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Stress cracking of nylon polymers in aqueous salt solutions

Part 2 *Nylon–salt interactions*

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A previous investigation (*J. Mater. Sci.* **22** (1987) 1707) has shown that nylon polymers are susceptible to stress cracking by aqueous calcium chloride at slightly elevated temperatures (50° C). In the present study, the nylon–salt interactions were investigated using thin films of both nylon 6 and nylon 6,6. Chemical, thermal, infrared and dynamic mechanical analyses were performed along with tensile property determinations. Weight gain measurements indicated that above 50° C large increases in sorption occurred for films immersed in either aqueous calcium, lithium, or magnesium chlorides. Both salt ions and water were absorbed at the elevated temperature. In contrast to these results, the data for sodium chloride indicated that only water was absorbed at all temperatures. The sorption process was shown to be physically reversible since the absorbed salt could be removed by immersion in pure water. Moreover the sorption of the salt solution at 100° C did not produce chemical degradation or significant crystallization of the nylons. At higher temperatures the absorbed salt did modify the recrystallization behaviour and increase the T_g of the nylons. Significant reductions in tensile modulus were observed for nylon films equilibrated in the salt solutions and tensile elongations at rupture were increased. The effect of increasing temperature and salt type on the sorption process parallels the previously observed stress-cracking activity of the aqueous salt solutions. It is therefore suggested that a plasticization-like mechanism is responsible for the salt-induced crazing of the crystalline nylons.

1. Introduction

Both organic liquids and inorganic salt solutions can cause environmental stress cracking of nylon polymers [1, 2]. Results discussed in a previous paper [3] demonstrated the role of polymer–liquid solubility in the stress cracking of nylon by organic solvents. Rapidly sorbed liquids were observed to plasticize the surface, allowing homogeneous stress relaxation to occur in competition with craze growth. To minimize this surface plasticization effect a subsequent study of nylon cracking in aqueous salt solutions employed a fracture mechanics approach [4]. With this technique the failure characteristics of razor-cut precracked specimens of nylon polymers were examined. Preliminary results indicated that salt-induced cracking occurred only at elevated temperatures (above 50° C). Moreover, the total failure time was determined largely by the craze growth kinetics. Crack growth occurred rapidly only after a crazed region had propagated across nearly the entire sample cross-section. In addition, the previous results showed that nylon 6 was more susceptible to cracking than nylon 6,6, while nylon 11 was essentially immune to stress cracking. Though differences in susceptibility for the various polymers can be attributed to differences in crystallinity and/or chemical structure (amide group concentration), the temperature dependence of the stress-cracking phenomenon is not readily explained by these factors.

The present study further addresses the mechanism of salt-induced cracking of nylon polymers by examining the sorption of salt solution in nylon 6 compared with nylon 6, 6 and by defining the effect of absorbed salt on the structure and properties of these polymers.

2. Experimental procedure

2.1. Materials

Extruded films of nylon 6,6 and nylon 6 were provided by E. I. duPont, Wilmington, Delaware, USA (Zytel 2781) and Allied, Morristown, New Jersey, USA (Capron ER20), respectively. The film thicknesses were 0.0027 cm for nylon 6, 6 and 0.0034 cm for nylon 6. Saturated aqueous solutions of sodium, calcium, lithium, and magnesium chlorides were prepared at room temperature. The latter was in the form of a hydrate, $MgCl_2 \cdot 6H_2O$. Analytical reagent grade salts were used. No attempt was made to compensate for the increased solubility of the salt at higher temperatures.

2.2. Weight gains

Weight gains were measured using the thin films to assess the percentage and rate of absorption in various inorganic salt solutions at 50, 75 and 100° C. Films were die-cut to give a 2.5 cm × 2.5 cm sample. Upon

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removal from the salt solution samples were dipped in water to remove excess salt on the film surface, blotted with tissues, and weighed. Preliminary experiments had shown that the brief immersion in water was necessary to give reproducible results. In addition, selected samples were immersed in water at 100° C to desorb the salt solution in order to assess the amount of extractable material in the films. The film weights were used as an indication of the completeness of the desorption process and the retained water was subsequently removed by drying at 100° C in a vacuum oven.

2.3. Chemical analysis

Nylon film samples which were equilibrated in salt solutions at various temperatures were also analysed for their cation content. The films remained in the heated salt solutions until just prior to the analysis to prevent desorption at room temperature. The technique involved dissolving the sample in hydrochloric acid and subsequently determining the calcium, lithium, sodium, or magnesium concentration with a Model 46 Atomic Absorption Spectrophotometer (Perkin-Elmer, Norwalk, Connecticut, USA). Based upon the measured ion content and the total weight gain, the partitioning of the salt and water in the films was calculated.

