Low-temperature extrusion and properties of solid polyamide-6/calcium chloride complexes

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Solid polyamide-6/$CaCl_2$ polymer complexes with values of the salt/polymer repeat unit molar ratio (τ) as high as 40% were prepared by a new method involving room-temperature extrusion of a blend of polymer and salt powders in the presence of small amounts of methanol, followed by solvent elimination and drying. Complexation between polymer amide groups and salt ions was investigated by infra-red spectroscopy, wide-angle X-ray scattering and differential thermal analysis. Complexes were shown to absorb water more readily and to a greater extent than the parent polymer. The plasticizing effect of water on this type of material was demonstrated by dynamic mechanical measurements.

(Keywords: polymer/salt solid complexes; modified polyamides; ion–dipole interactions)

INTRODUCTION

Polymer–salt interactions have been widely studied[1], particularly in connection with protein denaturation[2–4]. Non-ionic polymers bearing polar groups such as ethers, ketones, amines and amides have been shown to complex with metal salts. Most of the involved salts were alkali and alkaline-earth metal halides, but a number of studies have been conducted with other cations (i.e. of transition and rare-earth metals) and anions (CN^-, SCN^-, ClO_4^-, $CF_3SO_3^-$, etc.).

Polymer/salt systems based on polyamides (PAs) have received relatively little attention. In the early 1940s, patents to Du Pont[5,6] claimed the invention of new solvents capable of dissolving PAs with at least two carbon atoms between successive amide groups. The claimed new solvents were solutions of inorganic metal salts, including thiocyanates, in lower, saturated or unsaturated aliphatic alcohols or mixtures thereof. However, the mechanism of PA solubilization was not explained in the invention.

In 1955, Barmby and King[7] found that PAs dissolved in molten arsenic and antimony trichlorides. On the basis of infra-red (i.r.) analyses, it was postulated that strong interactions between the trichlorides and the C=O groups of the polymer caused the N–H···O=C hydrogen bonds to break. Ford and Marshall[8] pointed out that the C=O stretching vibration frequency shift which followed dissolution of PAs in group IV tetrahalide/alcohol complexes persisted after elimination of the solvent. The authors ascribed this phenomenon to a direct coordination of the metal halide to the amide oxygen atom. Dunn and Sansom[9] likewise attributed the stress cracking of PAs by aqueous and non-aqueous solutions of metal salts to the formation of coordination complexes between the amide groups of the polymers and the ions resulting from salt dissociation. Frasci *et al.*[10] pointed out that the addition of low amounts of salt to PAs induced decreases in melting temperature and crystallinity which were not solely caused by a diluent effect. The authors concluded that there was an interaction between the polymer and the salt in the solid state.

In 1969, Sélégny *et al.*[11] studied the optical properties of chiral PAs. For solutions in saturated MeOH/$CaCl_2$, an anomaly in the optical rotatory dispersion curve was observed which was not detected for solutions in other solvents. These authors[12] also found that PAs with sufficiently high salt concentrations ($\tau = 40\%$) did not melt or burn. Thereafter, systematic studies of a complexation equilibrium were conducted[13–17] by investigating optical activity changes in solutions of PAs with varying proportions of MeOH, salt and polymer. The observed change in sign of the Cotton effect was attributed to the formation of ion/dipole adducts between salt molecules and polar amide groups of the polymer.

Models of the structure of PA/salt complexes generally postulate the existence of an interaction between cations and carbonyl groups, with the possible involvement of solvent molecules[9,18,19].

So far, the techniques used for preparing solid, non-ionic polymer/salt systems can be separated into two categories, according to whether they involve the use of a solvent or not. In the first category, complexation in solution followed by solvent elimination is the most commonly described process. Polymer and salt are dissolved either in the same solvent or in two miscible ones. PAs, for their part, are dissolved in a solution of the salt in a lower aliphatic alcohol[5,6]. Polymer/salt complexes in the solid state can then be obtained, either by solvent evaporation[8,10] or by coacervation. The latter procedure was used to precipitate fractions from solutions of PAs in MeOH/$CaCl_2$ by adding controlled amounts of non-solvent, e.g. salt-free ethanol[13]. These

