The Stress Cracking of Polyamides by Metal Salts.
Part I. Metal Halides

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Synopsis

The stress cracking of polyamides (nylons) by a number of metal salts, in aqueous and nonaqueous solutions, has been investigated. Many metal halides and halide-like salts were found to be active stress-cracking agents, while metal acetates and sulfates were inactive. Zinc chloride was found to be most active, and its activity was compared with other metal halides. Using a recording tensometer, time to crack initiation, time to crack-through and time to rupture were determined. These parameters were found to be dependent on temperature, moisture content of the nylon, concentration of the cracking agent and level of stress. High values of all these factors favored rapid cracking. Cracking parameters were shown to be mainly independent of the surface geometry of the nylon and the hydrogen ion concentration of the cracking agent. Metal halides did not appear to cause any chain scission in the nylon and stress cracking was not due to hydrolysis or metal-ion catalysed hydrolysis.

INTRODUCTION

The cracking and delamination of nylon 6 and nylon 66 mouldings in the presence of aqueous zinc chloride solutions ranging in concentration from 20–80% weight/volume,[1] and also in the presence of zinc dust and hydrochloric acid[2] had been reported. Weiske[3] has described the stress cracking of dry nylons by a number of solvents and the action of methanolic solutions of calcium chloride. Barmby and King[4] have shown that both silk and nylons are soluble in arsenic and antimony trichlorides with little apparent molecular chain degradation, and that silk precipitated from an aqueous lithium bromide solution is similar to silk precipitated from solution in antimony trichloride. Sarda and Peacock[5] have shown that lithium bromide and lithium and magnesium perchlorates in aqueous solution reduce the modulus properties of nylon 6 and 66 and also bring about modification of the infrared spectra of these polyamides. A comparison of the effects of a range of metal salts on polyamides has now been undertaken.

EXPERIMENTAL

Materials

Nylon 6 test specimens were cut from extruded nylon 6 sheet ("Trogamid" B; Dynamit-Nobel A.G., Troisdorf, Germany), as rectangular

strips $6 \times 1 \times 0.125$ in. Dumbell tensile specimens, with neck dimensions $2 \times 0.50 \times 0.040$ in. were stamped from nylon sheet using Die A, of ASTM-D412.[6]   Other nylon specimens were in the form of injection moulded dumbells conforming to British Standard BS 2782.[7]   The moulding compounds used were:

Nylon 6,   "Grilon" A25G, Natural (Emser Werke A.G., Switzerland)
Nylon 66,   "Maranyl" A100, Natural (Imperial Chemical Industries Ltd., England)
Nylon 610,   "Maranyl" B1001C, Natural (Imperial Chemical Industries Ltd., England)
Nylon 11,   "Rilsan" BMNO, Natural (Société Organico, France)

Where possible the metal salts employed were analytical grade and were used without further purification.   All solvents were laboratory grade and were purified by distillation and then dried.   Distilled water was used throughout.

Measurement of Stress Cracking Parameters

To assess the activity of metal salts, test specimens of nylon 6 were stressed horizontally between the grips of a Hounsfield tensometer at stress levels of 2000 and 4000 psi, and single drops of saturated solutions of
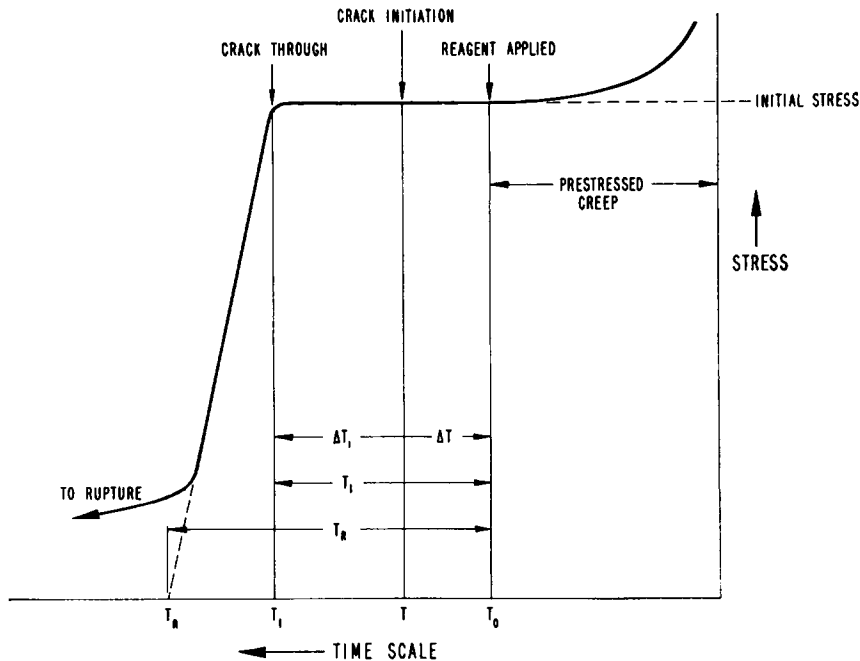

