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ORIGINAL CONTRIBUTION

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Carboxylic acid functionalization of nylon 6 by radiation grafting and conversion to zinc salts: effects on physical properties

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Abstract Functionalization of polymers by grafting monomeric species on to the backbone of molecular chains with the use of γ-radiation has been used extensively. In this work methacrylic acid was grafted onto a commercial grade of polycaproamide (Nylon 6) by preirradiating the polymer granules to 15 kGy at a rate of 1.0 kGy per hour and subsequently immersing these in a 10% aqueous solution of methacrylic acid in the presence of small quantities of $FeSO_4$ as homopolymerization inhibitor. The polymer was subsequently neutralized by mixing it with zinc acetylacetonate in a laboratory scale melt mixing device. The acid-grafting polymer modification resulted in an increase in glass transition temperature, while the addition of zinc acetylacetonate gave rise to two transitions: The lower transition corresponds to a miscible mixture of free polyamide and acid-grafted polymer, both plasticized with undecomposed zinc compound, while the upper transition corresponds to the zinc salt of the acid grafted polyamide. Through rheological measurements it was shown that both the acid-grafted polymer and the derived zinc salt have a branched structure, possibly containing also some crosslinked domains. Large improvements in solvent resistance were observed for both type of polymer modifications.

Key words Polymer functionalization – Nylon 6 – methacrylic acid – radiation grafting – glass transition temperature

Introduction

Grafting of functional groups onto polymer chains is a widely used method to modify the properties of existing polymers [1–3]. The introduction of acid groups on polymer chains, starting from either raw polymers or finished products, such as films and fibres, is a particularly attractive route to enhance properties, like adhesion, printability, barrier towards nonpolar liquids and dye receptivity [4, 5]. It is possible to neutralize, fully or partially, the acid groups in order to produce metal salts or ionomeric species within the structure in order to modify further the properties of the original polymer. This enables such polymers, for instance, to enter applications requiring special properties, such as membranes, battery separators and biomedical devices.

The main advantage of using ionising radiation for chemical grafting is the possibility to carry out the reactions at low temperatures. Moreover, when using highly hydrophilic monomers, such as those containing acid, amide or amino groups, it is possible to carry out the grafting reactions in water solutions, which enables the residual monomers and polymeric byproducts to be easily removed by extractions with water. Grafting with the use of peroxide initiators, on the other hand, is normally carried out at high temperatures in twin screw extruders by reaction processing methods. There can be some handling difficulties in these operations, however, arising from the volatility of monomers and the inability to completely strip off unreacted monomers and byproducts resulting from homopolymerization.

Very little has been reported in the literature on the grafting of acid functionalized groups on to polyamide chains. Mainly because these are already sufficiently hydrophilic and do not present the usual problems associated with lack of wettability and adhesion. Jin and Huang, however, have carried out a study on blending of polyacrylic acid with Nylon 6 for the production of membrane materials for pervaporation separation of acetic acid/water and ethanol/water mixtures [6]. The blend was found to be miscible and an increase in T_g was reported, which was attributed to the formation of anhydrides within the polyacrylic acid chains, as indicated by the appearance of an I.R. absorption band at 1750–1800 cm^{-1}.

Several studies have also been reported on the effects of adding inorganic salts to polyamides [7–9], indicating that complexation takes place between the metal ions and the amide groups in the polymer chains, which gives rise to an increase in glass transition temperature (T_g).

In some more recent studies, Molnar and Eisenberg [10] have shown that coordination between metal ions and amide groups can take place also in blends of polyamides with sulphonic acid salts in grafted polystyrene. It is interesting to note that even for the case when the blends were immiscible an increase in T_g was always observed for the polyamide phase, which can only be attributed to the migration of the metal ions and their complexation with the amide groups. A similar cation migration phenomenon has been reported by Mascia et al. for blends of an ionomer based on an ethylene terpolymer with the polyhydroxyether of bis phenol A [11, 12].

In the present study are examined the effects of grafting a polyamide with methacrylic acid and subsequently neutralizing the acid groups to produce the corresponding zinc salt, using zinc acetyl acetonate, on the physical properties and behavior towards solvents.

Experimental

Materials

The polymer examined was an extrusion grade of polycaproamide (Nylon-6) with a relative viscosity of 4 supplied by SNIA Ricerche in the form of cylindrically shaped granules (about 2.5 mm diameter and 3 mm long).

The monomer used for the acid functionalization of the polymer was methacrylic acid (MAA), 99.9% purity. An analytical grade of ferrous sulphate hexahydrate ($FeSO_4$) was used as homopolymerization inhibitor (13), and zinc acetyl acetonate dihydrate (ZnAcAc), also analytical grade, was used for the subsequent neutralization of the acid groups. (These were supplied by Aldrich Chemical.) The reason for choosing ZnAcAc to carry out the neutralization reaction is that acetyl acetone, formed as a product of the neutralization reaction, can be easily expelled from the polymer through volatilization during mixing (see later).