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fractions were found to have different molar masses but the same τ values. Dissolution of the polymer does not seem to be a prerequisite of complexation. Salt/polymer complexes can be obtained by immersing polymer films in saturated solutions of salts in non-solvents of the polymer[9]. In the second category, Frasci *et al.*[10] prepared complexes of polyamide-6 (PA6) and alkali halides by heating a stirred blend of salt and polymer powders in an inert atmosphere. Ciferri *et al.*[20] extruded blends of PA6 pellets and CaCl$_2$ powder at 260°C and obtained fibres with low salt contents ($\tau \leqslant 5\%$). An interesting alternative is the preparation of polymer/salt complexes by bulk anionic polymerization of lactams in the presence of small amounts of LiCl ($\tau \leqslant 5\%$)[21] or CaCl$_2$ ($\tau \leqslant 7.5\%$)[22].

In the present paper, we describe a new method for preparing and processing complexes with high salt contents ($\tau \leqslant 40\%$) at temperatures well below the polymer melting temperature. In the first step, PA6 and CaCl$_2$ powders were blended. Then, small amounts of MeOH were added to the mass. Finally, the resulting homogeneous blend was extruded and dried to eliminate volatiles. The extrudates were evaluated with respect to salt and volatile contents, crystallinity, water absorption, thermal and dynamic mechanical properties and non-oxidative thermal degradation.

EXPERIMENTAL

Materials

MeOH (99% grade, Prolabo) was used as received. PA6 powder (R grade 'Orgamide®', Atochem) was used as received, occasionally after vacuum drying for 24 h at 90°C. CaCl$_2$ granules (Prolabo) were ground before use and the resulting powder, in some instances, was dried in an oven at 300°C for at least 24 h. Complete elimination of water of hydration was checked by thermogravimetric and differential thermal analyses. Unless otherwise specified, all powders had a mean particle size less than 250 μm.

PA6/CaCl$_2$ blends

In a typical experiment, PA6 (390 g) and CaCl$_2$ (130 g) powders were carefully mixed. The resulting blend was then transferred to a container and a definite volume (365 cm^3) of MeOH was added stepwise to the mass. The mass was kneaded for 15 min at 20°C and then fed into a single-screw extruder (Brabender) set to operate at 55 rev min^{-1} and equipped with a cylindrical die.

Part of the PA6/CaCl$_2$ extrudates was dried in a vacuum oven for 24 h at 90°C, then ground under nitrogen and further vacuum dried for 24 h at 130°C. Another part of the freshly extruded material was formed into 0.5 mm thick sheets by compression at 120°C. These sheets were then vacuum dried under the following programme: 120 h at 50°C, 20 h at 60°C, 75 h at 70°C and 113 h at 80°C.

METHODS

Fourier transform infra-red (FT*i.r.*) *spectroscopy*

*FT*i.r. spectra were recorded on a Perkin–Elmer 1760 spectrometer flushed with nitrogen. KBr discs (1 wt% sample, 99 wt% KBr) were made from dried powders with a mean particle size smaller than 40 μm.

Wide-angle X-ray scattering

The apparatus used for wide-angle X-ray scattering (WAXS) was equipped with a cobalt source. Kα_1 and Kα_2 wavelengths (mean value 0.17902 nm) were used in the reflection mode. The scattered intensity was recorded in a multichannel analyser. Dried powder samples were used. Diffraction bands were assigned to CaCl$_2$ and hydrates with the help of ASTM tables.

Differential thermal analysis

Differential thermal analysis (d.t.a.) of samples was conducted on a Du Pont 910 apparatus. Baseline stability was checked with two empty pans and was found to be satisfactory up to 300°C. Measurements made on an indium standard were accurate to less than 0.5°C, and so no temperature corrections were applied. Typically, the powdered material (4 mg) was heated up to 280°C at 10°C min^{-1}. The sample was then quenched down to -40°C by placing a cooling can filled with liquid nitrogen on top of the measurement cell. Finally, the material was again heated up to 280°C at 10°C min^{-1}. Heat flow curves were recorded during heating steps. A nitrogen flow was maintained during cooling steps.

