

Compatibilization of Poly(vinylidene fluoride)/Nylon 6 Blends by Carboxylic Acid Functionalization and Metal Salts Formation. I. Grafting Reactions and Morphology

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ABSTRACT: An investigation was carried out to determine the feasibility of producing compatibilized blends of PVDF and nylon 6 using a procedure involving the grafting of carboxylic acid groups on the chains of either polymer component and, subsequently, producing the corresponding metal salts. The grafting reactions were carried out by irradiating the polymer with γ -rays at 15 kGy, followed by treatments in aqueous solutions of methacrylic acid. These conditions were established from preliminary work which also revealed that this monomer gives higher grafting yields than acrylic acid. The grafted polymers were found to have a heterogeneous structure, attributed to the presence of oligomeric, rather than unitary, side groups. Nevertheless, these modifications of the polymer chains were found to give rise to well-compatibilized blends, containing co-continuous phases which became much finer through the addition of zinc acetyl acetonate. FTIR analysis showed that the enhanced compatibilization resulted from the reactions between the acid groups in the PVDF component and the terminal amine groups of the polyamide chains. Since the addition of zinc acetyl acetonate was found to reduce the yield of amidized groups, it was inferred that the enhanced compatibilization has resulted from the complexation of zinc cations with the amide groups in the nylon 6 chains, which are shared with the carboxylate anions of the grafted PVDF component. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1911–1923, 1997

Key words: grafting functionalization; ionic associations; blends; PVDF; nylon 6; ionizing radiation

INTRODUCTION

Despite its high level of crystallinity (35–65%) poly(vinylidene fluoride), PVDF, dissolves readily in highly polar aprotic solvents, such as dimethyl formamide (DMF), and swells in esters and ketones, owing to the possibility for its dipoles to form strong H-bonding associations with carbonyl groups. For the same reason PVDF is miscible with a large

number of polymers containing fairly closely spaced carbonyl groups along the chains. Typically among these are the nonsterically hindered poly(alkylacrylates and methacrylates), poly(vinyl esters), and poly(vinyl alkyl ketones), which allow the above-mentioned interactive dipoles to reach close proximity.^{1–7}

PVDF has also been found to be totally miscible with polymers containing tertiary amide groups along the chains, such as poly(*N,N*-acrylamide) and poly(*N*-vinyl-2-pyrrolidone), and is partially miscible with polycaprolactone, that is, it is miscible with PVDF at concentrations < 30%.⁸

Strong interactions leading to miscibility have

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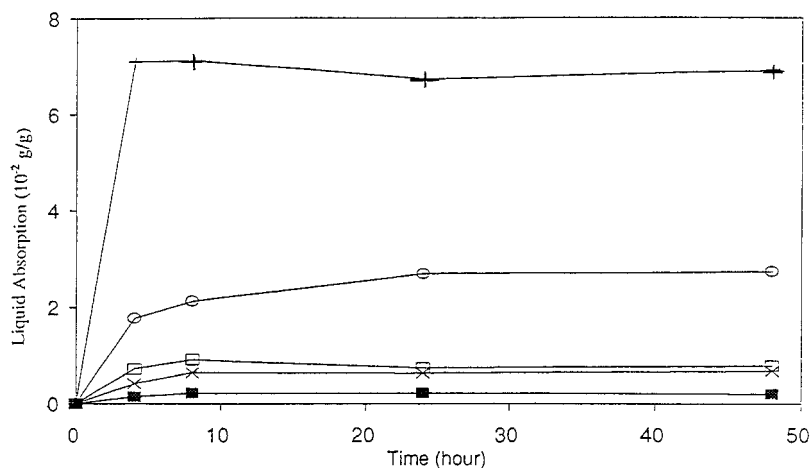


Figure 1 Absorption of water, monomer, and monomer solutions in PVDF plaques (0.5 mm thick) at 80°C. (■) water, (+) acrylic acid, (○) methacrylic acid, (□) 20% (v/v) acrylic acid in water, and (×) 5% (v/v) methacrylic acid in water.

also been reported for mixtures of PVDF and polypyrrole in its oxidized state.⁹

In a different category of behavior are the linear aliphatic polyamides, such as nylon 6 and nylon 66, which are also highly polar but are only soluble in highly protic solvents, such as formic acid and phenols, and are immiscible with other polymers. These polymers, however, would lend themselves to compatibilization owing to the possibility of forming intermolecular H bonds with groups in both polymers. (The term "compatibilization" is used to describe the process which pro-

duces finely dispersed phases of microscopic dimensions in blends of immiscible polymers.)

It has been found, in fact, that PVDF is totally miscible with ϵ -caprolactam¹⁰ owing to the formation of strong H bonds between the H atom linking the β carbon in the polymer and the lactam carbonyl groups. These associations become more difficult for the case of polycaprolactams owing to the large reduction in the entropic contribution to the free energy of mixing and the less favorable molecular interactions between the two polymer components of the mixture in comparison to the highly ordered H bonds between polyamide chains.

Nevertheless, the expected strong interactions between the two phases have been reported to give rise to the formation of finely dispersed particles of the minor component for either polymer.¹¹ Furthermore, the amine end groups of polyamides can readily react with acid or anhydride groups to produce graft copolymers which will act as compatibilizers for the nonreacted components.¹²⁻¹⁸ This suggests, therefore, that an *in situ* compatibilizer would be formed if the PVDF were to be functionalized with carboxylic acid groups prior to mixing with the polyamide. Such a modification would subsequently make it possible to utilize also the complexation characteristics of nylons with metal ions and their ionic associations with the acid groups in the PVDF chains.¹⁹

Several studies have been reported, in fact, on the possibility of enhancing the miscibility of polymers by promoting ionic interactions,²⁰⁻²² by sharing common cations to produce co-ionomeric mixtures.²³⁻²⁷

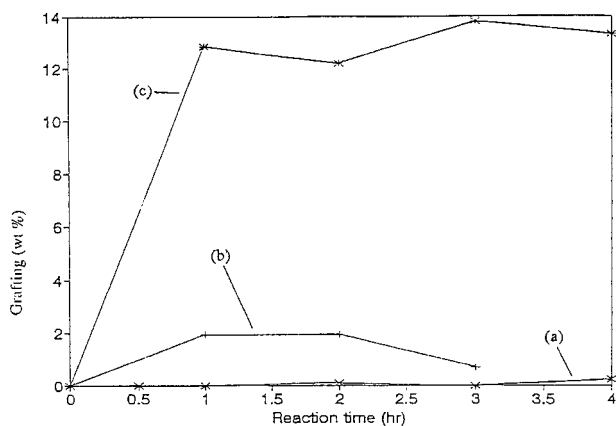


Figure 2 Effect of reaction time on the grafting yield (wt %) by the preirradiation method. (5 vol % monomer solutions $\pm 0.1M$ $FeSO_4$, reacted at 8p°C). (a) Acrylic acid reacted with PVDF powder irradiated at 1.5 kGy, (b) methacrylic acid reacted with PVDF powder irradiated at 1.5 kGy, (c) methacrylic acid reacted with PVDF powder irradiated at 15 kGy.

