JOURNAL OF MATERIALS SCIENCE 13 (1978) 243–252

Stress-cracking of nylons induced by zinc chloride solutions

A. C. REIMSCHUESSEL, YOUNG JOON KIM*
Allied Chemical Corporation Chemical Research Center, Morristown, New Jersey 07960, USA

Swelling, orientation, and stress-cracking experiments with nylons in various zinc chloride solutions show that a low degree of solubility of the polymer in the stress-cracking agent is a prerequisite for cracking. As demonstrated by scanning electron microscopy, dissolving, yielding, and tearing occur during the solvent stress-cracking process.

1. Introduction

Stress-cracking is defined as catastrophic failure of a material at a much lower stress than its ultimate strength due to the combined effects of stress and environment. In the case of polymers Howard [1] distinguished between environmental, solvent, and thermal stress-cracking. In his definition, environmental stress-cracking is surface-initiated by an agent functioning through an absorptive mechanism without producing other effects. The particular emphasis here is that the cracking agent is not a solvent or even a swelling agent. On the other hand, solvent stress-cracking involves physical swelling of the polymer. Thermal stress-cracking involves morphological changes within the material through exposure to thermal energy. The morphological changes result in impairment of the strength. We shall adopt the terminology used by Howard in this paper.

The mechanism of environmental crazing in a polymer glass (PMMA) has been studied by Andrews and Bevan [2]. They showed that the crazing behaviour is strongly dependent on temperature and governed by both solubility parameters and the swelling characteristics of the solvent for the polymer. These and other aspects of crazing, such as nucleation and growth of voids, plastic deformation, strain hardening and solvent craze-growth, have been reviewed by Andrews [3] and Haward [4].

According to MacNulty [5] the final mechanism of polymer fracture by either pure stress or by liquid and stress is the same, however Henry [6] and Singleton [7] suggest that in glassy thermoplastics and in polyethylene, environmental stress-cracking agents weaken the intra- and intermolecular bonds and the cohesion between "macro" structural elements, such as fibrils and lamellae. Hannon [8] discussed environmental stress-cracking of polyethylene and copolymers of polyethylene in terms of "intercrystalline links" of lower density which bear the stress concentrations, fracture, and cause the formation of microvoids. According to Hannon, the process of hole nucleation and hole growth is followed by viscoplastic deformation and strain hardening of the molecules surrounding the voids.

Dunn and Sansom [9–11] conducted extensive investigations on the stress-cracking of polyamides in aqueous or methanolic solutions of various metal salts. They concluded that two different physical mechanisms apply for two different groups of metal salts. Chemically, both groups of metal salts form complexes with polyamides with the aid of the solvents, but in different manners. Group I salts plasticize the polymer matrix by diffusion, lower the yield strength, and as a consequence induce the stress-cracking. Group II metal salts dissolve polyamides, and the dissolution causes the stress-cracking. The authors further

---

*Present address: Chemelex Inc., Redwood City, California, USA concluded that zinc chloride, the most active halide for polymer stress-cracking, belongs to Group I salts.

Our observations showed evidence that various zinc chloride solutions have solvent action on polyamides. A close relationship between the solvent action of zinc chloride solution and the stress-cracking was observed. Experimental results are presented which indicate the stress-cracking of polyamides by aqueous, alcoholic or ether solutions of zinc chloride is based upon solvent stress-cracking.

2. Experimental

2.1. Polymer samples

The following are the resins used in the experiments:

(1) Nylon 6 (Type A): Molecular weight Mn = 28 000; water extractable content 1.7%. (Allied Chemical Corporation).

(2) Nylon 6 (Type B): Molecular weight Mn = 21 000; water extractable content 0.8%. (Allied Chemical Corporation).

(3) Nylon 6 (Type C): Molecular weight Mn = 21 000; water extractable content 7%, lubricant content 0.5%. (Allied Chemical Corporation).

(4) Nylon 11: Plasticized–Plasticizer type and content are unknown (Acquitaine–Organico).

(5) Nylon 12: Unplasticized (Chemische Werke Huels AG).

(6) Nylon 6–12: Copolymer of 20 mol% Caprolactam and 80% Laurylactam unplasticized (Chemische Werke Huels AG).

2.2. Swelling test

Nylon pellets were ground in a Spex's Freeze Mill at liquid nitrogen temperature. The ground resins were screened through 60 mesh openings and the particles which were smaller than 60 mesh were collected. 1 g of the polymer powder was mixed with 20 ml of the appropriate zinc chloride solution in a 50 ml Erlenmeyer flask. The mixture was continuously shaken on a hand-action shaker and periodic visual inspections were made for 24 h. To conduct the experiment at an elevated temperature the lower half of the flask was immersed in a shallow oil bath. The bath temperature was maintained at 60° C while shaking was continued.

After 24 h the treated samples were examined visually. They were classified as "unaffected" in the case when the particles had remained separate and did not show any sign of swelling, as "swollen and aggregated" when the particles had formed a single mass in which the original shape of the particles was still recognizable, and as "dissolved" when a viscous fluid had formed. For comparison, 60 mil* nylon 6 strips were immersed in a 50% zinc chloride solution.