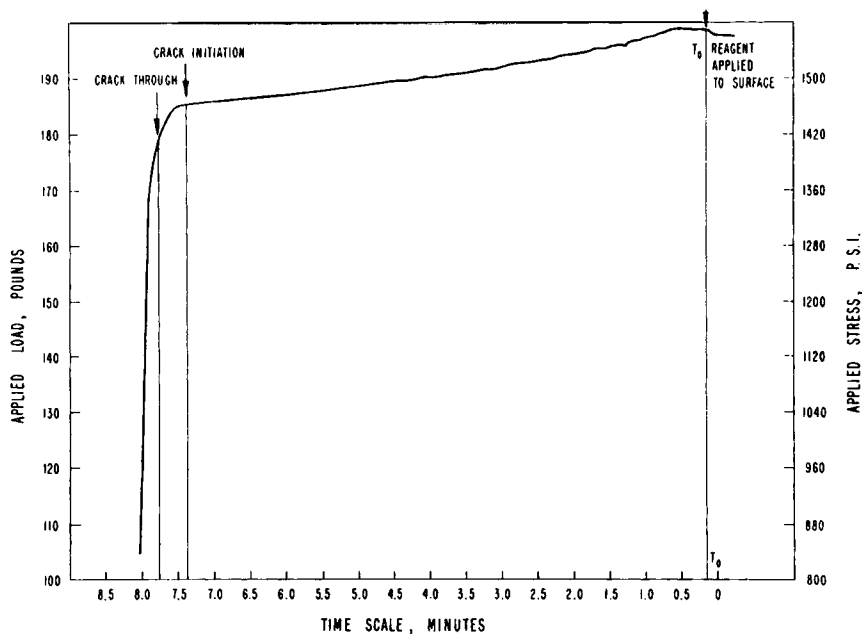
Fig. 1. Schematic stress-time curve.

Fig. 2. Typical experimental stress-time curve for nylon 6 (moisture content, 3.5%) stress cracked by saturated methanolic ZnCl₂ solution, at 21°C.

the reagent applied to the surfaces. The initiation of cracking within 48 hr was taken as proof of stress cracking activity. Initially a simple separation into highly active, active, weakly active and inactive categories was carried out on the basis of whether total rupture of the specimen occurred rapidly, within the period of the test, failed to occur even though crack initiation took place, or no cracking occurred. Some reagents failed to cause cracking but caused swelling of the nylon and this was always described as weak activity.

To quantitatively investigate the activity of the metal salts, stressed specimens at constant strain were treated with the reagent and the stress, which decreased as cracking took place, was continuously recorded. The stress was recorded by means of a Phillips pick up in contact with the spring beam of the tensometer; the output of the pick up was indicated on a Sargent model SRL variable speed recorder.

All specimens were prestressed and then allowed to relax under creep until the stress remained nearly constant before the reagent was applied to the surface. Thus, stress-time curves of the type shown schematically in Figure 1 were obtained. A typical curve for nylon 6 stress cracked by methanolic zinc chloride solution is shown in Figure 2 and a typical cracked specimen in Figure 3.

The cracking process was followed visually by observing the nylon surface through a mounted, moveable large magnifier, fitted with inbuilt fluorescent illumination. Initiation of cracking was detected using low

