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Stress cracking of nylon polymers in aqueous salt solutions

Part 3 *Craze-growth kinetics*

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Craze-growth kinetics were measured for nylon 6 and nylon 6,6 immersed in aqueous salt solutions. Under all conditions of stress level, temperature, and salt type examined, the craze-growth data exhibited a steady state growth rate which was linear with time. Comparison of these results with available mechanistic models for craze growth suggests that salt-induced crazing of nylon polymers is an example of relaxation-controlled craze growth. Activation energies for crazing are $2.1 \times 10^5\,\mathrm{J\,mol^{-1}}$ for nylon 6 and $3.9 \times 10^{-5}\,\mathrm{J\,mol^{-1}}$ for nylon 6,6. These values are similar to the activation energies for the alpha relaxation (glass transition) of the nylons. Although the activation energies depend to some extent on the initial stress intensity factor level and salt type, the results indicate that the polymer type is the primary factor determining the temperature dependence of craze growth. The effect of salt type on cracking was shown to correlate with the charge density ratio of the salt cation, namely Q/R, where Q is the oxidation number and R is the ionic radius. These results indicate that the stress cracking susceptibility of nylon polymers can be predicted based upon the polymer chemical structure, glass transition temperature, degree of crystallinity, and the Q/R ratio of the specific salt in question.

1. Introduction

The previous papers on the stress cracking of nylon polymers by aqueous salt solutions have shown that the occurrence of crazing is highly temperature dependent [1, 2]. Moreover, under constant tensile load the total failure time was determined largely by craze growth. Crack growth occurred rapidly only after a crazed region had propagated across nearly the entire sample cross-section. The mechanism for salt-induced cracking was not clearly defined by the previous studies though it was established that sorption of the salt solution occurred at the same elevated temperatures where crazing was observed. Also the analyses of the salt-solution-equilibrated nylon thin films demonstrated that no significant degradation or crystallinity changes were caused by the sorbed salt ions. Thus, in spite of the many studies showing strong effect of metal halides on the glass transition, melting, and crystallinity of nylons [3–7], the aqueous solutions used in this study appear to act only as swelling agents for the amorphous phase of the polymer.

Of particular note was the influence of absorbed salt solution on the tensile properties of the nylons. Specifically, the equilibrated films evidenced large decreases in modulus with increases in elongation, similar to the plasticizing action of sorbed organic liquids. Similarities between organic solvent crazing the salt solution crazing have previously been suggested based upon morphological evidence and diffusion chracteristics [8–10]. These observations, along with our previous results, suggested the possibility that mechanistic models for solvent crazing of glassy polymers [11–13] might also be applicable to salt-solution crazing of the crystalline nylons. The present study was, therefore, undertaken to measure the craze-growth kinetics for nylon 6 and nylon 6,6 in various salt solutions. The temperature dependence of craze-growth rate was also examined in order to calculate an activation energy for salt-induced crazing.

The effect of initial stress intensity level on the crazing kinetics and corresponding activation energy was also measured. In addition, the flow of salt solution into the sides of the growing craze was restricted in one experiment, in order to compare the corresponding kinetics with the case of unrestricted side flow [11, 12]. Finally, the possibility of regarding craze growth by increasing the degree of crystallinity of nylon 6 was examined both by annealing injection-moulded samples and by preparing a cast nylon 6 which inherently was of higher crystallinity.

The salts investigated included sodium chloride, lithium chloride, calcium chloride, and magnesium chloride. These salts were selected for study based upon a previous publication by Kim and Harget [14] which showed the effect of blending the salts (in the absence of any absorbed moisture) on the glass transition temperature (T_g) of nylon 6. In their study it was shown that, for equal molar concentrations of salt in the nylon 6, the T_g increased systematically with Q/R, where Q is the oxidation number of the cation and R

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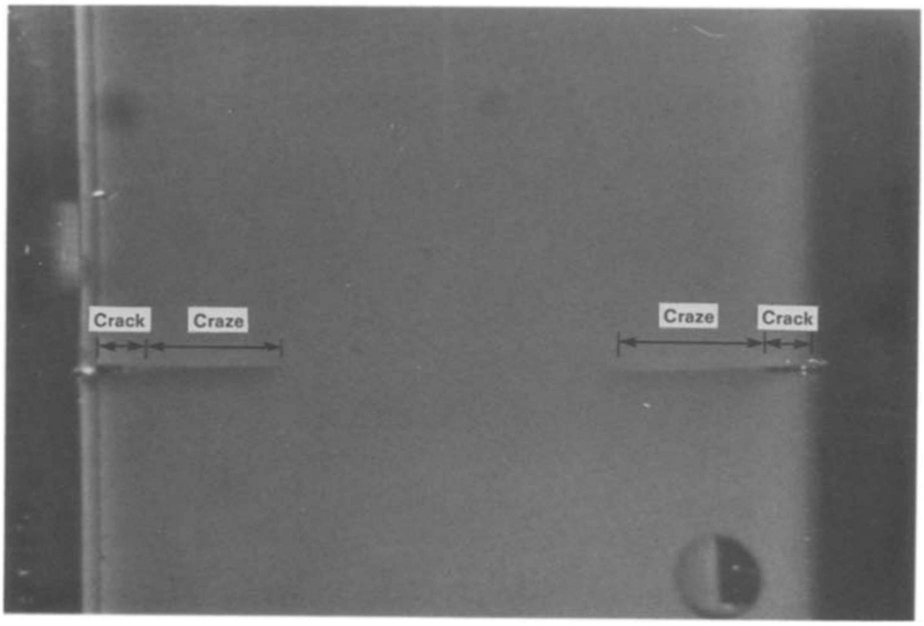

Figure 1 View of crazes growing from precracks in a nylon 6 tensile bar immersed in saturated aqueous calcium chloride at 50° C (× 7.25).

is the ionic radius. Thus, Q/R is a measure of ionic strength or charge density. Of course, the nylon–salt mixtures studied by Kim and Harget contained no water, whereas for the present stress cracking investigation it was the aqueous solutions which were of interest.