2.3. Stress-cracking tests

Two different methods were used to test the stress-cracking behaviour of nylons. One is essentially the Bell Laboratories bent strip test [12, 13]. Specimens of 0.5 in. x 1.5 in. were punched out from a 0.125 in. thick compression moulded sheet with a cutting die. A stress-raising slip 0.020 in. deep and 0.75 in. long was cut in the centre of one surface of each specimen parallel to the long axis of the specimen using a special razor-blade. The specimens were bent into an arch with the slit on the top surface. The bent strips were inserted in a sample holder consisting of an open rectangular channel of inside dimension 0.375 in. deep, 0.625 in. wide, and 6.5 in. long. The whole specimen holder with the mounted specimen was submerged in a test tube filled with a stress-cracking agent. Periodic inspections were made for 24 h to see whether or not the specimens were cracked. This test method was used to study the relationship between solubility and stress-cracking.

The second method involved testing under constant stress. This method was used to study the effects of both orientation and low molecular weight fractions on stress-cracking. The experimental set-up is shown in Fig. 1. Dumbbell-shaped specimens were cut from a compression moulded sheet. Each specimen was mounted horizontally between two clamps, one of which moved freely

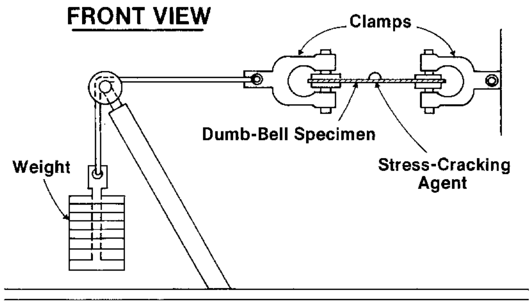


Figure 1 Stress-cracking tester (constant tensile load).

---

*1 mil = 10^{-3} in.

over a supporting roller. A desired level of stress was applied by adding weights at the end of the freely moving side. As soon as the specimen was loaded to the desired stress level, a drop of stress-cracking agent was placed at the centre of the neck of the dumbbell specimen. Time-to-break was measured from the time at which the stress-cracking agent was placed on the specimen to the time at which the specimen ruptured into two separate pieces. The test was conducted at room temperature. The dimensions of the neck of the unoriented dumbbell specimen were 0.03 in. x 0.25 in. x 1.0 in. In the oriented specimens, the dimensions of the neck were smaller; therefore, lower weight levels were applied to keep the stress constant at ~7000 psi.

2.4. Orientation

The dumbbell specimens were oriented by stretching on Instron tensile equipment at room temperature, at a rate of 0.1 in. min^{-1}. The neck dimensions of the unstretched dumbbell specimen were 0.03 in. x 0.05 in. x 1.0 in. After stretching, the specimens were held at the stretched state for 5 min before they were released from the Instron jaws. Resultant per cent elongation was determined 1 h after the specimens were released from the Instron by measuring the neck portion of the dumbbell. The stress-cracking test was carried out a short time after measuring the elongation.

2.5. Scanning electron microscopy

Nylon 6 Type B polymer, nylon 11 and nylon 12 were selected to study the effect of stress-cracking agents on the fracture morphology by scanning electron microscopy. Included for comparison were mechanically fractured specimens. All of the samples were compression moulded and quenched in air.

(a) Mechanically fractured surfaces were obtained by fracturing dumbbell-shaped specimens on a tensile impact device at room temperature. The cross-sectional area of the dumbbell measured 0.25 in. x 0.06 in.

TABLE I Swelling and stress-cracking of nylons in various zinc chloride solutions

Type of nylon	Expt. temp. (° C)	Stress-cracking agent		Degree of solvation of nylon powder	Stress-cracking of bent nylon strips†
		Solvent*	$ZnCl_2$ Conc.		
nylon 6	23	water	50 wt %	swelled and aggregated	cracked
		methanol	saturated	dissolved	not cracked, dissolved
		ethanol	saturated	dissolved	not cracked, dissolved
		ether	saturated	swelled and aggregated	cracked
nylon 11	23	water	50 wt %	not affected	not cracked
		methanol	saturated	not affected	not cracked
		ethanol	saturated	dissolved	not cracked, dissolved
		ether	saturated	swelled and aggregated	cracked
nylon 11	60	water	50 wt %	not affected	not cracked
		methanol	saturated	swelled and aggregated	cracked
		ethanol	saturated	dissolved	not cracked, dissolved
		ether	saturated	‡	‡
nylon 12	23	water	50 wt %	not affected	not cracked
		methanol	saturated	not affected	not cracked
		ethanol	saturated	not affected	not cracked
		ether	saturated	swelled and aggregated	cracked
nylon 12	60	water	50 wt %	not affected	not cracked
		methanol	saturated	swelled and aggregated	cracked
		ethanol	saturated	dissolved	not cracked, dissolved
nylon 6 and 12 copolymer	23	water	50 wt %	not affected	not cracked
		methanol	saturated	swelled and aggregated	cracked
		ethanol	saturated	dissolved	not cracked, dissolved
		ether	saturated	swelled and aggregated	cracked

* None of these solvents caused stress-cracking without zinc chloride.

† All of the specimens which are marked "cracked" failed within 1 h.

‡ The data could not be obtained due to the rapid evaporation of ether at 60° C. However, the zinc chloride saturated ether solution tends to dissolve both nylon 11 and nylon 12 when the temperature is increased from room temperature.

(b) Brittle fracture was achieved by precooling the test specimens in liquid nitrogen for a minimum of 5 min.

(c) The stress-cracked surfaces were prepared by cracking nylon strips in the stress-cracking agents at room temperature and at 60° C. Nylon strips measuring 2.5 in. x 0.25 in. x 0.06 in. were bent into loops and the open ends were tied together to keep the specimens under a bending stress. The stressed specimens were submerged in the cracking agents and failure occurred within a period of less than 1 h. The cracked specimens were removed from the agent, rinsed with distilled water, and dried in the atmosphere.

