The effect of metal halides on the deformation mechanism of thin films of nylon*

A. P. More and A. M. Donald†
Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK
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Soaking of nylon 6 and 66 films in saline solutions modifies their deformation response to an applied tensile stress. Unsalted films do not show conventional crazes. Instead they are seen to deform by a mixture of shear and fibrillated shear, the latter involving chain disentanglement. Dried salt-soaked films are, however, dominated by scission crazing for all temperatures below the glass transition temperature. Salt treatment modifies intermolecular bonding, strengthening it in the process, and stiffens the polymer chains. Such modifications act to suppress shear and chain disentanglement. Calcium and zinc chlorides both reduce the temperature dependence of the strain for deformation onset and embrittle films, with nylon 6 much more affected than nylon 66. Sodium chloride acts only as a weak crazing agent for both nylon types.

(Keywords: electron microscopy; crazing; fibrillated shear; nylon; salting)

INTRODUCTION

Several authors have reported that various different metal halides lead to embrittlement of nylon macrosamples. Dunn and Sansom[1] considered a wide range of different halide salts in both aqueous and methanolic solutions. They concluded that plasticization was an important contributing factor, and that the stress cracking was promoted by chemical means. Further their i.r. study[2] of thin films identified the occurrence of complexing of the metal cation with the carbonyl oxygen atom of the amide group for certain metals, including zinc and copper (termed Group I). The effect of this was thought to be a disruption of the hydrogen bonding leading to susceptibility to stress cracking. Other metals (termed Group II) including calcium, were shown to form proton donating solvated species which were thought to act directly as solvents for the nylon.

More recently Wysgoski and Novak considered the response of nylon macrosamples to aqueous salt solutions as a function of temperature[3], and again thin film i.r. spectroscopy was used to study salt–nylon interactions[4]. Craze growth kinetics was also studied[5]. They concluded that NaCl had no effect on bulk nylon at any temperature (ductile behaviour being recorded as with pure water), but that $CaCl_2$, $MgCl_2$ and LiCl all led to a transition to a brittle response at elevated temperatures. A possible link with the glass transition temperature (T_g) was suggested, with cracking occurring above the T_g. They also recorded a large increase in the weight gain due to the salt as the temperature was raised.

I.r. thin film studies therefore suggest that a change in the nature of the bonding is responsible for the embrittlement observed in bulk samples, but the way in which this affects the detailed molecular mechanism of crazing and cracking is not explicitly discussed. The purpose of this paper is to try to bridge between the studies on the salt–nylon interactions, and the understanding of mechanisms of crazing in an air environment largely developed for amorphous polymers.

For amorphous polymers such as polystyrene (PS), an extensive picture has now been built up of the molecular processes that take place as the void–fibril structure of a craze forms ahead of a crack[6,7]. Both the advance of the craze tip and the lateral growth of the craze interface propagate via the meniscus instability[6,8,9]. Using the model for this mechanism[6,10] it is possible to compute the required stress for the craze to grow, given the geometry of the fibril bases and the surface energy of the freshly created fibril surface. Since amorphous polymers are entangled, this surface energy term depends on whether the necessary voids have been created by the chains being broken or disentangling. For a polymer such as PS, which has a comparatively low density of entanglements, the energy cost associated with scission is not unduly high at room temperature (relatively few scission events are required to create the topology of the craze), but for more densely entangled polymers such as polyethersulphone or polycarbonate this is not the case and shear becomes the preferred mode of deformation at ambient temperatures[11]. For these polymers, which tend to be tough at room temperature, as the temperature is raised the alternative mechanism for void creation via disentanglement of the chains becomes increasingly probable. This mechanism permits crazing to occur at a lower stress than shear, and so the response may change from

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† To whom correspondence should be addressed

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ductile to brittle[12]. For PS, on the other hand, the stress for crazing via scission only drops rather slowly with increase in temperature, and in practice shear usually becomes more dominant as the temperature is raised so that the transition is to a ductile response as T_g is approached. The exception to this is if the molecular weight of the chains is sufficiently low that disentanglement starts to occur, in which case crazing is observed right up to T_g, particularly at low strain rates[13,14].

