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The morphology and mechanism of crack propagation in nylons in the presence of inorganic salts

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The morphology of fracture surfaces has been examined for inorganic salt-induced stress cracking of polyamides. A variety of inorganic salts and solvents were found to have markedly different activity but a common order of topography across the fractured cross-section. Crazes and other features resemble those found in the solvent cracking of glassy polymers. Tensile tests on treated polyamides suggested a conjoint action of salt and solvent.

1. Introduction

The importance of crazing as a significant and distinct form of deformation in glassy polymers has been reflected in recent years by a large output of literature [1–3].

The mechanism of crazing in amorphous polymers has been extensively studied [4–8]. Fracture mechanics approaches have been successfully applied [9–10], although most investigations have been directed towards understanding the physical behaviour of polystyrene, polymethyl methacrylate and polycarbonate. Additional information has been gained in elucidating crazing behaviour in these materials (in the absence of craze-promoting agents) by extending conditions of temperature and strain rate (e.g. [11–14]). Furthermore, the commercially important phenomenon of environmental stress cracking has been well characterized in glassy polymers [15, 16], but with the exception of detergent cracking in polyethylene [17–20], relatively little attention has been paid to craze and crack formation in semicrystalline materials. The emergence of a broader variety of polymers in which crazing can (under suitable conditions) be promoted, suggests that this mode of deformation is of universal importance. Examples include low-temperature crazing in polypropylene [21] and craze-like phenomena in polyvinyl chloride [22].

There are several reasons why craze formation in crystallizable polymers have not been widely investigated. Although the microstructural organization of lamellae within the spherulitic matrix has been extensively characterized, attempts to explain mechanical properties including deformation [23, 24], have been limited by the absence of direct, unambiguous, molecular-level information. The heterogeneous nature of this class of polymers makes stress analysis particularly difficult at the microscopic level. Similarly, diffusion, cavitation and other craze-initiation processes are inherently more difficult to interpret than in amorphous polymers. Semicrystalline polymers have low transparency, retarding visual observation of craze growth, and the lower incidence of crazing "under normal conditions" (compared with polystyrene, for example) has also hindered progress.

Since the landmark investigations by Dunn and Sansom [25, 26] fracture in nylons caused by inorganic salts is now well recognized. Recently, the fracture mechanics of nylon (in the absence of crazing agent) [27] and the fracture morphology of nylons with inorganic salts [28] have begun to

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be documented. The physical mechanism of failure however, remains to be thoroughly investigated.

This paper provides the results of an extensive programme, in which nylons were strained in the presence of a variety of salt solutions, and under many test conditions. The fracture morphology of a great many specimens was examined, so that a generalized mechanism of craze formation and breakdown could be deduced.

While there is some opinion that a universal description of the molecular dynamics of craze and crack growth will not be easily achieved, it has been established [29] that for a wide range of systems involving the conjoint action of a stress and an aggressive solution that the characteristics of crack propagation are uniquely determined from a measurement of the crack velocity as a function of the stress intensity. A schematic diagram is shown in Fig. 1 depicting five regions of behaviour. A brief interpretation of these regions in terms of solvent-induced cracking of polymers will aid the description of the fracture morphologies revealed in this study.

Region IA. For specimens that do not contain a sharp starter notch, there will exist an initiation period in which a craze will commence at some stress concentration and grow to a critical size that will then initiate a crack. It is known that for unnotched specimens this process may consume a large fraction of the total life of the specimen.

Region I. The crack propagates through preformed craze, the controlling factor being associated with an agent-induced molecular relaxation. The transport of aggressive solvent is adequate to maintain the propagation of the preformed craze.

Region II. There exists some uncertainty about this region but it has been suggested [2] that the limiting parameter is the transport of the solvent through the craze and diffusion into bulk polymer in the vicinity of the crack tip. Although the diffusion rate may be accelerated by the presence of a tri-axial stress system at the front of the crack, the high rate of change of K with V will mean that in this present experiment this region will exist only for a relatively short distance.