Prior to examination, all of the fractured surfaces were vapour-coated with a thin (~ 150 Å) film of Au/Pd to render them conductive, a prerequisite for examination with the scanning electron microscope. The instrument used was a JEOL JSM–2, operated at an accelerating voltage of 25 kV. Photomicrographs were prepared at a scan speed of 50 sec per frame.

3. Results and discussion

3.1. Swelling and stress-cracking

The results of both the swelling experiment and the bent strip tests shown in Table I indicate that the stress-cracking of nylons in various zinc chloride solutions is closely related to their swelling and "limited" or low solubility characteristics. Whereas nylon strips stress-cracked in the medium that had caused swelling and aggregation of the corresponding polymer powder, no stress-cracking was observed in strips exposed to agents that had not caused swelling or partial dissolution of the powder. The observation that a low degree of solubility is related to stress-cracking is consistent with previously reported work on solvent stress-crazing by Stuart *et al.* [14]. The authors believed that wetting and swelling is necessary for organic plastic to craze.

The fact that the same agent causes stress-cracking at an elevated temperature while it does not at a lower temperature, suggests that the purely physical approach attempted by Stuart *et al.* [14] is justifiable. The authors treated the causes of the crazing of organic plastics from this point of view, although they were aware of the fact that there could exist chemical interaction involving some type of secondary bonds, which in turn, may cause the solubility. Dunn and Sansom [10] showed that the zinc chloride solutions form a complex with nylon molecules. The formation of the complex would cause nylon stress-cracking

TABLE II Stress-cracking resistance of oriented nylon 6 in aqueous zinc chloride solution

Type of resin	Type of specimen cooling*	Initial extension (%)	Resultant† extension after recovery (%)	Stress† applied (psi)	Time-to-break† (min)
Type A:	AC	0	0	7350	15.3
MW = 28 000	AC	10	Nil	7350	1.5
water extractable = 1.7%	AC	100	70	7380	>1440.
	QQ	0	0	6630	0.85
	QQ	10	Nil	6910	0.37
	QQ	10	75	7480	>1440.
Type B:	AC	0	0	7020	5.0
MW = 21 000	AC	10	Nil	7490	0.56
water extractable = 0.8%	AC	100	63	6870	>1440.
	QQ	0	0	8580	0.74
	QQ	10	Nil	7500	0.34
	QQ	100	75	6650	>1440.
Type C:	AC	0	0	4490	2.8
MW = 21 000	AC	10	Nil	8630	0.63
water extractable = 7%	AC	100	50	7390	18.
max as lubricant = 0.5%	QQ	0	0	4800	0.18
	QQ	10	Nil	7940	‡
	QQ	100	83	7420	333.

* Key: AC = cooled in air temperature. QQ = quickly quenched in water at approximately 15° C.

† The values shown are the average of two tests.

‡ The samples were stretched upon applying the stress. The time-to-break was not measured on these samples.

only if it involves a particular degree of solubility. In other words, the complexation alone is not a sufficient condition for the nylon stress-cracking. For instance, nylon 12 in zinc chloride saturated ethanol solution probably forms the type of complex Dunn and Sansom suggested regardless of whether the solution is at room temperature or at 60° C. However, due to the difference in the degree of solvent power of the stress-cracking medium at a given temperature, nylon 12 cracks at room temperature, but dissolves rather than cracks at 60° C.

A significant difference in swelling characteristics between the powders and the bulk strips was observed with the effective stress-cracking agents. Whereas nylon 6 powder started to show signs of swelling and aggregation a few minutes after the submergence in 50% aqueous zinc chloride solution, 60 mil strips did not show any appreciable change even after two months of submergence. The result suggests that the thickness of the polymer layer into which the stress-cracking agent had penetrated and swollen the polymer during that period is limited. Further investigation of this observation may help to illustrate the physical aspect of the solvent stress-cracking mechanism. By recognizing the limited growth of the swollen layer thickness, we may explain the physical mechanism of nylon stress-cracking in zinc chloride solutions.

As soon as the zinc chloride solution wets the polymer, some chemical complex between the polymer and the stress-cracking agent is formed. The complexation has not only a plasticizing and swelling effect but also some barrier effect against further diffusion of electrolyte solution into the polymer matrix. The barrier effect may be steric or ionic, or both, and limits the total thickness of the swelled layer. However, at the apex of microcracks the agent can diffuse further into the polymer forming a new swollen layer of limited thickness. Crack propagation will continue due to the combined effects of stress concentration and softening until the material fails.

Increasing the solvent power of the stress-cracking agent will result in the formation of very thick swollen layers and the loss of stress concentration at the tips of microcracks. The microcracks will eventually collapse in the rapidly growing gel, and dissolution rather than stress-cracking will be the cause of failure.

In short, limited solubility and a limitation of the equilibrium thickness of the swollen layer appear to be a requirement for the stress-cracking of nylons in zinc chloride solutions.

3.2. Effect of orientation, low molecular weight fractions, and cooling rate

In oriented nylon 6, resistance to zinc chloride stress-cracking increased significantly parallel to the direction of orientation. These results are shown in Table II. Although no quantitative test was conducted, it was observed that stress-cracking resistance decreased in the direction perpendicular to the orientation.

The following observations can be made from the stress-cracking data of nylon 6 shown in Table II.

