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Compatibilization of poly(vinylidene fluoride)/Nylon 6 blends by carboxylic acid functionalization and metal salts formation

Part 2. Mechanism and effects on physical properties

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A study was made of the mechanism for the compatibilization of blends of PVDF and Nylon 6, induced first by grafting the chains of the two polymers with methacrylic acid and, subsequently, by the formation of zinc salts. The physical properties and rheological behaviour of the blends were examined in order to elucidate the mechanism. It was found that for blends containing minor amounts of PVDF effective compatibilization was achieved only when either grafted Nylon 6 was blended with pristine PVDF, or zinc acetyl acetonate was added to blends of grafted PVDF and pristine Nylon 6. This second effect was attributed to the interfacial sharing of zinc cations between the carboxylate anions in the PVDF phase and the amide groups of the Nylon component. At high concentrations of grafted PVDF compatibilization was observed even in simple mixtures with Nylon 6, owing to the greater propensity of interfacial amidation reactions during mixing. As in the previous case compatibilization of the blends was enhanced by the addition of zinc acetyl acetonate. The type of improvements in mechanical properties, resulting from compatibilization induced by the addition of ZnAcAc, however, was found to depend on the nature of the component forming the main phase. A large increase in tensile strength was observed in blends with PVDF as the main component, while a higher ductility was achieved when the polyamide formed the main phase. Dynamic mechanical property measurements have revealed that an appreciable level of molecular miscibilization takes place within the amorphous domains of the blend, which is more easily discerned for blends in which the Nylon component forms the main phase. No evidence for the formation of ionomeric clusters for either components or the corresponding blends could be found for acid grafted systems neutralized by the addition of ZnAcAc. © 1997 Elsevier Science Ltd.

(Keywords: grafting functionalization; ionic associations; blends)

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) has the highest strength, wear resistance and creep resistance of all fluoropolymers and exhibits the typical oxidative and UV resistance of highly fluorinated compounds.

The polymorphism of PVDF and the alternation of CH_2 and CF_2 groups along the polymer chains provide a unique polarity which is responsible for its solubility in aprotic solvents.

Polyamides possess a very high melting point and excellent mechanical properties, which are maintained up to high temperatures. Their main limitations arise from their poor thermal oxidation and UV stability and their high water absorption.

Combining the properties of these two classes of polymers constitutes, therefore, a solid basis for the development of high performance engineering polymers. However, these polymers were found to be immiscible with each other[1], despite the fact that PVDF is soluble in ε-caprolactam and is partially miscible with polycaprolactone, that is for PVDF concentrations up to 30%[2]. PVDF is fully miscible, however, with non-sterically hindered poly(alkylacrylates and methacrylates), poly(vinyl esters) and poly(vinyl alkyl ketones)[3–7].

Compatibilization of blends of polyamides was generally achieved by promoting chemical reactions between its terminal amine groups and the acid or anhydride groups of another component of the blend. The graft copolymers formed will then act as compatibilizers for the main polymer components[8–16]. Grafting of acid or anhydride groups on to inert polymers is a widely used approach to enhance the compatibility[†] of blends with polyamides. Polypropylene is a favourite polymer companion for Nylon blends in view of its high melting point and its non-polar nature.

Reactive functional grafts were introduced by reactions with maleic anhydride through reaction processing methods (i.e peroxide initiation) and with water soluble monomer through radiation processing (i.e. γ-radiation initiation)[17].

Owing to the presence of tertiary hydrogens in the repeating units, polypropylene has a similar degradation susceptibility to polyamides and, therefore, cannot provide the thermal and UV ageing resistance that is expected from blends with PVDF.

By infrared analysis Serpe *et al.*[9] have revealed the formation of succinimide groups in blends of polyethylene grafted with maleic anhydride with Nylon 6, and through studies carried out on similar blends, using ^{13}C n.m.r., Van Duin *et al.*[15] reported the formation of linear imide acid

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[†] The term compatibility is used to describe the formation of finely dispersed phases and the development of strong interfacial bonding in polymer blends.

groups when the blends were heated to 180-220°C and cyclic imides at temperatures above 220°C.

In addition to compatibilization by chemical reactions the combination of polymers containing acid groups with polyamides offer the possibility of inducing compatibilization through complexation with metal cations. This will increase the strength of intermolecular associations by the sharing of cations between carboxylate anions and amide groups through co-ordination[18-20].

Ionomer based blends are interesting not only for their compatibilization efficacy which results from the strong intermolecular associations but also for the substantial enhancement in physical properties that they bring about. In fact, ionomers have long been reputed for such properties as solvent resistance and mechanical properties at high temperatures, which has made them attractive for a variety of applications[21]. The grafting of acid groups on to PVDF chains, followed by the formation of the corresponding metal salts, would be expected to improve its solvent resistance. Owing to its very high dielectric constant, however, the extent of grafting required for cluster formation is expected to be very large and is likely to have an adverse effect on its mechanical properties and its processing characteristics. For the case of ionomers based on ethyl acrylate copolymers, in fact, the development of clusters has been observed only at concentrations of the acid containing monomer in excess of 12 mol%[22,23]. Consequently blending is a more suitable route to enhance the solvent resistance.

In a study published elsewhere the authors reported a procedure for the grafting of carboxylic acid groups on PVDF chains from preirradiated polymer powder which was subsequently reacted with methacrylic acid in aqueous solutions[24]. In this work it was also shown that substantial improvements in compatibility are achieved in blends with Nylon 6 through the addition of zinc acetyl acetonate, as a result of the formation of carboxylate salts and complexation with amide groups.

The purpose of the present study is to analyze the thermal properties, dynamic mechanical spectra and rheological behaviour of such blends in order to elucidate the type of interactions which underlie the compatibilization mechanism and to examine the effects of the induced compatibilization on mechanical properties.

EXPERIMENTAL

Materials

1. Polyvinylidene fluoride. An emulsion polymer, Kynar 461 from Atochem North America inc., having a weight average molecular weight equal to 5.34×10^5 g mole^{-1}, melting point around 156-160°C and particle diameter in the region of 0.2 μm.
2. Nylon 6. A high viscosity grade in granular form, Sniamid ads 40, obtained from SNIA Ricerche, having a relative viscosity of 4 and a melting point around 220-223°C.
3. Nylon 6 cast films 20 μm thick, produced from Sniamid ads 40, also obtained from SNIA Ricerche.
4. Methacrylic acid at 99.9% purity, supplied by Aldrich Chemicals.
5. Ferrous sulphate hexahydrate (homopolymerization inhibitor) 99.9% purity, supplied by Aldrich Chemicals.
6. Zinc acetyl acetonate dihydrate (cation donor), 99.9% purity, supplied by Aldrich Chemicals.

