it appears that 20 wt% of PC makes PVDF completely brittle. However, modification of PVDF by 20 wt% of PMMA or poly(MMA-co-AA), increases the elongation at break. A two times higher additive content improves further ϵ_b , particularly in the case of PMMA. In contrast to the fully neutralized copolymer, partial neutralization of poly(MMA-co-AA) has a very beneficial effect on ϵ_b when used at the lower content of 20 wt%. Increasing this content up to 40 wt% is advantageous although moderately. Fig. 7 shows that beyond 40 wt% of PMMA, poly(MMA-co-AA) and PZn50 in PVDF, a transition from ductility to brittleness occurs. When PZn100 is concerned, 20/80 PC/PVDF blends are brittle whatever the additive amount (Fig. 8B). This behavior is the direct consequence of the brittleness of the PVDF/PZn100 blend, which actually forms the continuous phase in the 20/80 PC/modified PVDF. The tendency of Zn carboxylate groups to self-associate into multiplets and/or clusters in PZn100/PVDF blends is more likely responsible for this brittleness. It must also be noted that reaction of PC with PZn100 in the melt (235°C) leads to crosslinked material, which might also have a detrimental effect on ϵ_b of the polyblends. The same behavior was observed in case of the reactive compatibilization of polyester/vinylacetate copolymer blends, catalyzed by high content of dibutyltin oxide (Bu_2SnO) [30]. The situation however changes when the PVDF/PZn100 blend is the dispersed phase in the 80/20 PC/modified PVDF blends (Fig. 9B).

The yield tensile strength is not significantly modified when the PVDF phase dispersed in PC is modified by 20 and 40 wt% additive, respectively (Fig. 9A). Although, the neat 80/20 PC/PVDF is brittle (Fig. 9B), addition of 20 wt% PMMA or poly(MMA-*co*-AA) to PVDF remarkably increases the elongation at break (to 71%), expectedly in line with improved interfacial adhesion. Small additional effect is observed at higher content of these additives (40 wt%), the elongation at break being then nothing but the elongation at break of the PC continuous phase ($\epsilon_{PC}=75\%$). Compared to what happened for these blends modified by PMMA and poly(MMA-*co*-AA), partial neutralization of the poly(MM-*co*-AA) additive has no beneficial effect on ϵ_b .

The same qualitative observations are reported for the blends of co-continuous two-phase morphology [3] (Fig. 10 and Fig. 11). The addition of 20 or 40 wt% of PMMA or poly(MMMA-*co*-AA) neutralized or not improves slightly the yield tensile strength of the neat blends (Fig. 10 and Fig. 11). Fig. 10 and Fig. 11 show that in the absence of compatibilizer, the interface is weak and the blends are brittle. The addition of 20 wt% of PMMA to PVDF does not improve the elongation at break for the 40/60 PC/PVDF blends (Fig. 10B), although 20 wt% of poly(MMA-*co*-AA) and PZn50 dramatically increases ϵ_b . Once again no improvement in ϵ_b is observed when the copolymer is totally neutralized. The same general comments can be extended to the 60/40 PC/modified PVDF blends (Fig. 11B), except for PMMA which improves now ϵ_b when 20 wt% are added to PVDF.

As a rule, addition of 20 wt% of PMMA and poly(MMA-*co*-AA) to PVDF (no reactive blending) very significantly improves the adhesion with PC. When PVDF is the major phase (60 or 80 wt%), partial neutralization of the random copolymer (reactive blending) improves further ϵ_b , and thus the interfacial adhesion (Fig. 8 and Fig. 10). This beneficial effect of the grafting reaction that occurs in the presence of Zn carboxylate is no longer detectable when the amount of additives is as high as 40 wt%. Except when PVDF is the minor component (20 wt%), addition of PZn100 is very detrimental to the mechanical properties of the PC/PVDF blends, more likely because of the crosslinking of the interfacial region.

The elongation at break of the blends has been compared to the values calculated by the linear additivity rule (Eq. (4)).

$$P_{av} = x_1 P_1 + x_2 P_2 \quad (4)$$

where P_{av} is the average value of the property P and x_i is the weight fraction of component i . In this case, 1 is PC and 2 is PVDF containing 20 and 40 wt% of additive whatever it is. Deviation from the additivity relationship, which fingerprints the ideally compatibilized system, is an estimate of the extent of compatibilization, small deviations indicating better compatibility [31-32].

Deviation of the elongation at break with respect to ideality (in %) is plotted in Fig. 12 against the wt% of PC in the PC/modified PVDF blends, PVDF phase being modified by 20 and 40 wt% of PMMA containing additives, respectively. As a rule, deviation is maximum for the 20/80 and 40/60 PC/PVDF blends modified by 20 wt% PMMA in PVDF (Fig. 12A), and becomes less important when the content of PMMA in PVDF is increased up to 40 wt% (Fig. 12B), whereas substitution of PMMA by the poly(MMA-*co*-AA) containing 2.8 mol% of zinc carboxylate (PZn50) provides much less deviation when only 20 wt% is premixed within PVDF, in line with improved interfacial adhesion. Conversely, modification of PVDF by the fully neutralized poly(MMA-*co*-AA) remains not beneficial.