Monomer absorption from water solutions

Some preliminary experiments were carried out to determine whether fairly large quantities of monomer would be absorbed into the polymer granules from water solutions. Small amounts (i.e. about 1 g) of granules were immersed in 10 ml of liquid consisting of pure MAA, water, 10% and 30% water solutions, respectively, and heated for various lengths of time at 80 °C. The increase in weight was measured at regular intervals for up to 48 h.

Grafting procedure

The polymer granules were vacuum-dried at 70 °C for 48 h and placed in polyethylene lined paper envelopes and sealed to prevent the absorption of water during handling and storage. These were irradiated with a cobalt 60 source at 1 kGy/h to a total dose of 15 kGy and, after being conditioned for 48 h at room temperature, the envelopes were subsequently stored in a freezer, for up to 1 month, prior to use. The conditioning at room temperature was deemed to be necessary to maximize the formation of peroxide groups from the reaction with atmospheric oxygen surrounding the granules [14].

About 100 g of irradiated granules were placed in a 1 l flask, fitted with a condenser, containing 500 ml of 10% MAA solution in distilled water and $FeSO_4$ was subsequently added in an amount to produce a 0.01 M solution. After bubbling nitrogen gas through the solution for about 1 h to expel the dissolved free oxygen the temperature was increased to 80 °C and the solution was heated for 3 h with continuous stirring. The monomer concentration in the water solution and the reaction time were determined from previous monomer absorption studies and preliminary grafting reactions carried out over different lengths of time. The granules were subsequently filtered and then washed several times with boiling water to remove the dissolved unreacted monomer and any free polymethacrylic acid formed as byproduct. These were dried at 100 °C and the % grafted monomer was calculated from the weight increase. The grafting yield was estimated to be 11%, with a variation of about 5%.

FTIR analysis

Infrared spectra were obtained from measurements on films pressed at about 240 °C to a thickness of 5 μm, using a Nicolet 20 DXC spectrophotometer. The % grafted MAA was estimated by measuring the area absorbance ratio for $COOH/CH_2$ groups at 1714 and 2900 cm^{-1} using a calibration curve previously obtained from a series of ethylene acrylic acid terpolymers (respectively, AC 672, AC 540 and AC 5120 obtained from Allied Signals) and montanic acid (supplied by Aldrich). The FTIR method gave results about 15% higher than the values obtained gravimetrically. This discrepancy is attributed to the leaching out of some low molecular weight species from the polymer, such as lubricants, during the grafting reaction and subsequent washing stage.

SEM examinations

Samples of granules of grafted polymer were fractured in liquid nitrogen and the fractured surface was examined by SEM using a Cambridge Stereoscan 360 instrument.

Specimens preparation

Samples of both grafted and virgin granules were melted and homogenized in a Brabender Plastograph, fitted with a 25 ml mixing chamber and conventional rotors for thermoplastics, using a rotor speed of 80 rpm and a preset temperature of 220 °C. Immediately after melting the granules a stoichiometric amount of ZnAcAc was added to neutralize the acid. The same amount of ZnAcAc was also added to the virgin polymer granules, as a control experiment. The acid groups already present as terminal groups in the original polymer were ignored for the purpose of the calculation as these amounts were deemed to be very small. Mixing was carried out for a period of 15 min from the end of the melting stage and the addition of the ZnAcAc. The melt was discharged from the mixing chamber in the form of small slugs, which were quickly squashed between metal plates to produce preforms about 3–4 mm thick. These were stored in a desiccator and used to produce compression moulded plaques (100 × 100 × 0.5 mm) at 240 °C using PTFE impregnated fine weave glass cloth for mould release purpose and ensuring that the plaques were cooled at a reasonably constant cooling rate while maintaining the pressure.

Differential scanning calorimetry

The thermal properties of the compression moulded specimens were examined on a Du Pont DSC apparatus, model 2000, using about 10 mg samples and a scanning rate of 20 °C/min with a flow of nitrogen of 60 ml/min. To obtain data on samples with a uniform thermal history a second heating cycle was carried out after holding the temperature constant at 260 for 1 min. In addition to recording the thermal transitions and the respective enthalpy data, the % crystallinity was calculated using a fusion ΔH value of 190.8 J/g for a 100% crystalline sample [15].

