

The influence of salt type in the environmental fracture of nylons

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The fracture surfaces of nylons strained in the presence of inorganic salt solutions have been analysed using energy dispersive X-rays. Correlations are made between surface morphology and ion distribution so that the role of salts in craze formation and breakdown could be determined. Differences between cations binding directly to the polymer chain from those in which solvent molecules form a bridge, are reflected in the ion distribution. Initial studies of the nature of salt uptake into the polymer are also described.

1. Introduction

Two prevalent examples of environmental stress cracking (E.S.C.) of polymers are the failure of amorphous polymers in the presence of organic liquids [1-3] and the failure of polyethylene in the presence of detergents [4-6], but there now exists a third interesting case which can be described as the failure of hydrogen-bonded polymers in the presence of agents capable of disrupting that bonding [7-9].

As discussed by Burford and Williams [10], the mechanism of E.S.C. of nylons 6 and 66 in the presence of inorganic salts can be discussed using the same morphological description as that developed for amorphous polymer-solvent E.S.C. However, there arises a number of interesting problems associated with the transport of the ions during fracture. In this study a scanning electron microscope will be used to determine the position of ions relative to particular surface morphologies.

1.1. Polymer-salt interactions

Compared with the considerable advances made in understanding the complicated mechanism of selective binding between cations and macromolecules including proteins and nucleic acids, there has been relatively modest and recent activity in

the field of synthetic polymer-cation complexation. Of interest are the study of changes in solution properties caused by the addition of salts [12-14], characterization of solids complexes of both model low molecular weight compounds, and polymers, with anhydrous salts [15-18], spectroscopic studies of polymers with absorbed ions [7, 8, 11, 15] and diffusion analysis, with emphasis more on solvents than salts [20, 21].

Bulk properties of synthetic polymer-inorganic salt systems have also been investigated [22, 23].

The results of Dunn and Sanson [7, 8, 18] and Wissbrun and Hannon [19, 24] are of particular relevance. The former investigators determined by infra-red and nuclear magnetic resonance methods, that of the many salts found to promote cracking strongly in nylons, some bound directly to the carboxyl oxygen in the polymer whilst the rest complexed normally with a hydroxylic solvent molecule. These salts were classified Type I (e.g. zinc chloride) and Type II (e.g. lithium chloride).

Wissbrun and Hannon [24] have characterized complexes formed between calcium thiocyanate and inorganic nitrates with polyvinyl esters and alcohols. In their second paper [19], infra-red measurements were employed so that a model, essentially the same as that of Dunn and Sanson's

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could be developed for the polymer–salt complex. They also concluded that nitrate counterions remain in close proximity to the cation.

Whilst the phenomenon of solvent cracking and swelling of nylons by inorganic salts has been well known for over a decade, the morphological study by Reimschuessel and Kim [9] is isolated. Using zinc chloride and various nylons, they concluded that the polymer will environmentally stress crack when it has low solubility in the salt solution, although our own studies [10] have shown that these processes include crazing mechanisms.

In this study, energy dispersive X-ray analysis proved to be an ideal tool. The method is singularly applicable to the polymer–salt system, because the X-ray analyser discriminates for elements with an atomic number greater than 11. Hence, salts can be readily discriminated from the low atomic number elements in the nylon. The method is not generally applicable to organic solvent–amorphous polymer systems where all atomic numbers are too low. It will be shown that not only can correlations between fracture morphology and salt distribution be made (providing information about the mechanism of failure), but that also the distinction between salts made by Dunn and Sansom is in accord with two modes of failure.

2. Experimental details

2.1. Materials and specimen preparation

Preparation of Nylon 66 test pieces were as described previously [10]. Fracture surfaces were prepared by straining test pieces (ASTM D638, Type 1) in either an Instron TT-DM machine, or a small tensile rig, with the agent applied just prior to testing. Uptake studies were conducted by full immersion of the polymer into the appropriate salt solution. Cross-sections were obtained from the wiped sample by cutting with a razor blade.