(1) Time-to-break values of Type A polymer are consistently higher than those of Type B. Considering the relatively low water extractable content for both polymers, it can be concluded that the difference is due to the difference in molecular weight. Comparing polymers Type B and Type C,

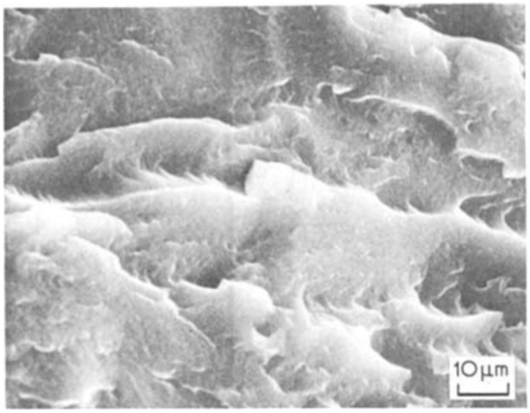


Figure 2 Nylon 6, tensile impact test, fractured at – 180° C.

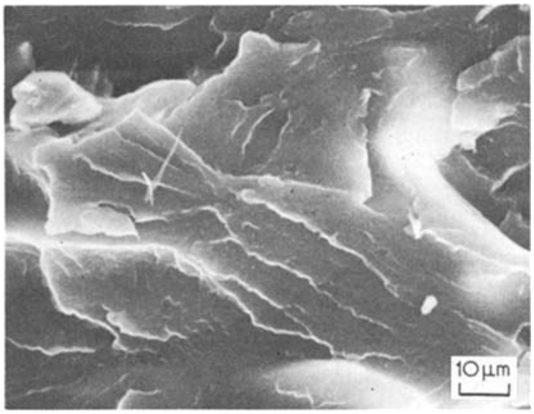


Figure 3 Nylon 6, tensile impact test, fractured at room temperature.

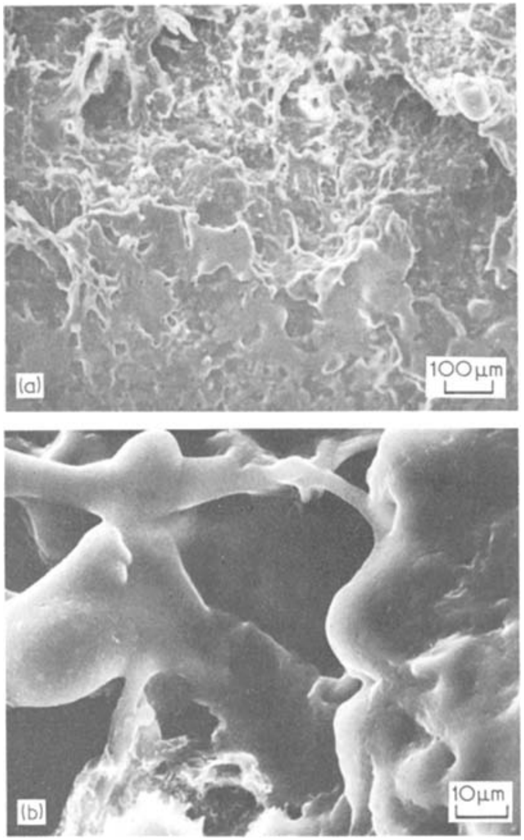


Figure 4 Nylon 6, stress-cracked in aqueous $ZnCl_2$ solution (50%) at room temperature.

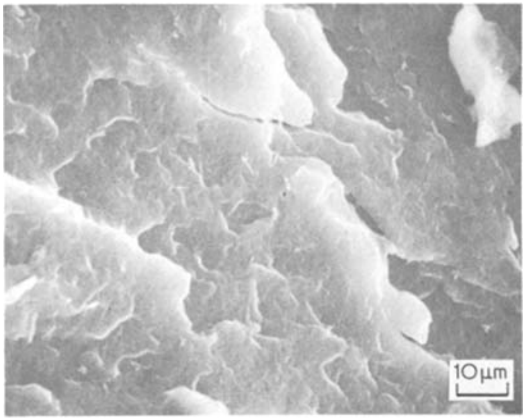


Figure 5 Nylon 11, tensile impact test, fractured at −180° C.

it is shown that polymers of the same average molecular weight but different water extractable content differ in their time-to-break value. This is especially pronounced in the oriented samples. Type C, the material with the higher water extractable content, i.e., higher content of low molecular weight fractions, fails within a shorter period. As indicated by these data, low average molecular weight and high content of low molecular weight fractions adversely affect the stress-cracking resistance of nylon 6 in aqueous zinc chloride solution.

(2) All of the specimens which had been slightly stretched and relaxed produced consistently lower time-to-break values than either unstretched samples or the samples which had been stretched and permanently oriented. It is assumed that the number of microcracks or surface defects increased due to the stretching and relaxation treatment. The presence of such cracks appears to play a significant role in the stress-cracking of nylon 6 aqueous zinc chloride solution.