Dynamic mechanical thermal analysis

Dynamic mechanical spectra were obtained with the use of a Polymer Laboratory DMTA apparatus, model PL 706. Rectangular specimens about 10 mm wide and 35–40 mm long, cut from the compression moulded plaques, were clamped in a medium frame, centrally loaded, dual cantilever testing jig, with a 4 mm free length. The tests were carried out at 1 Hz with 4 mm oscillations amplitude over the temperature range varying from −100 to +100 °C at a heating rate of 5 °C/min.

Rheological measurements

The rheological properties were measured on a Rheometric RDA II Dynamic Analyser using a 25 mm diameter parallel-plate fixture. Sample discs of approximately 27 mm diameter were cut from the plaques and placed within the plate of the rheometer. Prior to commencing each experiment the rheometer was allowed to equilibrate at the test temperature for 10–15 min. After melting the sample, the gap was reduced to exactly 500 μm and the normal forces allowed to relax to a final level of less than 10%, removing the excess melt at the periphery of the plates, prior to starting the experiments. Logarithmic frequency sweeps were taken over a frequency range of 0.1 rad/s to 500 rad/s with 5 measurement points per decade. A fixed strain of 5% was used at test temperature of 240 °C and the results were expressed as plots of the complex viscosity versus angular frequency on a logarithmic scale.

Solvent sorption tests

Rectangular specimens, about 10 wide and 30 mm long, were cut from the compression moulded plaques and dried in a vacuum oven at 80 °C for 24 h. These were weighed and immersed in 150 ml of solvent, respectively chloroform and butyl acetate (analytical grades from Aldrich Chemical), for 72 h at room temperature. The specimens were then wiped with a paper tissue and reweighed.

Results and discussion

In Fig. 1 are reported plots of the weight increase (g/g) of the polyamide granules as a function of immersion time in methacrylic acid (MAA) solution in water relative to pure water and pure MAA. These show that solutions are absorbed more readily than the pure monomer. Moreover while at 10% monomer concentration the ultimate weight increase was about 35%, which occurred in 48 h, with a 30% monomer solution the maximum weight increase was about 100% and was achieved in only 3 h. These data provide, therefore, a clear confirmation that the monomer can be made to penetrate deep within the granules so that it would be possible to achieve a fairly uniform reaction with the radicals generated on the polyamide chains by the radiation treatment. As the desired extent of grafting was targeted to be in the range of 10–15%, the solution with monomer concentration of 10% was chosen to carry out the grafting reactions.

The micrographs in Fig. 2, on the other hand, reveal the presence of a very thin layer (about 12 μm) of a porous cortex around the granules during the grafting reaction. This corresponds, however, to only approximately 1% of the volume of the granules, and since the overall extent of grafting recorded is in the region of 11–13%, it can be deduced that the grafting reactions have indeed occurred deep into the granules. This has been affirmed by Chapiro and Stanner (51) and later by El-Azmirly et al. (50) on the radiation grafting of polyamide fibres with unsaturated monomer. These authors have also reported that the swelling

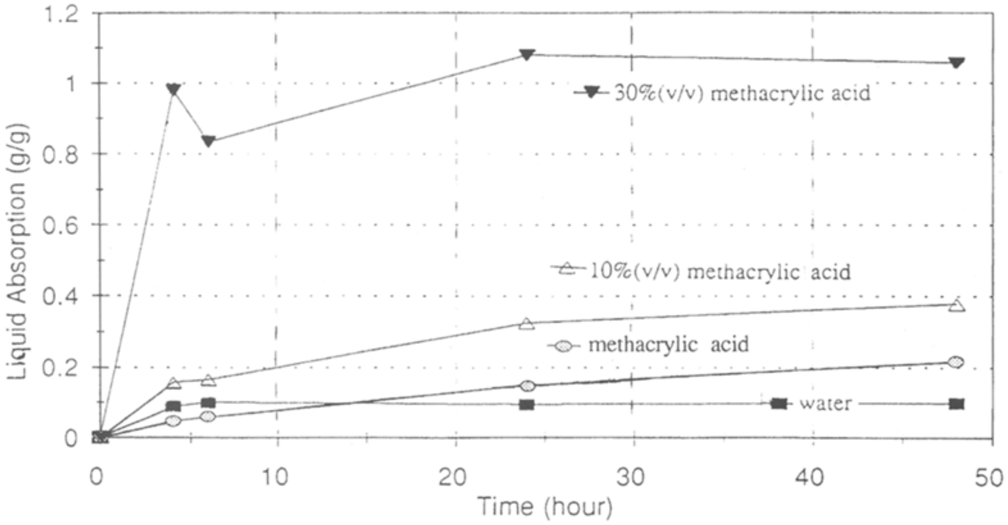


Fig. 1 Absorption of water, monomers and water solutions of monomers by Nylon 6 granules at 80 °C