2.4. Molecular weight determinations

Gel permeation chromatography (GPC) curves of the nylons were obtained from samples dissolved in freshly distilled *m*-cresol heated to 60° C at a polymer concentration of 0.5 wt %. The filtered solutions were injected into a Waters 150-C ALC/BPC Chromatograph (Millipore Inc., Milford, Massachusetts). The columns contained polystyrene–divinyl benzene gels and were purchased from the Shodex Corporation of Japan. The columns were heated to 110° C. Molecular weights of the nylons were obtained from the GPC curves using a universal calibration curve. The Mark–Houwink coefficients (*K* and *a* values) for the nylons were calculated using injection-moulded nylon 6 samples of known molecular weights which were supplied by the Allied Corporation.

2.5. Infrared spectroscopy

A Perken-Elmer Model 283B infrared spectrometer was used to obtain transmission infrared spectra of thin films of nylon. Initial experiments with the extruded films indicated that they were too thick for transmission spectroscopy. Therefore, thinner films were prepared by casting from formic acid solutions (10 wt %). The films were dried in a vacuum oven at 100° C for 2 h to remove the solvent. Changes in the infrared spectra were recorded for films before and after equilibration in saturated aqueous calcium chloride at 100° C.

2.6. Differential scanning calorimetry (DSC)

DSC was employed to determine the effect of the absorbed calcium chloride solution on the T_g and the melting behaviour of the nylon. For this purpose scans were made at 20° C min^{-1} using a sample size of 4 to 5 mg. After the first heating to above the melting temperature, a repeated scan was made. Since most of the water is driven off during the first heating, the second DSC trace presumably indicates the effect of absorbed calcium chloride alone, whereas the first scan indicates the combined effect of absorbed salt and water.

The DSC was also used to determine the percentage crystallinity of nylon 6 and nylon 6,6. For these measurements 10 mg samples were used with the DSC in the time-base mode. Melting peak areas were measured with a planimeter and the corresponding percentage crystallinity was based upon heats of fusion of 191 and 196 J g^{-1} for nylon 6 and nylon 6,6, respectively. These values are the averages of several reported values for each polymer [5].

2.7. Dynamic mechanical measurements

The T_g was difficult to define from the DSC traces. To more clearly define the effect of the absorbed solution on the T_g, dynamic mechanical properties were measured using the Rheovibron DDV-II-C (Toyo Baldwin Co. Ltd.). Extruded film samples (0.5 cm × 3.0 cm) were run at a heating rate of 1° C min^{-1} and a fixed frequency of 11 Hz.

2.8. Tensile property measurements

Die-cut specimens (ASTM Type C) were equilibrated at 100° C in saturated aqueous calcium chloride and maintained at this temperature in solution until just prior to testing. Upon removal from the solutions, the films were dipped in water to remove excess salt on the surface, blotted with tissues and mounted in the Instron tester. During the few minutes required for this procedure, the film temperature had decreased to room temperature. Elongation was calculated based upon the initial grip separation. The crosshead speed was 5 mm min^{-1}.

3. Results

3.1. Weight gains

Figs 1 and 2 show the effect of temperature and time on the weight gains for nylon 6 and nylon 6,6 thin films immersed in saturated aqueous calcium chloride

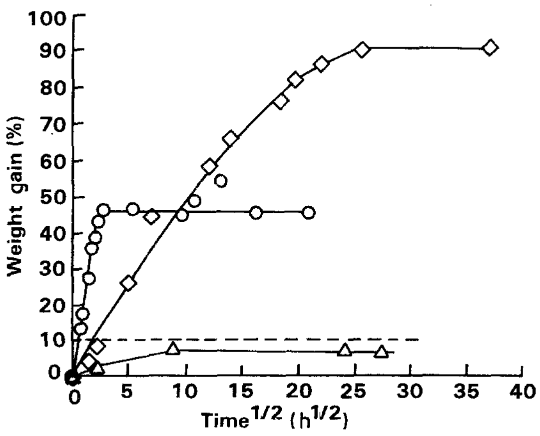

Figure 1 Effect of temperature on the weight gains of nylon 6 thin films in saturated aqueous calcium chloride: (△) 50° C, (◇) 75° C, (○) 100° C. For comparison the equilibrium level for nylon 6 in water at 100° C is shown by the dashed line.

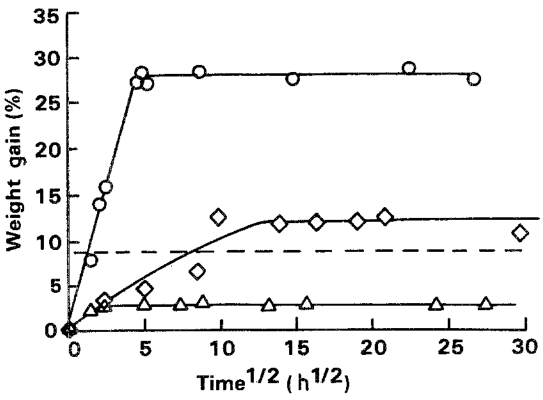

Figure 2 Effect of temperature on the weight gains of nylon 6,6 thin films in saturated aqueous calcium chloride: (△) 50° C, (◇) 75° C, (○) 100° C. For comparison the equilibrium level for nylon 6,6 in water at 100° C is shown by the dashed line.

solutions. Comparing the results for the two polymers it is noted that relatively low weight gains are observed at 50° C, though the nylon 6 absorbs more than the nylon 6,6. At higher temperatures significant increases are observed with equilibrium values being greater than the weight gains observed in pure water (dashed lines in Figs 1 and 2). For nylon 6,6 the equilibrium weight gain increases systematically as temperature increases. However, in the case of nylon 6 a greater weight gain occurs at 75° C than at 100° C.