2. Experimental techniques

2.1. Materials

Injection-moulded nylon 6,6 tensile bars (ASTM D-638, Type I) for craze-growth studies were prepared from Zytel 101, a product of E. I. duPont. Similarly, nylon 6 bars were moulded using Capron 8202 from Allied Corporation.

Saturated aqueous solutions of the salts were prepared at room temperature. Analytical reagent grade calcium, lithium, and magnesium chlorides were used. The latter was in the form of a hydrate, $MgCl_2 \cdot 6H_2O$. No attempt was made to compensate for the increased solubility of the salts at higher temperatures.

2.2. Cast nylon 6

A cast nylon 6 was prepared via the anionic polymerization of ε-caprolactam. The plaque was hand poured from a mixture of 98.44 parts caprolactam, 0.57 parts sodium hydride, and 0.99 parts toluene diisocyanate. Polymerization occurred in a vertically held mould which was preheated to 160° C and maintained at this temperature for 3 min. The thickness of the 203 mm square plaque was 3.0 mm. Test specimens 12.7 mm × 203 mm were mill-cut from the plaques.

2.3. Craze growth kinetics

The constant load apparatus, environmental chamber, and procedure for stress cracking experiments were described previously [1]. Double edge-notched samples were prepared by razor cutting precracks, 1.0 mm deep, on each side of injection-moulded or cast nylon tensile bars. The stress intensity factor, K_I, at the crack tip was calculated from the sample geometry and constant applied load [1].

The growth of crazes from the precracks was observed directly using a Bausch and Lomb Stereozoom 7 Microscope. Craze lengths were measured with a micrometer eyepiece. In most cases, the entire sample was surrounded by the aqueous salt solution. This arrangement is referred to as an unrestricted side flow experiment since the salt solution can reach the tip of the porous craze structure either by flowing through the precrack and along the entire craze length or by the generally shorter flow path through the sides of the crazed region [11, 12].

In one case, glass slides were used to cover the sides of the crazed region (i.e. the entire sides of the tensile bar were covered). This changed the previously employed unrestricted side flow experimental arrangement to one of restricted side flow. Stopcock grease was applied to the slides to provide a seal to the 12.7 mm wide faces of the nylon tensile bar. Thus craze growth should occur only as a result of salt solution through the razor-cut precrack and along the entire length of the crazed region.

3. Results

3.1. Nylon 6

Fig. 1 shows the crazes advancing from two precracks in a nylon 6 specimen immersed in saturated aqueous calcium chloride and loaded to provide an initial stress intensity factor, K_I, of 0.66 MPa $m^{1/2}$. The crazed region may consist of numerous crazes or craze bundles rather than a single large craze. For this study the advance of the tip of the crazed region was measured and no attempt was made to distinguish between single or multiple crazes in this zone.

Fig. 2 shows the craze growth results for dry injection-moulded nylon 6 at 50° C in saturated aqueous calcium chloride. Data are shown for both the left and right sides of the sample to demonstrate the similarity of the growth rates. These results show that there is an initial rapid growth of the craze to a length of approximately 1 mm followed by a decrease in rate to a steady state growth condition.

The temperature dependence of salt-induced craze

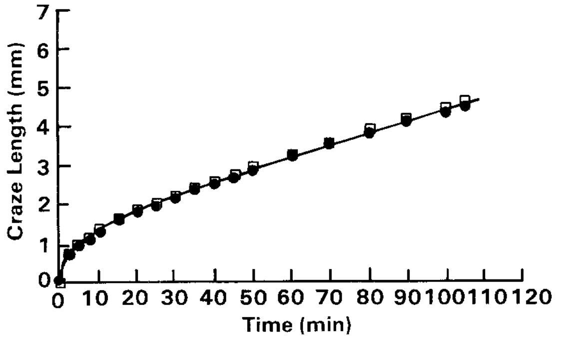

Figure 2 Rate of craze growth for nylon 6 immersed in saturated aqueous calcium chloride at 50° C. (□) Left side, (●) right side.

growth in nylon 6 is shown in Fig. 3 where results are plotted for one side only of the double edge-cracked specimen (similar data were obtained for each side). At all temperatures the craze initially grew more rapidly to a length of about 1 mm, then an apparent steady state growth rate was observed, until finally the specimen ruptured. The craze length at the time of rupture was reasonably constant at 4 to 5 mm. As the sample is 12.7 mm in width, with the initial precracks being 1 mm from each side, it is apparent that craze growth proceeds across 8 to 10 mm out of a possible 10.7 mm before crack growth initiates and rupture occurs. This confirms in a quantitative manner the major role of craze growth in the overall environment cracking process.

3.2. Salt type

The fact that the craze length exhibits a steady state growth rate which is linear with time indicates that the kinetics follow the relaxation-controlled growth models proposed by previous investigators [11, 12]. This was further substantiated by craze-growth data for nylon 6 in magnesium chloride (Fig. 4) and in lithium chloride (Fig. 5). As with the calcium chloride, crazes were observed to initiate and grow only at the razor-cut precracks and the growth rate increased systematically with increasing temperature. In all cases a steady state growth rate can be identified.