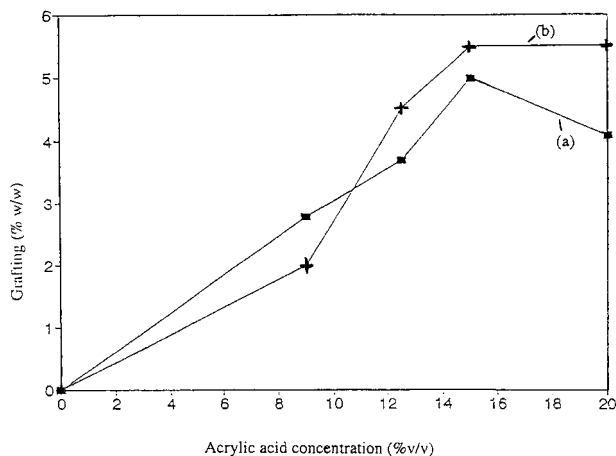


Figure 3 Effect of acrylic acid concentration on grafting yield (wt %). PVDF irradiated to 15 kGy reacted for 3 h at 80°C in 100 mL monomer solutions containing 0.1M FeSO₄. (a) Percent grafting measured gravimetrically, (b) percent grafting measured by FTIR.

Grafting of acid functionality on polymers is widely used commercially through reaction processing and radiation-assisted methods. The latter are particularly attractive owing to the possibility of using water solutions of unsaturated monomers, such as acrylic acid and methacrylic acid, to induce reactions with peroxy radicals formed on the polymer chains by irradiation in the presence of air.²⁸⁻³²

The aim of this study was, therefore, to develop a suitable procedure for the grafting of acid-containing monomers from water solutions onto the polymer chains, starting from powders which

have been subjected to γ -radiation and to examine the extent to which compatibilization can be achieved through reactions with the end groups of the polyamide chains, and also through complexations and ionic associations developed by the addition of a cation donor compound to the mixture.

EXPERIMENTAL

Materials

Poly(vinylidene fluoride) is an emulsion polymer, Kynar 461 (Atochem North America, Inc.), having a weight average molecular weight equal to 5.34×10^5 g/mol, melting point ~ 156 – 160°C , and particle diameter in the region of $0.2 \mu\text{m}$. nylon 6, a high viscosity grade in granular form, Sniamid ADS 40, was obtained from SNIA Ricerche (Italy), having a relative viscosity of 4 and a melting point ~ 220 – 223°C . nylon 6 cast films, $20 \mu\text{m}$ thick, were produced from Sniamid ADS 40 and also obtained from SNIA Ricerche. The acid functionalizing monomers used were acrylic acid and methacrylic acid, both at 99.9% purity. Ferrous sulfate hexahydrate, 99% purity, was used as homopolymerization inhibitor; zinc acetyl acetonate dihydrate, 99% purity, was used as the cation donor; and polyacrylic acid, 98% purity, was used as the acid calibration compound for FTIR analysis. All materials not mentioned specifically were obtained from Aldrich Chemical Co. (UK).

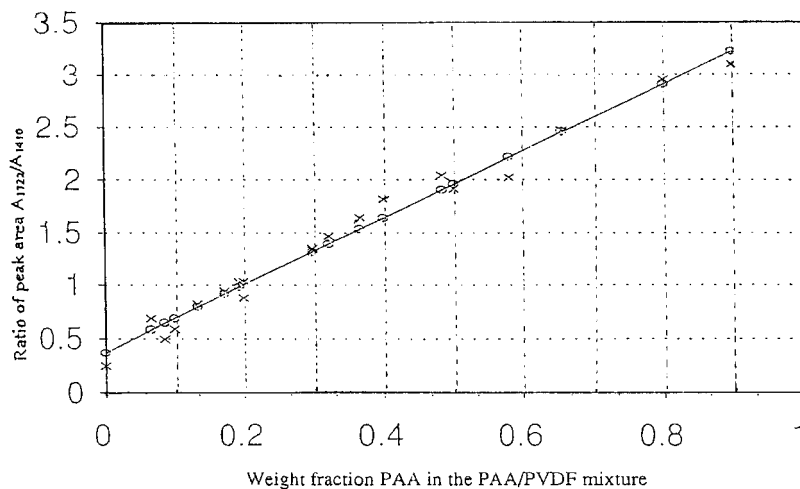


Figure 4 FTIR calibration curve for “Ratio of peak absorbance areas A_{1722}/A_{1410} ” against “Weight ratio of polyacrylic acid in mixtures with PVDF.”

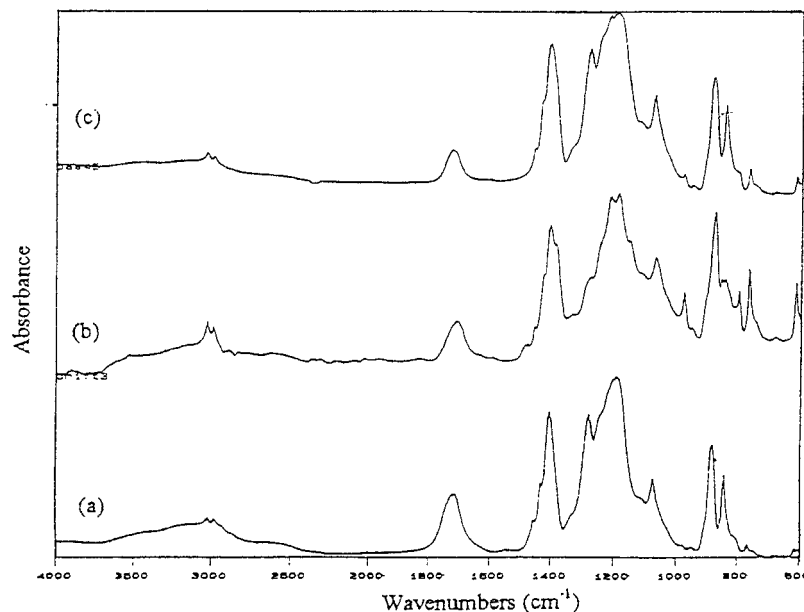


Figure 5 Examples of FTIR spectra for (a) mixtures of polyacrylic acid and PVDF, (b) PVDF grafted with methacrylic acid, and (c) PVDF grafted with acrylic acid.

Monomer Absorption

The extent of monomer absorption by PVDF was determined by immersing small pieces ($10 \times 10 \times 0.5$ mm, cut from compression-molded plaques) in both pure monomer and monomer solutions in water at 80°C for different periods of time until equilibrium was reached.