Repeated measurements using multiple samples demonstrated that the reproducibility of the equilibrium weight gains was poor. For example, at 75° C nylon 6 films gave maximum weight gains ranging from 65 to 110%. This scatter is attributed to the distortion of the films when highly swollen and to the associated difficulties in rinsing and blotting the surfaces in a reproducible manner. Generally less scatter was noted (and less distortion) for nylon 6,6. Due to the inaccuracy of these data it is not possible to characterize the sorption kinetics (Fickian as against Case II) or to accurately assess differences in rate for the nylon 6 compared with nylon 6,6. However, in spite of the inaccuracy it is possible to conclude from these results that nylon 6 absorbs greater amounts of the calcium chloride solution at all temperatures compared to the nylon 6,6. Moreover, the effect of the increasing temperature on sorption parallels the effect of increasing temperature on stress cracking of both polymers in the salt solution [4].

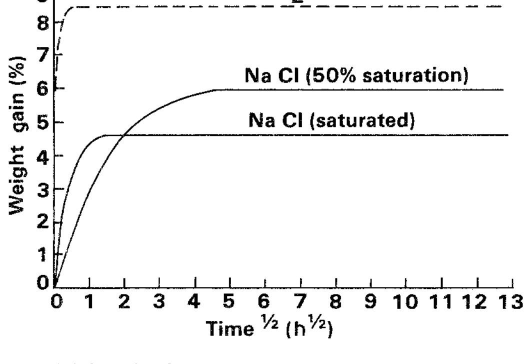

Figure 3 Weight gains for nylon 6,6 thin films in water or in aqueous sodium chloride solutions at 100° C.

TABLE I Equilibrium weight gains for nylon 6,6

Aqueous solution	Concentration (M)	Temperature (° C)	Weight gain (%)
NaCl	6.1*	100	4.6
$CaCl_2$	6.7*	100	28.5
LiCl	15.0*	100	25.9
$MgCl_2$	5.7*	100	23.8
$CaCl_2$	5.7	100	23.0
LiCl	5.7	100	8.7
$CaCl_2$	3.3	100	12.4
$CaCl_2$	6.7*	85	17.4
LiCl	15.0*	85	14.3
$MgCl_2$	5.7*	85	22.6

*Saturated solutions.

The weight gains for nylon 6,6 films immersed in water or aqueous sodium chloride solutions are shown in Fig. 3. As the concentration of salt increases the maximum weight gain decreases. Thus the sodium chloride acts as a diluent lowering the concentration (and thus the activity) of the water with a resultant decrease in the equilibrium sorption level of water. This behaviour differs markedly from that observed for nylon 6,6 films in the calcium chloride (Fig. 2).

Results for nylon 6,6 in lithium and magnesium chloride solutions were similar to that in the calcium chloride as shown in Table I. For these saturated solutions at 100° C the amount of absorbed salt and water was greater than 20% in all cases. This demonstrates that all three of these salt solutions interact strongly with the nylon in contrast to the results for sodium chloride.

Solutions having equimolar concentrations were also investigated by diluting the calcium and lithium chloride to give 5.7 M solutions, the same as the saturated magnesium chloride. Weight gains for nylon 6,6 equilibrated in these solutions are also shown in Table I. There is a significant reduction in the weight gain in the diluted lithium chloride compared to the saturated solution.

Data for nylon 6,6 in a calcium chloride solution diluted to 50% of the saturation (3.3 M) is also shown in Table I. The results suggest that the equilibrium weight gain is directly proportional to the amount of calcium chloride in the solution. For example, in 6.7 M calcium chloride a weight gain of 28.5% was observed, while in the 3.3 M solution the weight gain was 12.4%.

For direct comparison with craze growth kinetics data (to be reported [6]), weight gains were also measured at 85° C. Compared to the higher temperature, the equilibrium weight gains decreased, with magnesium chloride being the most soluble followed by calcium and lithium chlorides. The precision in the data is insufficient to determine whether the order of solubility at 100° C is reversed compared to 85° C.