angle illumination and observation.   A plane mirror sited under the speci-
mens, together with low angle illumination, was used to observe when the
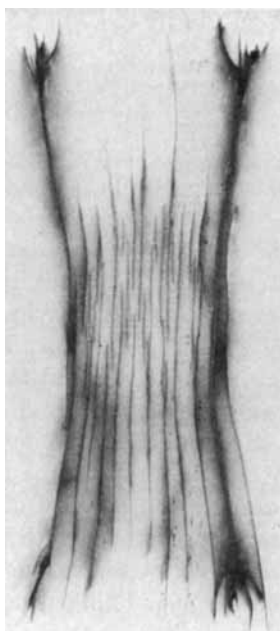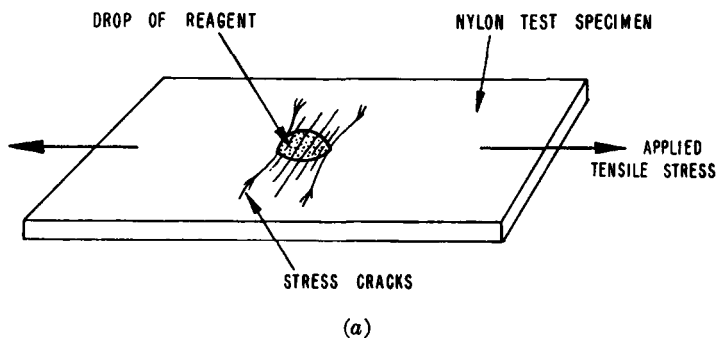crack appeared at the under surface.

(a)

(b)

Fig. 3. (a) Typical experimental procedure.   (b) typical stress cracking: nylon 6 stress
cracked by aqueous (80%) ZnCl₂ solution.   The water soluble dye, Nigrosine G140, was
added to the solution in order to indicate the stress cracking pattern.   The initial stress
was 2000 psi, and the test temperature, 21°C (× 4 magnifications).

From visual observation, and the stress-time curves, the following crack-
ing parameters were obtained.
   Crack Initiation Time (ΔT): the crack initiation time is defined as the
period between application of a drop of the test reagent and the first visible

cracking of the surface of the test specimen. Without observation, this parameter cannot be derived from the stress-time curve.

Crack-through Time (T_1): the crack-through time is defined as the period between application of the test reagent to the upper surface of the test specimen and the first appearance of visible cracking on the underside of the specimen. In practice it is found that this corresponds to the time interval T_1-T_0 shown on the typical stress-time curve. After crack-through the stress decreases rapidly.

Time to Rupture (T_R): the time to rupture is defined as the period from initial application of the test reagent to the time of final rupture of the specimen (zero stress). In some cases where the stress, after reaching a low value, failed to decrease at the previous rate an extrapolated value for T_R (Fig. 1) was used.

Crack-through Propagation Period (ΔT_1): the crack-through propagation period is defined as the period elapsed between crack initiation and crack through, that is $\Delta T_1 = T_1 - \Delta T$. From this period the crack propagation rate, K, may be calculated (section G). This represents a useful semiquantitative method of ranking the activity of various cracking agents under the test conditions. Although numerical values are employed, emphasis should only be placed on the order of magnitude.

RESULTS

A. Qualitative Assessment of Stress Cracking Agents

The activities of metal halides on stressed nylon 6 are shown in Table I. Certain metal halides and halide-like salts were active stress cracking agents in aqueous solution. Other soluble salts such as sulfates and acetates were inactive. Some agents, such as vanadium chloride and chloroauric acid were weakly active in aqueous solution, and caused surface swelling and softening of the stressed nylon.

In saturated methanolic solution many of the metal halides found to be active in aqueous solution had their activity enhanced, while others such as nickel$_{II}$ chloride, manganese$_{II}$ chloride and calcium chloride which were inactive in aqueous solution became active. Only two salts, aluminium chloride and mercuric chloride, which were active in aqueous solution were found to be inactive in methanolic solution.

Solutions of lithium chloride, cobalt$_{II}$ chloride and zinc chloride in acetone, ethanol, n-propanol, and amyl alcohol were also active cracking agents, but solutions of these salts in dimethyl sulfoxide and ethylene glycol were inactive. None of these solvents showed any stress cracking activity.

B. Reproducibility of Results

For any given set of conditions the cracking parameters are not completely reproducible. However a probability of crack initiation, crack-

through and rupture within certain time limits can be determined.   Generally time to rupture (T_R) was more reproducible than time of crackthrough (T_1).   Typical results showing the probability of rupture with zinc chloride solutions are shown in Table II.