These results also demonstrate that the craze-growth rate depends upon salt type with the most rapid growth in magnesium chloride and the least rapid in lithium chloride. This is shown by the comparison of craze growth rates at 55° C in Fig. 6. It is interesting to note that the saturated aqueous solutions of calcium and lithium chloride are more concentrated (6.7 M and 15.0 M, respectively) than the magnesium chloride (5.7 M). Thus the rate of craze growth is not simply related to the number of cations in the aqueous solutions. The higher craze-growth rate in magnesium chloride does correlate with the higher weight gain which has been reported for nylon 6 thin films in this salt solution [2].

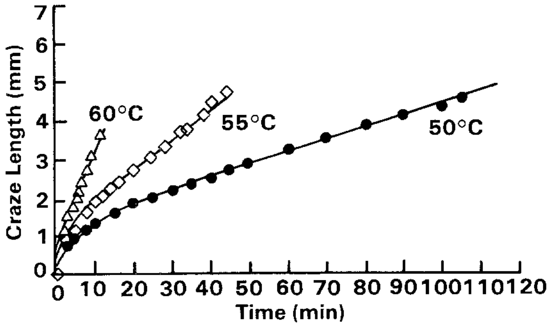

Figure 3 Temperature dependence of craze growth for nylon 6 immersed in saturated aqueous calcium chloride (K_I = 0.66 MPa m$^{1/2}$).

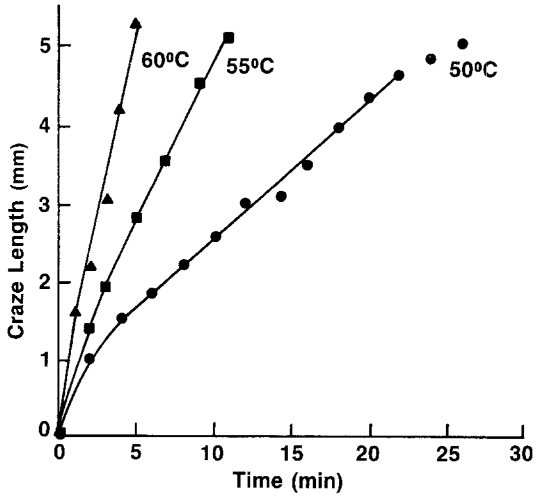

Figure 4 Temperature dependence of craze growth for nylon 6 immersed in saturated aqueous magnesium chloride (K_I = 0.66 MPa m$^{1/2}$).

3.3. Nylon 6,6

For injection-moulded nylon 6,6, measurements were taken at higher temperatures and at a constant K_I = 0.35 MPa m$^{1/2}$. Both the temperature range and K_I level were selected from previous data on the stress-rupture behaviour of nylon 6,6 [1]. The craze growth kinetics in saturated aqueous calcium chloride are shown in Fig. 7. As with the nylon 6, a steady state craze-growth rate is apparent beyond a craze length of about 1 mm. The craze length at rupture was generally less than that noted for nylon 6 at the lower temperatures even though the K_I level was lower.

Attempts were made to obtain comparative craze-growth data for nylon 6,6 at 85° C in the different salt solutions. Although a reduced growth rate was observed in the lithium chloride solution, no growth was observed in aqueous magnesium chloride at this

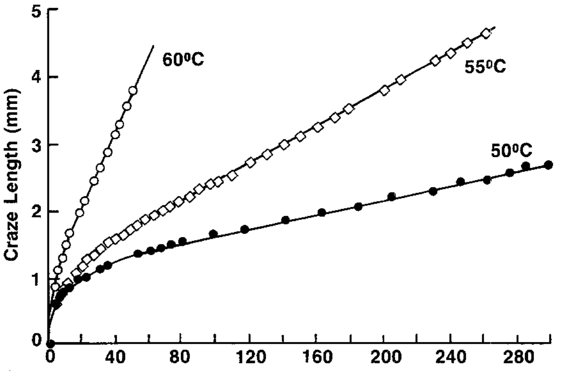

Figure 5 Temperature dependence of craze growth for nylon 6 immersed in saturated aqueous lithium chloride (K_I = 0.66 MPa m$^{1/2}$).

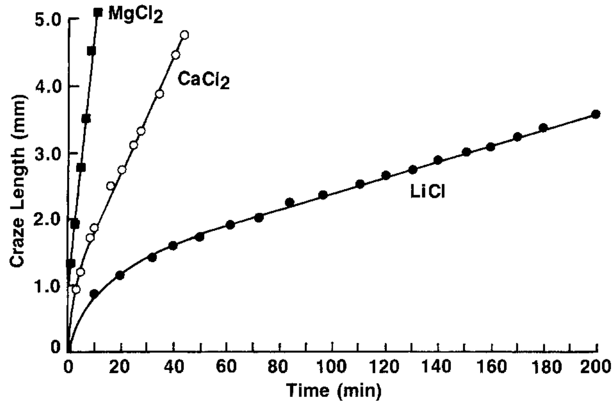

Figure 6 Rate of craze growth at 55° C for nylon 6 immersed in various saturated aqueous salt solutions ($K_I = 0.66\,\mathrm{MPa\,m^{1/2}}$).

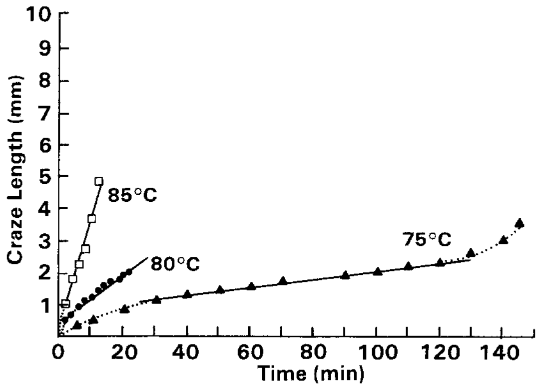

Figure 7 Temperature dependence of craze growth for nylon 6,6 immersed in saturated aqueous calcium chloride ($K_I = 0.35\,\mathrm{MPa\,m^{1/2}}$).