Data for nylon 6 films are listed in Table II. The results indicate that in the 50% saturated (3.3 M) calcium chloride the nylon 6 showed a similar weight gain to the nylon 6,6 (12.9% compared with 12.4%, respectively). Also in the equimolar (5.7 M) solutions considerably less absorption occurred in the lithium chloride. At 55° C, for the saturated solutions, a significantly higher sorption of aqueous magnesium

TABLE II Equilibrium weight gains for nylon 6

Aqueous solution	Concentration (M)	Temperature (° C)	Weight gain (%)
$CaCl_2$	6.7*	100	44.8
$CaCl_2$	3.3	100	12.9
$CaCl_2$	5.7	100	25.0
LiCl	5.7	100	8.5
$MgCl_2$	5.7*	100	26.6
$CaCl_2$	6.7*	55	1.6
LiCl	15.0*	55	1.3
$MgCl_2$	5.7*	55	13.6

*Saturated solutions.

chloride was observed. Results at 55° C for the other two salt solutions were lower than expected. Repeated measurements indicated considerable scatter in results for calcium and lithium chlorides though maximum weight gains were always below 10%. In magnesium chloride the weight gains were consistently above 10% though the rate of sorption was not necessarily more rapid than for the other salts. This will be discussed further in conjunction with craze growth kinetics [6].

3.2. Chemical analysis

To more clearly define the composition of the sorbed solution, the equilibrated films were analysed for their sodium, calcium, lithium, or magnesium content. Weight gains were recorded for each film sample used in the analysis with immersion times based on the results in Figs 1 and 2. From the cation determination the total salt content (assuming electrical neutrality) and the water content were calculated. Tables III and IV list the measured results along with the calculated values. At 50 and 100° C in calcium chloride, replicate experiments were performed, and in these cases the values given in Table III are averages. As noted previously, considerable scatter occurred for nylon 6 equilibrated at 75 or 100° C, but not for nylon 6,6.

For the calcium chloride (Table III) the analysis confirms that both salt and water were absorbed into the nylon at all temperatures. A significant increase in the amount of the absorbed calcium chloride occurred above 50° C, paralleling the increase in overall weight gain for both materials. An apparent maximum weight gain was noted at 75° C for the nylon 6 (Fig. 1). On the other hand, the partitioning of the salt solution ($CaCl_2/H_2O$ molar ratios) in each of the nylon polymers indicates that the effective concentration of salt solution in the polymer films increases systematically with temperature. A much greater temperature dependence is indicated for the nylon 6,6 even though the weight gains are generally lower. In all cases, the concentration in the films is less than the concentration of salt in the saturated liquid. For example, saturated aqueous calcium chloride is 6.7 M, which is significantly above the salt/water concentrations in the nylon, even at 100° C.

For nylon 6 the increase in temperature from 50 to 75° C was seen to affect the total weight gain in a much more dramatic manner than it affected the relative amounts of calcium chloride and water. The reason why the total weight gain decreased at 100° C compared to 75° C is not known; however, the distortion of the films and lack of precision suggest further studies are needed to confirm this. Comparing these results with the previous stress-rupture data [4], it is noted that the total weight gain correlates well with stress-cracking activity rather than the salt concentration in the nylon.

For lithium and magnesium chloride solutions data were taken only at 100° C for nylon 6,6. Results are given in Table IV. In both cases the analysis confirms that the increased weight gain, compared to pure water, is due to the sorption of both salt and additional water.

The weight gain and chemical analysis results demonstrate that a partial solvation of the nylon matrix occurs at these slightly elevated temperatures in aqueous salt solutions. Whether the solvation is confined to the amorphous (rather than crystalline) regions, and whether it induces chemical degradation or a true plasticization of the nylon (as water does), are discussed in the following sections.

3.3. Molecular weight determination

The number average ($\bar{M}_n$), weight average ($\bar{M}_w$), and z-average ($\bar{M}_z$) molecular weights of the extruded nylon films are given in Table V. The effect of calcium chloride exposure on the molecular weight was examined to assess whether degradation of the polymer occurred in the salt solution. Since some uncertainty existed in the initial molecular weight averages of the nylon 6 film, studies were conducted using the nylon 6,6 film. The results in Table V indicate that no degradation occurred after four days of immersion at 100° C for the nylon 6,6. Considering the relatively rapid time scale of the environmental crazing and cracking [4], this result suggests that chemical attack of the nylon by the salt solution is not responsible for the salt-induced cracking. After 30 days of immersion, there is some indication that the nylon is degrading since the molecular weight is decreasing. In view of the

TABLE III Analysis of nylon films equilibrated in saturated aqueous calcium chloride

Sample	Temperature (° C)	Weight gain (%)	Composition (wt %)			Concentration in film (M)
			Ca	$CaCl_2$	H_2O	
Nylon 6	50	7.8	0.6	1.8	5.5	3.0
	75	78.2	4.5	12.3	31.6	3.5
	100	42.0	3.1	8.5	20.4	3.9
Nylon 6,6	50	3.0	0.2	0.6	2.4	2.4
	75	22.0	2.3	6.3	11.7	4.9
	100	28.5	3.1	8.5	13.8	5.6

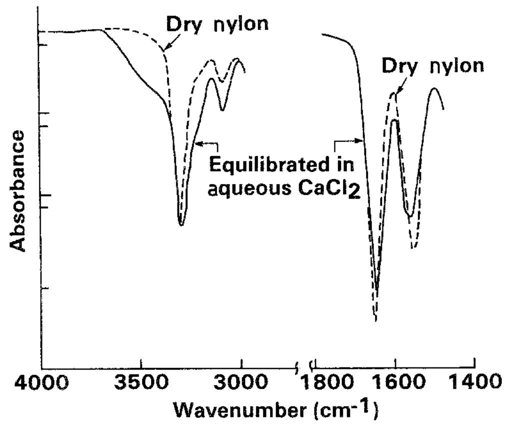

Figure 4 Infrared spectra of cast nylon 6 film before and after equilibration in saturated aqueous calcium chloride at 100° C.

magnitude of the decrease, even after 30 days, it is reasonable to presume that the previously observed effect of the salt solution on stress-rupture behaviour in short time exposures is primarily physical in nature rather than an irreversible chemical degradation. Of course, at the lower temperatures, such as 50 or 75° C, degradation is even less likely to occur.