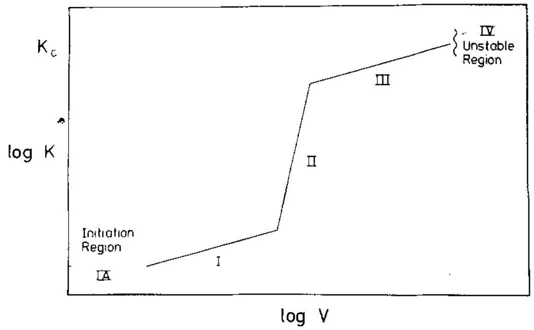

Figure 1 Crack velocity (V) as a function of stress intensity (K), according to Williams [29].

Region III. The crack velocity has now exceeded any solvent transport process and the craze formed will be the same as that formed if the experiment was conducted in air. The crack proceeding behind the craze will now be traversing a different craze structure to that in Region I and II.

Region IV. As the stress intensity increases, the crack velocity will exceed the craze velocity and the crack process will become unstable with a rapid increase in speed. The fracture surfaces will show very little evidence of any visco-elastic deformation that would absorb energy.

2. Experimental details

2.1. Materials

Nylon 66 with a vicsocity average molecular weight of 18 000 (determined in 90% aqueous formic acid) with a crystallinity of 47% (by specific gravity measurement) was used in the form of ASTM D638 Type I test pieces. Nylon 6 has a molecular weight of 87 000 (85% aqueous formic acid) and a crystallinity of 17%. Samples complied with ASTM D638 Type IV specifications.

Compression-moulded films of nylon 66 (Maranyl A100) and nylon 6 (Maranyl F.103) were generally prepared by melting granules between glass slides coated with a silicone release agent and applying a pressure of 25 to 50 MPa (depending on desired film thickness). Each film was allowed to cool slowly or was quenched, as desired.

2.2. Tensile testing

Quantitative tensile testing was performed using an Instron machine at a test temperature of 20 ± 2° C. Films (thickness less than 0.20 mm) were tested either in the Instron machine, or alternatively in simple tensile machines which could be accommodated under the viewing stage of an optical microscope (Zeiss Ultraphot II). The latter method enabled direct observation of changes in the morphology of the specimen during the test, but no mechanical data were produced. The stress crazing agent was applied to the specimen using a calibrated syringe and straining commenced. After testing, each sample was either mounted in a miniature fixed strain jig for insertion into the scanning electron microscope (*in situ* crazes) or simply attached to a specimen stub (fractured specimens).

Using the terminology of Dunn and Sansom [25], the following range of salts were examined

Type I: $ZnCl_2$, $CoCl_2$

Type II: LiI, LiBr, $Mg(ClO_4)_2$

in aqueous solution at 1 M concentration unless otherwise noted. Because Type II salts are said to function as crazing agents via an intermediary solvent molecule, the following additional solvents were examined with lithium iodide: methyl cyanide, 1,2-dihydroxyethane and dimethyl sulphoxide.

It was considered desirable in this study of an apparently new type of stress crazing system to attempt to examine as large a range of morphologies as possible. Appropriate fracture mechanics methods are limited to relatively small ranges of crack speed and would not, therefore, have conveniently covered the expected range of fracture surfaces. The droplet test method gave results which were internally consistent and reproducible when efforts were made to keep test conditions constant. Once straining has commenced, deformation was extremely localized and this contributed to the consistency of the results obtained.

Two approaches were used to examine the stress–strain behaviour in the presence of salts. In the first method, tensile tests were conducted on specimens that had been allowed to equilibrate to give particular contents to water and/or zinc chloride. The aim of these experiments was to determine the overall mechanical behaviour of homogeneous material. After equilibration, some test specimens were dried in vacuum at 120° C until constant weight was achieved. All specimens were strained at 20° C using a cross-head speed of $1\ mm\ min^{-1}$. The second method entailed application of small droplets of 1 M solution to the test piece just prior to the commencement of straining.

Tests were also conducted with nylon 6 in the anhydrous, as received (3% wt/wt H_2O) or with a high water content (10% wt/wt H_2O).

2.3. Scanning electron microscopy

Stress-crazed fracture samples were washed quickly with distilled water, dried and gold and/or carbon coated. Conditions for viewing were optimized by using uniform coatings, high tilt angles within the microscope and high condenser lens currents. Lower voltages (less than 10 kV) were avoided, and it was noticeable that in most experiments, charging was reduced by thorough removal of residual stress crazing agent.