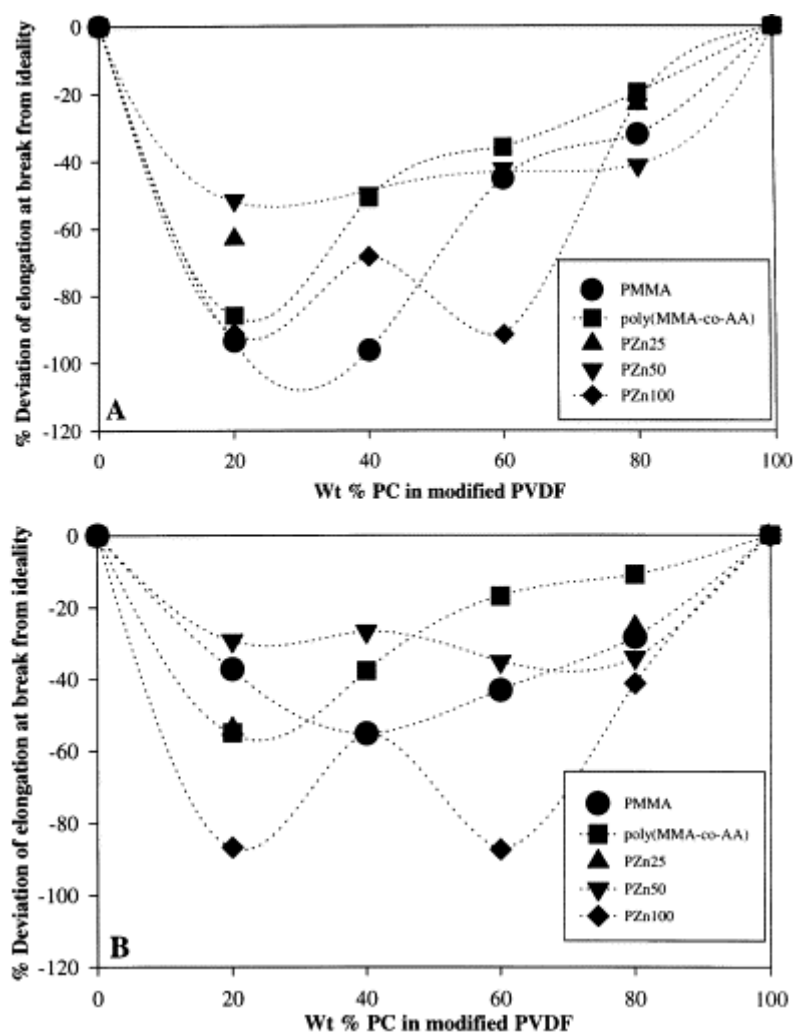


Fig. 12. Deviation of the elongation at break from the additivity rule for PC/PVDF blends, in which the PVDF phase has been modified by (A) 20 wt% and (B) 40 wt% of PMMA containing additives (experimental data for PZn 25 are only available in blends containing 20 and 80% PVDF).

When PC is the major phase (60 and 80%), deviation is usually small and almost independent of the type of modifier, except for PZn100 which is still inefficient. Then, the additive content (PZn25, PZn50) in the whole blend is smaller when PVDF (modified by 20 wt% additives) is the minor phase rather than the major one. As result, less graft copolymer is formed at the interface. Although this amount is large enough to stabilize the phase morphology against coalescence [33], it is too small to improve the toughness of the interface, which strongly depends on the amount of block or graft copolymer added to the blends [34].

4. Conclusions

Reaction between PC and PMMA has been studied at high temperature in solution (benzophenone, 240°C) and in the bulk (235°C), and analyzed by FTIR and SEC. In solution, PC does not react with PMMA, although a grafting reaction occurs when PMMA contains 6 mol% acrylic acid neutralized or not by Zn cations. A substantial progress of the reaction is observed after 20 min.

In the melt (235°C; 8 min) no reaction occurs between PC and poly(MMA-co-AA), although the partial neutralization of the acid groups PZn25, PZn50 is enough to trigger the expected grafting reaction. In case of full neutralization, the major part of the PC/PZn100 blend gets crosslinked.

When the PVDF phase of PC/PVDF blends is modified by a random poly(MMA-co-AA) copolymer containing 6 mol% of AA and partly neutralized by Zn cations, melt blending at 235°C results in modifications of the phase morphology and the tensile properties, in agreement with formation of PMMA-g-PC copolymer at the interface.

Indeed, the average size of the dispersed phases is significantly decreased and the phase morphology is stabilized compared to the parent blends in which the PMMA additive is known for lack of reaction with PC. Furthermore, the elongation properties of the reactive blends, in which PVDF is the major phase, agree with good stress transfer across the interface that is the usual signature of polyblends properly compatibilized by block or graft copolymers. However, when the 6 mol% of acrylic acid of the random copolymer are completely neutralized, grafting density and possibly crosslinking become exceedingly high, making the blends more rigid and decreasing the elongation at break.

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