Absorption experiments were not carried out on nylon 6 films as it was already established from previous work that the amount of monomer uptake from water solutions is in the region of 30 wt %.³³

Grafting Reactions

Grafting Procedure for PVDF Powders

Amounts in the region of 100 g were placed in polyethylene-lined paper envelopes and irradiated with a ^{60}Co at a dose rate of 1 kGy/h to a total dose of 15 kGy. After irradiation the polymer was found to be still completely soluble in DMF, indicating that no crosslinking takes place under these conditions. The irradiated powder was conditioned at room temperature for 48 h in order to allow the formation of peroxy groups to take place from reactions with atmospheric oxygen before being stored in a refrigerator at -40°C for a period of up to 1 month for subsequent use.

One-hundred-gram quantities were suspended

in 500 mL of a 10 wt % methacrylic acid solution in deionized water within a 2-L flask, containing a 0.1M quantity of FeSO_4 . A stream of nitrogen was bubbled through the solution for 2 h to expel any dissolved oxygen and then heated for different times at 80°C under reflux conditions. The treated powder was filtered and then washed several times with boiling water to remove any unreacted monomer or homopolymer formed as by-product and subsequently dried for 48 h at 80°C in a vacuum oven. The powder was weighed accurately before and after the reaction in order to determine the approximate grafting yield. Both monomer concentration and reaction conditions were determined from preliminary experiments carried out on a smaller scale (i.e., ~ 10 g of powder) by monitoring the percent yield as a function of reaction time. Both acrylic and methacrylic acid (MAA) were used in these studies.

Grafting Procedure for Nylon 6 Films

A number of polyamide films were weighed and sandwiched between low density thick paper mats capable of allowing a free flow of solution through the fiber interstices. These were dried in a vacuum oven at 80°C , sealed in a polyethylene-lined paper envelope, and subsequently irradiated and conditioned and stored under the same conditions as the PVDF powder in previously described experiments.

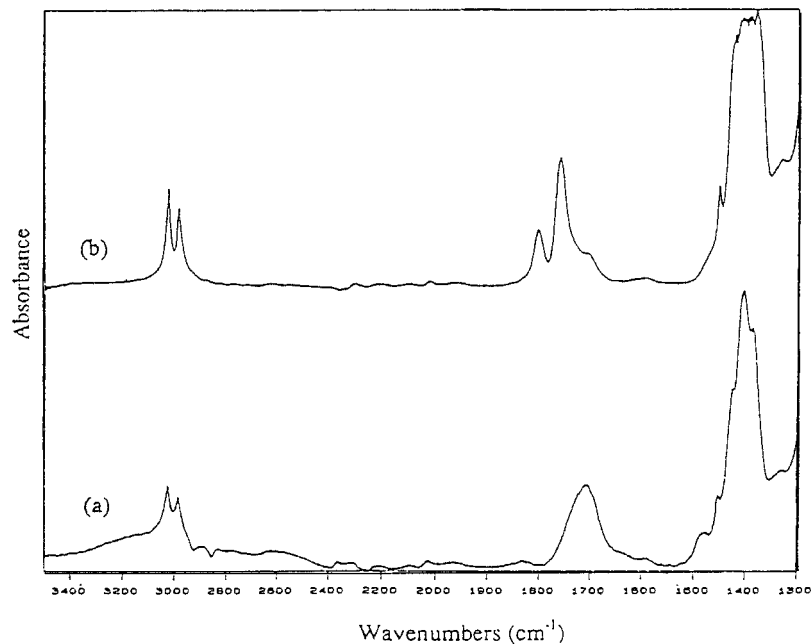


Figure 6 FTIR spectra for PVDF powder grafted with 5 wt % methacrylic acid (PVDF-*g*-MAA5). (a) DRIFT technique using powders, (b) thin films produced by compression molding.

The irradiated paper mats/polyamide films sandwiches were rolled and immersed in a large flask containing 2 L of 10% MAA solution in water

to which were added the required amount of FeSO_4 to give a 0.01M concentration. The solution was flushed with nitrogen gas for ~ 1 h and

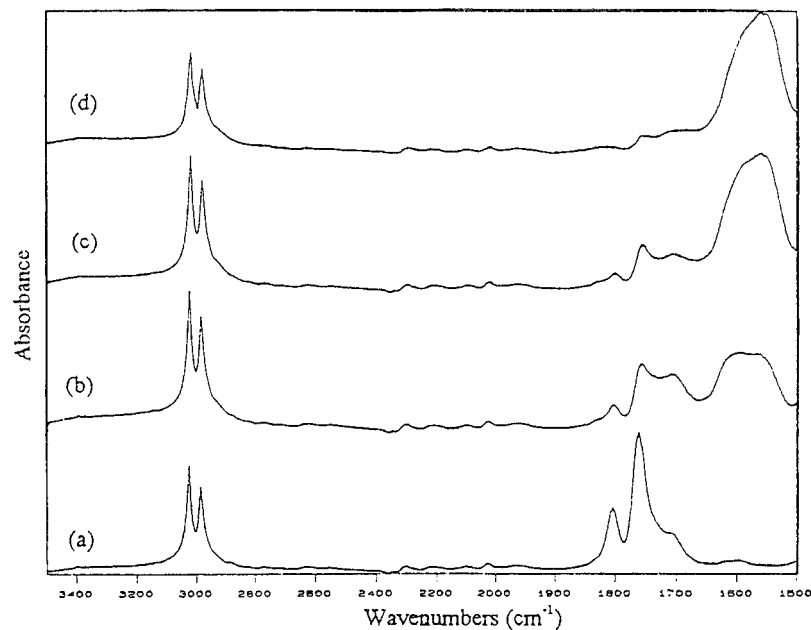


Figure 7 FTIR spectra of grafted PVDF and corresponding zinc salt. (a) PVDF-*g*-MAA5 (as described in Fig. 6), (b) PVDF-*g*-MAA5 + zinc acetyl acetonate (ZnAcAc) (0.5 molar ratio), (c) PVDF-*g*-MAA5 + ZnAcAc (1.0 molar ratio), (d) PVDF-*g*-MAA5 + ZnAcAc (1.5 molar ratio).

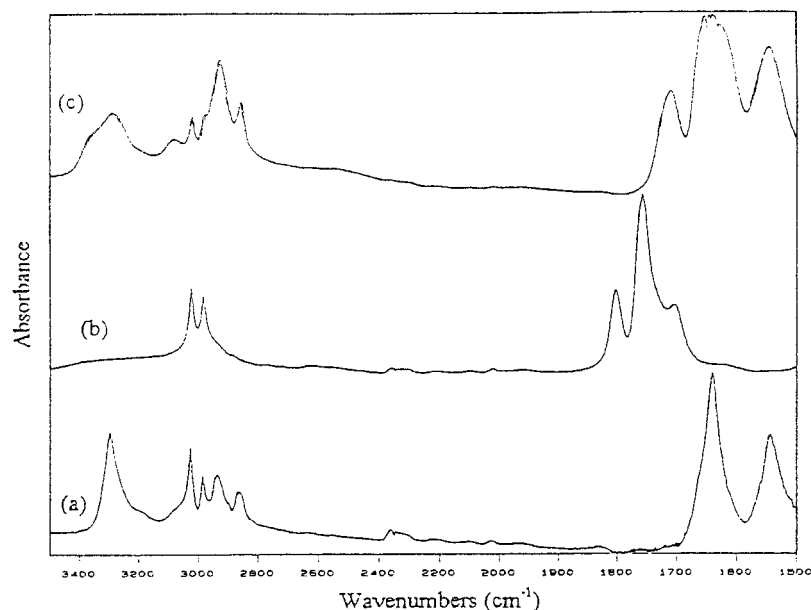


Figure 8 FTIR spectra for (a) blend of PVDF and nylon 6 at 80 : 20 weight ratio (PVDF/N6), (b) PVDF grafted with 10 wt % methacrylic acid (PVDF-g-MAA10), (c) blend PVDF-g-MAA10/nylon 6 at 80 : 20 weight ratio.