Dynamic mechanical testing

PA6/CaCl$_2$ dogbone specimens for dynamic mechanical testing were stamped out from freshly made sheets. In the case of PA6, dry powder was pressed at 220°C and the resulting sheets had to be plasticized in water for 48 h to allow dogbone stamping. Both PA6 and some PA6/CaCl$_2$ specimens were dried as described above, whereas the remaining salted specimens were conditioned for 15 days at 25°C and 55% relative humidity (*RH*). In the area of homogeneous stress, dogbones were 0.5 mm thick, 4 mm wide and 20 mm long.

Dynamic mechanical tests were performed on a Rheometrics RSA2 apparatus in the tension–compression mode. The temperature-regulating fluid was a mixture of liquid and gaseous nitrogen that flowed over an electrical resistor. A static stress (about 10% of the maximum allowed stress) was superimposed upon the dynamic stress. The dynamic strain had an amplitude of 0.05% and its frequency was varied stepwise from 0.16 to 16 Hz at selected temperatures. The heating rate was set at 5°C min^{-1}.

Thermogravimetry

Thermogravimetry was performed on a Du Pont 951 thermogravimetric analyser. Samples (6 mg) were analysed at a heating rate of 5°C min^{-1} under nitrogen, the maximum temperature being set at either 280°C for tests aimed at checking sample dryness or 550°C for studies of non-oxidative thermal degradation. In the latter case, powders with a water content smaller than 0.2% were used.

Karl–Fischer analyses

Karl–Fischer analyses were performed on a Metrohm apparatus. Samples were dissolved in a 90/10 (v/v) *m*-cresol/MeOH mixture. For calibration purposes, known amounts of water were added to the same solvent system.

Water uptake

Comparable volumes of dry, powdered material were stored at 25°C over salt-saturated aqueous solutions of definite *RH*, namely NaCl ($RH=75.1\%$) and LiCl ($RH=11.1\%$). The mass gain was determined gravimetrically at definite time intervals.

RESULTS AND DISCUSSION

PA6/CaCl₂ blending and processing

On addition of MeOH, the PA6/$CaCl_2$ powder blend took on a dough-like texture along with a translucent, green-blue glowy appearance, and progressively became easier to knead. The resulting homogeneous mass was then used directly for low-temperature extrusion.

A preliminary study was conducted to evaluate the possible effects of the following factors on blend extrudability: (i) molar ratio τ; (ii) salt/MeOH molar ratio; (iii) extrusion temperature; and (iv) water content of PA6 and $CaCl_2$ powder precursors. Extrudability partly depended on the amount of heat generated within the machine by the extrusion process, because it was not possible to control the temperature of the mass within the extruder. An extruder jam was observed whenever excessive volatilization of the solvent occurred. Therefore, the effect of each of the selected parameters might have been different had the extrusion temperature been controlled.

Under the investigated experimental conditions, τ was found to have the biggest influence on extrudability. Blends with a τ value smaller than 30% could not be extruded. The effect of the salt/MeOH molar ratio appeared to be smaller. Lowering this ratio seemed to have a positive effect on extrudability. The other factors apparently did not bear any significant influence, at least within their variation domain. As a consequence, starting materials thereafter were not subjected to drying before extrusion. *Table 1* summarizes the conditions under which the PA6/$CaCl_2$ blends were found to be extrudable. Parts of the C and D extrudates were further ground or formed into sheets for later analysis.

Elimination and assay of volatiles

Thermogravimetry of undried, salted samples showed mass losses mainly within two temperature intervals, the first one centred at 70°C and the second centred at 130°C. After extensive drying, PA6/$CaCl_2$ powders still contained about 0.4 wt% low-molecular-weight material, which was shown thermogravimetrically to be eliminated between 175 and 200°C. By contrast, complete elimination of volatiles occurred below 100°C for pure PA6. This difference might result from the existence of stronger interactions between these small molecules and the PA6/$CaCl_2$ complex[9].

PA6/$CaCl_2$ sheets dried by the same procedure as that used for the extrudates underwent dimensional changes and even popped, probably because the elimination of volatiles was too quick. Consequently, conditions were determined which ensured drying while preserving geometrical integrity. PA6/$CaCl_2$ sheets from which specimens for dynamic mechanical testing were made contained about 7.8 wt% residual low-molecular-weight material. Karl–Fischer analysis showed that water made up about 20 wt% of these volatiles.