K_I level and temperature. In view of the relatively high weight gain for nylon 6,6 thin films immersed in this salt solution [2], the lack of craze growth is considered to be related to the unexplained crack-tip blunting noted earlier [1].

3.4. Stress intensity factor

The stress intensity factor was held constant at $0.66\,\mathrm{MPa\,m^{1/2}}$ for the nylon 6 craze-growth data reported earlier. This value was arbitrarily selected to provide convenient time scales for the measurements. To determine the influence of higher and lower initial loads, data were taken for nylon 6 in both lithium chloride and calcium chloride at initial stress intensity factor levels of 1.1 and $0.33\,\mathrm{MPa\,m^{1/2}}$, respectively. Results are shown in Fig. 8 for craze growth in lithium chloride with the dashed lines being the data of Fig. 5 for the lower K_I. As expected, more rapid craze-growth rates are observed at higher K_I, although the general shapes of the curves are similar with definite steady state growth rates indicated as before.

For the more potent crazing agent, calcium chloride, measurements were made for both nylon 6 and nylon 6,6. In both cases the change in K_I level had less effect on craze-growth rates than that noted for lithium chloride. Consistently higher growth rates are observed at the higher K_I. This is discussed further in a later section.

3.5. Cast nylon 6

Craze-growth kinetics for the anionically polymerized cast nylon 6 material are shown in Fig. 9. Reduced craze-growth rates were observed at all temperatures compared to the injection-moulded material. Also, data could be recorded over a 20° temperature range for the cast nylon 6 because rapid fracture did not occur at the higher temperatures. Unlike the injection-moulded nylon 6, the samples did not rupture immediately once the crazed regions reached the mid-point. This indicates that the breakdown of the crazed regions was also retarded for the cast nylon 6. The more stable structure is believed to be due to the higher molecular weight of the sample ($M_W = 124\,000$ compared to 48 000 for the injection-moulded nylon 6) whereas it is suspected that the retardation in craze-growth rates is related to the crystallinity.

3.6. Crystallinity

Differential scanning calorimetry measurements confirmed that the cast nylon 6 was 46% crystalline whereas the injection-moulded nylon 6 was only 31% crystalline. Thus the degree of crystallinity correlated well (inversely) with the craze-growth rate. This factor was examined further by measuring the craze-growth kinetics for injection-moulded nylon 6 which was annealed at 200° C for 1.5 h to increase its crystallinity to 36%. Fig. 10 shows that the effect of the increased crystallinity was to dramatically reduce craze-growth rates, even lower than that observed in the cast nylon 6.

Though confirming the effect of increasing crystallinity, these results also show that the per cent crystallinity alone does not dictate the craze-growth rate. A further distinction in comparing annealed injection-moulded nylon 6 with the cast material is the craze length at the time of rupture. Values less than 2 mm

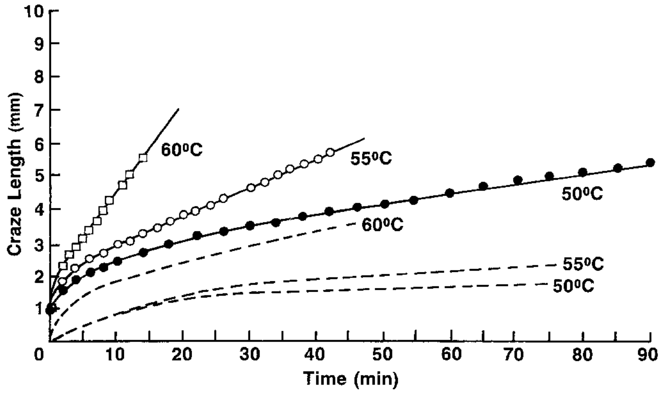

Figure 8 Craze-growth kinetics for nylon 6 immersed in saturated aqueous lithium chloride at a higher stress intensity factor level ($K_I = 1.1\,\mathrm{MPa\,m^{1/2}}$). Dashed lines are data from Fig. 5 at $K_I = 0.66\,\mathrm{MPa\,m^{1/2}}$.

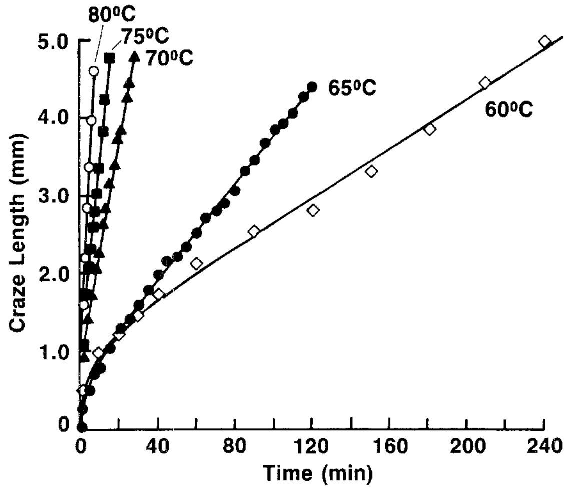

Figure 9 Rate of craze growth for cast nylon 6 immersed in saturated aqueous calcium chloride at various temperatures (K_I = 0.66 MPa m$^{1/2}$).