heated for 3 h at 80°C under a stream of nitrogen to expel atmospheric oxygen. After washing in hot water and dried at 100°C the films were weighed to calculate the extent of grafting. This was found to be 3.1%. The procedure was repeated using only a 500 mL solution of 10% MAA, while the concentration of FeSO_4 was reduced to 0.001M. The latter procedure was found to give a grafting yield of 11.3%.

Calibration Procedure for FTIR Measurements of Grafting Yield

PVDF (0.3 mg samples) and polyacrylic acid powders at different weight ratios were mixed with 0.15 g KBr in a mortar and pressed into discs with a 15-ton pressure for 10 min. These were examined by FTIR using a Nicolet 20 DXC spectrophotometer. The absorbance area and peak

Table I Ratio of Peak Absorbance Height and Peak Absorbance Area of NH_2 Group at 3300 cm^{-1} to CH_2 Group at 2939 cm^{-1}

Blend	Absorbance Ratio NH_2/CH_2	
	Peak Height	Peak Area
80 PVDF/20 N6	1.31	3.13
80 PVDF-g-MAA10/20 N6	0.66	2.04
80 PVDF-g-MAA10/ZnAA(1)/20 N6	0.88	2.78
80 PVDF/20 N6-g-MAA3	1.45	2.93
80 PVDF-g-MAA10/20 N6-g-MAA3	0.58	1.88
80 PVDF-g-MAA10/ZnAA(1)/20 N6-g-MAA3	1.10	2.59
80 PVDF/15 N6/5 N6-g-MAA11	1.30	2.82
80 PVDF-g-MAA10/15 N6/5 N6-g-MAA11	0.65	1.99
80 PVDF-g-MAA/ZnAA(1)/15 N6/5 N6-g-MAA11	1.17	2.56

Data were derived from the FTIR spectra of various blends. Abbreviations are defined in the text. The number before the stated polymer represent the amount in the blend. The digit (1) after ZnAA represents the molar fraction of cation used relative to the total amount of free acid groups present (i.e., stoichiometric amount for full neutralization).

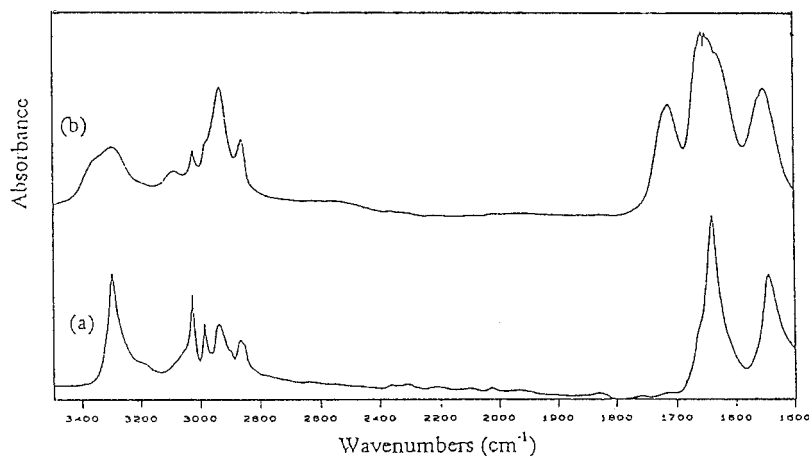


Figure 9 FTIR spectra for (a) blend of PVDF and nylon 6 film grafted with 3 wt % methacrylic acid (N6-*g*-MAA3) at 80 : 20 weight ratio, (b) blend PVDF-*g*-MAA10/N6-*g*-MAA3 at 80 : 20 weight ratio.

height ratios for the C=O stretching at 1722 cm^{-1} from the polyacrylic acid and the CH_2 bending at 1410 cm^{-1} from the PVDF component were measured and plotted against the amount of polyacrylic acid in the mixture to produce a calibration curve for subsequent use.

FTIR Analysis of Grafted Polymers and Blends

The washed and dried PVDF powder after the grafting reaction was analyzed by FTIR using the same procedure as described earlier, and the grafting yield, were estimated using the calibration curve produced previously.

For the case of nylon 6 films and blends the FTIR analysis was carried out on films pressed at 210°C between polytetrafluoroethylene (PTFE) sheets to a thickness of 5–7 μm . Only qualitative evaluations were made in the latter cases to determine whether the expected reaction had taken place.

Blending Procedure

PVDF and grafted PVDF powders alone or in mixtures with nylon 6 granules and/or grafted nylon 6 films at a weight ratio of 80 : 20 were blended in a Brabender Platicorder fitted with a 25 mL mixing chamber for a total of 15 min and a rotor speed of 80 rpm. The temperatures used were 180°C for PVDF and 240°C for nylon 6 and any blend of the two polymers. Whenever the presence of ZnAcAc was required for the neutralization of the acid groups, this was added during the initial

melting period over ~ 5 min and mixing was subsequently continued for 10 min. For the control experiments the amount of ZnAcAc added was equivalent to that required for the full neutralization of the acid groups in the related sample.

Preparation of Test Plaques

Plaques (110 \times 110 \times 0.5 mm) were produced by compression-molding at 180°C for PVDF and 240°C for blends with nylon 6. PET films were used for mold release of PVDF plaques and fine-weave glass cloth impregnated with PTFE for the pressing of the blends. The plaques were cooled under pressure by the circulation of cold water through the platens of the press before being removed from the mold.

Scanning Electron Microscopy

A Cambridge Stereoscan 360 scanning electron microscope was used to examine the morphology of the blends and its components. Appropriate samples were fractured in liquid nitrogen and vacuum-coated with gold to render the surface conductive.