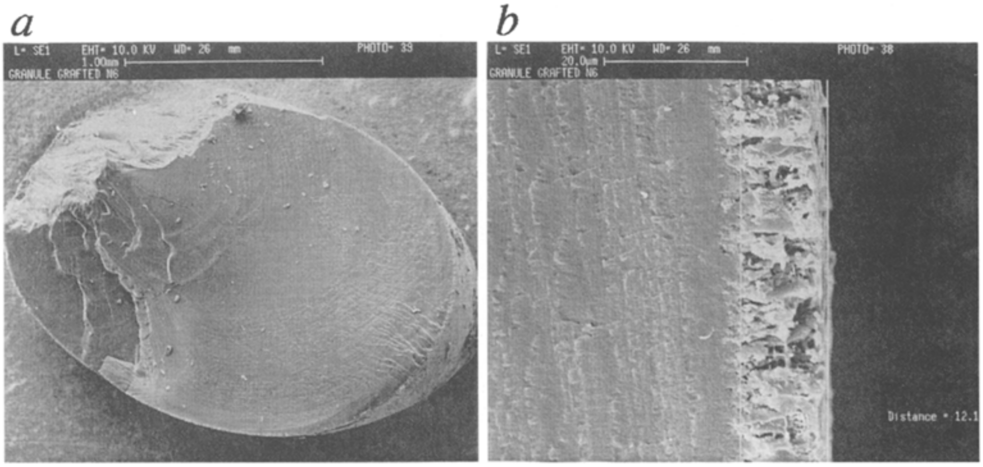


Fig. 2 Scanning electron micrographs of cross-section of Nylon 6 granules after grafting with 11 wt% methacrylic acid. (a) Overall view; (b) Surface layer

produced by the absorption of water and monomer contributes considerably to the achievement of a uniform distribution of grafted species through the mass. The porous skin observed on the surface of the Nylon 6 granules can be assumed to have resulted from the dissolution of free polyacrylic acid which is likely to be produced particularly in the outer surface layer owing to the very high concentration of monomer in these regions. For the same reason it can be presumed that in these outer layers the nature of the grafts may be oligomeric or polymeric, rather than unitary.

A careful inspection of the topology of the fractured surface of the granules suggests that the surface roughness appearing almost over the entire surface, except for a small area in the central region, may be indicative of the depth of penetration of the grafting monomer, which gives rise to the formation of a heterogeneous morphology. SEM examinations of the fractured surface of thin films of the same polymer (20 μm thick), grafted under analogous conditions and to the same extent of grafting, have revealed a heterogeneous morphology (see Fig. 3), which suggests that the distribution of the methacrylic acid grafts is not homogeneous but may be present in localized regions or clusters. Such a thin film is, obviously, expected to be grafted through the entire cross section in a fairly even manner [16]. These observation suggest that although an amount of polymer from the middle regions of the granules is almost certain to have not been affected by the grafting process, it is expected that the largest proportion of material has been grafted.

The thermograms in Fig. 4 and the thermal data in Table 1 show that the melting point and the heat of fusion and crystallization are reduced considerably as a result of the grafting reactions on the polymer chains, which also causes a delay in the onset of crystallization through the requirement of larger degree of supercooling. It is interesting to note, however, that when the acid groups are neutralized, to produce the corresponding Zn salt, the melting point (T_m) and peak crystallization temperature (T_c) are very close to that of the pure polyamide, whereas the degree of crystallinity remains at the same level as the parent acid-grafted polymer. This suggests that there is a fractionation of the amorphous polymeric salt from the ungrafted polymer; this represents the only direct evidence that grafting has not occurred in the central regions of the granules. The presence of free grafted polymer, also, cannot be excluded and, indeed, the small drop in T_m (see Table 1) may be considered an experimental verification for this hypothesis.

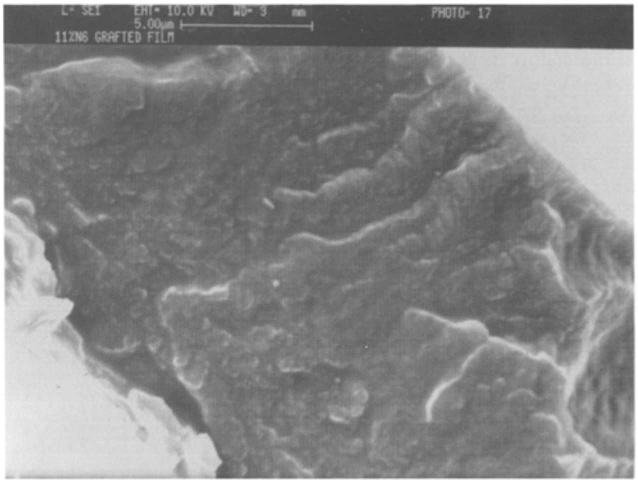


Fig. 3 Scanning electron micrograph of the fracture surface of a Nylon 6 film (20 μm thick) after grafting with 11 wt% methacrylic acid