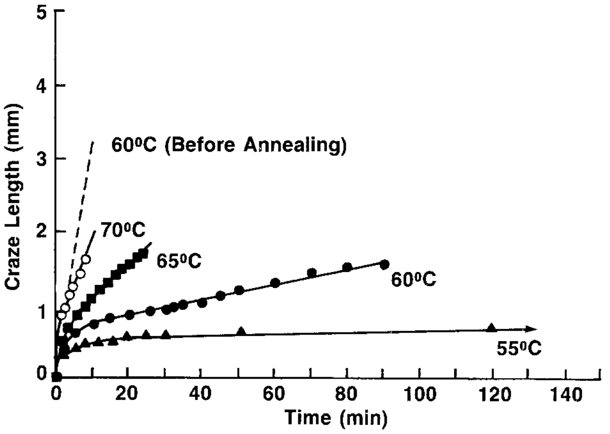

Figure 10 Craze-growth kinetics for annealed injection-moulded nylon 6 immersed in saturated aqueous calcium chloride (K_I = 0.66 MPa m$^{1/2}$). Data for unannealed sample (dashed line) are shown for comparison.

were noted in the former, whereas cast nylon supports craze growth to lengths of more than 4 mm, i.e. across the entire width of the tensile bar. The practical significance of this difference can be seen by comparing the time to complete rupture for the two materials at 60° C (Figs 9 and 10). Although craze growth is more rapid in the cast nylon 6, the more stable craze structure results in a longer time to complete rupture for this sample compared to the annealed injection-moulded sample. Thus both crazing and cracking kinetics must be considered in assessing resistance to salt solutions. Although the differences noted here are primarily attributed to molecular weight, other factors such as morphology or residual monomer may also be contributing to the craze-growth kinetics.

3.7. Restricted side flow experiment

When glass slides were used to prevent salt solution contact with the faces of the tensile bar, the steady state craze-growth rate was significantly retarded and the shape of the craze length against time curve was changed. This is shown in Fig. 11a. The apparent steady state growth rate was reached after 5 min compared to 2 min for the case of unrestricted side flow (dashed line). However, an alternative representation of these data is shown in Fig. 11b in which the square root of time is used as the abscissa. Although significant scatter is observed for short times (where it is more difficult to see the craze tip region), the entire data set can be fitted to a straight line. A linear relationship with $t^{1/2}$ is predicted for this restricted side flow experiment by published models for solvent crazing kinetics of glassy polymers [11, 12]. The results shown here are compatible with these models. Attempts to take further data were not successful because of the difficulty in viewing the craze tip in this type of experiment and problems with the sealing of the glass slides at high temperatures. Thus the results are not considered conclusive.

3.8. Activation energies for crazing

As the craze length against time plot at each temperature reached a constant slope characteristic of a steady state growth process, it was possible to calculate an activation energy for craze growth from the well-known Arrhenius relationship. Values for craze growth in nylon 6 and nylon 6,6 immersed in calcium chloride (data from Figs 3 and 7) are given in Table I. In spite of the uncertainty in the calculated values, due to the limited temperature range, it is apparent that a significant difference exists for the two types of nylon. The activation energy for craze growth in the cast nylon 6 is similar to the injection-moulded material. The latter value is based upon measurements at five temperatures (i.e. 20° range rather than 10°). This provides further evidence that the activation energy is strongly influenced by the polymer type.

The annealed nylon 6 exhibits an increased activation energy apparently reflecting the retarded craze growth rates for this sample. This result suggests that more extensively annealed nylon 6 may be comparable to nylon 6,6 in terms of craze-growth rate, activation energy for crazing, and crystallinity. However, the results for cast nylon 6, along with previous data [2], indicate that it is difficult to correlate the salt solution crazing and sorption behaviour to crystallinity alone.

From the temperature dependence of craze growth in the different types of salt solution, the corresponding activation energies which were calculated are given in Table II. Comparing these results with the propen-

TABLE I Activation energies for calcium chloride-induced craze growth in nylons

Sample	Activation energy (10^5 J mol^{-1})
Nylon 6,6	3.9
Nylon 6	1.9
Annealed nylon 6	3.0
Cast nylon 6	1.7

TABLE II Activation energies for aqueous salt-solution-induced craze growth in nylon 6 at 0.66 MPa m$^{1/2}$

Salt	Activation energy (10^5 J mol^{-1})
LiCl	2.5
$CaCl_2$	1.9
$MgCl_2$	1.5

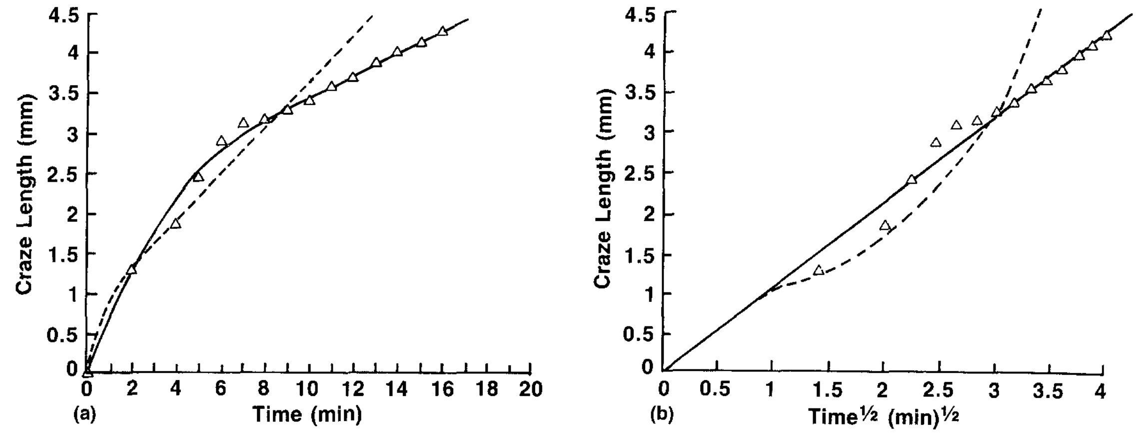

Figure 11 Rate of craze growth for nylon 6 immersed in saturated aqueous calcium chloride at 60° C under conditions of restricted side flow. Data are plotted against (a) time and (b) time$^{1/2}$ (K_I = 0.66 MPa m$^{1/2}$). Dashed lines represent previous data for unrestricted side flow conditions.

sity of the salt solution to cause craze growth (Fig. 6), indicates that the activation energy decreases as the craze-growth rate increases.