Fracture samples were alternatively washed with distilled water or merely wiped to remove excess agent, and then coated with carbon and/or gold prior to insertion in a Seimens Autoscan scanning electron microscope (SEM). Energy dispersive X-ray analysis was conducted using a nuclear Chicago energy dispersive X-ray detector and a Packard Multi-channel Analyser. For analysis 20 kV was used and results were improved when a high tilt eccentric focusing stage was employed. Ordinarily $K\alpha$ and $K\beta$ X-rays of elements with atomic numbers greater than 11 (i.e. sodium) were collected. Selection for both anions

and cations was possible, so that distribution of zinc chloride, for example, could be determined by obtaining either a line scan or “X-ray map”, discriminating for either zinc or chloride. Care was taken to avoid specimen damage, at slow raster speeds, high voltages and high magnifications.

3. Results and discussion

3.1. Fracture morphologies caused by zinc chloride and lithium iodide

The generalized scheme for stress cracking in nylons has been described in detail [10]. There are as many as five morphologically distinct zones designated Regions IA, I to IV. Region IA is essentially featureless, being an area of gross plasticization and crack initiation. Region I is characterized by highly elongated but discrete craze filaments and comprises remnants from rupture of agent-induced crazes. Region III contains a fracture surface showing identical features to that found for specimens fractured in air. In this region the crack velocity has exceeded the velocity of transport of the active fluid, and therefore craze formation and breakdown proceeds independently of the environment. The intermediate Region II, represents a transition between Region I and III where the fluid transport is the limiting factor. The exact nature of the morphology of this region is not known. The last region (Region IV) is the brittle fracture zone where crack growth is unstable. As indicated previously the existence and extent of each of these regions depends on several experimental conditions which include the physical state of the polymer, strain rate, temperature and type of agent present. This last aspect is the object of this investigation.

A typical fracture surface for a stress cracked nylon is shown in Fig. 1. In this example, where 5 M aqueous zinc chloride was applied, substantial crazing has occurred to leave a “honeycomb” structure in the fracture surface (Region I). The central area, containing the typical hyperbola features, represents Region III and rapid unstable brittle fracture has occurred in the remainder (Region IV). Region II is not at present readily identified but as discussed previously [10] it would only exist over a relatively short distance that the specimen was stretched at a constant strain rate. Higher magnification of the area near the origin of the fracture (right hand edge) reveals a featureless zone (Region IA) where gross plasticization and swelling has occurred.

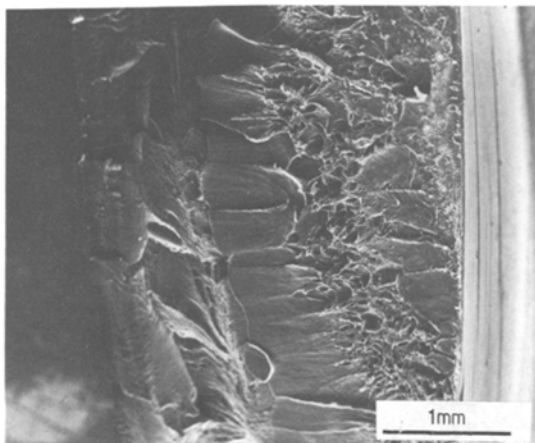


Figure 1 Fracture surface of nylon 66, stressed in presence of 5 M zinc chloride solution, showing “honeycomb-like” Region I.

3.2. Energy dispersive X-ray analysis

Four examples have been selected to distinguish between the mechanism of crazing and cracking with Type I salts from that of Type II salts. Nylon 66 samples which have failed with either zinc chloride or lithium iodide are examined in both “washed” and “unwashed” conditions. Normally, when specimens are fractured in the presence of an aggressive solvent, solvent transfer to other regions can be ignored on the assumption that the solvent will quickly evaporate, not altering the fracture surface or leaving a residue. In this case, however, it is possible to draw fallacious conclusions for the obvious reason that the inorganic salts transferred to other regions during the last stages of fracture, may or may not remain after washing and drying.