TABLE I
Activity of Metal Halides on Stressed Nylon 6

	Activity in aqueous solution (saturated)		Activity in methanolic solution (saturated)	
	At 4000 psi stress	At 2000 psi stress	At 4000 psi stress	At 2000 psi stress
LiCl	+	−	++	++
LiBr	+++	+++	+++	+++
LiI	−	−	++	++
LiNO₃	−	−	+	+
NaCl	−	−	−	−
KCl	−	−	−	−
NH₄Cl	−	−	−	−
CuCl₂	+	−	+	−
Chloroauric acid	+	−	0	0
MgCl₂	+	−	+	+
CaCl₂	−	−	++	++
MgClO₄	+++	+++	0	0
SrCl₂	−	−	−	−
BaCl₂	−	−	−	−
BaI₂	−	−	++	++
BaBr₂	−	−	+	+
ZnCl₂	+++	+++	+++	+++
ZnI₂	+++	+++	+++	+++
CdCl₂	−	−	−	−
CdBr₂	−	−	+	+
CdI₂	+	−	+	−
HgCl₂	+	−	−	−
AlCl₃	+	−	−	−
InCl₃	++	++	++	++
YCl₃	+	0	0	0
Rare earth chlorides[a]	++	0	0	0
SnCl₂	−	−	−	−
PbCl₂	−	−	−	−
VCl₂	+	+	++	0
CrCl₃	++	−	++	0
FeCl₃	++	−	++	+
CoCl₂	++	++	++	++
NiCl₂	−	−	+	0
PtCl₄	++	++	0	0
PdCl₂	+	−	0	0

Key to Table I: +++, highly active; ++, active; +, weakly active; −, inactive and 0 not tested.

[a] The chlorides of the following rare earths were used: yttrium, lanthanum, praseodymium, neodymium, samarium, gadolinium, yerbium, dysprosium, holmium, erbium, europium, ytterbium.

TABLE II
Typical Times to Rupture for Zinc Chloride Solutions on Stressed Nylon 6[a]

	Time to rupture, min	
Probability of rupture	Aqueous 80% ZnCl₂ solution	Saturated methanolic solution
90% of specimens ruptured	Within 21	Within 10
60% of specimens ruptured	Within 14.5	Within 4.2
50% of specimens ruptured	Within 12.5	Within 3.5
40% of specimens ruptured	Within 12	Within 2.75
20% of specimens ruptured	Within 10.8	Within 2.4
10% of specimens ruptured	Within 9.5	Within 1.5

[a] Conditions: Nylon 6 specimens, 3.5% water content, initial stress 2500 psi, 21°C.

C. Effect of Concentration

With zinc chloride solutions ranging in concentration from 50–80% (w/v), stress cracking data indicated that the concentration did not greatly affect the time to crack initiation. However, with further decreasing concentration the time to rupture increased and the crack propagation rate decreased. Below 30% concentration, crack initiation was extremely slow.

D. Effect of Moisture Content of the Nylon

The moisture content of nylon 6 had a marked effect on the rate of cracking. Dry nylon 6 specimens under stress (3600 psi) showed no crack initiation within 4300 min while samples conditioned to 2.5–3.5% water content were completely ruptured in 20–60 min, and samples conditioned to a water content of about 10% were ruptured within 8 min.

Investigation of the effect of other conditioning agents for nylon, showed that water alone was not essential to the cracking process. Nylons conditioned in methanol, iso-propanol, acetone, ethylene glycol, or even water emulsifiable oil, were all susceptible to stress cracking by aqueous and methanolic solutions of metal salts (Table III).

TABLE III
Effect of Conditioning[a] Agent on Stress Cracking[b]
of Conditioned Nylon 6 Specimens

	Times to crack initiation, sec						Time to rupture, sec					
Cracking agent	A	B	C	D	E	F	A	B	C	D	E	F
80% aqueous ZnCl₂	20	5	60	120	35	15	70	40	105	170	70	85
Saturated methanolic ZnCl₂	30	4	4	4	23	3	40	6	7	6	27	6

[a] Conditioning: Dry samples were conditioned by immersion, at room temperature, for 1 week in: A, distilled water; B, methanol; C, isopropanol; D, acetone; E, ethylene glycol; and F, water emulsifiable oil.
[b] Stress conditions: 2500 psi at room temperature.

As shown in Table III, saturated methanolic zinc chloride was a more active cracking agent than 80% zinc chloride solution, irrespective of the conditioning agent used. Samples conditioned with nonaqueous agents were more rapidly attacked by methanolic zinc chloride than samples conditioned with water.