A similar effect was observed by increasing the stress intensity factor level. This is shown by the activation energies in Table III for craze growth in either lithium chloride or calcium chloride solutions. The magnitude of the change in activation energy is small for the more potent crazing agent, calcium chloride, in both nylon 6 and nylon 6,6.

The effect of stress intensity factor level and salt type on the activation energy for craze growth can be understood by considering that the growth rate is determined by some additive contribution of three variables; namely, the solubility of the salt solution, the stress intensity factor level, and the temperature. Thus, for solutions of higher solubility or at increased stress levels, lower temperatures are required to achieve a given craze growth rate, and the corresponding activation energy is decreased. However, the available results indicate that the polymer type is the primary factor determining the magnitude of the activation energy, not the salt type or stress level. The dependence on polymer type also indicates that the activation energies for craze growth are not due to the temperature dependence of salt solution viscosity, otherwise similar values would be expected for nylon 6 and nylon 6,6.

4. Discussion

4.1. Craze-growth mechanism

The growth of a craze at the tip of a sharp crack has been investigated extensively by Kramer and Bubeck [12] and earlier by Williams and Marshall [11]. In a fluid environment the craze growth is controlled by the transport of liquid through the porous craze structure to the craze tip, particularly at high K_I. At lower K_I or, at long times, relaxation-controlled growth can occur. For this case, the craze tip is considered to advance as a result of the stress relaxation of the fibrils in the mature liquid-saturated craze. This is shown schematically in Fig. 12. The overall stress borne by the craze fibrils is considered to balance the tremendous stress concentration which exists at the crack tip,

TABLE III Effect of stress intensity factor on the activation energy for salt-induced craze growth

Sample	Salt	Stress intensity factor (MPa m$^{1/2}$)	Activation energy (10^5 J mol^{-1})
Nylon 6	LiCl	0.66	2.5
		1.1	2.0
	$CaCl_2$	0.33	2.1
		0.66	1.9
Nylon 6,6	$CaCl_2$	0.35	3.9
		0.66	3.6

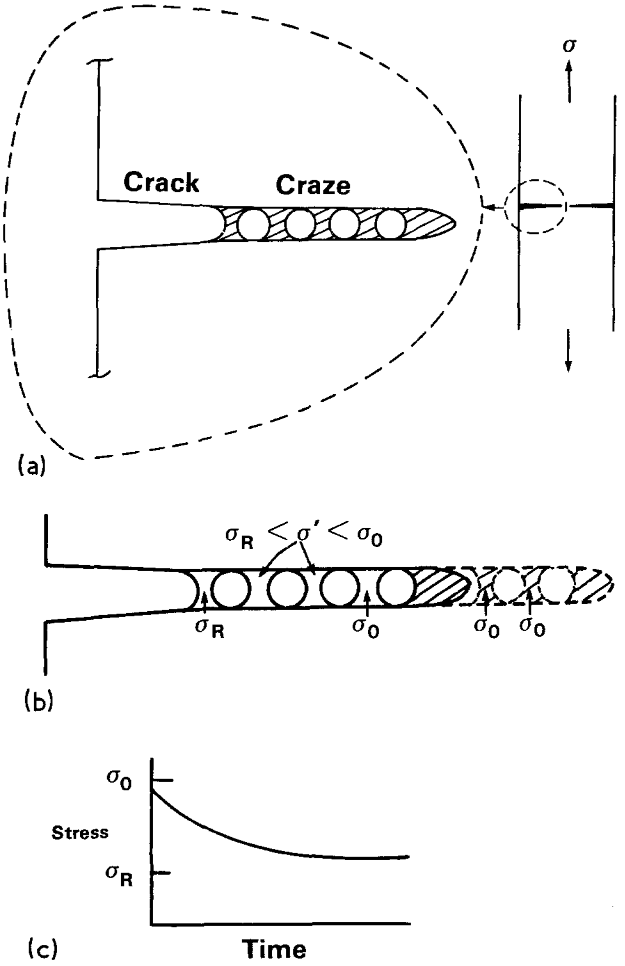

Figure 12 (a) Schematic view of a craze at a crack tip and, (b) craze tip advance to generate new fibrils at stress level, σ_0, as (c) stress in craze fibrils, σ_0, relaxes with time to σ_R.