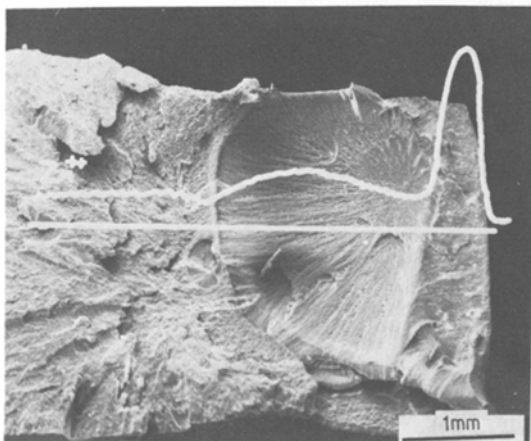


Figure 2 Washed anhydrous nylon 66 strained in presence of 5 M zinc chloride solution – line scan corresponding to zinc concentration is superimposed.

3.2.1. Zinc chloride-treated nylon 66 – washed

An anhydrous nylon 66 specimen strained in the presence of 5 M aqueous zinc chloride revealed fracture surfaces shown in Fig. 2. Regions I, III and IV are readily identifiable (Region IA can be seen at higher magnifications) and the superimposed X-ray line scan indicates the level of zinc firmly bound to the nylon despite the thorough washing of the fracture surfaces with distilled water

In Region I there are very high levels of zinc suggesting strong water resistant binding, but across the interface into Region III there is a sharp decrease in the level of zinc.

3.2.2. Zinc chloride-treated nylon 66 – unwashed

When the corresponding unwashed fracture face is analysed for zinc, it is found that high concentrations have carried over into Regions III and IV. The level of zinc in Region III is found to be comparable with that in Region I (Fig. 3), and the corresponding zinc X-ray map confirms that a relatively uniform distribution of zinc covers most of the fracture surface.

During the crazing process in Region I, the zinc cation binds strongly to the nylon and remains fixed during subsequent washing with water. Zinc chloride solution is evidently also transferred into Region III at some later stage after the craze and crack process has passed through that region. However, because Region III contains orientated filaments in the craze material, uptake of zinc chloride solution will be slow with the result that

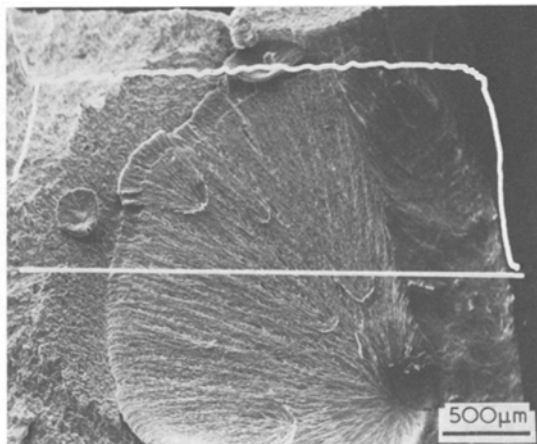


Figure 3 Unwashed nylon 66 fracture surface, with line scan corresponding to zinc concentration, illustrating transfer of zinc into Region III.

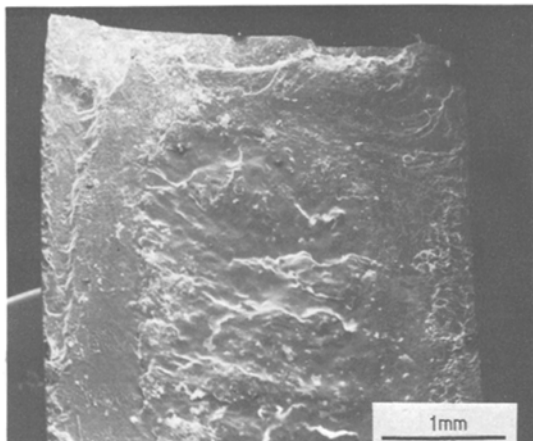


Figure 4 Fracture surface of lithium iodide treated nylon 66 – washed sample.

this area can be washed free of the majority of the salt.