Dry nylon or nylons with low equilibrium moisture content, such as nylon 11, were resistant to stress cracking by solutions of metal halides. Nylon 11 specimens however, conditioned for one week in methanol and then stressed at 2500 psi, cracked after 24 hr in contact with 80% zinc chloride solution, and after 1 min in contact with saturated methanolic zinc chloride. Nylon 11 specimens conditioned in a similar manner in distilled water and tested under the same stress conditions failed to show crack initiation with either reagent.

E. Effect of Temperature

Temperature has a marked effect on the rate of cracking of nylons by aqueous zinc chloride. Stressed nylon 6 specimens (water content, 3.5%) take greater than 250 min to crack-through at 3°C compared with 20–24 min at 21°C and 2–19 min at 27°C. Hot aqueous zinc chloride solutions (80°C) caused rapid cracking in stressed specimens.

F. Effect of Surface Conditions

Stressed nylon specimens with surfaces prepared by flame polishing, abrasion with course and fine emery, and notched both parallel and at right angles to the applied stress were shown to exhibit similar stress cracking parameters.

Specimens were tested with varying areas of contact between the stress cracking agent and the nylon surface. With the nylon cracking agent air interface unrestricted and the contact area between the cracking agent and the nylon determined only by drop size (as determined by the quantity of cracking agent applied) it was found that quantity and/or area of contact were not major factors in determining the rate of crack initiation. However, they could be important factors in determining the rate of crack propagation from initiation to crack through. For most determinations, drops of cracking agent were applied to the nylon surface with a micrometer syringe.

G. Comparison of Activity

As shown in Table IV aqueous zinc iodide, zinc chloride and lithium bromide at similar concentrations show the same order of activity.

Saturated aqueous solutions of cobalt$_{II}$ chloride were slower in action. The comparative activity of a range of lithium salts in both water and methanol is given in Table V.

Other metal halides were active in aqueous solution, in the order: $CoCl_2$, rare earth chlorides, $PtCl_4$, $CrCl_3$, $FeCl_3$, $HgCl_2$, $AlCl_3$, LiCl, $MgCl_2$. In

TABLE IV
Stress Cracking Activity of Aqueous Zinc Chloride and Zinc Iodide

Initial stress, psi	Time to crack-through, min at 21°C		
	$ZnCl_2$[a]	ZnI_2[a]	LiBr[a]
1400	36.5	75.5	—
2000	23.0	38.0	27.0
2500	8.2	12.3	—
3300	5.0	6.5	—
4300	3.4	4.0	—

[a] Solution concentration, 80% (w/v).

TABLE V
Stress Cracking Activity of Lithium Salts

Solution (saturated)	Time to crack initiation, min	Time to rupture, min
LiCl in water	>3000	[b]
LiCl in methanol	0.5	60
LiBr in water	10	23
LiBr in methanol	3	6
LiI in water	>1500[a]	[a]
LiI in methanol	400	405
Li acetate in water	>1500[a]	[a]
Li acetate in methanol	>1500[a]	[a]
Li nitrate in water	>1500[a]	[a]
Li nitrate in methanol	Approx. 1400	3000

[a] No crack initiation occurred.
[b] Crack initiation occurred very slowly.
Conditions: Nylon 6 specimens, 3.5% water content, initial stress 2000 psi, 21°C.

methanolic solution, activity of these salts was greatly enhanced. Methanolic solutions of $NiCl_2$, $MnCl_2$, and $CaCl_2$ also cause cracking of stressed nylons.

The comparative activity of stress cracking agents was assessed by determination of the rate of crack propagation through the nylon specimen.

The crack propagation rate (K), is defined by,

$$K = \frac{t}{T_1 - \Delta T}$$

where

t = thickness of the specimen
T_1 = period of crack-through
ΔT = period of crack initiation

Crack propagation rates for solutions of zinc, lithium, cobalt, and calcium chlorides on stressed nylon 6, as shown in Table VI, indicated that methanolic zinc chloride is the most active agent. The stress cracking activity of metal halides was also determined using a dynamic rupture technique in

TABLE VI
Crack Propagation Rates of Metal Halide Solutions[a]

Solution	Number of determination	Crack propagation rate (K), in. per min		
		$K_{max}{}^m$	$K_{min}{}^m$	K_{mean}
Aqueous ZnCl$_2$, 80%	16	0.028	0.005	0.010
Saturated methanolic ZnCl$_2$	10	0.059	0.010	0.030
Saturated methanolic LiCl	2	0.002	0.002	0.002
Saturated methanolic CoCl$_2$	2	0.001	0.001	0.001
Saturated methanolic CaCl$_2$	4	0.0005	0.0005	0.0005