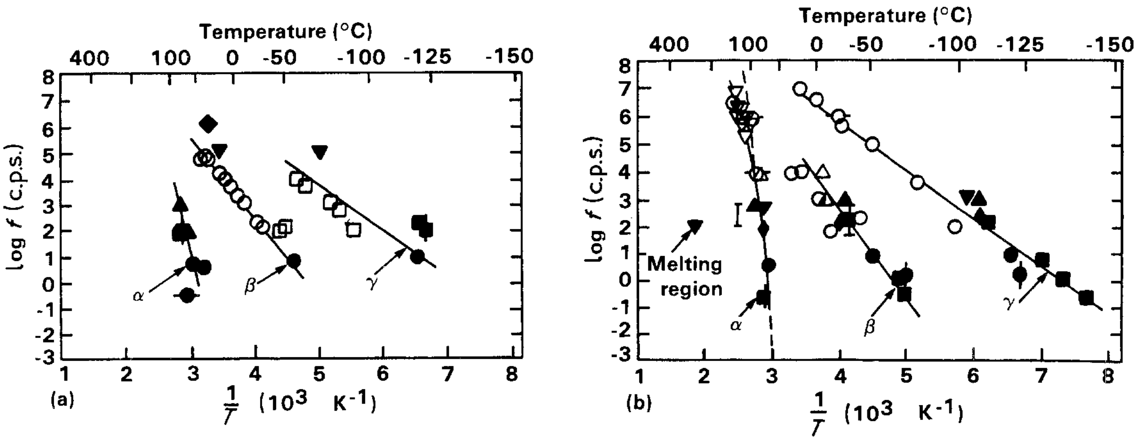

Figure 13 Frequency–temperature dependence of relaxations in (a) nylon 6 and (b) nylon 6,6 (reprinted from [15], open points are dielectric data, closed points are mechanical data, from a variety of literature reports).

Fig. 12a. As the craze fibrils absorb liquid and undergo stress relaxation, the craze tip advances in order to generate new fibrils which maintain the overall stress balance, Fig. 12b. For example, newly formed fibrils are at a stress level of σ_0, but with time the fibril stress, σ', approaches σ_R, Fig. 12c. Of course fibril stress relaxation can occur in air, but occurs at an accelerated rate in the presence of a plasticizing liquid environment. Mathematical expressions have been derived for the craze length as a function of time based upon the relaxation-controlled growth concept and assumptions concerning the stress distribution in the craze [11–13].

As mentioned previously, the shape of the craze length against time curve for nylon 6 and nylon 6,6 is similar to that derived for the general case of relaxation-controlled craze growth at constant K_I. In all cases examined an apparent steady state craze-growth rate can be defined which is linear with time under the experimental conditions of unrestricted side flow. The limited data for the case of restricted side flow followed a square root of time dependence which is also in accord with the craze-growth models for glassy polymers. In order to apply this solvent crazing model to the present results on nylon, it is imperative that the salt solution act as a partial solvent to accelerate stress relaxation within the nylon craze structure. The results of the previous study indicate that this is the case [2]. Although the aqueous calcium chloride behaves in some ways distinctly differently from organic solvent, it is similar to a solvent in a glassy polymer in its effect on the mechanical properties of the semicrystalline nylon. In particular, the diffusion of aqueous calcium chloride into the nylon will definitely result in a relaxation of stress in the polymer as indicated by the significantly lower modulus of the salt-solution-equilibrated films [2]. Thus, from this standpoint, the relaxation-controlled growth mechanism is a feasible mechanism for salt-solution-induced crazing of nylon.

4.2. Activation energy interpretation

From the available literature and mechanistic models, it is apparent that several steps occur in the overall process of environmentally induced crazing. A dry craze forms at the flaw or crack tip, fluid flows into the craze, the craze fibrils absorb fluid, the fibrils undergo stress relaxation, and the craze tip (which may still be a dry craze) advances. Based upon this physical model it was of interest to provide an interpretation for the activation energies associated with crazing. For example, why is the activation energy for crazing nylon 6 in calcium chloride only $2.1 \times 10^5\ \mathrm{J\,mol^{-1}}$, whereas, it is $3.9 \times 10^5\ \mathrm{J\,mol^{-1}}$ for nylon 6,6? In attempting to relate these values to the various steps in the process of solvent crazing, it was recalled that the onset of significant stress cracking with increasing temperature paralleled the onset of the T_g in these two polymers [1]. Although the T_g is sometimes treated as a fixed temperature, it is a manifestation of a kinetic event during which the molecules in the amorphous phase begin to undergo large-scale oscillations.

Moreover, the frequency dependence of the T_g, or alpha relaxation, has been widely studied for nylon polymers. Fig. 13 shows a replot of data from McCrum *et al.* [15] on the various relaxations of nylon 6 and nylon 6,6. These data are a collection of all previously published results in the literature. Over a broad temperature interval the rate dependence of the alpha relaxation cannot be fitted with an Arrhenius expression. In fact, it is well known that the Williams–Landel–Ferry (WLF) equation is more appropriate for describing the temperature dependence of viscoelastic processes above T_g [15]. However, over a limited range of temperatures just above T_g (covering the range used here for craze-growth measurements) a straight line corresponding to the Arrhenius relationship can be fitted to the data. The referenced authors had, in fact, drawn in a straight line for the nylon 6 data as shown in Fig. 13. For nylon 6,6 the dashed line shown in the α relaxation data was drawn by the present authors.

From the slopes of the lines in Fig. 13, activation energies can be calculated for the alpha relaxation for comparison with those determined independently from the craze-growth kinetics. The results are given in Table IV where it is seen that the agreement is excellent. Considering that on the one hand we are determining an activation energy for segmental molecular motion in the pure polymer (i.e. as moulded in the absence of any absorbed salt) and on the other hand we are determining a value for the process lead-

TABLE IV Comparison of activation energies for craze growth and the alpha relaxation (T_g) of nylon

	Activation energy ($10^5\,\mathrm{J\,mol^{-1}}$)	
	Craze growth	Alpha relaxation
Nylon 6	2.1	2.0
Nylon 6,6	3.9	4.0

ing to complete rupture of the polymer in salt solution, the agreement is remarkable.