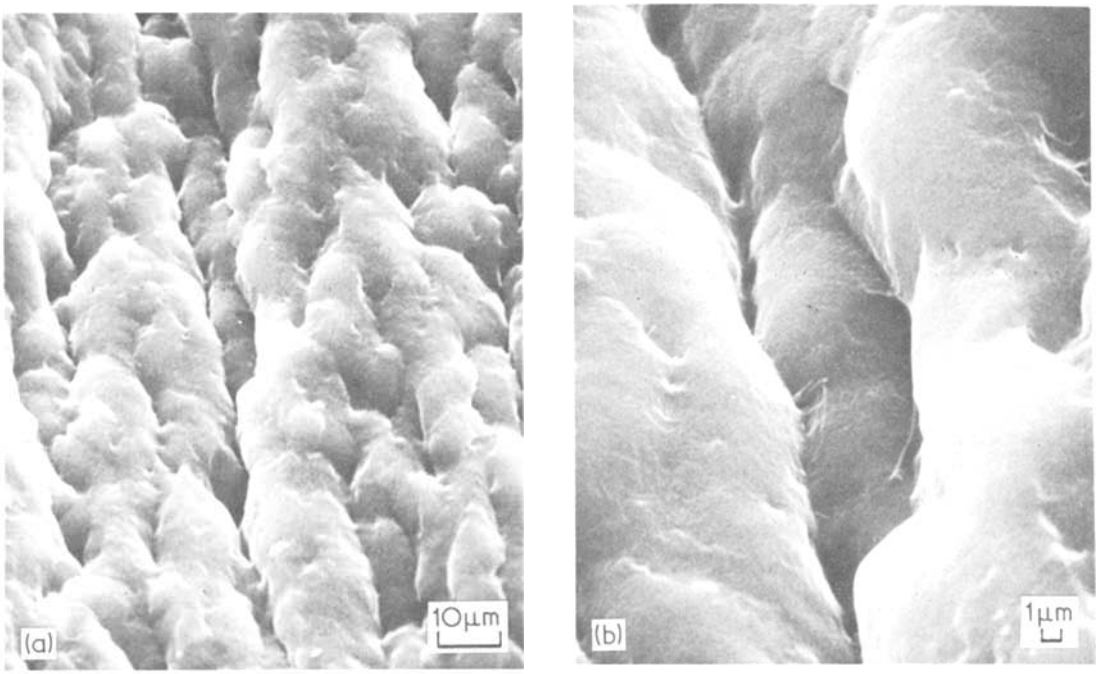
(3) All of the air-cooled samples showed consistently higher time-to-break values than quick-quenched samples. Both environmental stress-cracking [1] and thermal stress-cracking [16] showed the reverse trend in crystalline polymers. The observed trend that slow cooling improved the solvent stress-cracking resistance may be related to differences in the morphology of the samples investigated.

3.3. Interpretation of the fracture morphology

As would be expected, all of the low temperature fracture surfaces shown in Figs. 2, 5 and 8, show brittle fracture characteristics regardless of whether they are nylon 6, nylon 11, or nylon 12.

With the exception of the nylon 6 specimen, the texture of surfaces obtained by fracture at room temperature differed significantly from that obtained at liquid nitrogen temperatures. As shown in Figs. 6 and 9, the fracture of both nylon 11 and nylon 12 specimens involved deformation phenomena. It is assumed that the interconnected bead-like or globular protrusions are partially deformed spherulites. Fracture apparently proceeded along spherulite boundaries, which may be taken as an indication of the inherent weakness of this interspherulitic less-ordered region. For comparison, photomicrographs taken in polarized transmitted light from sections of the specimens obtained near the fractured surface are included. Both the range of the diameter and the orientation of the "rows" of spherulites shown, suggest a relation between this morphology and that of the fractured surface.

It should also be noted that both nylon 11 and nylon 12 specimens showed signs of necking, i.e.



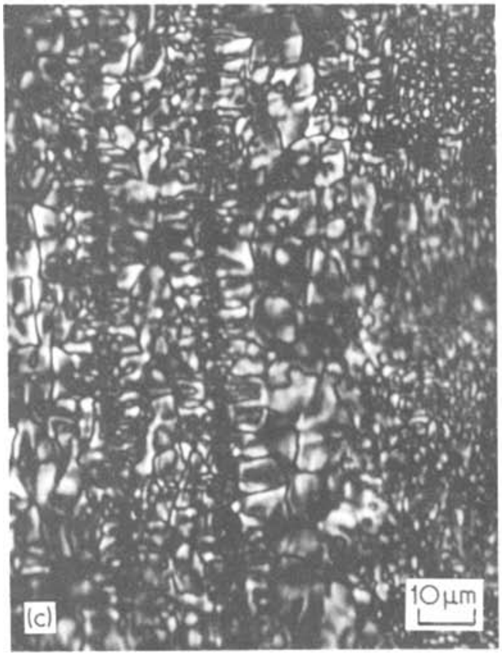


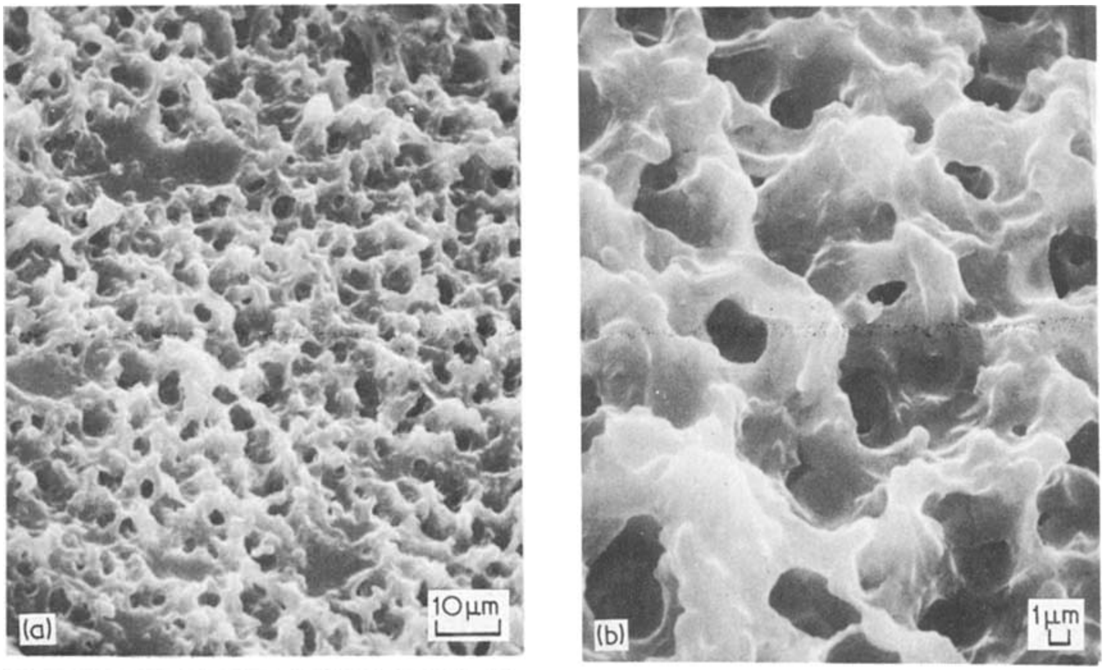
Figure 6 Nylon 11, tensile impact test, fractured at room temperature. (a) and (b) Scanning electron micrographs of fractured surface; (c) Photomicrograph of cross-section (transmitted polarized light).