[a] Conditions: Nylon 6 specimens, 3.5% water content, initial stress 2000 psi, 21°C. The specimens were 0.125 in. thick. A smaller number of determinations was carried out for less active agents because of the slower cracking rate. Where cracking occurred more slowly, results were much more reproducible. However, results are still only quoted to one significant figure.

which nylon 6 test specimens were extended at a rate of 0.0625 in./min and the load continuously recorded while in contact with the cracking agent. The time to rupture (T_R) was determined and an activity factor (A) then derived from the equation $A = 1/T_R \cdot (1)/(M)$
where

T_R = time to rupture of specimen
M = molar concentration of cracking solution

The activity factors for some cracking agent solutions, as shown in Table VII, show that methanolic zinc chloride is the most active agent followed, in order, by methanolic cobalt$_{II}$ chloride, aqueous zinc chloride, methanolic calcium chloride and methanolic lithium chloride.

TABLE VII
Stress Cracking Activity of Metal Halides under Dynamic Stress Conditions[a]

Agent	Number of determinations	Average time to rupture, min	Activity factor, min^{-1} mole^{-1}
Aqueous ZnCl$_2$, 80%	2	11.5	0.015
Aqueous ZnCl$_2$, 40%	1	12.35	0.028
Saturated methanolic ZnCl$_2$	4	5.55	0.041
Saturated methanolic LiCl	3	19.7	0.005
Saturated methanolic CaCl$_2$	4	42.0	0.011
Saturated methanolic CoCl$_2$	3	19.43	0.032

[a] Conditions: Nylon 6 specimens, 3.5% water content, 21°C. The specimens were 0.125 in. thick.

H. Effect of Stress

As with all other stress cracking phenomena, the initiation of cracking, rate of crack-through, rate of crack propagation and time to rupture in the cracking of nylon by metal halide solutions are stress dependent quantities.
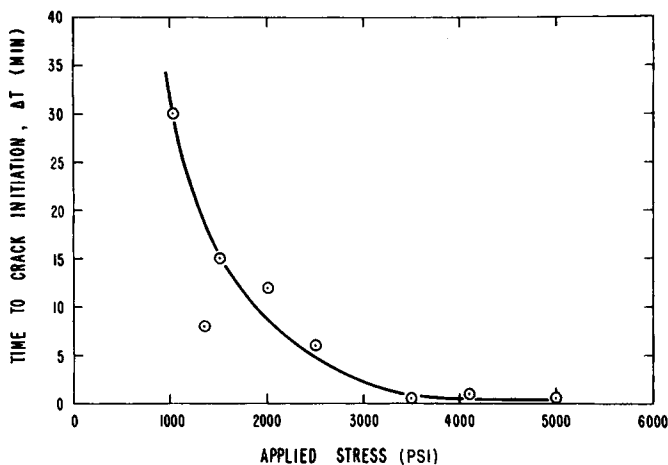
Fig. 4. Effect of stress on time to crack initiation for nylon 6—stress cracked by 80% aqueous $ZnCl_2$ solution, at 21°C.
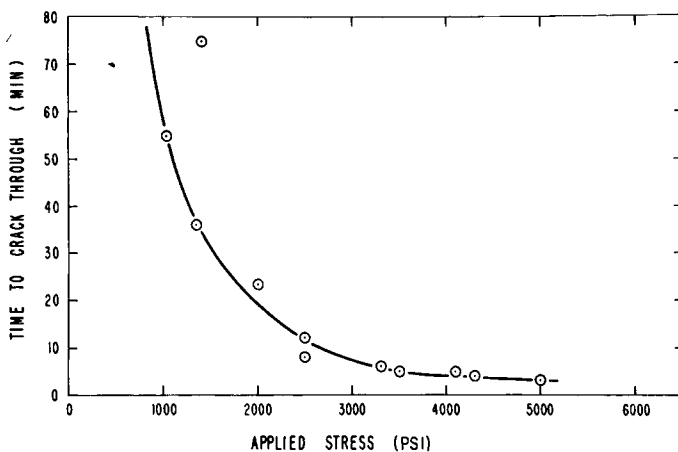

Fig. 5. Effect of stress on time to crack-through for nylon 6—stress cracked by 80% aqueous $ZnCl_2$, at 21°C.