Table 1 Conditions for extrusion of PA6/$CaCl_2$ complexes

τ (%)	$CaCl_2$/MeOH molar ratio (%)	Drying	Extrusion temperature (°C)	Extrudate designation
30	8	No	50	A
30	13	No	30	C
30	8	Yes	30	B
40	10	No	50	D

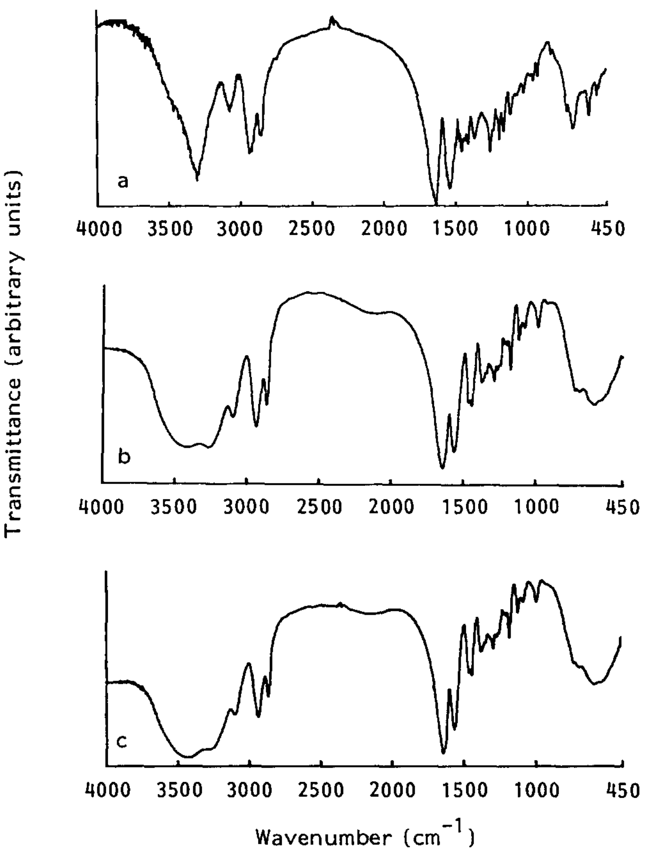

Figure 1 Infra-red spectra of (a) pure PA6, (b) sample C (PA6 + $CaCl_2$; $\tau=30\%$) and (c) sample D (PA6 + $CaCl_2$; $\tau=40\%$)

Infra-red absorption

The main differences between spectra (*Figure 1*) taken on powders of initial PA6 and salted samples (C and D) are summarized in *Table 2*. Comparisons between results from various sources[9,23,24] are difficult because of varying salt contents, salt solution compositions, extents of sample drying, sample physical states, etc.

For PA6, a broad absorption zone was observed above 3400 cm^{-1}, which might be caused by residual volatiles, either in the KBr pellets[25] or in the polymer (about 0.4 wt%). For samples C and D, absorption above 3400 cm^{-1} appeared to be more intense and to increase with salt content. Dunn and Sansom[9] ascribed these changes in absorption to free N–H groups, the corresponding hydrogen-bonding interactions being disrupted in the presence of the salt. Similar modifications were observed in i.r. spectra of copolyamide/$CaCl_2$ complexes which were prepared in alcoholic solutions[23]. Absorption in that range was considered to result in part from the formation of alcohol/Ca^{2+} solvates.

Spectra of salted samples C and D exhibited a downward shift of the 3300 cm^{-1} band and a convergence of the amide I (1640 cm^{-1}) and amide II (1540 cm^{-1}) bands, which occurred mainly through a 20 cm^{-1} upward

Table 2 Characteristic i.r. absorption bands for PA6 and PA6/CaCl$_2$ samples

Position of band		Salt content (mol%)	Assignment
PA6 (cm^{-1})	PA6/CaCl$_2$ (cm^{-1})		
3300	3260	30	N–H stretch (hydrogen bonded)
	3265	40	
3074	3088	30, 40	Overtone of amide II
1639	1637.50	30, 40	C=O stretch (amide I)
1542	1561	30, 40	C–N stretch + N–H bend (amide II)

shift of the latter. These observations agree with the previous studies on PA6/CaCl$_2$[24] and copolyamide/CaCl$_2$[23] complexes.