deformation near the fractured region when subjected to the tensile impact test, whereas no necking was observed in the nylon 6 specimens.

The stress-cracked nylon 6, nylon 11, and nylon 12 specimens differed from each other with respect to their surface morphology. Fig. 4 shows deep cracks, fissures and holes to be present on the surface of the nylon 6 specimen. These features, together with the smooth rounded-off areas shown in Fig. 4, are assumed to be indicative of localized partial dissolution of the polymer.

As shown in Fig. 7, the surface of the stress-cracked nylon 11 specimen exhibited numerous pits and bead-like protrusions. It is assumed that the globular aggregates represent the core or more densely packed portion of spherulites. The pits, comparable in diameter to the globules or beads, appear to correspond to sites from which spherulites may have been torn out on cracking. The spherulitic morphology of this specimen is illustrated in Fig. 7c.

It should be noted that the nylon 11 represented a plasticized resin, whereas both nylon 6 and nylon 12 materials did not contain plasticizer. The plasticizer acting as a diluent or similar to a low molecular weight fraction may have segregated out during crystallization [17, 18] into the spherulite boundary region. This less-ordered and "diluted" region was more easily attacked by the swelling agent, therefore yielding more rapidly during crack tip propagation. The topography of the stress-cracked nylon 12 shown in Fig. 10 is characterized



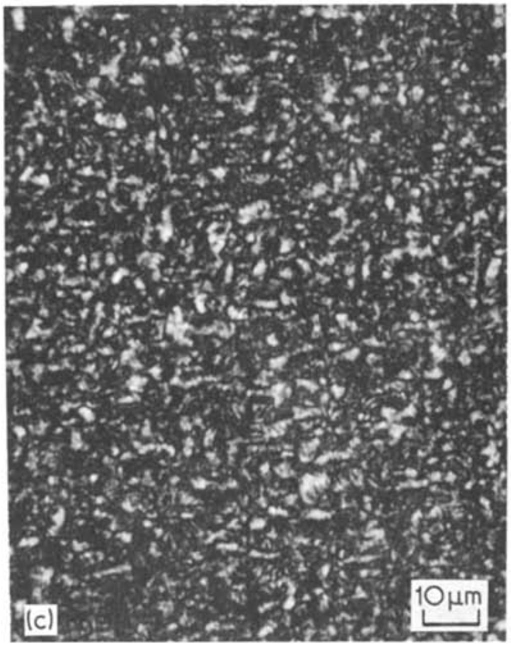


Figure 7 Nylon 11, stress-cracked in saturated solution of $ZnCl_2$ in methanol at 60° C. (a) and (b) Scanning electron micrographs of stress-cracked surface; (c) photomicrograph of cross-section (transmitted polarized light).