3.4. Infrared spectroscopy

Since nylon 6 generally absorbed larger amounts of the salt solution, infrared studies were conducted using this polymer. The infrared spectra of nylon 6 both before and after equilibration in saturated aqueous calcium chloride at 100° C are shown in Fig. 4. Changes in the shape and/or location of the absorption bands are observed at 3300, 1640 and 1550 cm^{-1}. These bands are attributed to vibrations of –N–H, –C=O, and –C–N molecules in the nylon chain, respectively [7]. The slight shift in frequency, or broadening, for each of these bands is in the direction expected for a change in environment of the molecules from an unassociated state to a more associated state [8]. Similar band-shifts are not observed for nylon 6 saturated with water, and non-polar diluents induce an opposite shift. Since an extensive intermolecular hydrogen bonding network is known to exist in nylon polymers [9], the infrared results suggest that the calcium chloride solution does not simply disrupt this network, but in fact replaces it with some form of association of the hydrated ions and amide groups in the nylon.

The infrared spectra of the salt-equilibrated film also shows a broad band at 3400 cm^{-1} as a shoulder on the sharper –N–H absorption band at 3300 cm^{-1}. In a previous study of a cast nylon film which contained only calcium chloride, (i.e. no water) an intense broad absorption was also observed at this frequency [10]. This was attributed to free, or non-hydrogen-bonded, N–H groups in accordance with the results of Trifan and Terenzi [9] for salt-free nylon. However, the 3400 cm^{-1} absorption reported here may also be attributed to the O–H groups of the absorbed water. A similar, though less intense, absorption was noted in this study in the infrared spectra of a nylon 6 film which was saturated with water. Also, vacuum drying at 100° C decreased the intensity of this band. Assuming that this band at least in part is due to free N–H groups, the existence of such groups seemingly contradicts the extensive broadening of the 3300 cm^{-1} band on the lower-frequency side. That is, the absorbed calcium chloride would appear to be causing an increase in both free N–H and more associated N–H. To avoid this contradiction it is tentatively suggested that the 3400 cm^{-1} band is entirely due to the large amount of absorbed water in the nylon films used in this study.

3.5. Differential scanning calorimetry

The DSC trace of a dry nylon 6 film is shown in Fig. 5. A slight endotherm occurred above 100° C, perhaps due to release of residual moisture or other impurity. The major transition for the polymer is the crystalline melting endotherm at 220° C with an indication that some recrystallization occurred above 160° C (exotherm just prior to melting). A repeated run of the dry nylon after melting and quenching gave a similar result to the initial trace.

The DSC analysis of nylon 6 after equilibration in saturated calcium chloride at 100° C is also shown in

TABLE IV Analysis of nylon 6,6 films equilibrated in saturated aqueous salt solutions at 100° C

Solution	Concentration (M)	Weight gain (%)	Composition (%)			Concentration in film (M)
			Cation	Salt	Water	
$CaCl_2$	6.7	28.5	3.1	8.5	13.8	5.6
LiCl	15.0	25.9	0.6	3.4	17.1	4.7
$MgCl_2$	5.7	23.8	1.1	4.4	14.8	3.1
NaCl	6.1	4.6	0	0	4.6	–
H_2O	–	8.5	0	0	8.5	–

TABLE V Molecular weights of nylon films

Sample	Description	$\bar{M}_n$ ($\times 10^4$)	$\bar{M}_w$ ($\times 10^4$)	$\bar{M}_z$ ($\times 10^5$)
Capron ER20	Extruded film nylon 6	4.72	~ 60*	~ 800*
Zytel 2781	Extruded film nylon 6,6	4.30	14.4	4.78
Zytel 2781	4 days at 100° C in sat. $CaCl_2$	4.32	14.5	4.67
Zytel 2781	30 days at 100° C in sat. $CaCl_2$	3.96	12.3	3.99

*Sample had a high molecular weight tail giving uncertain $\bar{M}_w$ and $\bar{M}_z$.