Extraction Tests

Rectangular pieces (10 \times 35–40 mm) were cut from compression-molded plaques (0.5 mm thick) and dried in a vacuum oven at 80°C for 24 h. These were placed between stainless steel gauzes with a very fine mesh, weighed, and immersed into 150

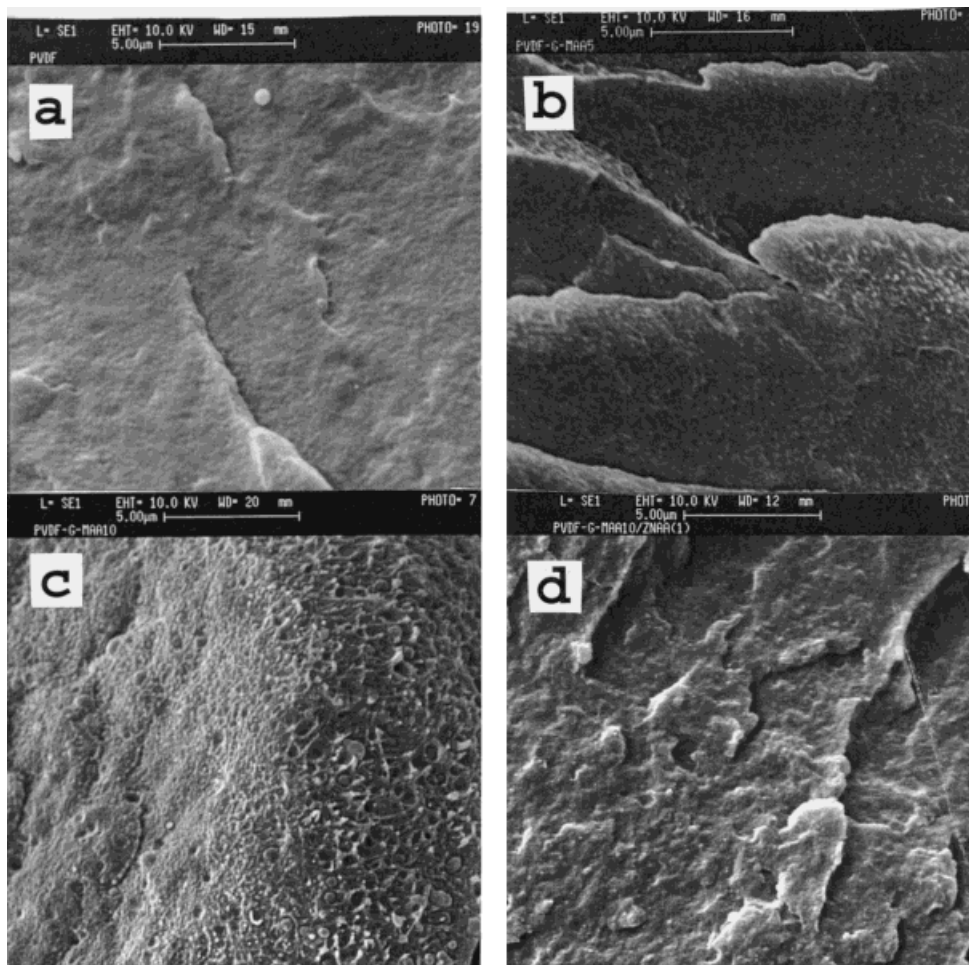


Figure 10 SEM micrographs of cryogenically fractured plaques. (a) PVDF, (b) PVDF grafted with 5 wt % methacrylic acid (PVDF-*g*-MAA5), (c) PVDF grafted with 10 wt % methacrylic acid (PVDF-*g*-MAA10), (d) PVDF-*g*-MAA10 + ZcAcAc (previously described) (1.0 molar ratio).

mL boiling water for 72 h. The samples were dried in a vacuum oven at 80°C for 48 h and reweighed. Each test was carried out in triplicate.

Tensile Tests

These were carried out at room temperature on dumbbell-shaped specimens (ASTM D638) cut out from compression-molded plaques, using a Lloyd 2000R tensile testing machine at a clamp separation rate of 5 mm min⁻¹. A minimum of five specimens were tested for each sample. The elongation at break and both yield strength and fracture stress were recorded when applicable.

Rheological Studies

The rheological properties of the blends and their components were evaluated by means of a Rheome-

trics RDA type II Dynamic Analyzer using a 25-mm-diameter parallel plates fixture. Sample discs ~ 27 mm in diameter were cut out from compression-molded plaques. Measurements were made after the specimens were equilibrated at the test temperature for 10–15 min and the residual compressive stress generated in squeezing the specimens into contact with the plates had relaxed almost completely, i.e., > 90%. Logarithmic frequency sweeps were taken over a frequency range of 0.1 to 500 rad s⁻¹ with five measurement points per decade. A fixed strain of 5% was used at test temperature of 200°C for PVDF and 240°C for all samples containing nylon 6.

RESULTS AND DISCUSSION

In Figure 1 are presented plots of the weight increase of PVDF plaques against immersion time

Table II Effects of Grafting Methacrylic Acid on PVDF Chains and Subsequent Salt Formation on Properties of the Resulting Modified Polymer

	Elongation at Break in Tensile Tests (%)	Water Absorption after 72 h Immersion (%)
PVDF (original polymer)	276	0.01
PVDF- <i>g</i> -MAA5	79	—
PVDF- <i>g</i> -MMA10	30	5.2
PVDF- <i>g</i> -MMA5/ZnAA	18	—
PVDF- <i>g</i> -MAA10/ZnAA	14	2.4

at 80°C in both pure monomers and corresponding aqueous solutions, while in Figure 2 are shown plots for the percent grafted monomer on irradiated PVDF powder from monomer solutions.

A comparison of these diagrams suggests that there is no correlation between monomer absorption and grafting yield, and that the grafting reaction from MAA solutions occurs more readily than with acrylic acid solutions. Additional confirmation of the lower reactivity of acrylic acid is demonstrated by the plots in Figure 3, which show that even by increasing the monomer concentration of acrylic acid to 20% the extent of grafting is considerably lower than that achieved with MAA at 5% concentration. This diagram demonstrates also the good agreement that exists between the gravimetric estimates and the results from the FTIR assessment of the grafting yield. (The calibration graph used for the FTIR analysis of the grafted powders is shown in Fig. 4.) The slightly lower values for the gravimetric method are probably due to the loss of additives, such as lubricants, during the grafting reaction.

The confirmation of the presence of acid groups grafted on the PVDF chains and the similarity in absorption characteristics of polyacrylic acid with the grafted acid groups on the polymer chains can be inferred from an inspection of the FTIR spectra in Figure 5. It is interesting, however, to compare the spectra obtained directly on the grafted powder by the DRIFT technique with those obtained on thin films pressed out from small pieces of a compression-molded plaque after being melted in a Brabender Plastograph. The spectra in Figure 6 for the latter determinations reveal the presence of two additional carbonyl absorption peaks, one at 1811 cm⁻¹, corresponding to anhydride groups,

and another at 1769 cm⁻¹, corresponding to carbonate groups, which result from dehydration of acid groups during the melting and pressing operations. These results are, in fact, in agreement with the findings of Grant and Grassie,³⁴ derived from studies of the decomposition of polyacrylic acid when heated to 200°C. In addition to the acid carbonyl groups at 1714 cm⁻¹, these authors have reported the occurrence of an absorption band at 1795 cm⁻¹ and one at 1750 cm⁻¹.