3. Results

3.1. Fracture surfaces

All the inorganic salts chosen produced failures at abnormally low stresses and although it was possible to qualitatively see differences in the ease of stress cracking, it became clear that the surface morphology of the various systems produced essentially the same sequence of fracture regions. For this reason we shall refer only to the fracture surface studies of that produced by 1 M aqueous zinc chloride. A similar comment applied to any distinction between nylon 6 or nylon 66. Determination of the severity of the agents would require a quantitative fracture mechanics approach and this is presently being undertaken.

A composite photograph of the entire process of failure of a nylon 66 specimen treated with 1 M aqueous zinc chloride and the approximate position of the various regions is provided in the montage in Fig. 2.

Region IA. The area where the fracture originates can be traced back to an almost featureless initiation region as seen in Fig. 3. This surface is in marked contrast to the neighbouring highly voided structure of Region I. The length of the initiation region was inversely related to the applied stress and it was clear that this region had, at one stage, existed as a crazed region but the presence of the aqueous zinc chloride solution during a comparatively long initiation time had produced a retraction of the fibrils and a general smoothing of the surface.

If the aggressive agent is a particularly good solvent for the polymer, then an extreme case for the extent of the initiation region will occur. Crazes formed will rupture at low elongation and rapid retraction of the fibrils will produce an almost featureless fracture surface over most the width of the specimen. An example of this behaviour was evident from examining the fracture morphology of nylon specimens strained in the presence of 99% wt/wt formic acid.

Region I. Examples of fracture surfaces in this region are shown in Figs. 2 and 4 and it is interest-

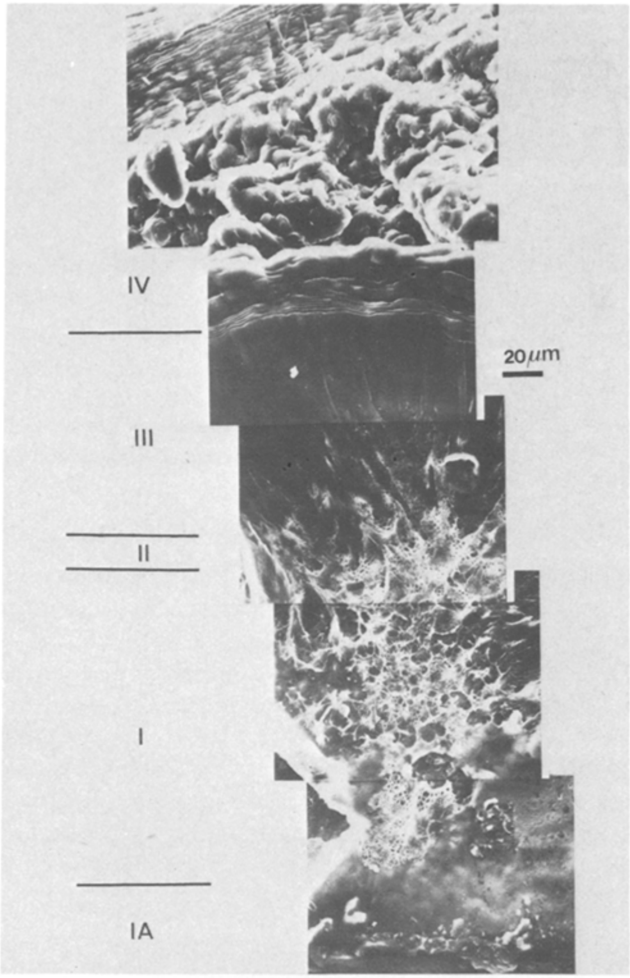

Figure 2 Fracture surface of nylon 66 treated with 1 M aqueous zinc chloride, showing morphologically distinct regions.

ing to note that they appear to be very similar to regions found [6] in many solvent-crazed amorphous polymers.

Observation of an immature craze (Fig. 5) revealed that in common with solvent-induced crazes in other polymers [30], pores are interconnected allowing transmission of solution (or solvent) to the craze front.