3.2.3. Lithium iodide-treated nylon 66 – washed

Lithium iodide-treated specimens gave rapid and extensive fracture at relatively low stresses (Fig. 4). The X-ray map of the washed fracture surface (Fig. 5) showed that only low levels of iodide remain. At the magnifications used, it is assumed that for overall ionic neutrality, the distribution of lithium cations is the same as for iodide anions [24].

3.2.4. Lithium iodide-treated nylon 66 – unwashed

The unwashed fracture surface is shown in Fig. 6 and the corresponding iodide distribution in the

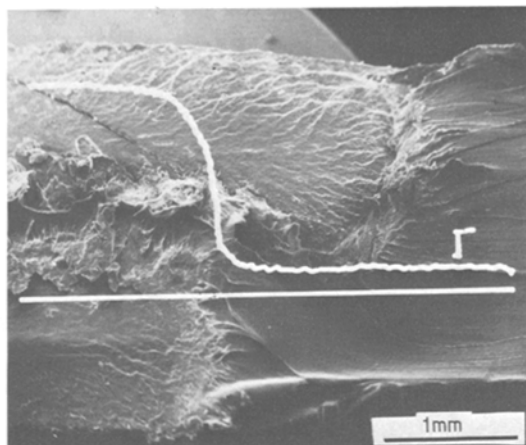


Figure 6 Unwashed fracture surface of nylon 66 treated with lithium iodide, with line scan superimposed.

X-ray map (Fig. 7). In Region I high levels of iodide are found, but although this specimen remained unwashed, no agent was carried over into Region III. These results are to be contrasted with that found for the washed specimen.

The results of these experiments on washed and unwashed stress-cracked nylons support the proposed [7] models of complexes formed from the salt, solvent and amide group of the nylon. Lithium iodide was classified as Type II complex with the hydroxylic solvent forming a bridge between the cation and the carboxyl oxygen in the amide group. Thus, washing with distilled water could rapidly remove the complex. In contrast, zinc chloride is classified as a Type I complex with the cation directly associated with the carboxyl oxygen of the amide group – solvent molecules are then attached to the cation. Washing with

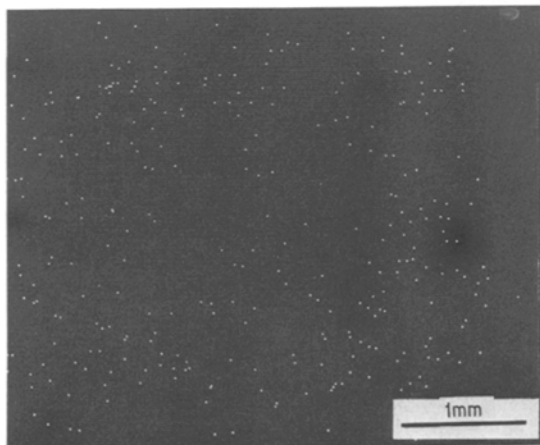


Figure 5 X-ray map of iodide ions, corresponding to surface shown in Fig. 4.

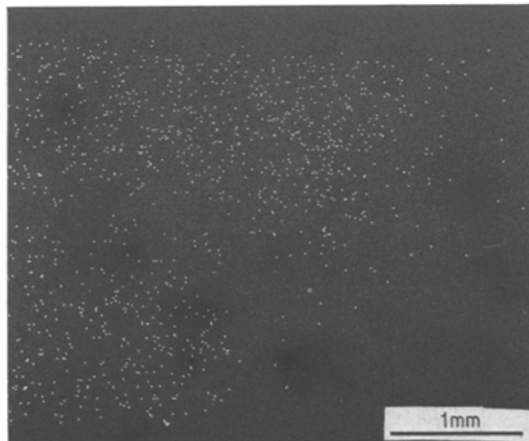


Figure 7 X-ray map of iodide ions corresponding to surface shown in Fig. 6.

distilled water did not appreciably lower the concentration of cations confirming that the zinc cations are held relatively tightly by the complex.