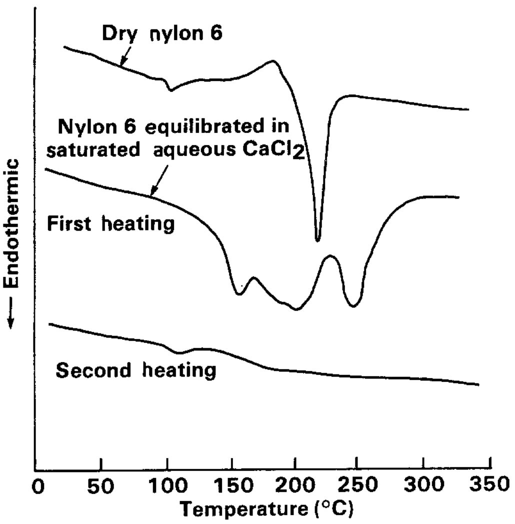

Figure 5 Differential scanning calorimetry traces of nylon 6 film showing the effect of absorbed aqueous calcium chloride on the melting behaviour.

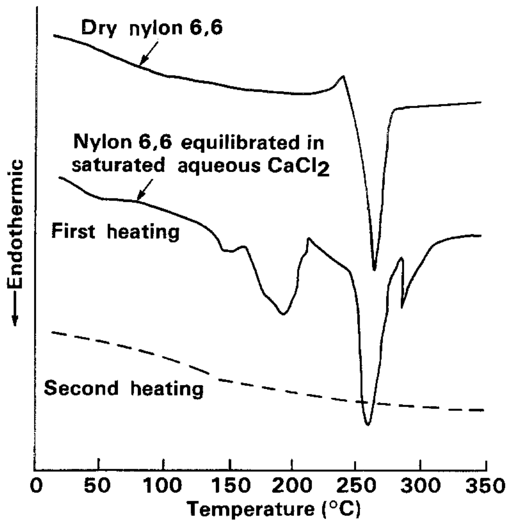

Figure 6 Differential scanning calorimetry traces of nylon 6,6 film showing the effect of absorbed aqueous calcium chloride on the melting behaviour.

Fig. 5. The initial trace is complex, particularly above 150° C, where multiple melting peaks are observed. After melting and quenching, the repeated run indicates that the nylon 6 film was completely amorphous with some indication of a broad T_g above 150° C. The latter is 100° C above the normal 50° C T_g of nylon 6. The effect of absorbed salt (in the absence of water) in preventing crystallization of nylon 6 has been previously reported [11]. Presumably much of the water is evaporated during the first DSC scan leaving primarily a nylon–salt mixture. The complex melting behaviour observed in the initial DSC heating is believed to be an indication that recrystallization occurs more readily for the nylon 6 containing both salt and water, in contrast to the effect of salt alone. Films equilibrated at 50 and 75° C also exhibit the multiple melting peaks, and also could be quenched to an amorphous or near-amorphous condition. However, if the equilibrated films were dried in vacuum to partially remove water prior to DSC analysis, the resultant DSC traces show much less intense premelting phenomena.

Similar DSC results were observed for nylon 6,6 films. Fig. 6 shows the DSC scans for the control and the salt solution-equilibrated film. Although the nylon 6,6 melts at a higher temperature than nylon 6 (265 compared with 220° C), the effect of absorbed salt and water is the same; namely, a complex melting and recrystallization was noted which is absent in the dry nylon 6,6. Again the reheat showed that the melted and quenched sample was amorphous (or melts above 325° C) with indications of a T_g near 125° C. As with the nylon 6, it is suggested that the initial effect of the salt and water is to promote recrystallization of the nylon 6,6 at lower temperatures (above 135° C); however, once the water has evaporated, the salt alone inhibits the recrystallization process allowing a quenched sample to be totally amorphous.

The DSC results do not establish whether the nylon films are less crystalline or more crystalline after equilibration in the saturated aqueous calcium chloride at 100° C. To address this question, crystallinity measurements were made for films which were soaked in water after prior equilibration in salt solutions. The water soaking removed the absorbed calcium chloride as verified by weight losses. To remove the water, the films were dried to constant weight in vacuum at 100° C. In the subsequent DSC measurements, these films gave a single melting endotherm, similar to unmodified dry nylon, with no evidence of lower melting forms and with relatively small recrystallization exotherms.

Crystallinity determinations are given in Table VI along with the amount of extractable material. The

TABLE VI Percentage crystallinity and extractables for equilibrated nylon films

Sample	Treatment	Crystallinity (%)	Extractables (%)
Nylon 6 (film)	None	26	–
	Water, 50° C	28	0
	Water, 100° C	30	1.4
	$CaCl_2$, 75° C	28	0.7, 0.7*
	$CaCl_2$, 100° C	33	3.2, 5.6*
Nylon 6 (injection-moulded)	None	31	–
Nylon 6,6 (film)	None	29	–
	Water, 50° C	34	0
	Water, 100° C	33	1.2
	$CaCl_2$, 100° C	32	0, 3.2*
Nylon 6,6 (injection-moulded)	None	37	–

*Repeated measurement.

latter refers to the amount of material extracted from the nylon films by water or by the aqueous calcium chloride during the weight gain experiment. For example, the nylon 6 film in water at 100° C evidenced a 1.4% loss in weight (determined after vacuum drying). Only small increases in crystallinity are observed due to immersion in the salt solution. Similar increases are noted after immersion in water. The uncertainty in these measurements is at least $\pm 2\%$ based upon repeated runs of the same sample. Also, if the extracted material is assumed to contribute to the amorphous content initially, then extracted samples should evidence an apparent increase in crystallinity. Based upon these considerations, it is clear that only minor changes, if any, occur in crystallinity as a result of the equilibration of either type of nylon in calcium chloride solutions. For comparison, a sample of nylon 6 annealed at 200° C in air for 24 h was determined to have a crystallinity of 48%. Thus, a significant increase is attainable for the nylon, but apparently the rate of recrystallization is not significant at 100° C even for the highly swollen films.