Grafting of PVDF from powders

About 100 g of PVDF powder were placed in polyethylene lined paper envelopes and irradiated with a ^{60}Co at a dose rate of 1 kGy h^{-1} to a total dose of 15 kGy. The irradiated powder was conditioned at room temperature for 48 h and then stored in a refrigerator at −40°C.

The grafting reactions were carried out by suspending 100 g quantities of preirradiated powder in 500 ml of a 10 wt% methacrylic acid solution in deionised water within a 2 l flask, containing a 0.1 M quantity of $FeSO_4$

A stream of nitrogen was bubbled through the solution for 2 h to expel the dissolved oxygen and then heated for different times at 80°C under reflux conditions. The grafted powder was filtered and then washed several times with boiling water to remove any unreacted monomer or homopolymer, formed as a by-product of the grafting reactions, and dried for 48 h at 80 C in a vacuum oven.

The amount of grafted monomer was estimated by FTIR analysis[24] using a calibration chart for the absorbance band at 1514 cm^{-1}.

Grafting of nylon 6 from films

A number of polyamide films were sandwiched between paper mats capable of allowing a free flow of solution through the fibre 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 previous described experiments.

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 was added homopolymerization inhibitor, $FeSO_4$, at 0.01 M concentration. The solution was first flushed with nitrogen gas for about 1 h and then heated for 3 h at 80°C. After washing in hot water and drying in an oven at 100°C the films were weighed to estimate the extent of grafting, which was found to be equivalent to 3.1% MAA. The procedure was repeated using only 500 ml solution of 10% MAA, reducing the concentration of $FeSO_4$ to 0.001 M. The latter procedure gave a yield of 11.3% grafted MAA.

Blending procedure

PVDF and grafted PVDF powders alone or in mixtures with Nylon 6 granules and/or grafted Nylon 6 films at 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. The zinc acetyl acetonate (ZnAcAc) required for the neutralization of the acid groups (when applicable) was added during the initial melting period over about 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.

Thermal analysis

The thermal properties of the blends and respective control samples were examined by differential scanning calorimetry using the Dupont 2000 apparatus. Small shavings were cut out from the plaques and 10 mg samples were placed in the aluminium pan with a lid, using a similar empty pan as reference. All experiments were carried out at a heating rate of 10°C min^{-1} under a nitrogen stream of

60 ml min^{-1}. To ensure a uniform history the PVDF samples were first heated at to 200°C and held at this temperature for 5 min. before being cooled at the same rate down to 70°C. After 1 min. the samples were reheated to 200°C at the same heating rate. The thermal data were obtained on both the first cooling rate and the second heating cycle. For samples containing Nylon 6 the same procedure was used going to a maximum temperature of 260°C and cooling to 70 °C after 1 min, both at 20°C min^{-1}. The % crystallinity of each phase was calculated separately from the normalized heats of fusion[25,26] using the values of 190.8 J g^{-1} for Nylon 6 and 104.7 J g^{-1} for PVDF both at 100% crystallinity.

Preparation of test plaques

Plaques (110 × 110 × 0.5 mm) were produced by compression moulding at 180°C for PVDF and 240°C for blends with Nylon 6. PET films were used for mould 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 mould.

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.

These were carried out at room temperature on dumbbell shaped specimens (ASTM D638) cut out from compression moulded plaques, using a Lloyd 2000R tensile testing machine at a clamp separation rate of 5 mm min^{-1}. A minimum of 5 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 its components were evaluated by means of a Rheometrics RDA type II dynamic analyzer using a 25 mm diameter parallel plates fixture. Sample discs approximately 27 mm diameter were cut out from compression moulded 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. more than 90%. Logarithmic frequency sweeps were taken over a frequency range of 0.1 to 500 rad s^{-1} with 5 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.