In Figure 7 are shown the spectra for grafted PVDF after the addition of ZnAcAc in amounts corresponding to 50, 100, and 150% stoichiometric levels required for neutralization. These spectra show that when an excess amount of ZnAcAc is used for the neutralization reactions, the acid carbonyl and anhydride absorption bands disappear completely and are replaced by the corresponding carboxylate anion absorption peak at 1571 cm⁻¹. Both peaks are present, on the other hand, when lower amounts of ZnAcAc are used. From this it is inferred that an amount of free ZnAcAc will always likely be present even when stoichiometric quantities are used, due to kinetic factors related to the decomposition of ZnAcAc and the subsequent neutralization reaction with the carboxylic acid groups.

The spectra in Figure 8 show that for blends at 80 : 20 ratio of PVDF and nylon 6 the characteristic absorbance peaks of the two components are not affected, whereas for the corresponding blend containing PVDF grafted with 10% MAA (PVDF-*g*-MAA10) a new peak appears at 1712 cm⁻¹, which corresponds to the carbonyl conjugated double bonds of the type O=C—N—C=O, resulting from the well known reaction between acid groups along the chains of PVDF-*g*-MAA10 and the terminal groups of the polyamide chains. The occurrence of this reaction is also confirmed by the reduction in the absorbance at 3300 cm⁻¹ and the disappearance of the carbonyl triple peaks.

The data in Table I show that the absorbance ratio for NH₂/CH₂ with respect to 80 : 20 blends of PVDF-*g*-MAA10 with nylon 6 (N6) decreases by more than 50% with respect to that for the corresponding blend based on nonmodified PVDF. For 80 : 20 blends of nonmodified PVDF with nylon 6 films grafted with 3% MAA (N6-*g*-MAA3) and mixtures of nylon 6 and nylon 6 grafted with 11% MAA (N6/N6-MAA11 at 3 : 1 weight ratio) there is no indication of any reduction in the NH₂/CH₂ ratio (Table I) associated with the formation of conjugated carbonyl groups through intramolecular reactions [Fig. 9(a)]. The formation of the

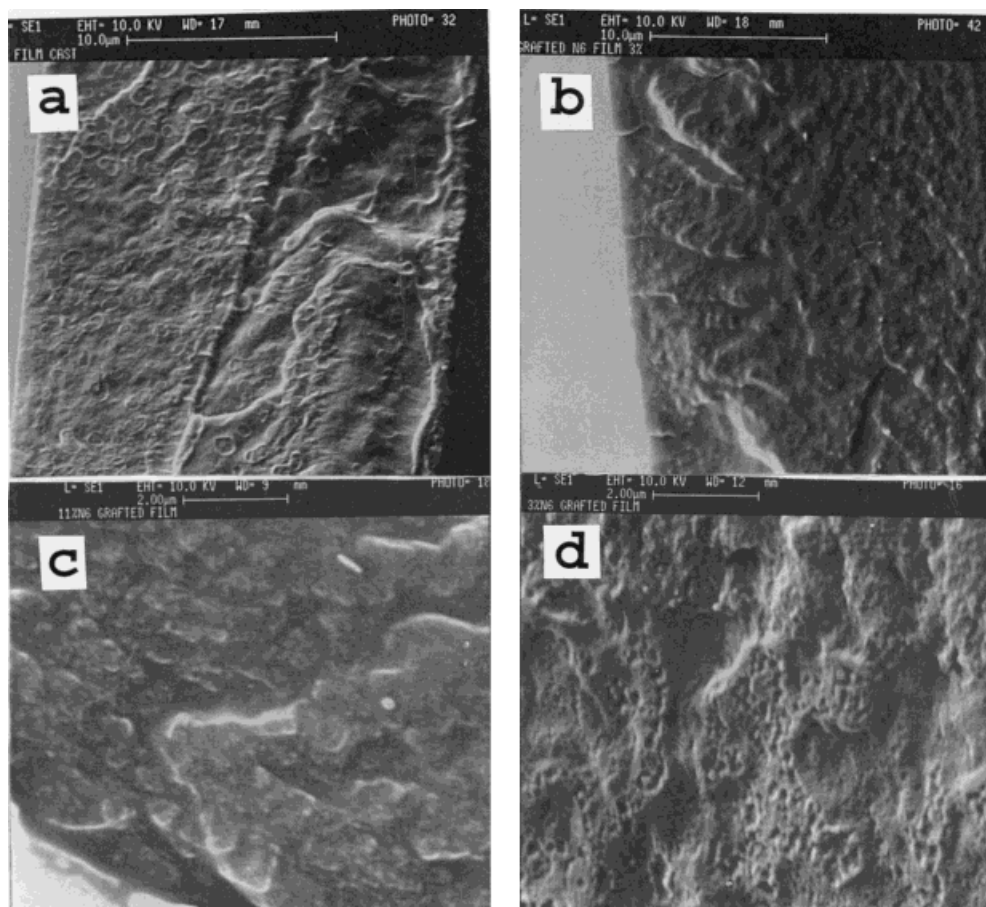


Figure 11 SEM micrographs of cryogenically fractured films. (a) nylon 6, (b) nylon 6 grafted with 3 wt % methacrylic acid (N6-g-MAA3), (c) nylon 6 grafted with 11 wt % methacrylic acid (N6-g-MAA11), (d) N6-g-MAA3 at higher magnification.

peak at 1714 cm^{-1} and a reduction in the height of the amine absorbance peak, on the other hand, is clearly visible in the spectra for blends based on PVDF-*g*-MAA10 at the same weight ratio [Fig. 9(b) and Table I]. There are some indications, however, that the amidation/imidation reactions occur to a slightly larger extent in the latter case.

The data in Table I show, furthermore, that the presence of ZnAcAc during mixing of the blend causes a substantially smaller reduction in the NH_2/CH_2 absorbance ratio for the 80 : 20 blend of PVDF-*g*-MAA10 with N6 and an even smaller reduction when grafted nylon is used in the blend, but does not affect the disappearance of the conjugated carbonyl groups. From this it is also deduced that the presence of ZnAcAc in the blend during mixing and subsequent processing interferes with the reaction between acid groups and amine groups in the two polymer components.