Crystallinity

The WAXS spectrum taken on PA6 (*Figure 2a*) exhibited two rather thin peaks centred at $2\theta = 22.2°$ and $2\theta = 26.6°$, characteristic of crystalline moieties. However, these peaks could neither be assigned to the γ crystalline form, for which a single band is usually detected[26], nor to the α (monoclinic) crystalline form of PA6, since reported values of the scattering angle for the latter form[26,27], after correction for the difference between Co and Cu source wavelengths, were, on the average, higher than ours by 0.7°.

A WAXS analysis was performed on a 60/40 wt% blend of PA6 and CaCl$_2$ as a blank. The observed bands (*Figure 2b*) were assigned to uncomplexed CaCl$_2$ and its hydrates.

By contrast, samples C and D exhibited spectra which were typical of essentially amorphous polymers (*Figures 2c* and *2d*). The fact that no crystalline CaCl$_2$ was detected might be ascribed to complexation of salt ions by the polar moieties of the polyamide, although ion clustering might also occur to some extent within the polymer matrix.

These findings agree well with previous data on PA6/CaCl$_2$ complexes formed by coacervation[17], as well as with those gathered on systems with a sufficiently high salt content[28,29].

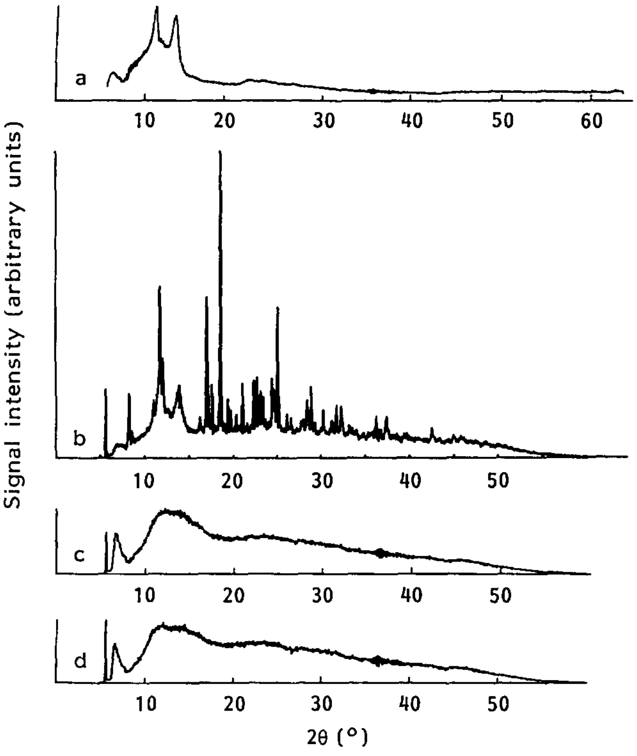

Figure 2 WAXS spectra of (a) pure PA6, (b) a powder blend of PA6 and CaCl$_2$ (60/40 wt%), (c) sample C (PA6 + CaCl$_2$; $\tau = 30\%$) and (d) sample D (PA6 + CaCl$_2$; $\tau = 40\%$)

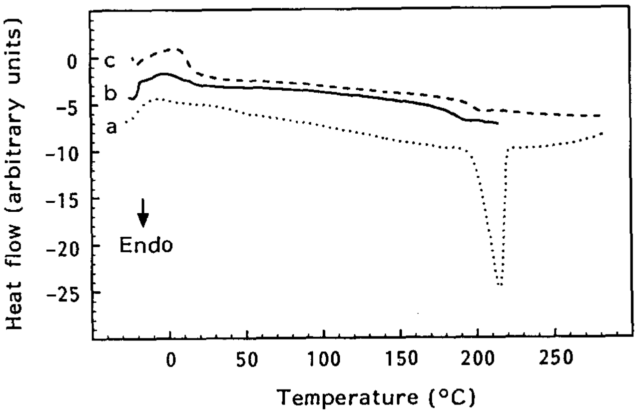

Figure 3 D.t.a. curves of (a) pure PA6, (b) sample C (PA6 + CaCl$_2$; $\tau = 30\%$) and (c) sample D (PA6 + CaCl$_2$; $\tau = 40\%$)