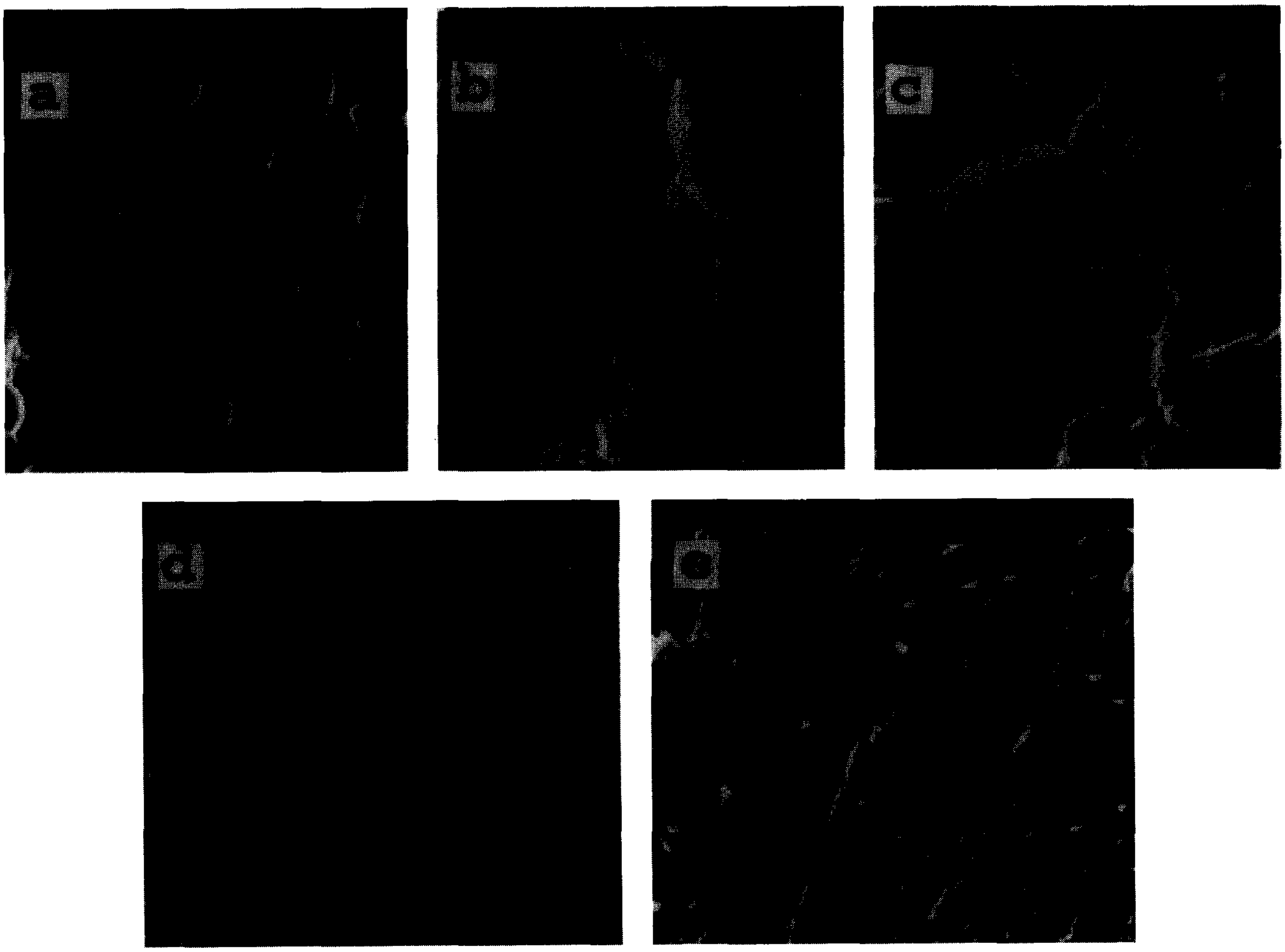

Figure 1 SEM micrographs of the fractured surface of blends based on PVDF/Nylon 6 systems at 20/80 weigh ratio. (Magnification is approximately 4400 in all cases) (a) PVDF/Nylon 6 (control) (b) PVDF grafted with 10 % MAA/Nylon 6 (c) (PVDF grafted with 10% MAA/Nylon 6) + ZnAcAc (d) PVDF/Nylon 6 grafted with 11 % MAA (e) (PVDF grafted with 10% MAA/Nylon 6 grafted with 11% MAA) + ZnAcAc

RESULTS AND DISCUSSION

The micrograph in *Figure 1* shows that, for blends in which PVDF is the minor component (i.e. 20 wt%, corresponding to 13 vol%), effective compatibilization is not achieved by the grafting of methacrylic acid on the PVDF chains. This suggests that the reaction between the grafted acid groups in the PVDF and the terminal amine groups in the polyamide cannot have taken place to a significant extent. Extensive compatibilization of the two phases is observed, in contrast, when either ZnAcAc is added to neutralize the acid groups in the PVDF phase or acid-grafted Nylon 6 is used in blends with pristine PVDF (micrographs *c* and *d* in *Figure 1*). The rheological curves for various individual polymers, shown in *Figure 2*, suggest that compatibilization of PVDF with acid-grafted Nylon 6 may have resulted from the closer matching of the viscosity/shear rate characteristics of the two polymer components of the blend.

However, this explanation is not applicable for the case in which ZnAcAc is added to the neutralize the acid groups of the grafted PVDF in blends with pristine Nylon 6, because the formation of the corresponding zinc salt does not affect significantly its rheological behaviour. The latter observation was attributed to the fact that the grafted species are immiscible with the non grafted polymer and will form dispersed particles which act as filler and, therefore, does not affect the viscosity[24]. Moreover the rheological data in *Figure 2* show that the migration of any small amount of ZnAcAc in the Nylon phase reduces its viscosity through plasticization effects, and accentuates further the difference in rheological behaviour of the two phases. Consequently the compatibilization mechanism in the latter case must be associated with both chemical interactions between the various components during mixing and to physical effects. This argument finds strong support from the rheological behaviour of the blends, illustrated in *Figure 3*, which reveal that compatibilized blends exhibit a rheological behaviour close to that of the PVDF component, whereas the behaviour of uncompatibilized blends is nearer to that of the Nylon 6 component, which constitutes the major (disperse) phase. Further, it was noted, that for blends where both polymers were grafted with MAA, and ZnAcAc was added to neutralize the acid groups, the compatibility is intermediate between the extreme cases (*Figure 1*, micrograph *e*) and that such behaviour is also reflected in their rheological behaviour (*Figure 3*).

In related work it was shown, in fact, that the addition of ZnAcAc reduces the extent of chemical reactions between acid groups and amine groups as the result of the formation of carboxylate salts[24].

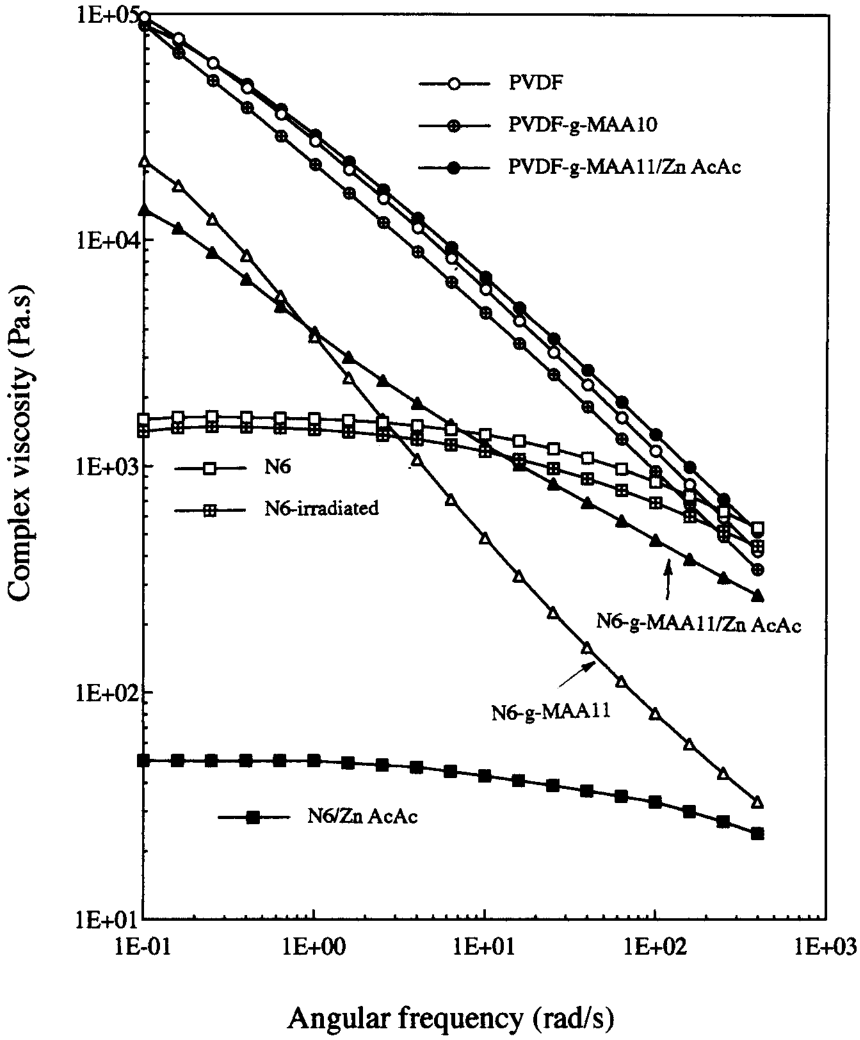

Figure 2 Complex viscosity as a fluiction of Angular frequency for various components of blends based on PVDF and Nylon 6. Codes: PVDF-g-MAA1O = PVDF grafted with 10 wt% methacrylic acid, PVDF-g-MAA1O/ZnAcAc = As above with addition of ZnAcAc, N6-g-MAAI 1 = Nylon 6 grafted with 11 wt% methacrylic acid N6-g-MAAI l/ZnAcAc = As above with addition of ZnAcAc

For blends in which the PVDF is the major component (i.e. 80 wt%, equivalent to 87 vol%) compatibilization takes place whenever the PVDF component contains grafted acid groups and that an even higher level of compatibility is achieved when the Nylon 6 component also contains grafted acid groups (*Figure 4*). It is noted that some compatibilization is also observed in blends based on virgin PVDF with Nylon 6 to which was added a minor amount of acid grafted Nylon 6 (micrograph (d)). From the rheological data shown in *Figure 5* it inferred that this cannot be attributed to a closer matching of viscosity characteristics of the components and that it must be associated with an increase in intrinsic phase miscibility (see later).