Although it was impossible to monitor directly the formation of COO^-Zn^{2+} groups by FTIR as their absorption band at 157 cm^{-1} is masked by the strong absorption at 1564 cm^{-1}, corresponding to –NH bending of the amide II peak, the spectra in Fig. 5 show that the absorption band at 1714 cm^{-1} corresponding to COOH groups has almost completely disappeared and that a small band has developed at around 1800 cm^{-1} for the formation of anhydride groups.

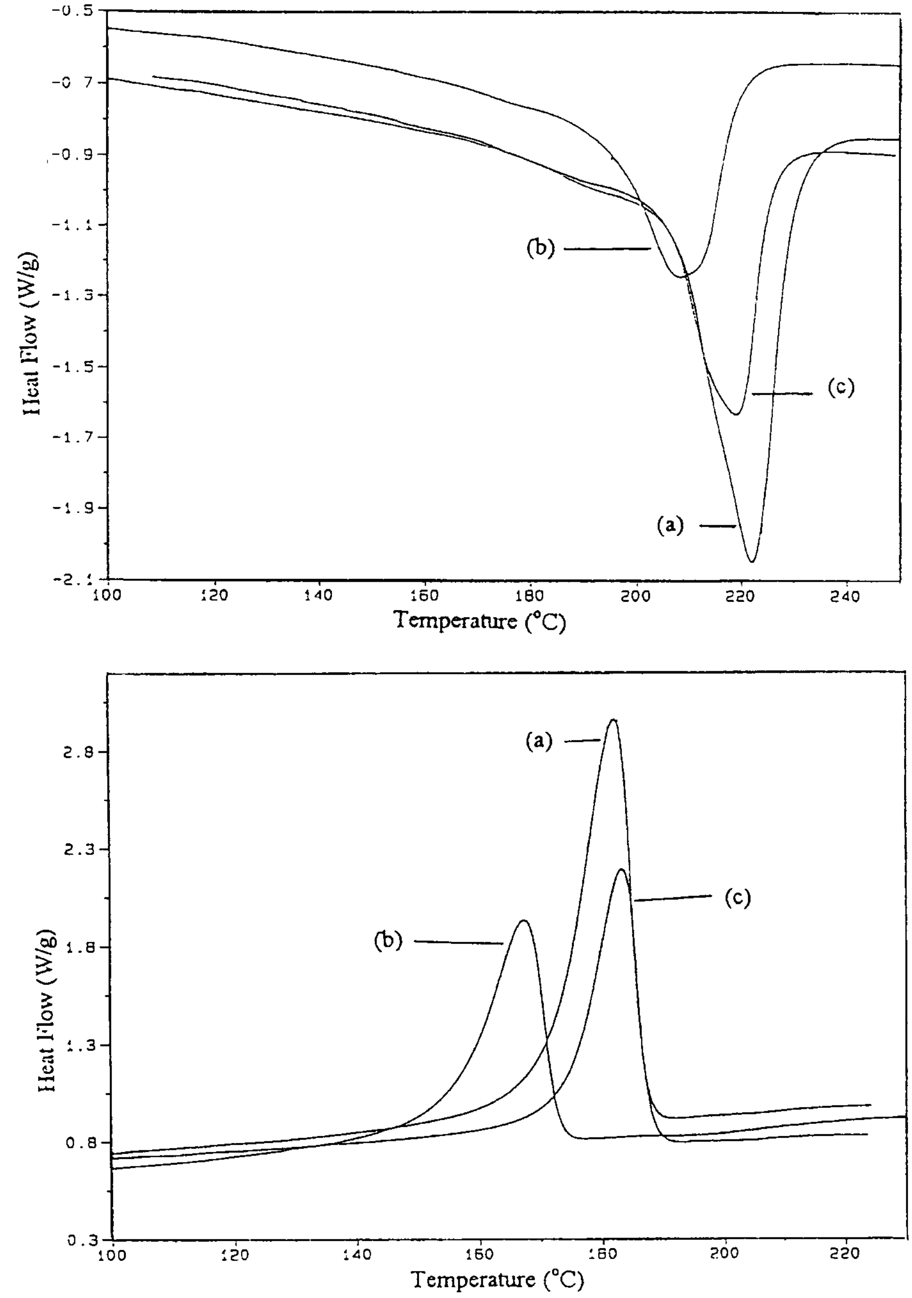
The dynamic mechanical spectra in Fig. 6 show that the acid-grafted polymer has a much higher T_g and a larger relaxation peak than the ungrafted polymer. These observations are consistent with the expected greater level of intermolecular attractions within the amorphous regions and the lower level of crystallinity found experimentally. The neutralized polymer, on the other hand, reveals the presence of two consecutive descrete relaxation processes with increasing temperature, one just below the relaxation peak for the pure polyamide and the other in the same region as the grafted polymer.