This has been demonstrated for the cracking of nylon 6 by both aqueous and methanolic zinc chloride.

The effect of stress in nylon 6, when treated with 80% aqueous zinc chloride, on the crack initiation time, on the crack-through time and on the time to rupture is shown in Figures 4, 5, and 6, respectively. The effect of stress in nylon 6, when treated with methanolic zinc chloride, on the crack-through time is shown in Figure 7.

These results indicate that a minimum stress level in nylon 6 of about 700–800 psi is required before stress cracking can be initiated by solutions of metal halides. Since injection moulded nylon components are also

rapidly cracked by solutions of zinc chloride[1] it is most probable that these components have internal stresses of a high order. The level of internal stress in nylon mouldings can be estimated by determination of the time to rupture when in contact with zinc chloride solution under standard conditions.
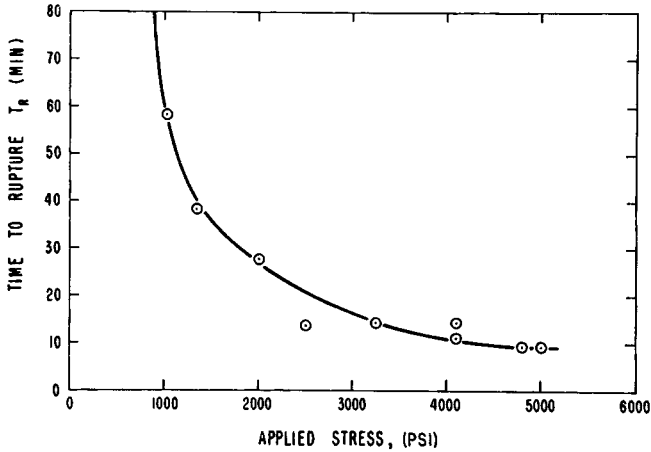

Fig. 6. Effect of stress on time to rupture for nylon 6, stress cracked by 80% aqueous ZnCl₂, at 21°C.
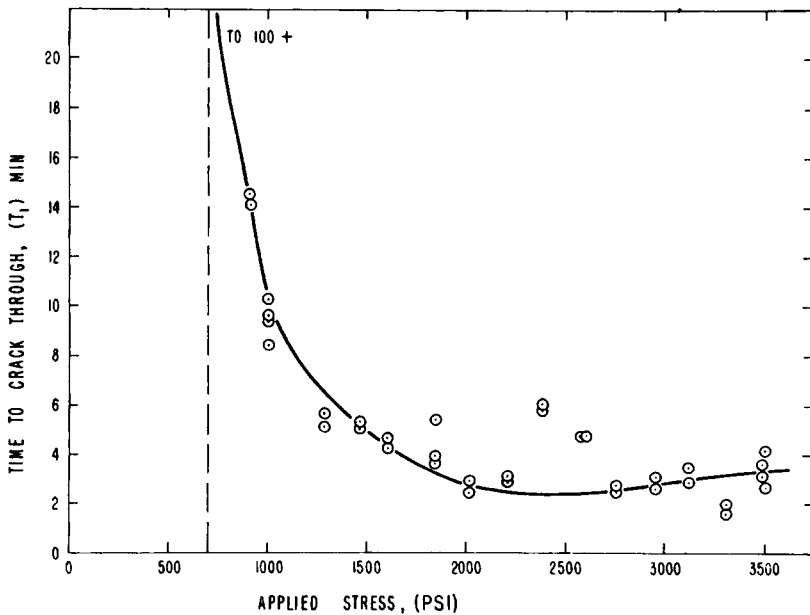

Fi . 7. Effect of stress on time to crack-through for nylon 6, stress cracked by saturated methanolic ZnCl₂, at 21°C.

Effect of Zinc Chloride on Unstressed Nylon

Unstressed, injection moulded, dry nylon 6 tensile test specimens were conditioned for various periods in distilled water and in 40% aqueous zinc chloride, after which they were washed clean and wiped dry. The tensile strengths of the specimens treated by these alternative conditioning agents were then determined and compared. The results (Table VIII) showed only minor differences between the water conditioned specimens and the zinc chloride conditioned specimens, and indicated that no embrittlement of the unstressed mouldings had occurred in the zinc chloride solution.