In any case these rheological data reveal that the more highly compatibilized blend, i.e. the blend containing zinc saks of both components, shows the typical positive deviation behaviour with respect to its viscosity characteristics.

The DSC traces in *Figure 6* provide a fingerprint identification of the state of the components of the blend. The control blends PVDF/Nylon 6 show the typical melting peaks of the two constituents at approximately the same temperature as for the individual components in isolation (see *Table 1*), whereas the introduction of acid groups in the PVDF component causes a large depression in melting point and a reduction in the heat of fusion in relation to the quantity of acid groups present in the PVDF (*Figure 6i*). It is worth noting that these correspond to the α-form of PVDF and to the γ-form of Nylon 6[1].

The addition of ZnAcAc to the blend causes the Nylon 6 phase to retain its original melting point, even at half the concentration required for presumed full neutralisation (see *Figure 6ii*, and note that the trace C was displaced slightly downwards for clarity). When both components contain acid groups the crystallisation of the Nylon component is completely suppressed (trace *b* in *Figure 7*), whereas the grafting of small amount of acid groups on to the Nylon has no effect in blends containing virgin PVDF.

This is in discordance with the comments made earlier with respect with micrograph *d* in *Figure 4*, which show a higher level of compatibility for blends containing acid groups in the Nylon phase. Although in both cases the total amount of carboxylic acid in the Nylon phase is the same (i.e. 3%), for the blend corresponding to micrograph *d* in *Figure 4* the Nylon phase consists of a mixture of Nylon 6 and heavily grafted Nylon 6 (i.e. 11%) which was found to be more miscible with PVDF. The difference in behaviour has to be attributed, therefore, to the greater capacity of the carboxylic acid groups, when grafted at higher level, to react with terminal amine groups of the polyamide. This is supported by the observation that the melting point (T_m) and peak crystallization temperature (T_c) of the polyamide phase are somewhat lower (i.e. 215°C and 185°C against 217°C and 189°C respectively) (see later).

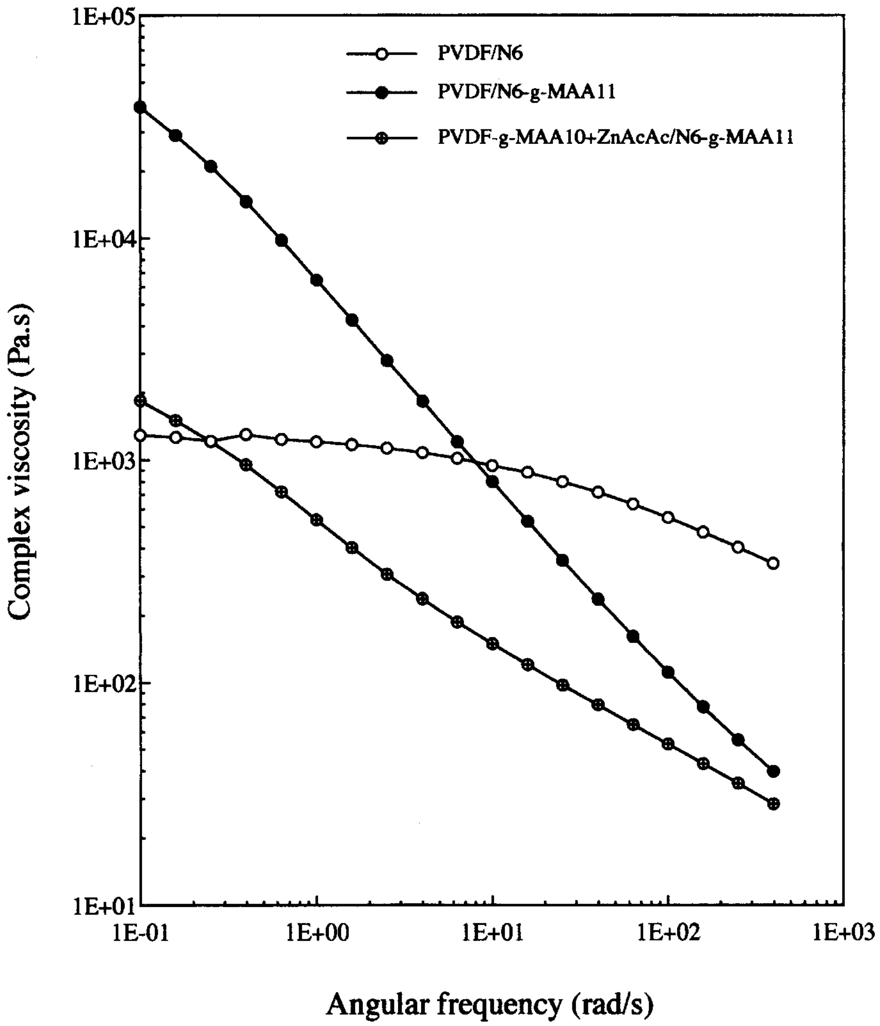

Figure 3 Complex viscosity as a ftmction of Angular frequency for various blends at 20/80 weight ratio of the components indicated (All codes are desribed in previous figures)