Thermal properties

Differential thermal analyses of thoroughly dried samples (water content $\leqslant 0.4$ wt%) were carried out in the −20 to 280°C range. Two heating runs were performed for each sample, the first one being intended to erase memory effects. Consequently, the following discussion will be based on the results obtained in the second heating runs. The PA6 thermogram (*Figure 3a*) exhibited a typical melting transition in the range 216–218°C, whereas under the selected experimental conditions no endotherm was detected in the temperature domain where the glass transition temperature (T_g) of PA6 was expected to lie (i.e. 40–52°C)[30]. In contrast, the thermograms for samples C and D (*Figures 3b* and *3c*) showed no melting transition but exhibited endotherms around 180 and 200°C, respectively. These endotherms might be ascribed to the occurrence of a glass transition. Although Turturro[31], assuming tetracoordination by the amide groups for LiCl and hexacoordination for CaCl$_2$, predicted a maximum T_g value of 92°C for fully coordinated PA6, it is noteworthy that higher T_g values have been observed for polyamide/CaCl$_2$ complexes prepared either by the dissolution–evaporation method[24] ($\tau \approx 25\%$; $T_g \approx 120°C$) or by internal mixing[32] ($\tau \approx 20$–30%; $T_g \approx 165$–$180°C$). The much higher T_g values which we found at salt contents well above the minimum theoretically required for complexation of all the available sites might be caused by ionic crosslinking. This type of crosslinking would also account for the different T_g values measured at the two CaCl$_2$ concentrations.

Dynamic mechanical properties

PA6 specimens were stamped from compression-moulded sheets rather than injection-moulded in order to avoid the marked anisotropy resulting from the latter process. For salted samples submitted to conditioning at 25°C and 55% *RH*, the volatile content was found to be 16 wt%. During dynamic mechanical measurements, the temperature-regulating fluid (a mixture of liquid and gaseous nitrogen) provided an oxygen-free and moisture-free atmosphere. A static stress was superimposed on the dynamic stress so that the total applied stress did not vanish at any time. Measurements were performed at dynamic strain values for which the material response could be considered linear. For PA6 these values were known from past experience, whereas for salted samples linearity was checked by testing predried C samples at two different temperatures (25 and 70°C) and two different frequencies (0.16 and 16 Hz). Later tests were conducted at dynamic strain values lying in the middle of the range thus determined. Maximum testing temperatures were kept below the values at which macroscopic changes occurred in specimens because of creep, volatile elimination, etc. These temperatures therefore differed for each type of material.

For predried C samples, values of the storage modulus E' in the glassy zone appeared to be close to those measured on dry PA6 (*Figure 4a*), thus showing little change in stiffness. The α relaxation zone was found to lie around 90°C, i.e. 20–25°C above the temperature for pure PA6 (*Figure 4b*). Above the α relaxation, E' decreased faster for sample C than for PA6 (*Figure 4a*). No plateau corresponding to a rubbery state was detected within the accessible temperature range.