Based upon these results, the complex melting phenomenon in the DSC scans is attributed to processes which occur at higher temperatures during the heating of the samples in the DSC. At 100° C (and below) the sorption of salt solution by the nylon is considered to be a physically reversible process with no large-scale changes in crystallinity resulting from the penetration of the solution into the amorphous regions of the nylon. It is also apparent from these measurements that the difference in crystallinity between nylon 6 and nylon 6,6 is not significant enough to explain the weight-gain differences or the corresponding susceptibility to stress cracking noted previously [4].

3.6. Dynamic mechanical measurements

The DSC results could not be used to clearly define the T_g of the nylon and the effect on T_g of the absorbed salt solution. The results did suggest that the salt alone increases the T_g, presumably due to the stiffening effect of the amide–salt complex formation reported by others [11]. Water, on the other hand, is well known to lower the nylon T_g, in the usual manner that diluents plasticize amorphous polymers [12]. The combined effect of absorbed salt and water has not been reported. Rheovibron measurements were therefore employed to reveal the effect of the absorbed salt solution.

Fig. 7 shows the change in loss factor, tanδ, with temperature for nylon 6,6 which was previously equilibrated at 100° C in saturated aqueous calcium chloride. Also shown is the effect of vacuum drying to remove water from the film, thereby indicating the influence of the calcium chloride alone. Following the usual convention, the various transitions in nylon are labelled α, β and γ with the α transition being identified with the glass transition of the nylon [13].

For the dry nylon the glass transition can be seen to initiate above 50° C with the peak in tanδ at 83° C. The absorbed calcium chloride solution dramatically shifts the T_g peak to higher temperatures (peak in tanδ at 130° C) and also causes a significant broadening of the peak. Such a shift in T_g suggests a restricting effect of the absorbed salt–water mixture on molecular motion in the amorphous phase of the nylon. However, due to the possible loss of water from the film during the Rheovibron test the exact location of the T_g of the equilibrated film is uncertain. Also the onset of T_g may not be shifted as much as the tanδ peak.

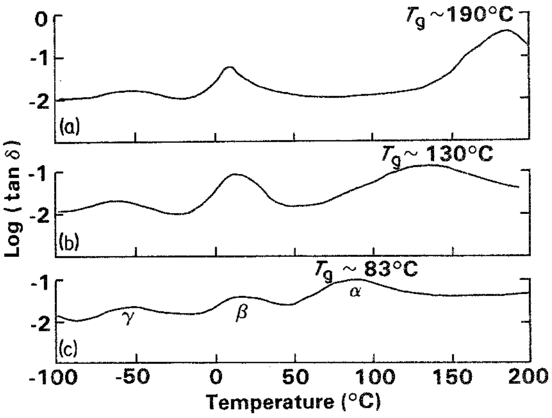

Figure 7 Dynamic mechanical loss factor (tanδ) against temperature showing the effect of absorbed calcium chloride solution on the transitions of the nylon 6,6. (a) equilibrated in $CaCl_2$, then vacuum-dried to remove water; (b) equilibrated at 100° C in saturated aqueous $CaCl_2$; (c) dry sample.

After water is removed from the swollen nylon 6,6 film by vacuum drying, the T_g tanδ peak is shifted to much higher temperatures with the maximum in tanδ near 190° C. This shows the strong effect of the salt alone in complexing with the nylon chains to completely suppress the segmental chain motions which normally would have initiated above 50° C. The T_g increase agrees with the DSC results reported here and by others [11]. These results suggest that the salt solution does not act as a conventional plasticizer for nylon; in other words, the T_g decrease expected from the large amount of absorbed solution is offset by the strong interactions with the salt ions.

The beta and gamma transitions are also affected by the absorbed salt solution with the beta loss peak especially being enhanced. Absorbed water has been reported to have a similar effect on this transition which is associated with carbonyl group motion [13]. Fig. 7 demonstrates that the removal of water causes a noticeable sharpening of the beta tanδ peak while the gamma tanδ peak is unchanged. In view of the latter being associated with local oscillations of non-polar methylene groups [13], this observation is not surprising and in fact confirms the infrared results in suggesting an association of the salt ions with the polar portions of the nylon.