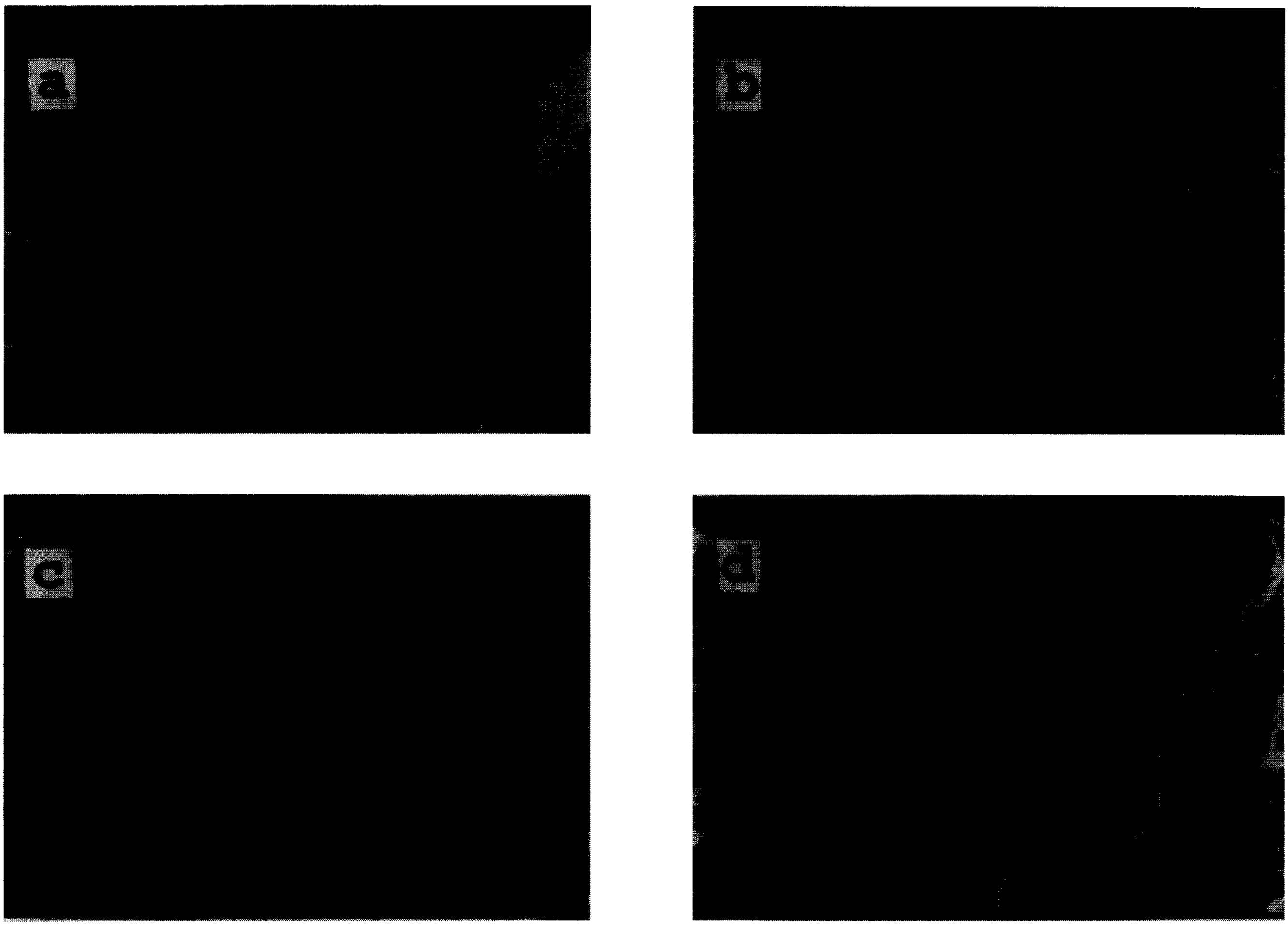

Figure 4 SEM micrographs of the fractured surfaces of blends based on PVDF/Nylon 6 systems at 80/20 weigth ratio (All codes are described in previous figures) (Magnification; can 4400 for (a) and (d); can 9000 for (b) and (c) (a) PVDF/N6-g-MAA3 (3 wt%) (b) PVDF-g-MAA1 0/N6-g-MAA3, (c) (PVDF-g-MAA10/N6-g-MAA3) + ZnAcAc, (d) PVDF/(Nylon6: N6-g MAAll @3:1 ratio)

The diagrams in *Figure 7* provide further confirmation that the addition of ZnAcAc causes the Nylon component to retain its original melting point but reduces the crystallization rate, as evidenced by the lower peak crystallization temperature and the broader crystallization endothermic on cooling.

In *Table 1* are shown the thermal data recorded for the two phases for the majority of the blends examined. For straight blends of PVDF/Nylon 6 one observes an antagonistic effect on the crystallization of both components, as evidenced by the lowering of T_m and T_c values and the reduction in melting and crystallization enthalpies. This suggests that a small level of miscibilization on a molecular scale has occurred in these blends, but it is possible that this may have resulted from the migration of residual oligomers or low molecular weight species that are likely to be present either from polymerization or formed during mixing and subsequent processing.

For blends in which the two components can react with each other, e.g. 80/20 blends of grafted PVDF and Nylon 6, the crystallization peak of the Nylon 6 phase is suppressed. This has to be attributed to the formation of branched molecular chains which hinder the crystallization process. It is noted that for the same combination of polymers at 20/80 weight ratio the effects are more pronounced with respect to the PVDF phase. In other words the magnitude of the effects appear to be directly related to the concentration of the interactive species in the blend.

It is remarked, however, that in none of the blends examined has been observed the overlapping of the crystallization of the two phases reported by Frensch and Junguickel[1]. In the studies made by these authors, however, the T_m of the PVDF was 178°C whereas in this work the value is 162–163°C. Since both polymers are expected to be present in their stable α-form, the disparity in melting point is likely to arise from the difference in the level of head-to-head defects along the chains which would affect the crystallization kinetics and final level of crystallinity in the polymer.

In examining the data in *Table 1* is instructive to note that while the melting point of the Nylon 6 phase remains at the same level as for the homopolymer in isolation when ZnAcAc is added to the blend, the degree of crystallinity of both phases is reduced considerably. In contrast, the T_m value for the PVDF phase is not affected by the addition of ZnAcAc and remains at the level exhibited by the grafted homopolymer, which is somewhat lower than for the virgin polymer.

From these observations it can be inferred that the complexation of zinc cations with the amide groups of Nylon 6 takes place in the amorphous phase and brings about a fractionation of the Nylon 6 crystals, expelling branched Nylon 6 chains and any solubilized PVDF containing species. It is worth noting, however, that these have no nucleation effect on the crystallization of pure Nylon 6, as evidenced by the fact that the peak crystallization temperature does not change.