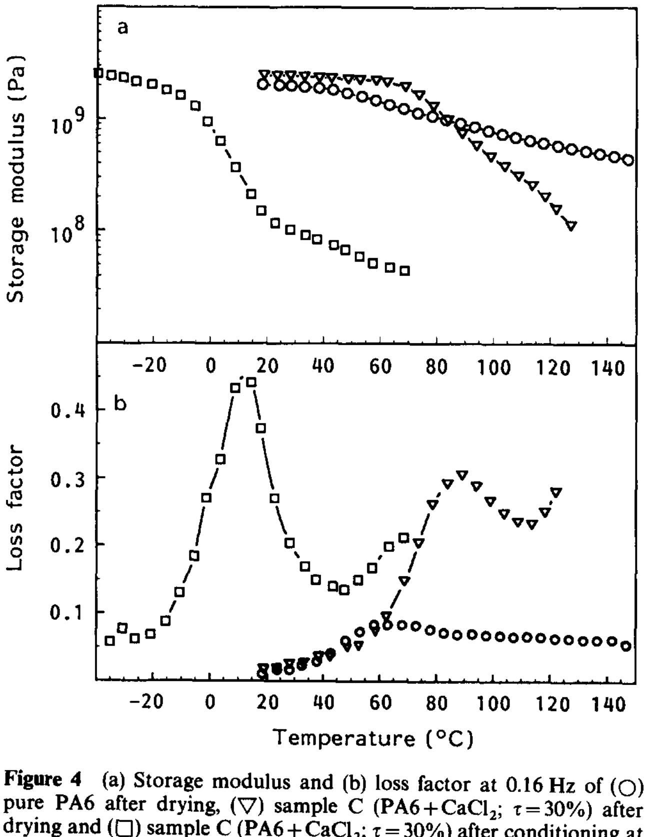

Figure 4 (a) Storage modulus and (b) loss factor at 0.16 Hz of (○) pure PA6 after drying, (▽) sample C (PA6+CaCl$_2$; $\tau=30\%$) after drying and (□) sample C (PA6+CaCl$_2$; $\tau=30\%$) after conditioning at 25°C and 55% *RH*

For samples preconditioned in a humid atmosphere, values of E' in the glassy zone remained comparable to those found for PA6 and predried C samples (*Figure 4a*). In contrast, moisture absorption caused an 80°C downward temperature shift of the α relaxation with respect to predried C samples, and a 50–55°C downward shift with respect to pure PA6 (*Figure 4b*). In the α relaxation zone and between 20 and 60°C, E' decreased faster than in the case of pure PA6. Above 60°C, the storage modulus of preconditioned samples tended to level off, while the loss factor increased.

The present dynamic mechanical data seem to be the first ever published on heavily salted PA6/CaCl$_2$ systems. More and Donald[33] merely mentioned slight variations in the loss factors of undefined PA6/CaCl$_2$ films whose salt contents probably were low, as evidenced by the small reported changes in crystallinity.

For predried PA6/CaCl$_2$ complexes in the glassy state, the curves shown in *Figure 4a* suggest that the presence of the salt somewhat balanced the loss of crystallinity. As far as the α relaxation is concerned (*Figure 4b*), a strong shift towards higher temperatures with respect to pure PA6 should have been observed according to the above-mentioned hypothesis of ionic crosslinking. Shifts of the α relaxation zone have indeed been reported for other PA6/salt systems[34–36]. The strong discrepancy between observed temperature shifts for the α relaxation (about 20°C) and glass transition (140–150°C) probably stems from the fact that the specimens differed with respect to their contents in plasticizing residual volatiles. Thus, specimens used for d.t.a. analyses had a volatile content of at most 0.4 wt%, whereas predried C samples used for dynamic mechanical analyses contained 7.8 wt% residual volatiles, including about 1.5 wt% water. Finally, the observed higher extent of the α relaxation for salted samples, as compared to pure PA6, has been reported elsewhere[37] and may be explained by the lack of crystallinity.

The high intensity of the α relaxation of preconditioned C samples and its shift towards lower temperatures, as compared with salt-free PA6 or with predried C samples, apparently reflects plasticization by sorbed water. Similar results on other PA6/salt systems have been published[38]. Above the α relaxation, the apparent tendency of the storage modulus to level off (*Figure 4a*) probably results from the progressive elimination of residual volatiles, which induces a stiffening of the material.

Non-oxidative thermal degradation

Curves of relative residual mass *versus* temperature were recorded for PA6 as well as for samples C and D (*Figure 5*). For samples C and D, non-oxidative degradation was found to start around 370°C, as compared to 300°C for PA6. According to the literature, the thermal degradation of PA6 should begin between 345 and 425°C, whereas somewhat lower temperatures have been reported for PA6 containing salts other than CaCl$_2$[29,39].

In contrast, the rate of degradation increased with the salt content (*Figure 5*). The temperatures of maximum degradation rate were 436, 421 and 414°C for PA6, C samples and D samples, respectively. The temperature of

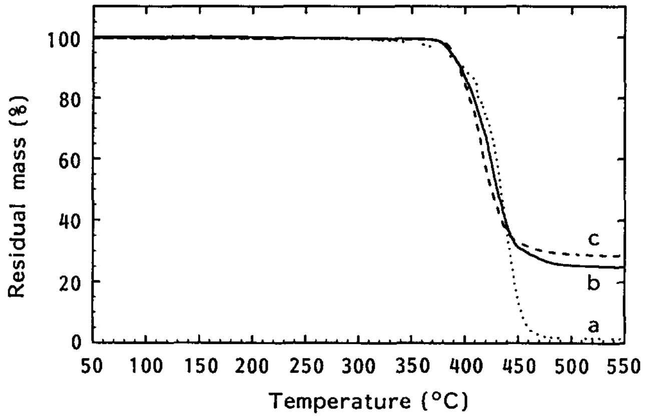

Figure 5 Thermogravimetry curves of (a) pure PA6, (b) sample C (PA6+$CaCl_2$; τ=30%) and (c) sample D (PA6+$CaCl_2$; τ=40%)