The curve for the ungrafted polyamide, to which was added the same amount of ZnAcAc, shows an even larger reduction in glass transition temperature and displays a similar dual relaxation behavior as the polymer salt.

Table 1 DSC data for (a) Nylon 6, (b) acid-grafted Nylon 6 (N6-g-MAA), and (c) Zn salt of acid-grafted Nylon 6 (N6-g-MAA/ZnAcAc)

	T_m (°C)	ΔH_f (J/g)	T_c (°C)	ΔH_c (J/g)	Crystallinity (%)
Nylon 6	222.0	87.6	182.2	72.6	45.9
N6-g-MAA	208.0	61.1	167.6	50.0	32.0
N6-g-MAA/ZnAcAc	218.8	62.7	183.2	54.8	32.9

Fig. 4 DSC thermograms. Top: Heating cycle; Bottom: Cooling cycle. (a) Nylon 6, (b) Nylon 6 grafted with 11 wt% methacrylic acid (N6-g-MAA), (c) Methacrylic acid grafted-Nylon 6 (11 wt%) + ZnAcAc (stoichiometric amount) (N6-g-MAA/ZnAA)



These are indicative of the occurrence of plasticisation by ZnAcAc, the extent of which decreases when added to the grafted polymer owing to its decomposition to produce the carboxylate salt. Although the stoichiometric amount of ZnAcAc was used the observed reduction in T_g indicates that the neutralization reaction did not procede to completion.

The relaxation region at the higher temperature for the three modified polyamides seem to occur over the same temperature region, albeit the hight of the peaks is different. The acid-grafted polymer displays the largest peak and the ungrafted polyamide/ZnAcAc mixture the smallest relaxation peak. Even in the latter case it seems that a certain amount of ZnAcAc decomposes to produce Zn ions which form complexes with the polyamide chains.

The results for these systems are at variance with those found by several others regarding the effects of inorganic salts on the secondary transitions of polyamides. In the latter cases it has generally been found an increase in T_g as a result of the enhanced molecular interactions

Fig. 5 FTIR spectra for (a) Nylon 6, (b) Nylon 6 grafted with 11 wt% methacrylic acid (N6-g-MAA), and (c) Methacrylic acid grafted-Nylon 6 (11 wt%) + ZnAcAc (stoichiometric amount) (N6-g-MAA/ZnAA)

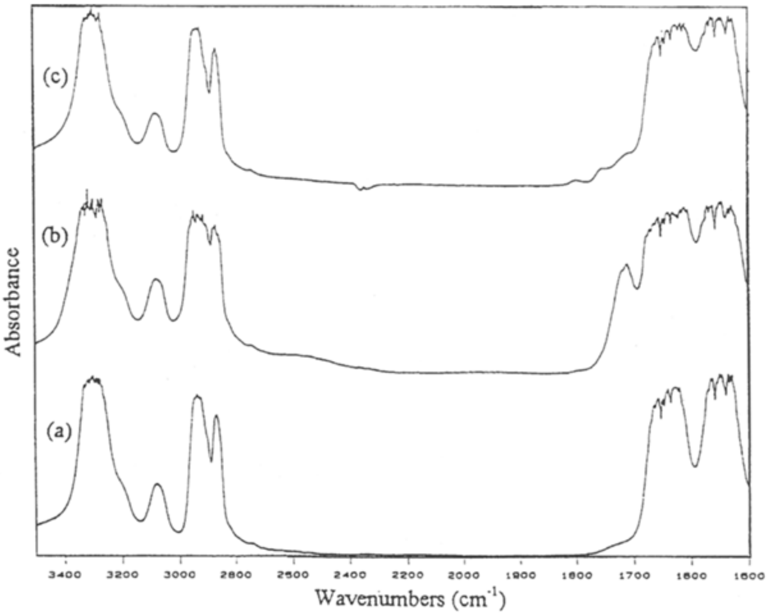
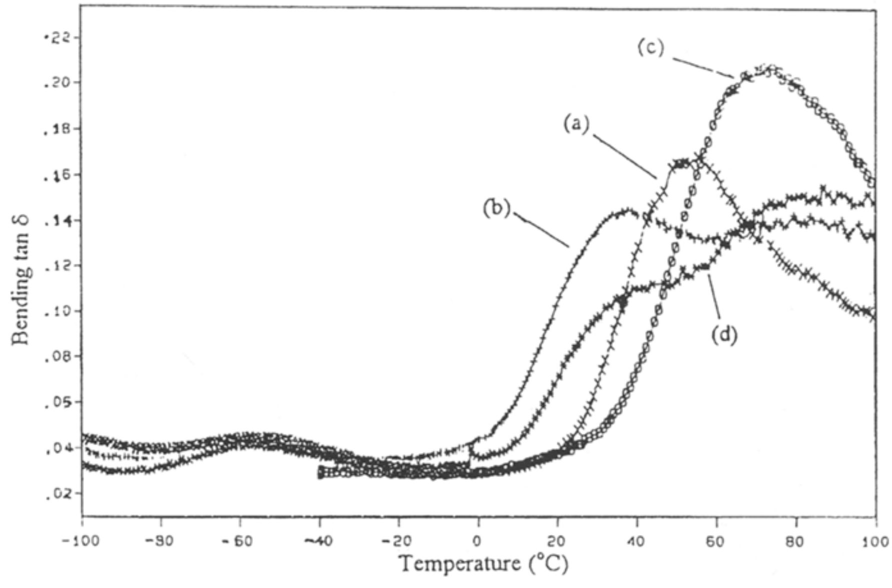