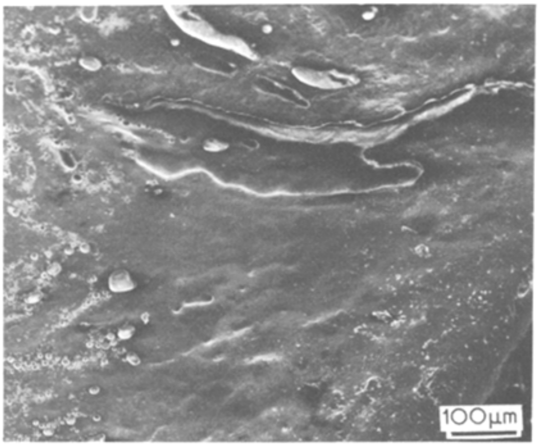

Figure 3 Featureless topography of initiation zone.

Region II. As discussed previously, there is some uncertainty regarding the position and character of this region. If the rate of transport has now become the factor limiting craze growth, it is not expected that there will exist a sharp transition but rather a graduation in morphology from Region I and II. As less agent is able to diffuse into the bulk polymer at the crack tip, so limited plasticization will gradually change the stress–strain character of the cavitation process.

It has been shown in some complementary work [31] that the concentration of zinc ions markedly decreases in the vicinity of this region indicating that the transport rate of the solution is now less than the crack velocity.

Region III. The crack velocity has now exceeded

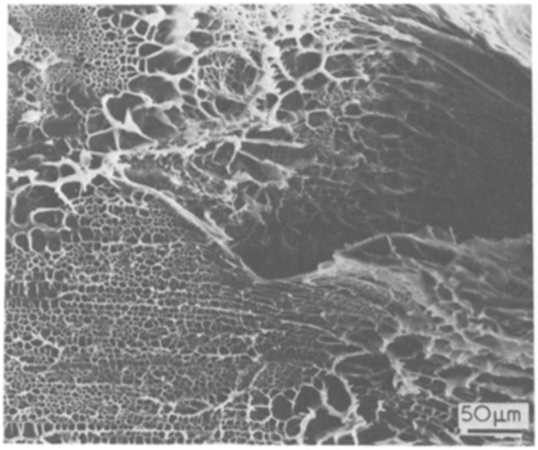

Figure 4 Agent-induced craze morphology of nylon 66 strained in presence of zinc chloride.

the transport velocity of the solution and the surface adopts a markedly different morphology (Fig. 2) with considerably reduced texture. The crack is now proceeding independently of the presence of the aggressive solution of zinc chloride and therefore the fracture morphology should be identical to the corresponding region of a specimen fractured in air at the same temperature. Direct comparison of similar regions in specimens fractured in the presence of aqueous zinc chloride (Fig. 6) and in the absence of aqueous zinc chloride (Fig. 7) reveal similar textures and the common feature of hyperbola markings. The hyperbola markings are an indication of cavity formation ahead of the main crack front [37] and their presence supports the contention that the Region III crazing mechanism operates independently of the aqueous salt solution.

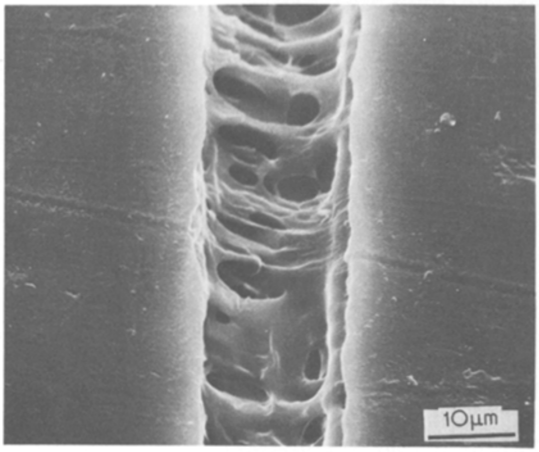

Figure 5 An intact nylon 66 craze, showing interconnected vesicles.

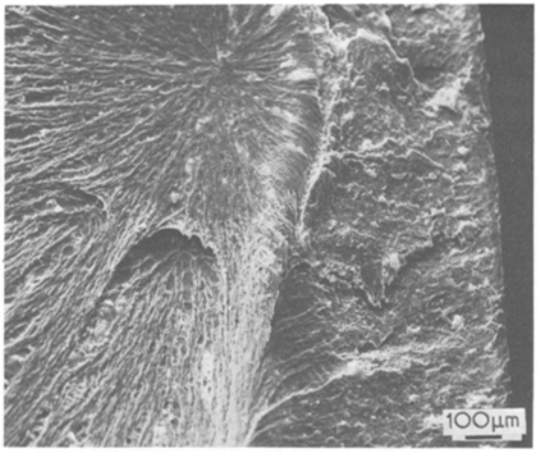

Figure 6 Fracture surface of nylon 6, strained in presence of zinc chloride.