This correlation of activation energies for the alpha relaxation and craze growth can be readily understood in terms of the relaxation-controlled craze-growth model. The comparison suggests that the rate-controlling step is the degree to which molecular segmental motion occurs in the amorphous phase of the nylon (with an associated volume expansion and disruption of hydrogen bonding). This expansion and liquid-like fluidity of the nylon chains permits a more rapid infusion of salt solution and concurrent stress relaxation of the nylon, specifically relaxation of the fibrils in the crazed region.

In addition to providing a possible explanation for the different temperature dependence of crazing in nylon 6 and nylon 6,6 the correlation of crazing with the alpha relaxation has other implications. Most notably it can explain why crazing does not occur at room temperature. Also it suggests a key role for the nylon T_g in establishing the temperature range where salt solution crazing will occur. The effect of increased crystallinity in reducing craze-growth rates is also compatible with the above association, For example, a reduction in the amorphous content should improve resistance to crazing by reducing sorption rate and amount. Also the increased activation energy for craze growth can be understood in terms of the restricted mobility of the amorphous phase chain segments after the recrystallization induced by annealing.

It would be of interest to measure the activation energy of the alpha relaxation after annealing in order to compare it with the value reported here for craze growth. Preliminary dynamic measurements have confirmed that the alpha relaxation shifts to a higher temperature after annealing, demonstrating restricted chain mobility in the amorphous phase. Unfortunately, an activation energy could not be calculated from the limited frequency range used for the measurements.

4.3. Effect of salt type

Although some influence of salt type was noted previously in the overall stress rupture data for nylon 6,6 [1], the craze-growth data presented here for nylon 6 provided a clearer quantitative assessment of the relative effect of different salts. From the available results and the concentrations of the various salts in water, it appears that there is no simple relationship between craze-growth rate and the number of cations in solution. However, it does appear possible to understand the relative ranking of the aqueous salt solutions based on the behaviour of the nylon-salt system in the absence of water. For example, the previous publication by Kim and Harget [14] had shown that the increase in T_g of nylon 6 could be used as a measure of the strength of the nylon–salt ion interaction. Moreover, it was shown that the increase in T_g could be correlated with the ratio of the cation ionic charge, Q, to the ionic radius, R. Thus, on an equal molar basis a greater increase in T_g occurred upon addition of the salt having the highest Q/R ratio. Data were shown indicating a relative ranking of salt cations in the order Na < Li < Ca < Mg. This is the same order observed in the present study for craze-growth rates in saturated aqueous solutions of these salts. For example, no crazing occurred in aqueous sodium chloride while in the other salt solutions craze growth occurred at an increasing rate in the order Li < Ca < Mg chloride (Fig. 6).

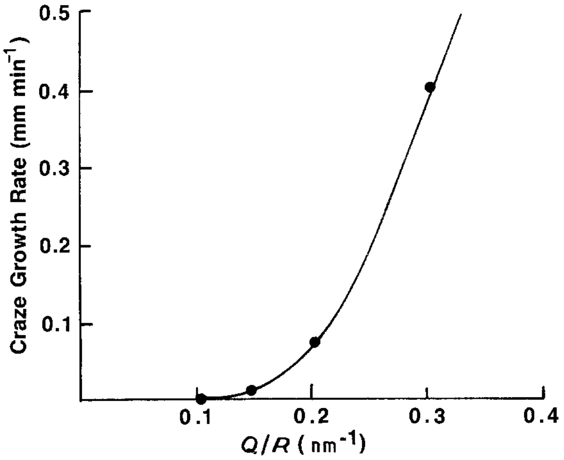

Figure 14 Relationship between craze-growth rates in various aqueous salt solutions for nylon 6 at 55° C, and the Q/R ratio of the salt cation ($K_1 = 0.66\,\mathrm{MPa\,m^{1/2}}$).

The relationship between craze-growth rate and Q/R is shown graphically in Fig. 14. Although equimolar solutions were not employed, the relative ranking of craze-growth rates would not be expected to change, as the most potent crazing agent, $MgCl_2$, was the least concentrated, while the LiCl was the most concentrated and the least severe crazing agent.

The correlation with Q/R suggests that the possibility exists to predict the susceptibility to environmental crazing of nylons based upon the known characteristics of the salt cation. The results also suggest that the role of water is to modify, by dilution, the interaction of the salt ions with the nylon polymer. Even if the Q/R correlation is not valid for all salts, as some evidence suggests [4], it may still be possible to predict the susceptibility of nylon to crazing by salt solutions from an experimental measure of the strength of the nylon–salt interaction in the absence of water or other solvent. For this purpose the straightforward determination of the T_g increase of the nylon–salt mixture may be a viable approach.

4.4. Predicting stress cracking behaviour

The results of previous investigations, as well as the data presented in this study, provide the following general framework for predicting stress cracking susceptibility of nylons to aqueous salt solutions. First, the T_g of the nylon represents (for all practical purposes) a critical temperature. Above T_g cracking occurs, and below T_g cracking will not occur. Second, more severe cracking will occur for less crystalline nylons and for those having higher concentrations of amide groups. Third, a prediction of the relative severity of cracking can be made based upon the specific type of salt. This can be approached by calculations of the Q/R ratio of the cation as well as by examining published experimental measurements of the increase in T_g of the nylon–salt mixture.

5. Conclusion

The investigation of stress rupture behaviour and nylon–salt interactions, as well as the measurements of craze-growth kinetics, lead us to suggest that the salt-induced cracking of nylon polymers at slightly elevated temperatures is a specific case of the more general phenomenon of solvent stress cracking of polymers. The results not only indicate that the nylons exhibit relaxation-controlled craze-growth in the salt solutions, but also it is suggested that the specific molecular relaxation which controls the kinetics of craze growth is the alpha relaxation of the nylon.

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