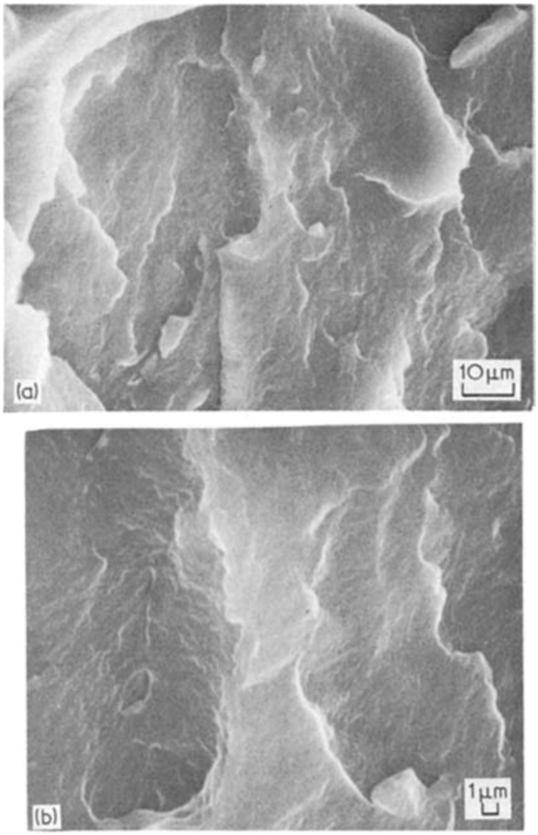
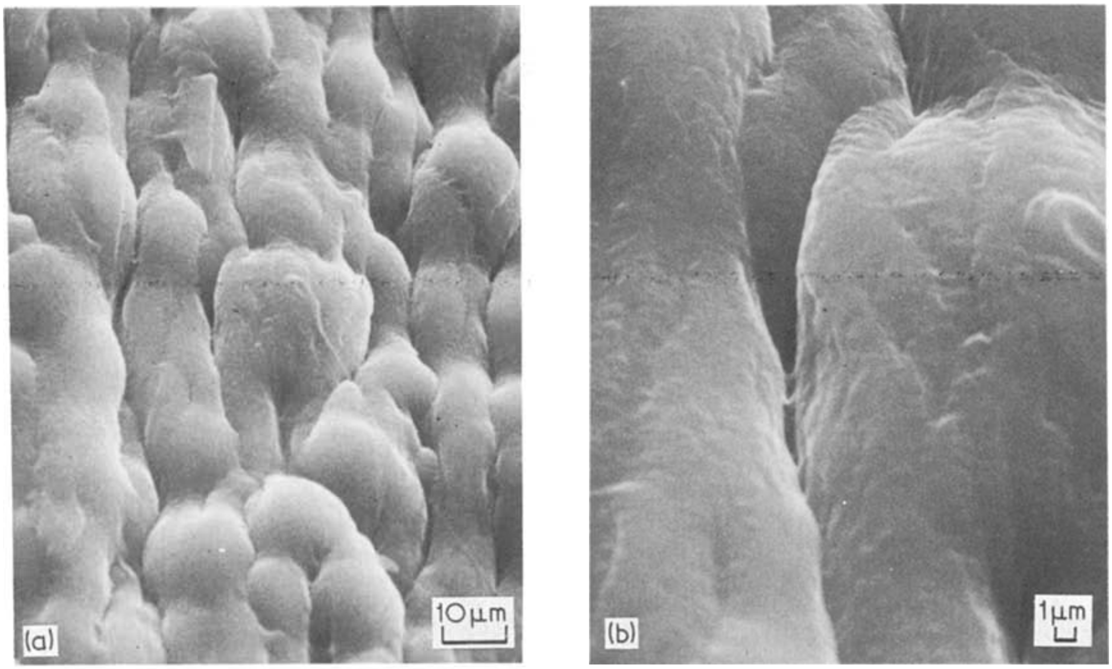


Figure 8 Nylon 12, tensile impact test, fractured at −180° C.

by the presence of sheets, fibrils, shallow pits and some isolated small globular protrusions.

Whereas preferred swelling and yielding of the interspherulite regions was assumed to be responsible for the stress-cracking of the plasticized nylon 11, rupture of the nylon 12 specimen appeared to have involved mainly tearing along sheets of lamellae and fibrils. The presence of pits and globules in addition to the sheets and fibrils



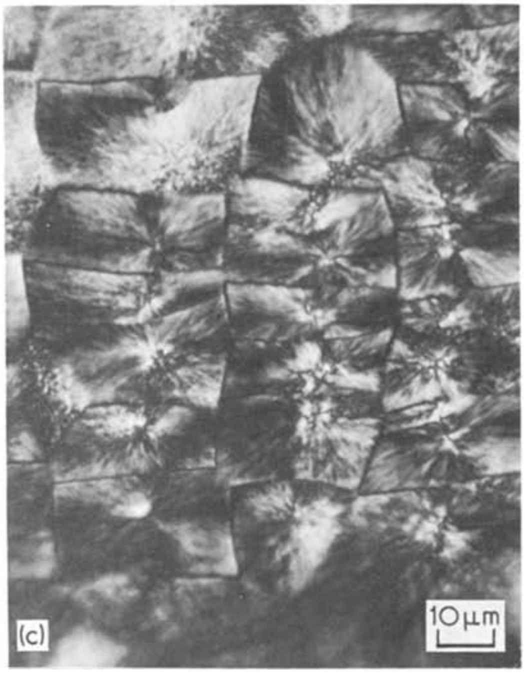


Figure 9 Nylon 12, tensile impact test fractured at room temperature. (a) and (b) Scanning electron micrographs of fractured surface; (c) Photomicrograph of cross-section (transmitted polarized light).

indicates that a more complex fracture mechanism is involved in the stress-cracking of this material.

The characteristics of the fractured surfaces obtained at either liquid nitrogen temperature, room temperature, or in a stress-cracking medium differ significantly. This would be expected from the different fracture modes, and from differences between the starting materials with respect to crystallinity and morphology, such as size and distribution of spherulites. The differences in the surface morphology between the stress-cracked nylon 6, nylon 11, and nylon 12 materials, however, appear to be related not only to morphological differences of the starting materials but to their swelling and solubility characteristics.

4. Conclusions

Accepting Howard's [1] classification of polymer stress-cracking as environmental, solvent or thermal processes, the stress-cracking of nylons in various zinc chloride solutions can be termed solvent stress-cracking. A prerequisite for this process to occur is the limited solvent power of the stress-cracking agent.

Nylon stress-cracking in zinc chloride solutions is accelerated by the presence of low molecular weight components and retarded by orientation of the polymer. The crack propagates by partially dissolving, yielding and tearing of the polymer proceeding as in the case of mechanical fracture along the weakest path.