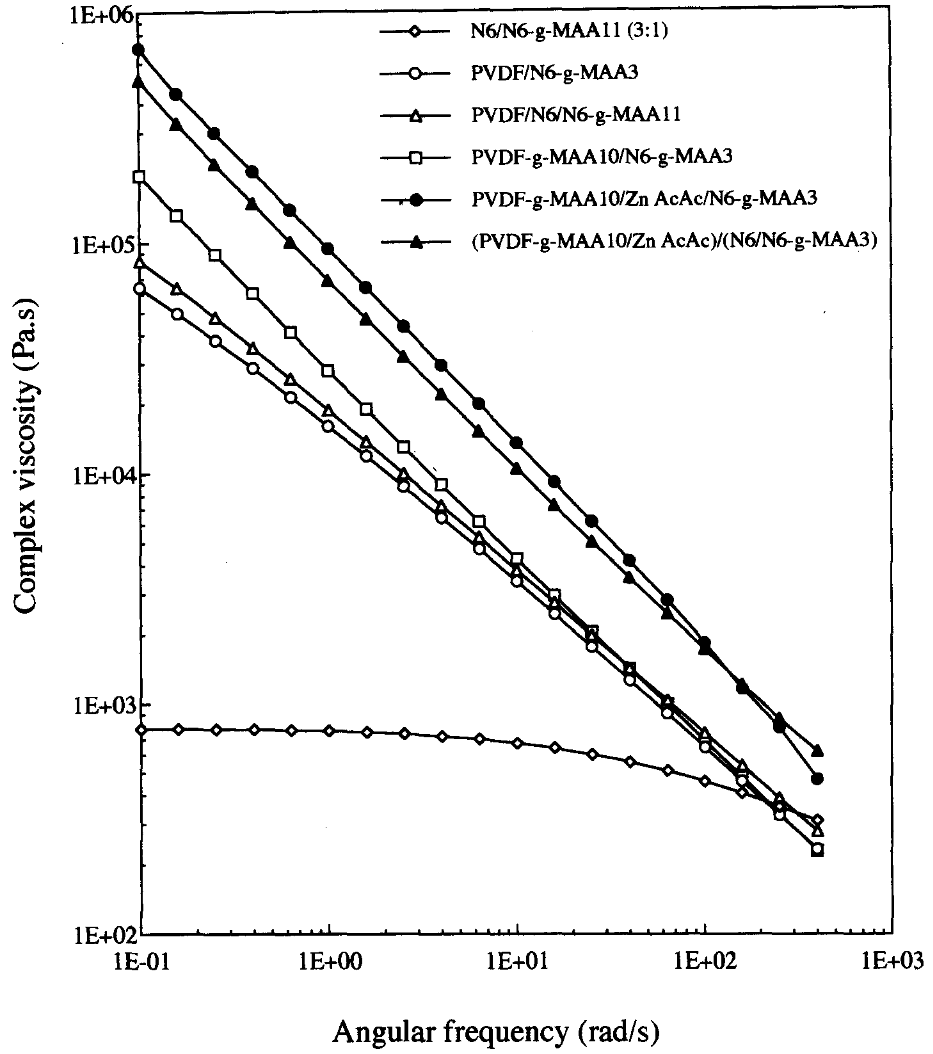

Figure 5 Complex viscosity as a function of Angular frequency for various blends at 80/20 weight ratio. (All codes are described in previous figures)

For the case of the PVDF phase such fractionation does not take place as a result of the addition of ZnAcAc as long as the PVDF component constitutes the main phase. However, at low concentrations of PVDF both the melting point and the degree of crystallinity are reduced substantially. Since the degree of crystallinity of the Nylon 6 phase is also reduced for the same blends, it can be concluded that molecular miscibilization of the two components has occurred in the amorphous phase.

The deductions about the morphology and the physical state of the two phases present in the blends derived from the SEM examinations and thermal analysis find also support from the dynamic spectra. In *Figure 8i* it is shown that the general shape of the curves for tan δ as a function of temperature is not substantially affected by the grafting of methacrylic acid on the PVDF chains and by the subsequent formation of the zinc salts. The reduction in the level of energy dissipation resulting from the modification of the PVDF chains is attributed to the particulate nature of dispersed phase containing the grafted chains and corresponding zinc salts.

Although no data are available for the relaxation behaviour of these systems in the temperature range between 100 and 180°C, there are no indications in the dynamic spectra in *Figure 8i* and the rheological data in *Figure 2* of the possible existence of new transitions related to the formation of ionomeric clusters.

The dynamic spectra in *Figure 8ii* confirm the validity of the suggestion made in the analysis of thermal data that, even in the absence of any grafts, there is phase miscibility in blends of Nylon 6 and PVDF evidenced by the large downward shift of the glass transition of the Nylon 6 phase. A reduction of about 20°C is estimated from the displacement of the of the peak-tan δ temperature for blends containing 20 wt% PVDF. This reduction in T_g is very large and is approximately equal to the value calculated on the basis of full miscibility of the amorphous phases of the two components using the reciprocal weighted average rule. Although it is not possible to make a similar calculation for the blend in which the PVDF is the main phase, the spectra in *Figure 8ii*, show a clear plasticization effect for the polyamide phase and a substantial increase in the tan δ values for the PVDF phase in the very "lossy" region above 60°C.

When grafted PVDF is used in blends with 20 % Nylon 6 the peak-tan δ temperature is reduced to about 80°C from a value of about 120°C and the breadth of the relaxation curve is reduced, whereas the T_g for the polyamide phase remains in the same region as for blends containing virgin PVDF.

The partial replacement of Nylon 6 with the acid grafted homologue and the addition of ZnAcAc to the blend based on grafted PVDF decreases the values of tan δ in the more energy dissipative regions, i.e. above 60°C. When ZnAcAc is added to the blend containing grafted acid groups in both

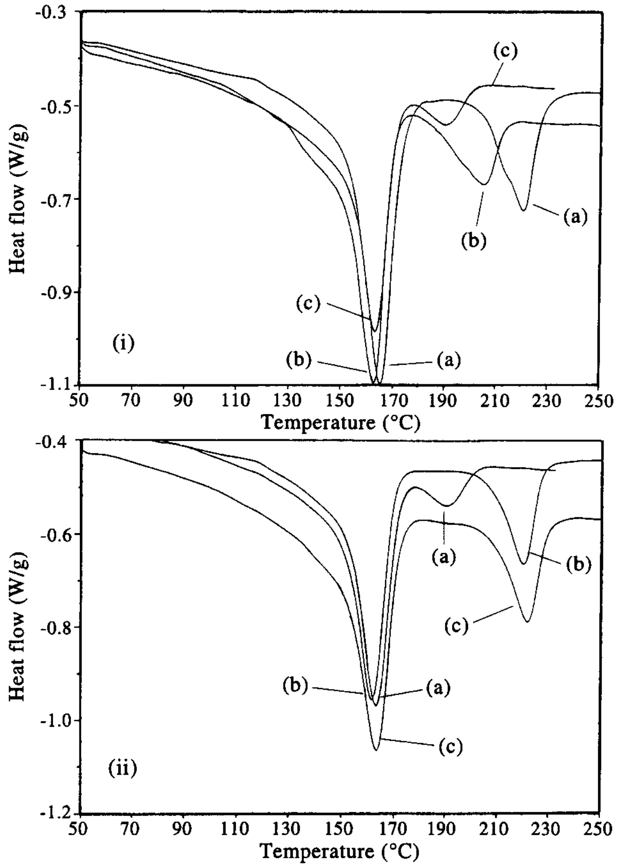

Figure 6 DSC trace for the second heating cycle of the thermal analysis for blends at 80/20 weight for the components shown below. (All codes are described in previous figures; the number 0.5 or 1 after ZnAA is the molar ratio with respect to the grafted acid groups)For top diagram (i): a) PVDF/N6; b) PVDF-g-MAA5/N6; c) PVDF-g-MAA 10/N6 For bottom diagram (ii): (a) PVDF-g-MAA 10/N6; (b) (PVDF-g-MAA10/N6) + 0.5 ZnAcAc; (c) (PVDF-g-MAA10/N6) + 1.0 ZnAcAc

components of the blends the peak-tan δ temperature is shifted downwards from the previous value of 80°C to about 55°C and the transition occurs over a more narrow temperature interval *Figure 9*.