Accordingly, the above observations demon-

strate that the end groups of the polyamide chains are easily accessed by the acid groups within the PVDF phase, which may be favored by the enhanced miscibility of the acid-containing segments of the PVDF with the polyamide. From this it can be deduced that the precipitated particles seen in the SEM micrographs of grafted PVDF [Fig. 10(b,c)] are probably species containing large sequences of oligomeric MAA units which are capable of diffusing easily into the nylon phase, either directly or progressively through consecutive reactions with the amine end groups. In inspecting the micrographs in Figure 10 one observes that the addition of ZnAcAc to acid-grafted PVDF causes such precipitated particles to diffuse into the surrounding matrix. This difference in morphology is reflected in the mechanical properties and water absorption characteristics (Table II). Both the amount of water absorbed by the blend and the elongation at break, measured

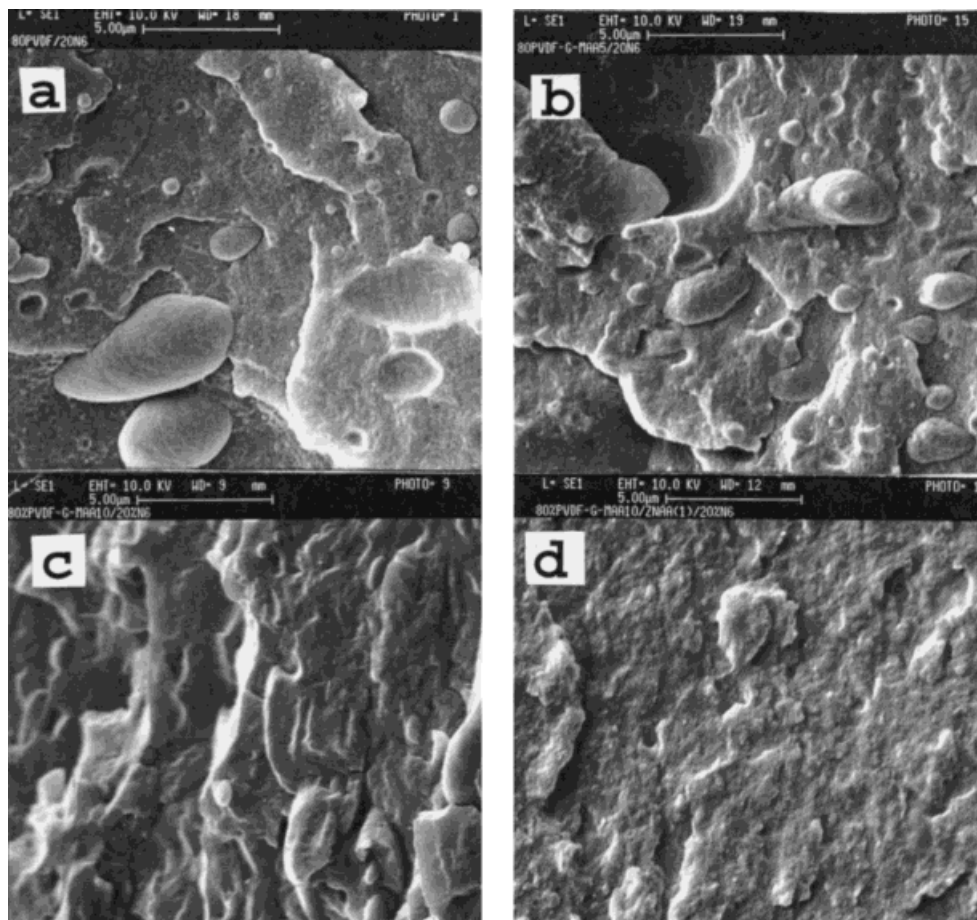


Figure 12 SEM micrographs of cryogenically fractured compression-molded plaques from various blends at 80 : 20 weight ratio of the following components. (a) PVDF/nylon 6, (b) PVDF-*g*-MAA5/nylon 6, (c) PVDF-*g*-MAA10/nylon 6, (d) (PVDF-*g*-MAA10/nylon 6) + ZnAcAc. All codes are described in previous figures.

in tensile tests, decrease as a result of the addition of ZnAcAc. Both phenomena are indicative of a change in morphology from particulate to cocontinuous phases.

The presence of a cocontinuous microstructure is also evident in the case of grafted nylon 6 film [Fig. 11(c–d)]. Although the MAA was found to dissolve readily in the polyamide film, achieving equilibrium absorption levels in the region of 40% from the aqueous monomer solution,³³ the micrographs in Figure 11 suggest that the grafting reactions within the nylon film take place in a heterogeneous manner, that is, in localized regions, and that the formation of dispersed particles may arise from the formation of side branches consisting of oligomeric MAA units, as in the case of PVDF.

The morphology of the blend at 80 : 20 weight ratio for various PVDF/N6 systems is illustrated

in Figure 12 (micrographs a–d) and shows that the blends of ungrafted polymers and those containing small amounts of grafted MAA on the PVDF chains form a distinct two-phase morphology, the minor phase being dispersed as particles (micrographs a and b). Diffused cocontinuous morphologies are formed, on the other hand, when using grafted PVDF with the higher level of MAA (micrograph c) and an even finer morphology develops as the result of the addition of ZnAcAc (micrograph d).

The rheological data for the above blends reported in Figure 13 show that the blends containing grafted PVDF have a lower viscosity than the corresponding blends of nongrafted polymers, whereas the blends produced with the addition of zinc acetyl acetate (i.e., PVDF-*g*-MAA10/ZnAcAc/N6) display a much higher viscosity.

The rheological curves in Figure 14 demon-

strate first that the reduction in viscosity of the blends containing grafted PVDF is not due to chain scission reactions, which could arise from the radiation and/or subsequent heat treatments, and second that the large increase in viscosity resulting from the addition of zinc acetyl acetate cannot be due to ionization of the carboxylic acid groups in the PVDF component. Consequently, compatibilization in this latter case must have occurred through extensive intermolecular attractions between the two polymer components, arising through the coordination of zinc cations in the carboxylated PVDF and the amide groups of nylon 6. This type of interaction has been widely reported by other authors for blends of ionomers of sulfonic acid functionalized polystyrene and nylon 6.²⁰⁻²²

CONCLUSIONS

The main conclusions that can be derived from this work are as follows: (1) Grafting of MAA from aqueous solutions on preirradiated PVDF produces species that are immiscible with the unaffected polymer chains, forming dispersed parti-

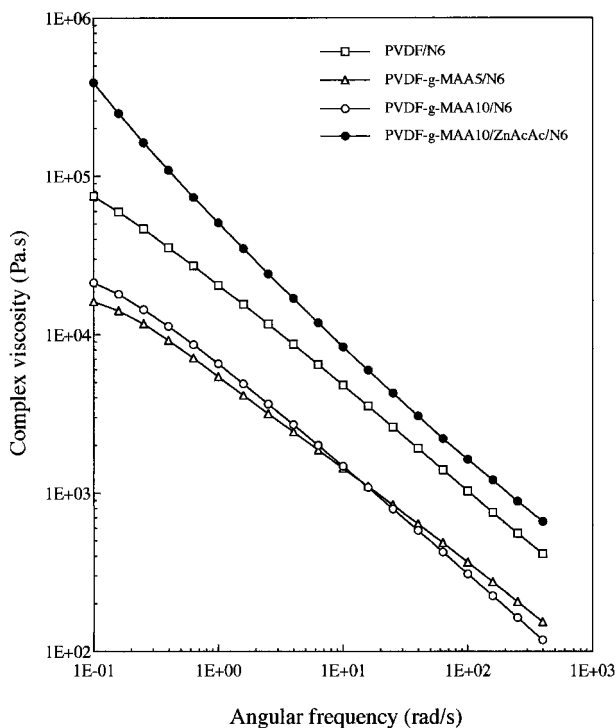


Figure 13 Plots of complex viscosity against angular frequency for various blends at 80 : 20 weight ratio. All codes are described in previous figures.