3.3. Diffusion of zinc chloride and lithium iodide into unstressed nylon 66

The energy dispersive X-ray analyser is an excellent tool for determining ionic penetration into a polymer and so studies of the uptake of zinc chloride into nylon have commenced. It is hoped that by understanding the influence of applied stress and molecular architecture of the polymer upon agent uptake, the factors controlling craze initiation might be discovered. The limited information so far obtained is that an accelerated uptake mechanism, as proposed by Peterlin [25], might apply.

When a nylon 6 specimen which has been immersed in 5 M zinc chloride solution for 28 days at 25°C is washed, dried, and a cross-section prepared, three regions are distinguished using the SEM (Fig. 8). The outer, porous material to the left is precipitated nylon 6–zinc chloride complex. The light grey area to the right is nylon devoid of salt. The corresponding X-ray map (Fig. 9) and line scans confirm that a uniformly high level of zinc is maintained up to a certain level of penetration, beyond which a rapid drop off to essentially background level occurs. This is analogous to the uptake of methanol in poly(methyl methacrylate) reported by Thomas and Windle [21] and is termed Case II transport. Lithium iodide also exhibited Case II diffusion but unfortunately the SEM method did not allow the accurate determination of the rate of uptake in

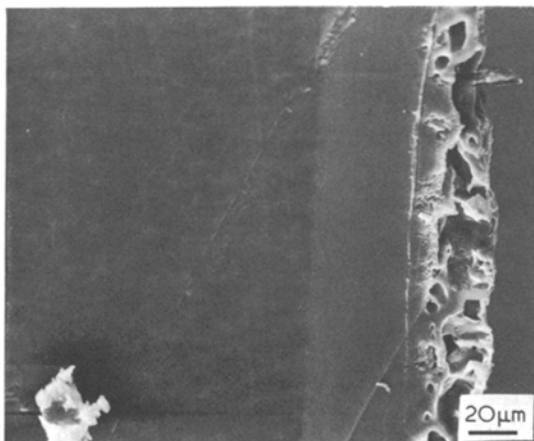


Figure 8 Cross-section of nylon 6, showing three distinct regions. Only the dark region (at left) is zinc deficient.

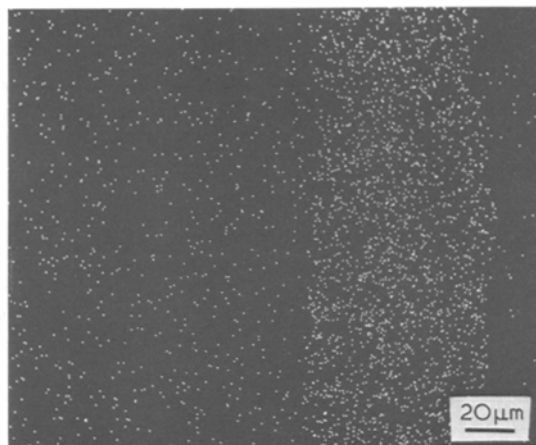


Figure 9 Zinc X-ray map, corresponding to Fig. 8.

this present system and no comparison could be made between zinc chloride and lithium iodide.

4. Conclusions

The morphology of nylons crazed in the presence of Type I salts (in particular zinc chloride) has been contrasted with that produced by Type II salts. Whilst both morphologies comply with the generalized mechanism previously proposed [10], changes consistent with salt solution mobility and found.

X-ray analysis has confirmed that Type I salts bind more strongly to nylon 66 than do Type II salts, and this is consistent with the classification of Dunn and Sansom.

Preliminary evidence for Case II transport of zinc chloride into nylon 66 is presented, and further information is currently being sought to clarify this aspect. Clearly changes in the morphology of the polymer would need to be monitored, as these strongly influence solvent uptake [26].

Acknowledgement

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