These are clear indications of further plasticization taking place within the amorphous regions of the PVDF phase, which have become the prevalent domains as the result of the reduction in the level of crystallinity. The enhanced plasticization of the amorphous PVDF phase, revealed by the dynamic spectra, for blends containing grafted acid groups in the chains of both polymers as a result of the addition of ZnAcAc is concordant with the hypothesis put forward in the analysis of the thermal data. In other words the expulsion of the grafted chains from the Nylon 6 phase during crystallization increases the quantity of such chains diffusing into the amorphous PVDF phase.

The mechanical properties were also found to be affected considerably by the changes in morphology of the blends and the physical state of the two phases. The results in *Table 2* for the single components show the typical fillers effect in polymers on tensile strength and elongation at break for grafted PVDF and corresponding zinc salt, which was discussed previously with respect to morphological considerations and rheological behaviour.

The data in *Table 3* illustrate the improvements in mechanical properties that result from the different levels of compatibilization of the blends. One general observation that can be made with respect to these data is the contrasting effect on mechanical properties that compatibilization brings about according to whether the Nylon 6 or the PVDF based component forms the main phase. In the latter case compatibilization of the components produces an increase in strength but the failure is always a brittle type. However, when the polyamide component forms the main phase compatibilization brings about an increase in ductility, that is to say that the elongation at break increases but the yield strength remains constant.

From these data is also evident that the most dramatic improvements in mechanical properties take place for blends containing zinc salts, respectively for blends of grafted PVDF and Nylon 6 at 20/80 weight ratio and grafted PVDF and grafted Nylon 6 at 80/20 weight ratio.

These effects cannot be related to the morphology of the blends revealed by the SEM examinations, partially because these are not sufficiently discriminatory but also because the physical state of the constituent phases can also have a

Table 1 DSC data for various blends of PVDF and Nylon 6 based polymers. (Note; The enthalpy values are normalized to 100% polymer component and the % crystallinity was calculated from the heat of fusion, ΔH_f)

Blend	PVDF phase				Nylon 6 phase			
	T_m (°C)	ΔH_f (J/g)	T_c (°C)	Cryst (%)	T_m (°C)	ΔH_f (J/g)	T_c (°C)	Cryst (%)
PVDF	165	65	135	63				
Nylon (N6)	111	111	111	111	222	88	182	46
PVDF-g-MAA5	163	64	136	61				
PVDF-g-MAA10	162	49	135	47				
80/20 PVDF/Nylon 6	165	54	128	51	221	56	182	29
80/20 PVDF-g-MAA5/N6	163	52	131	50	205	37	157	19
80/20 PVDF-g-MAA10/N6	163	33	132	32	191	12	none	6
80/20 (PVDF-g-MAA5/N6) + ZnAcAc	164	47	130	45	222	51	179	27
80/20 (PVDF-g-MAA10/N6) + ZnAcAc	164	45	132	43	222	50	186	26
20/80 PVDF/Nylon 6	161	27	120	26	221	70	183	37
20/80 PVDF-g-MAA5/N6	159	17	124	17	220	55	183	29
20/80 PVDF-g-MAA10/N6	160	19	130	18	218	58	187	30
20/80 (PVDF-g-MAA5/N6) + ZnAcAc	159	23	120	22	221	63	183	33
20/80 (PVDF-g-MAA10/N6) + ZnAcAc	159	21	127	20	222	59	187	32

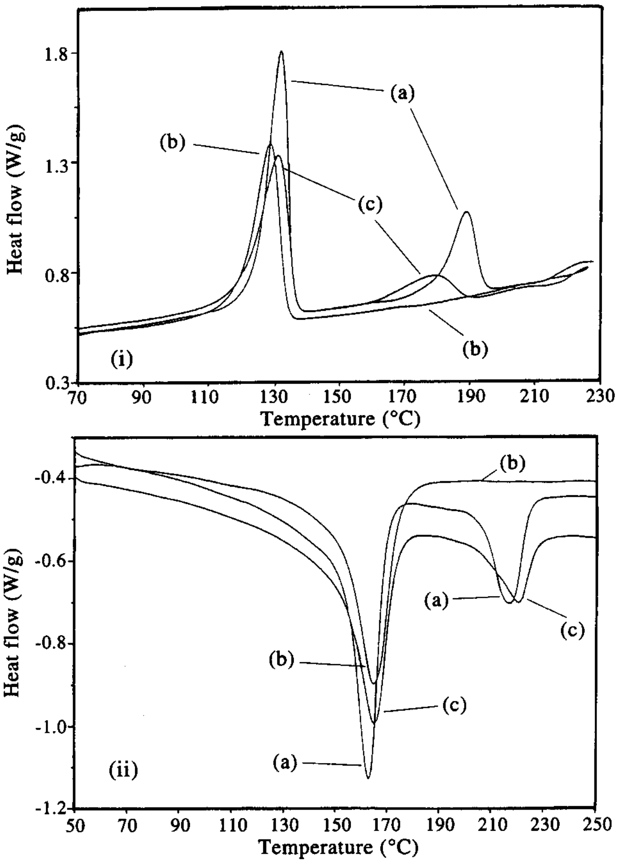

Figure 7 DSC traces for various blends at 80/20 weight ratio for various blends (All codes are described in previous figures). Diagrams at the top are for the second heating cycle. Diagrams at the bottom are for the cooling cycle, (a) PVDF/N6-g-MAA3: (b) PVDF-g-MAA1 0/N6-g-MAA3; (c) (PVDF-g-MAA10/N6) + ZnAcAc

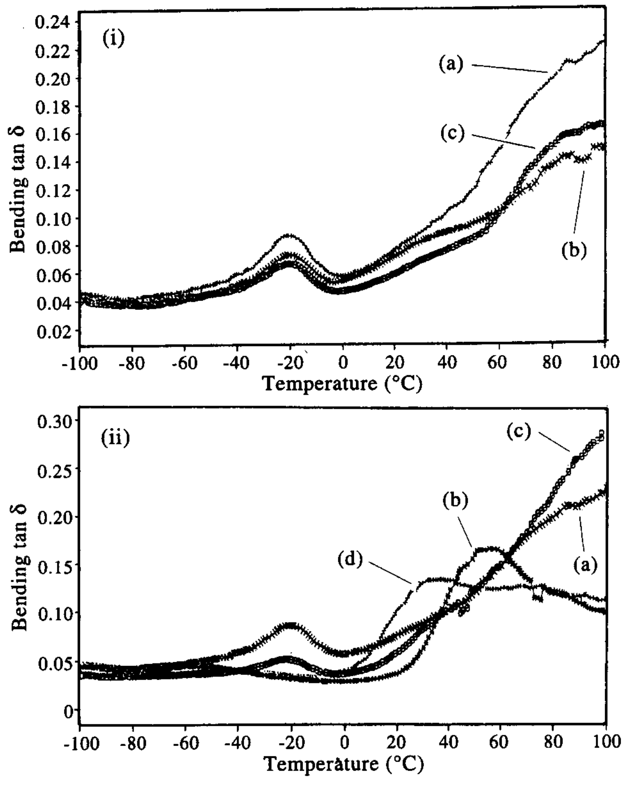

Figure 8 DMTA spectra for various components and blends. (All codes are desribed in previous figures). For top diagrams (i): (a) PVDF; (b) PVDF-g-MAA; (c) PVDF-g-MAA + ZnAcAc For bottom diagrams (ii): (a) PVDF; (b) Nylon 6; (c) PVDF/N6 (80/20);(d) PVDF/N6 (20/80)