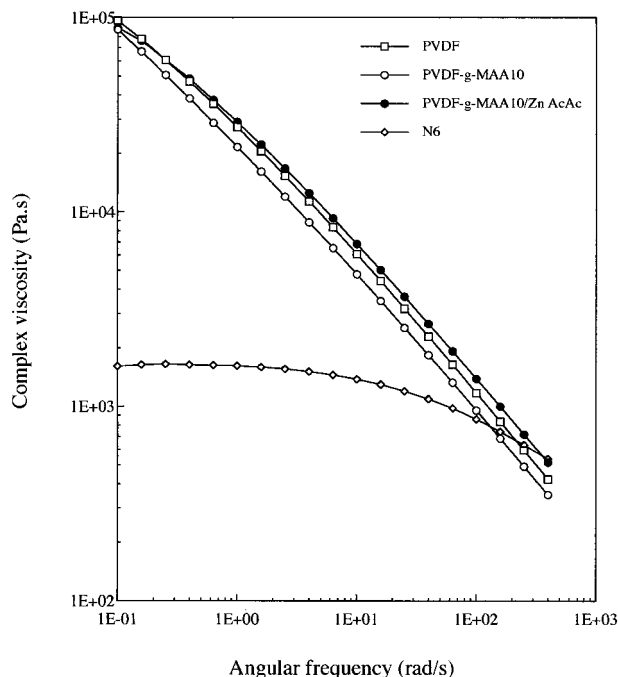


Figure 14 Plots of complex viscosity against angular frequency for the various components of the polymer blends examined. All codes are described in previous figures.

cles ~ 0.1 to $1.0 \mu\text{m}$. Neutralization of acid groups with ZnAcAc forces this second phase to become somewhat more diffuse, but do not assume the typical characteristics of ionomeric polymers, as it can be inferred by their viscosity, which increases only slightly from that of the unmodified polymer. (2) FTIR analysis can be readily used to monitor the progress of the reactions for both the grafting of carboxylic acid groups on the polymer chains and the subsequent formation of carboxylate anions through the addition of zinc acetyl acetate. (3) Blends of PVDF with nylon 6 are completely immiscible and, at 80 : 20 weight ratio, the nylon phase forms very small dispersed particles around $1-5 \mu\text{m}$. Grafting of acid groups result in the formation of continuous domains and become even finer when ZnAcAc is added to the mix.

The compatibilization associated with the changes in morphology is attributed to the reactions of the acid groups in the PVDF and the terminal groups in the polyamide component. The addition of ZnAcAc has the effect of decreasing these reactions and the further improvements in compatibilization can be attributed to complexation with the amide groups.

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REFERENCES

1. D. R. Paul and J. W. Barlow, *J. Macromol. Sci. Rev. Macromol. Chem.*, **8**, 109 (1980).
2. J. Mijovic, H. L. Luo, and C. D. Han, *Polym. Eng. Sci.*, **22**, 234 (1982).
3. T. K. Kwei, G. D. Patterson, and T. T. Wang, *Macromolecules*, **9**, 780 (1976).
4. T. K. Kwei, H. L. Frisch, W. Radigan, and S. Vogel, *Macromolecules*, **10**, 157 (1977).
5. G. Guerra, F. E. Karasz, and W. J. MacKnight, *Macromolecules*, **10**, 681 (1977).
6. M. Galin, *Makromol. Chem., Rapid Commun.*, **5**, 119 (1984).
7. Y. F. Chong, S. Y. Lee, and S. H. Goh, *Eur. Polym. J.*, **26**, 1145 (1990).
8. W. H. Jo, S. J. Park, and I. H. Karon, *Polym. Intern.*, **29**, 173 (1992).
9. P. Sunita and B. Narendra, *J. Appl. Polym. Sci.*, **54**, 201 (1994).
10. Z. H. Liu, Ph. Marechal, and R. Jerome, *Polymer*, **37**, 5317 (1996).
11. H. Frensch and B.-J. Jungnickel, *Colloid Polym. Sci.*, **267**, 16 (1989).
12. H. Raval, Y. P. Singh, M. H. Mehta, and S. Devi, *Polym. Intern.*, **26**, 105 (1991).
13. G. Serpe, J. Jarrin, and F. Dawans, *Polym. Eng. Sci.*, **30**, 553 (1990).
14. W. J. MacKnight, R. W. Lenz, P. V. Musto, and R. J. Somani, *Polym. Eng. Sci.*, **25**, 865 (1990).
15. F. Ide and A. Hasegawa, *J. Appl. Polym. Sci.*, **18**, 963 (1974).
16. A. Gonzalez-Montiel, H. Keskulla, and D. R. Paul, *J. Polym. Sci., Part B: Polym. Phys.*, **13**, 1751 (1995).
17. S. S. Dagli, M. Xanthos, and J. A. Biesemberger, *Polym. Eng. Sci.*, **34**, 1720 (1994).
18. Y. Jin and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **36**, 1799 (1988).
19. A. Molnar and A. Eisenberg, *Macromolecules*, **25**, 5774 (1992).
20. R. A. Weiss, C. Beretta, S. Sasongko, and A. Garton, *J. Appl. Polym. Sci.*, **41**, 91 (1990).
21. Z. L. Zhou and A. Eisenberg, *J. Polym. Sci., Part B: Polym. Phys.*, **21**, 17 (1984).
22. A. Molnar and A. Eisenberg, *Polymer*, **34**, 1918 (1993).
23. L. Mascia and A. Moggi, *J. Polym. Sci., Part B: Polym. Phys.*, **31**, 1441 and 1309 (1993).
24. L. Mascia, G. R. Hitchcock, and A. Valenza, *Colloid Polym. Sci.*, **168**, 272 (1994).
25. D. G. Peiffer, I. Duvedevani, P. K. Agarwal, and R. D. Lundberg, *J. Polym. Sci.: Lett. Ed.*, **24**, 581 (1986).
26. E. Hirasawa, Y. Yamamoto, K. Tadano, and S. Yano, *J. Appl. Polym. Sci.*, **42**, 351 (1991).
27. M. Jiang, C. Zhou, and Z. Zhang, *Polymer Bulletin*, **30**, 449 and 455 (1993).
28. J. C. Bonnefis and Y. R. Puig, *J. Appl. Polym. Sci.*, **15**, 553 (1971).
29. K. N. Rao, M. H. Rao, P. N. Mourthy, and A. Charles, *Polym. Lett. Ed.*, **10**, 893 (1972).
30. M. B. Huglin and B. L. Johnson, *J. Polym. Sci.: Part A-1*, **7**, 1371 (1969).
31. A. K. Mukherjee and B. D. Gupta, *J. Appl. Polym. Sci.*, **30**, 2643 (1985).
32. V. Koul, S. K. Guha, and Choudhary, *Polym. Int.*, **30**, 411 (1993).
33. L. Mascia and K. Hashim, *Colloid Polym. Sci.*, to appear.
34. D. H. Grant and N. Grassie, *Polymer*, **1**, 125 (1990).