Fig. 6 DMTA spectra for (a) Nylon 6, (b) Nylon 6 + ZnAcAc, (c) Nylon 6 grafted with 11 wt% methacrylic acid (N6-g-MAA), and (d) Methacrylic acid grafted-Nylon 6 (11 wt%) + ZnAcAc (stoichiometric amount) (N6-g-MAA/ZnAA)



through complexation of the cations with the amide groups [7–9].

The rheological curves in Fig. 7 show that the irradiation treatment *per se* causes only a very small reduction in the molecular weight of the polymer. The addition of ZnAcAc to the ungrafted polyamide, on the other hand, causes a very large reduction in viscosity (more than one order of magnitude) without altering the pseudo Newtonian characteristics of the base polymer. This is a clear manifestation of a platicisation phenomenon arising from the presence of free ZnAcAc, which can account also for the reduction in the glass transition temperature, discussed earlier (Fig. 6), whereas the presence of a relaxation peak at higher temperatures, on the other hand, has to be associated with the presence of domains in which the intermolecular attractions are stronger and can be assumed to result from the direct complexation of Zn cations.

A drastic change in rheological behavior is observed for the acid-grafted polyamide and the corresponding neutralized samples. These become highly non-Newtonian and acquire a large increase in viscosity at low shear rates, both arising from the presence of chain branches and gels in the polymer [11]. The formation of chain branches and crosslinks occur from the reaction of the grafted acid

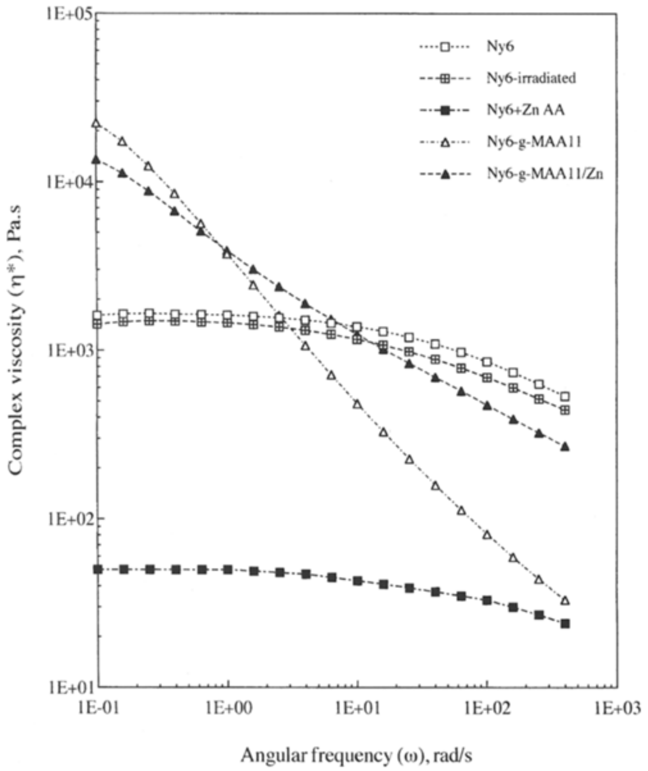


Fig. 7 Complex viscosity as a function of frequency for Nylon 6 and various modified systems, as specified in Fig. 6