3.7. Tensile property measurements

Table VII lists the properties of nylon 6 and nylon 6,6 thin films before and after equilibration in saturated calcium chloride at 100° C. Modulus and strength values were calculated using the dimensions of the dry films. A large decrease in modulus was observed for both nylons as a result of the absorption of aqueous calcium chloride. Lower strengths were also observed,

TABLE VII Tensile properties of nylon films equilibrated in saturated aqueous calcium chloride at 100° C*

Sample	Treatment	Modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
Nylon 6	Vacuum-dried control	1.06	42.4	8.0
	$CaCl_2$, 100° C for 1.5 h	0.32	24.8	18.5
Nylon 6,6	Vacuum-dried control	2.03	108.1	125
	$CaCl_2$, 100° C for 24 h	0.83	101.9	178

*Modulus and strength were calculated using dimensions of dry films, not swollen film dimensions.

especially for the nylon 6, and elongations at break were also increased for both polymers.

The tensile property measurements suggest that the effect of the diffusion of salt solution into the amorphous regions is to weaken the nylon matrix. Since these measurements were performed at room temperature, it must also be expected that at elevated temperature the effects reported here would be further enhanced. Thus even lower moduli and loss of load-bearing capability would be anticipated due to the absorption of salt solution at 50 to 100° C.

The reproducibility of the tensile property measurements was demonstrated by replicate experiments with both nylon 6 and nylon 6,6. In view of the infrared and dynamic mechanical measurements, some stiffening (modulus increase) had been anticipated rather than the observed softening. A direct comparison of these results is complicated by the uncertainty in the amount of water which evaporated from the samples. Since the elapsed time period (from removal of samples from the salt solutions to tensile testing) was considerably less than in the dynamic mechanical measurement of T_g, the tensile properties are thought to more nearly represent the equilibrated film conditions. The relation of the observed changes to the T_g of the equilibrated films will require further study. However, the tensile property changes reported here are representative of a plasticization-like action by the salt solution.

4. Discussion

The results of this investigation have shown that those aqueous salt solutions which were previously shown to cause crazing of nylon are also partially soluble in the material at elevated temperatures. This includes calcium, lithium, and magnesium chlorides. Sodium chloride, which showed no tendency to induce crazing, was also not absorbed into the nylon structure. The chemical analysis confirmed that both salt ions and water are absorbed into the nylon with the partitioning of the salt and water being dependent on temperature as well as on nylon type.

The crystallinity measurements of films previously equilibrated in salt solutions suggested that the salt is sorbed into the amorphous regions of nylon without inducing significant changes in crystallinity. Similarly no degradation in molecular weight was detected as a result of salt-solution absorption. Thus the evidence indicates that the sorption process is physically reversible and appears similar in this regard to the swelling of amorphous polymers by organic solvents.

However, the ionic nature of the salt solution coupled with the intermolecular hydrogen bonding of the nylon lead to a much more complicated polymer–liquid interaction than the van der Waals type of bonding in organic solvents. For example, the infrared spectroscopy results indicated that the absorbed calcium chloride formed an association with the amide groups in the nylon. This was observed in spite of the large amount of water in the equilibrated films. Evidence that the association of the amide groups with the hydrated salt ions stiffens the nylon chains was provided by the dynamic mechanical measurements which showed a shift of the glass transition to higher temperatures. Such a shift is indicative of a restricted mobility for the nylon polymer chains in the amorphous phase in the presence of the aqueous salt solution.

That absorbed salt alone restricts the amorphous phase mobility is shown by the very high T_g for the vacuum-dried film. DSC results also indicate an increased T_g for the second heating of equilibrated films. These films are also thought to contain very little water. This confirms the observations previously reported by others for nylon–salt systems [11]. For the film equilibrated in the aqueous solution, the loss of water during the dynamic test leaves some doubt as to the precise location of T_g. Since absorbed water decreases T_g while salt alone increases it, one expects an intermediate effect of the salt solution. The fact that salt solution induced crazing occurs at temperatures just above the T_g of the dry nylon makes the question of the T_g location of even greater interest. For example, if absorbed salt raises the T_g, the sorption process should in turn be retarded. On the other hand, a lowering of T_g is more compatible with solvent crazing models developed for amorphous glassy polymers. Unfortunately the available evidence does not allow a resolution of the question of the T_g of the salt solution equilibrated nylon films.

The tensile property measurements, on the other hand, indicate that the modulus is decreased as a result of the sorption process. The inference is that the T_g may also be reduced or at least substantially broadened. The reduction in modulus is considered very significant in terms of proposing a mechanism for salt-solution-induced crazing. It establishes a parallel between absorbed salt solution in nylon and absorbed organic solvents in glassy polymers, since the latter can also reduce modulus and increase tensile elongation. Thus relaxation controlled craze growth models developed for solvent crazing of glassy polymers [14, 15] may be equally applicable to salt solution induced craze growth in crystalline nylon. This will be examined in detail in the next paper in this series [6]. The results of the present study are compatible with a plasticization-like mechanism for salt-induced crazing since it has been clearly demonstrated that the salt solution penetrates the nylon structure without destroying the crystalline structure and without causing extensive recrystallization or molecular weight degradation.

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