Table 2 Mechanical properties of various PVDF and Nylon 6 polymers

Blend	Tensile yield Strength (Mpa)	Elongation at break (%)
PVDF	42.5	276
PVDF-g- M~AA5	41.6	79
PVDF-g-M~AA10	44.5	30
PVDF-g-M~AA10 + ZnAcAc	44.3	14*
Nylon 6	57.6	235

* Brittle failure.

Table 3 Mechanical properties of various blends of PVDF and Nylon 6 based polymers

BLEND	Tensile Strength (MPa)	Elongation at break (%)
20/80 PVDF/Nylon 6 (N6)	42.5	46
20/80 PVDF-g-MAA10/N6	53.6	78
20/80 (PVDF-g-MAA10/N6	53.9	188
80/20 PVDF/Nylon 6) + ZnAcAc	17.6*	4
80/20 PVDF-g-MAA10/N6	35.7*	6
80/20(PVDF-g-MAA10/N6) + ZnAcAc	33.3*	5
80/20 PVDF/N6-g-MAA11	35.4*	8
80/20 PVDF-g-MAA10/N6-g-MAA11	37.4*	6
80/20 (PVDF-g-MAA10/N6-g-MAA11) + ZnAcAc	50.6*	9

*Brittle failure.

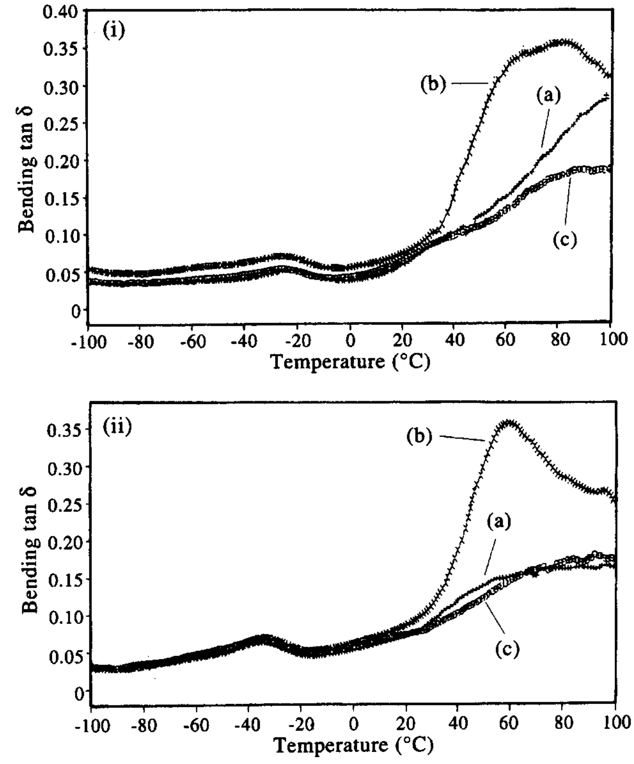

Figure 9 DMTA spectra of various blends (All codes are described in previous figures). For top diagrams (i): a) PVDF/N6 (80/20); b) PVDF-g-MAA1O/N6 (80/20); (c) [VDF-g-MAA1O/N6 (80/20)] + ZnAcAc. For bottom diagrams (ii): a) PVDF/N6/N6-g-MAA11 (80:15:5) (b) PVDF-g-MAA1O/N6/N6-g-MAA11 (c)[PVDF-g-MAA/N6/N6-g-MAA11 (80:15:5)] + ZnAcAc

significant effect on mechanical properties. The very high tensile strength observed for blends at 80/20 weight ratio of grafted PVDF and grafted Nylon 6, neutralized with ZnAcAc, can be attributed to extensive miscibilization of the amorphous PVDF domains which constitute the main phase. It is possible that the large amounts of Nylon present in this phase produce strong intermolecular interactions as a result of ionic associations and complexation of the zinc cations with amide groups. Although the simultaneous formation of chemical cross-links cannot be excluded it was shown in related work that the chemical reaction between acid groups and terminal amine groups occur to a much lesser when ZnAcAc is present in the mixture, because of the more favourable formation of zinc salts[24]. It is important to bare in mind that the value of 50.6 MPa for the tensile strength of the blend in question is much greater than that of the pure PVDF, despite the lower degree of crystallinity. Although some reinforcement can also be expected from the continuous polyamide phase, the contribution from this source can assumed to be very small in so far as the degree of crystallinity of the Nylon phase in the blend is rather low and the total amount present is quite small.

The high ductility of the 20/80 blend of grafted PVDF/Nylon 6 containing zinc cations can be attributed to the continuity of the polyamide phase and the presence of dispersed particles of the PVDF component, which are brought about by the suppression of the reactions between the two polymers as a result of the more favourable formation of zinc salts.

CONCLUSIONS

The main conclusions that can be drawn from this study are the following:

(1) PVDF and Nylon 6 form partially miscible blends with a typical two-phase morphology of particles dispersed in a continuous matrix of the major component. The mechanical properties are inferior to those exhibited by the individual polymers in isolation owing to the low interfacial adhesion between the two phases.

(2) Grafting methacrylic acid groups on the PVDF chains is effective in inducing compatibilization of the blends, evidenced by the formation of fine co-continuous phases. Compatibilization is enhanced by blending the components in the presence of zinc acetyl acetonate and takes place through both a reduction in the level of crystallinity of the two phases and an increased level of miscibility within the amorphous phases.

(3) For blends in which the main component consists of a grafted PVDF phase compatibilization by the addition of zinc acetyl acetonate brings about very large increases in tensile strength, which are attributed to strong ionic associations within the main PVDF phase. When the main phase consists of a grafted Nylon 6 component there are large improvements in ductility without any significant deterioration in tensile strength. This is attributed to the reduction in the extent of crosslinking reaction occurring between acid groups and terminal amine groups in the polyamide, as a result of the formation of carboxylate zinc salts.

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