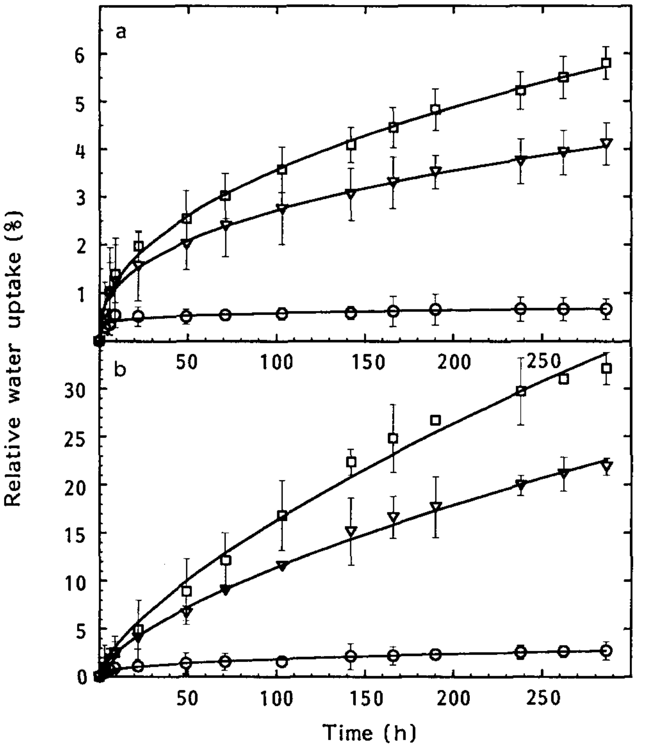

Figure 6 Relative water uptake plots of (○) pure PA6, (▽) sample C (PA6+$CaCl_2$; τ=30%) and (□) sample D (PA6+$CaCl_2$; τ=40%) at 25°C and (a) 11.1% *RH* and (b) 75.1% *RH*. Error bars correspond to 95% confidence intervals

maximum degradation rate for PA6 was reported by Ballistreri *et al.*[40] to lie around 425°C. Similar effects have been reported for other PA6/salt systems[29,39].

The value of the residual mass was around 1% for PA6, while values of 24.2 and 28.5%, which were obtained respectively for samples C and D, were in fair agreement with the corresponding salt mass fractions (23.1 and 28.6%) in the original materials.

Water sorption

Curves of mass gain as a function of time (*Figure 6*) showed that salted samples sorbed moisture more quickly and to a larger extent than pure PA6. The higher the salt content, the higher the moisture uptake. Apparently, equilibrium had not yet been reached after 300 h of storage, except for PA6 samples which had an equilibrium water content of 0.68% after storage at 11.1% *RH*. This last result is in agreement with previous work[41–43].

CONCLUSIONS

Our alternative method, based on the use of small amounts of solvent, allowed us to extrude solid complexes of polyamide-6 and $CaCl_2$ with high salt contents at temperatures far below the melting point of PA6. This method required much less solvent than the previously described dissolution–coacervation procedure.

Under the selected experimental conditions, extrudability was shown to depend on the salt/polymer molar ratio and, to a lesser extent, on the salt/solvent molar ratio. Complete elimination of plasticizing volatiles from salted extrudates appeared to be difficult, probably because some of the solvent molecules were engaged in the solvation of complexed species.

Evidence for complexation was gathered from the observation of salt effects on crystallinity, thermal properties and infra-red absorption. Salt-related T_g increases suggested reversible ionic crosslinking of PA6 chains by calcium ions. The results were very similar to those obtained on complexes prepared by the dissolution–coacervation method. The findings showed that handling large amounts of alcohols is no longer required to make PA6/$CaCl_2$ complexes with high salt contents.

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