Region IV. As shown in Fig. 8, the surface morphology changes abruptly from the crack predominantly travelling on one plane to multi-planar propagation. The crack length at the beginning of this sudden change will correspond to a critical crack length and thereafter the fracture process becomes unstable. The excess strain energy released is sufficient both to accelerate the crack and produce forking onto numerous planes. The result is a surface showing many facets and little indication of any gross visco-elastic deformation.

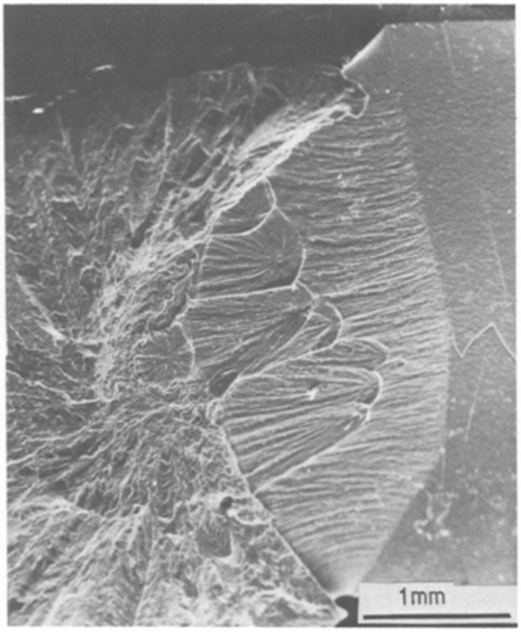

Figure 7 Surface of nylon 66 fractured in air, showing hyperbolic markings.

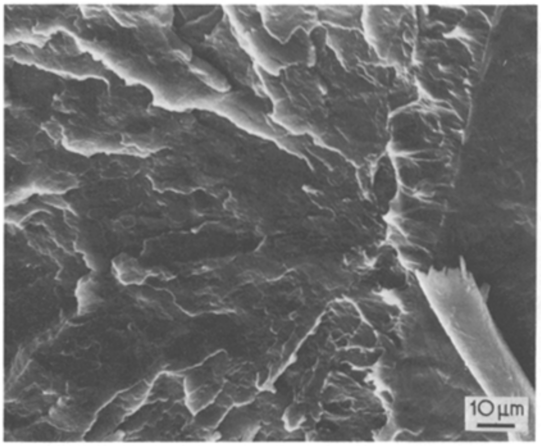

Figure 8 Morphology corresponding to unstable crack propagation through nylon.

3.2. Mechanical measurements

3.2.1. Equilibrium measurements

The stress–strain photos for the nylon 6 specimens equilibrated with their environment (specified in the figure) are shown in Fig. 9. As the content of water and zinc chloride is increased, the nylon adopts properties typical of that attributed to plasticization. However, in the specimen in which the water was later removed, it can be seen that the zinc chloride alone acts as an anti-plasticizer causing a marked increase in yield strength and a decrease in the elongation to failure.

3.2.2. Non-equilibrium measurements

Fig. 10 shows that for both zinc chloride and lithium iodide salts, the prior water content of the nylon 66 had a considerable influence on the stress necessary to cause failure. While it is obvious that water is necessary for the transmission of ions through the craze to the vicinity of the crack tip, it is interesting to note that water (or other hydroxylic solvents) is required to form complexes with the group and the inorganic cations.

3.2.3. Influence of solvents

The crazing activity of Type II salts in the presence of a different solvent is shown in Fig. 11. The results indicate that lithium iodide in methyl cyanide is very active, but is less active in DMSO and 1,2-dihydroxyethane. When water or methyl cyanide are solvents, low stresses are required for craze initiation and subsequent craze and crack propagation is rapid. They can all interact with hydrogen bonds and possess a small molecular size.