TABLE VIII
Effect of Zinc Chloride on Unstressed Nylon 6

Period of conditioning, days	Moisture content, % (approx)	Tensile yield strength, psi	
		Conditioned in water	Conditioned in 40% zinc chloride solution
Nil(Controls)		7000, 6850, 6720, 6700	
1.25	2	6020, 5800, 6120	6360, 6360, 6440
8	4	4150, 4150, 4160	4020, 3900, 3800
17	6	3800, 3860, 3870	3780, 3720, 3820
31	8	3670, 3640, 3620	3470, 3460, 3410
52	10	3320, 3420, 3320	3250, 3210, 3220
80	Saturated	3220, 3400, 3460	3220, 3120, 3300

Viscosity measurements of nylon 6 in formic acid solution showed that the intrinsic viscosity did not decrease, on standing, in the presence of zinc chloride, indicating that reduction of molecular weight due to chain scission did not occur. However, it was shown that the viscosity of nylon in formic acid solution was reduced in the presence of zinc chloride. Some modification of the polymer structure in the presence of zinc chloride had probably occurred.

DISCUSSION

Stuart, Markowski, and Jeschke[8] have described a mechanism of environmental stress cracking by solvents or other liquids capable of wetting the surface of polymeric materials. These are often capable of being absorbed, cause swelling of the polymer and induce critical localized stresses which cause fine cracks to appear at surface flaws. This is more likely to occur where such flaws are associated with boundaries between separate crystalline regions in the polymer. They also indicate that factors such as instantaneous increase in local notch stresses, "microplasticization" and also gross plasticization of the polymer due to the cracking agent are all important factors in the stress cracking process.

Methanolic and aqueous solutions of the metal halides are usually viscous and surface wetting does not occur readily. Also in most cases crack

initiation does not occur in the area under the droplet but at the nylon-reagent-air interface. The presence of gross surface imperfections does not appear to markedly affect the rate of crack initiation.

Microplasticization and gross plasticization occurs, since all of the cracking agents are effective swelling agents for nylon. The presence of water or other nonaqueous conditioning agents, which are also swelling agents, in the nylon is essential for stress cracking by metal halides to occur. This result for nylon is at variance with the effects of prior conditioning with swelling agents on the stress cracking of polythene described by Stuart et al.[8]

The presence of a metal halide in solution is essential for this type of stress cracking. It would appear that the role of the solvent, and the conditioning agent, is not only to act as a swelling agent, but also to provide a transport medium by which the metal halide can be absorbed into the nylon. We believe the absorbed metal halide mainly promotes stress cracking by chemical means.

TABLE IX
The Effect of pH on the Stress Cracking of Nylon 6[b]

Solution	pH	Crack initiation time, min	Rupture time, min
ZnCl₂ solution, (35%)	4.29	1	80–140
ZnCl₂ solution, (18%) adjusted with HCl	4.89	>1500	—
ZnCl₂ solution, (4.5%) adjusted with HCl	1.45	>1500	—
Hydrochloric acid (12 N)	0	nil[a]	nil[a]

[a] Extensive swelling and softening.

[b] Conditions: nylon 6 specimens, 3.5% water content, initial stress 2000 psi, temperature 21 °C.

Weiske[3] has described the stress cracking of dry nylons by polar solvents and in this case a simple physical mechanism is involved. He has also described the cracking of nylons by dilute mineral acids. Hydrochloric acid (5%) was reported to cause cracking in conditioned nylon 6 and 6.6 within 2-3 months and 2% hydrochloric acid caused embrittlement in one year. The mechanism proposed was one of simple hydrolysis, with the rate of crack initiation being a function of hydrogen ion concentration.

We found solutions of hydrochloric acid of equivalent hydrogen ion concentration to active zinc chloride solutions (80% ZnCl₂, pH 0; 20% ZnCl₂, pH 5.2) would not cause rapid stress cracking of nylon. Dilute solutions of zinc chloride, adjusted by the addition of hydrochloric acid to a hydrogen ion concentration equivalent to that of the more concentrated active solutions, were very slow cracking agents.

Results as shown in Table IX indicate that the stress cracking of nylon 6 by metal halide solutions is not a function of the hydrogen ion concentra-

tion, and it is unlikely that the mechanism is one of hydrolysis or metal-ion catalysed hydrolysis.

We believe the stress cracking mechanism involves reactions between the metal halide and the nylon. This has been investigated using infrared techniques and is described in Parts II and III.

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