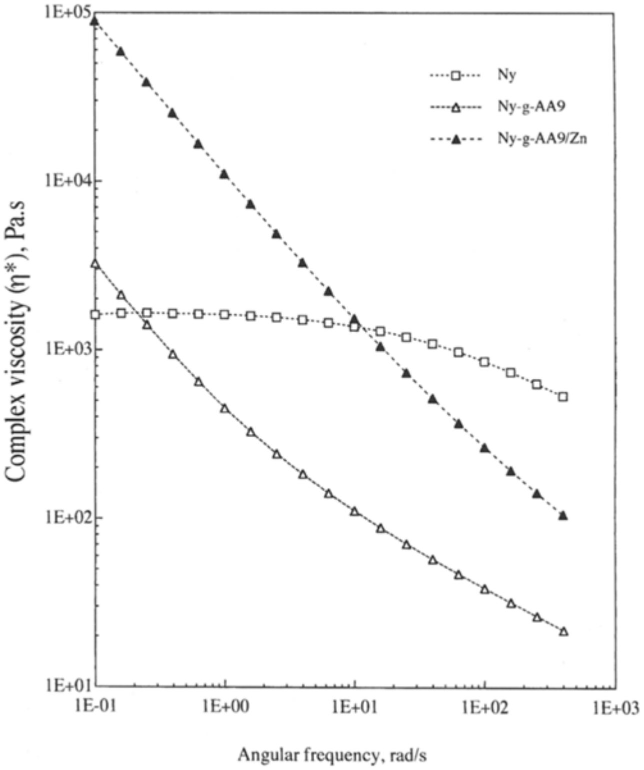


Fig. 8 Complex viscosity as a function of frequency for: (a) Nylon 6, (b) Nylon 6 grafted with 9 wt% acrylic acid (Ny-g-AA), and Nylon 6 grafted with 9 wt% acrylic acid and treated with a stoichiometric amount of ZnAcAc (Ny-g-AA/Zn)

groups with the existing terminal amine groups in the polyamide, as demonstrated by several authors on studies of blends of acid containing polymers with polyamides [17].

The curve for the neutralized polymer through the addition of ZnAcAc displays a slightly lower viscosity at low shear rates, but a much higher viscosity than the acid-grafted parent polymer at high shear rates. This provided further evidence that neutralization is not complete and that free ZnAcAc is present in the polymer, acting as a plasticizer. In this respect it is interesting to note that for systems where the polyamide was grafted with acrylic acid (instead of methacrylic acid) at about 9% level, in a series of related experiments, a considerably different behaviour was observed. The zinc salt of the acrylic acid-grafted polymer showed a very large increase in viscosity over the parent acid-grafted polymer over the entire range of shear rates. This suggests that the extent of ionization of the acid groups by ZnAcAc is much greater in the latter case due to the lesser steric hindrance around the COOH groups, which provide more favorable conditions for the interactions between the reacting species i.e. COOH and ZnAcAc (Fig. 8).

Table 2 Solvent absorption data (% weight increase) for tests in butyl acetate and chloroform on (a) Nylon 6, (b) carboxylic acid-grafted Nylon 6 (N6-g-MAA), and (c) Zinc salt acid-grafted Nylon 6 (N6-g-MAA/ZnAcAc)

	Butyl acetate	Chloroform
Nylon 6	– 29.0	3.67
N6-g-MAA	41.7	0.45
N6-g-MAA/ZnAcAc	0.22	1.13

Finally, the solvent sorption data for butyl acetate and chloroform shown in Table 2, demonstrate clearly that grafting of the polyamide with acid groups increases considerably the solvent resistance characteristics of the polymer. A further reduction in solvent absorption is experienced, for the case of butyl acetate after neutralization of the acids groups to produce the corresponding Zn salt. It is possible that for the case of the tests in chloroform, some species may have been extracted from the acid grafted polymer giving a lower weight increase than it would have otherwise been obtained. This would, therefore, mask the further reduction in solvent absorption for the corresponding zinc salt.

Conclusions

The conclusions that can be drawn from this study are as follows:

1) Grafting of methacrylic acid onto Nylon 6 can be readily carried out by preirradiating the polymer granules and subsequently immersing them in an aqueous monomer solution.

2) Zinc acetylacetonate is soluble in Nylon 6 and, therefore, is highly suitable for the neutralization of acid groups in polymer chains by melt mixing techniques.

3) A change in the rheological behavior from pseudo-Newtonian to highly non-Newtonian takes place during melt mixing. This is attributed to the reaction of acid groups with the amine terminal groups in the polyamide.

4) Very large improvements in solvent resistance are obtained as a result of the acid grafting reactions on the polyamide chains, and further improvements are achieved after subsequent neutralization to produce the corresponding zinc salt.

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