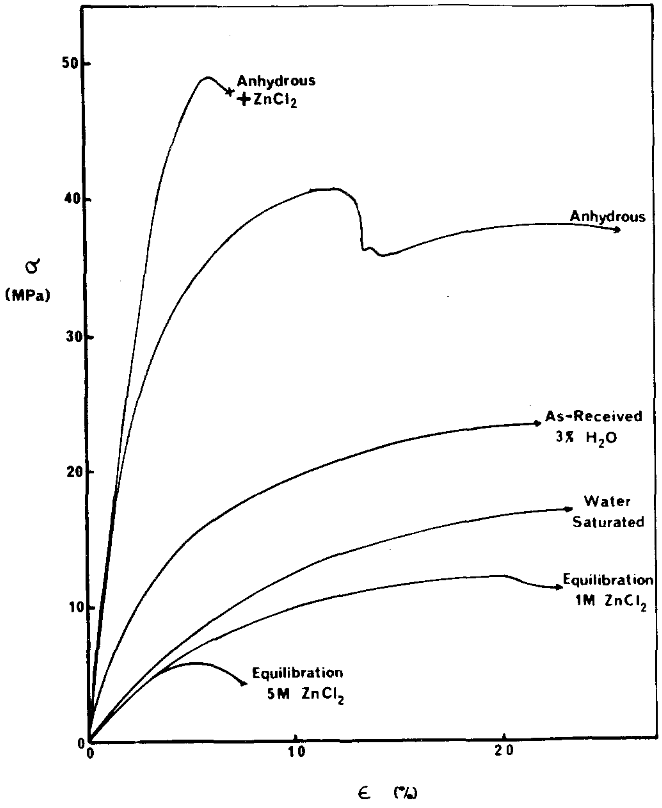

Figure 9 Influence of water and zinc chloride concentration upon mechanical behaviour of nylon 6.

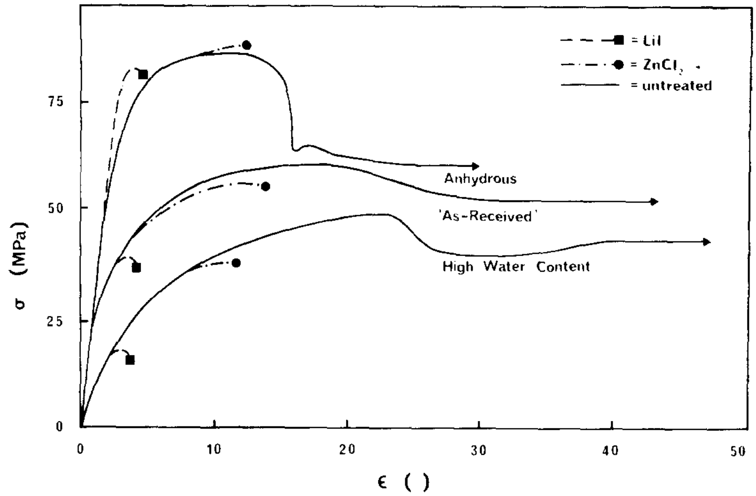

Figure 10 Influence of water content of nylon 66 upon stress to failure.

Dimethyl sulphoxide (DMSO) and 1,2-dihydroxyethane are both good ligands for cations and this may inhibit the crazing activity of the lithium iodide. As DMSO is a dipolar aprotic solvent, iodide ions are not solvated and would potentially be able to bind strongly to the amide moiety. The inactivity of lithium iodide in DMSO might suggest that cations, rather than anions have the more dominant role in the crazing process. A lithium–DMSO complex is aproptic and so is unable to hydrogen bond to the amide oxygen, with the result that weaker interactions arise (secondary forces which are possible are too weak to disrupt the secondary structure of the nylon). Didenate liganding of the 1,2-dihydroxyethane with lithium cations may produce large aggregates in which only a low concentration of actively modified protons can arise, compared with hydrated lithium ions. In addition, their size would make penetration into the polymer matrix more difficult than water and methyl alcohol. The reduced rate of uptake of agents with large solvent molecules into the nylon matrix is probably the rate-determining factor for craze initiation and crack growth.