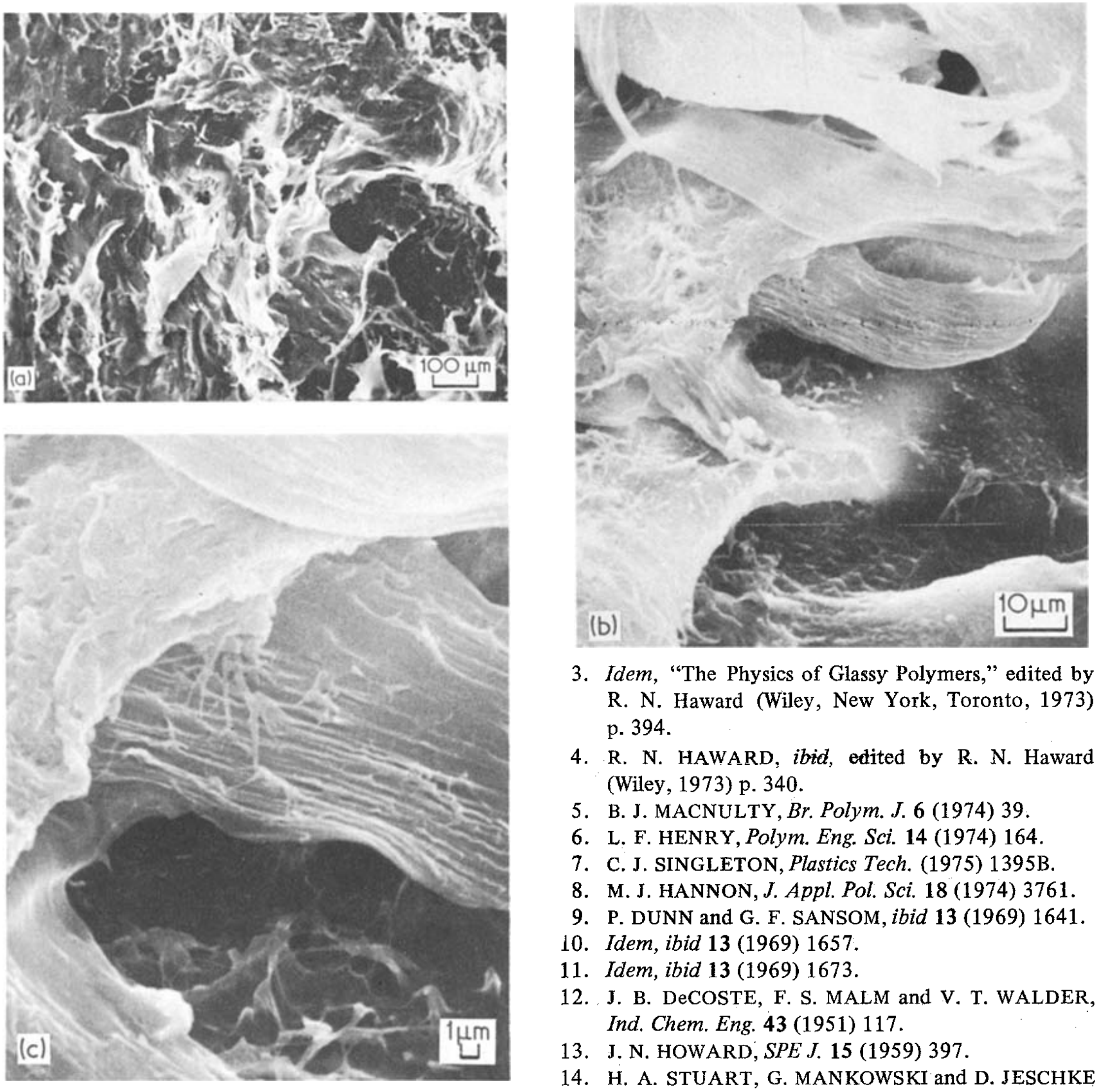


Figure 10 Nylon 12, stress-cracked in saturated solution of $ZnCl_2$ in methanol at 60° C.

References

1. E. BAER and J. B. HOWARD, "Engineering Design for Plastics" (Van Nostrand Reinhold, New York, 1964) p. 742.
2. E. H. ANDREWS and L. BEVAN, *Polymer* **13** (1972) 337.
3. *Idem*, "The Physics of Glassy Polymers," edited by R. N. Haward (Wiley, New York, Toronto, 1973) p. 394.
4. R. N. HAWARD, *ibid*, edited by R. N. Haward (Wiley, 1973) p. 340.
5. B. J. MACNULTY, *Br. Polym. J.* **6** (1974) 39.
6. L. F. HENRY, *Polym. Eng. Sci.* **14** (1974) 164.
7. C. J. SINGLETON, *Plastics Tech.* (1975) 1395B.
8. M. J. HANNON, *J. Appl. Pol. Sci.* **18** (1974) 3761.
9. P. DUNN and G. F. SANSOM, *ibid* **13** (1969) 1641.
10. *Idem, ibid* **13** (1969) 1657.
11. *Idem, ibid* **13** (1969) 1673.
12. J. B. DeCOSTE, F. S. MALM and V. T. WALDER, *Ind. Chem. Eng.* **43** (1951) 117.
13. J. N. HOWARD, *SPE J.* **15** (1959) 397.
14. H. A. STUART, G. MANKOWSKI and D. JESCHKE *Kunstoffe* **54** (1964) 618.
15. J. CRANK and G. S. PARK, "Diffusion in Polymers" (Academic Press, New York, 1968) 220.
16. Y. J. KIM and A. C. REIMSCHUESSEL, unpublished data, Allied Chemical Corporation, 1971.
17. H. D. KEITH and F. J. PADDEN, *J. Appl. Phys.* **34** (1963) 2409.
18. *Idem, ibid* **35** (1964) 1270.

Received 18 February and accepted 20 May 1977.