4. Discussion

Until now the significance of craze formation in "environmentally cracked" nylons has not been

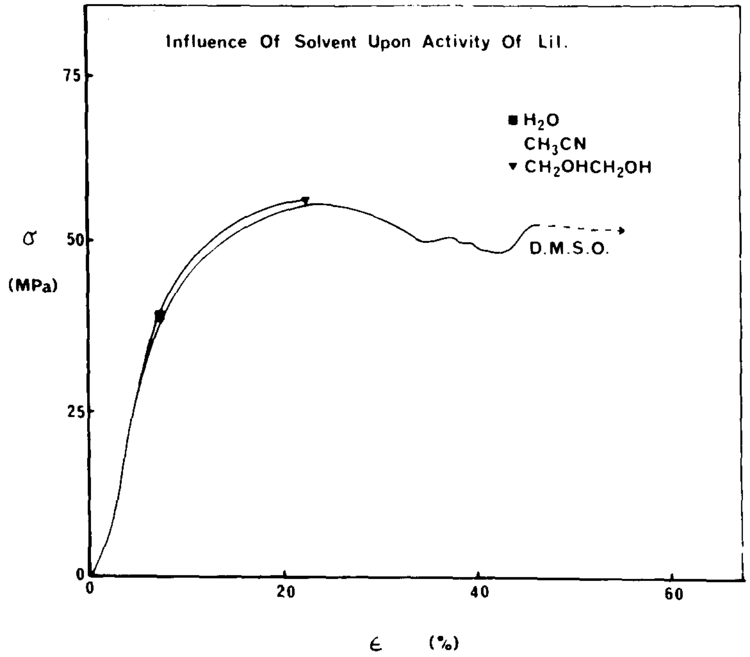

Figure 11 Influence of solvent upon activity of lithium iodide.

recognized. The work by Reimschussel and Kim [28] is the only instance where the morphological aspects of fracture in nylons has been described and the introductory examination did not identify the role of craze formation, and subsequent crack growth has been shown to follow the established pattern of development seen most commonly in solvent stress cracking of amorphous glassy polymers. While there were very obvious differences in activity for the various systems investigated it was apparent that the same morphological features were present despite changes in the types of agent, solvent or water content of the nylon.

The mechanism of interaction of the active salts with nylons originally suggested has been supported by further work both in solution and in the solid state [32, 33]. The mechanical behaviour of nylon, equilibrated with zinc chloride solution added further evidence to the proposal that the mechanism of interaction of zinc chloride and water with nylon can be explained by reference to the molecular model (Type I) suggested by Dunn and Sansom [25]. If the nylon is allowed to equilibrate with aqueous zinc chloride, the zinc cation binds directly to the carboxyl group and then is itself surrounded by water molecules. The water molecules effectively shield the zinc cations and the carboxyl group thus reducing the interchain attractions and lowering the strength. If the water molecules are removed by drying, the zinc cations remain and the increase in strength can be attributed to the pseudo cross-linking effect similar to that experienced by the addition of zinc cations to carboxylic acid polymers [36].

The solvents for the salts such as water and methanol themselves act as plasticizers producing significant movement in the α-relaxation peak [34] to lower temperatures but there was no indication that acting alone these solvents could induce stress cracking. Very strong solvents such as formic acid are able alone to cause stress cracking of nylons but in the case of the aqueous zinc chloride system, water appears to act in a conjoint manner in aiding the disruption of the hydrogen bonding.

It has been reported [35] that the glass transition temperature of nylon 6, previously soaked in aqueous zinc chloride, increased with the content of zinc chloride thus suggesting a conflict with the present results. However, the water content in the specimens was not quoted and it is possible that in the course of the torsion pendulum experiments the water content decreased sufficiently to allow the zinc cation anti-plasticizing effect to dominate.

In reviewing other studies of nylon–salt interaction, it is appropriate to comment on the two methods adopted to load the nylon with inorganic salt, and the resultant possible changes of structure. The first method (used in this study) was to allow the slow uptake of inorganic salt and solvent at room temperature, with no subsequent thermal treatment (except for the series dried at 120° C). Repeated absorption and desorption of strong solvents (phenol, formic acid) has been shown [35] to change the crystal structure of nylon 6 – weaker solvents such as water and methanol presumably only absorb into the amorphous phase. The second method used in other studies [32] was to intimately mix a mechanical blend of salt and polymer – subsequently the blend was temperature cycled above the melt temperature. This latter method has been shown [32] to dramatically alter the percentage crystallinity and produce a heterogeneous blend.

Acknowledgement

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