Armed with this picture of the response of amorphous polymers in air, it is helpful to reconsider the embrittling of nylon by salt solutions and to see whether explanations of changes in mechanism with temperature evolved for the less complex case where crystallinity does not intervene, can improve understanding of the environmental crazing situation. As a first step in this direction, we have examined the mechanical response of thin nylon films in air and after soaking in NaCl solutions (which Wysgoski and Novak reported did not embrittle nylon macrosamples[3]). These studies show[15] that as well as the two well-documented modes of deformation of shear and crazing, a third type of response is seen, termed 'fibrillated shear'. An example of this is shown in *Figure 1*. The mechanism by which this is formed appears to be similar to that described by Friedrich[16] for crazing, in that blocks of lamellae deform in concert so that they are still distinguishable after deformation. Fibrillated shear is thus more homogeneous than true crazing, although voids are also present. In this paper, the changes in mechanical response that occur following treatment of thin nylon films with NaCl, $CaCl_2$ and $ZnCl_2$ solutions are considered as a function of the temperature of deformation.

EXPERIMENTAL

Thin films for this study were produced in a manner similar to that of Lauterwasser and Kramer[17]. Nylon films were produced by drawing a glass slide from a 3 wt% solution of the polymer in formic acid at a rate of 1 mm min^{-1}. Nylon 6 ($M_w \sim 18\,000$, purchased from Goodfellows of Cambridge) and nylon 66 ($M_w \sim 48\,000$, supplied by ICI plc) were used for this study. Film thickness varied slightly due to the presence of a semicrystalline spherulitic microstructure. Films produced, however, were a maximum of ~1 μm thick, as determined by ellipsometry. The films were then floated off the glass slide onto a water bath. Some coaxing from the glass slide with a pair of blunted tweezers was necessary. Prior to removal from the slide, films for salt conditioning were immersed in 6 molal solutions of the salt (Analar grade) for 6 h at 25°C, then briefly rinsed in distilled water to remove any excess salt solution. Using the data of Burford and Harrauer[18], 6 h should permit diffusion of the salt solutions right through the film thickness to give a homogeneous distribution of the salt. NaCl, $CaCl_2$ and $ZnCl_2$ solutions were used for salting.

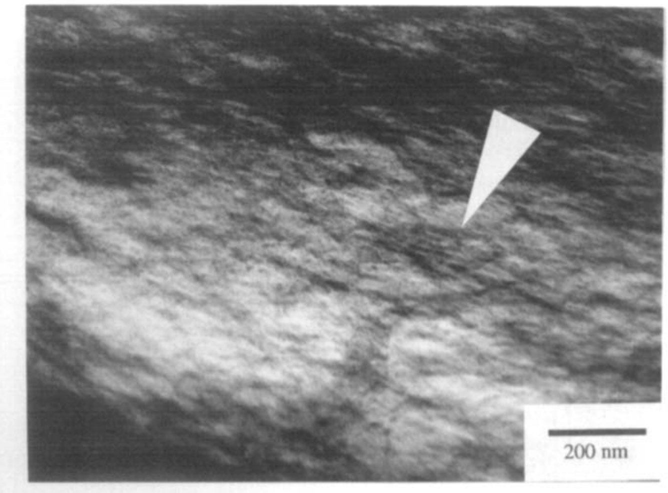

Figure 1 TEM micrograph of fibrillated shear developed in NaCl treated nylon 6, developed at ~50°C for a strain rate of ~1.3×10^{-3} s^{-1}. Blocks of lamellar spherulitic material are visible drawn into the deformed region (arrowed)

Films were transferred from the water bath on to copper grids which had previously been both annealed and nylon coated. The films were allowed to dry at room temperature prior to a few seconds exposure to solvent vapour (formic acid). Exposure to the acid vapour bonds the films to the copper grid in addition to smoothing out and relieving the stress within the films. They were then vacuum dried for 72 h at 80°C and strained.

The film coated grids were strained at a constant strain rate of ~3×10^{-3} s^{-1} in a variable temperature strain rig mounted on a Carl Zeiss Jenapol optical microscope. Strain for deformation onset (SDO) was recorded. SDO refers to the amount of strain the film undergoes prior to the appearance of dark deforming zones optically (at × 160 magnification). Individual deformed grid squares were subsequently cut from the copper grid for examination by transmission electron microscopy (TEM, Jeol JM 2000 EX at 200 kV) in order to determine the nature of the deformation developed.

Film crystallinity was estimated by d.s.c. Samples (10 mg) of untreated, NaCl and $CaCl_2$ treated nylon 6 and 66 were sealed in aluminium pans and scanned from 25 to 300°C at a rate of 10°C min^{-1} with a Mettler 30 DSC. Prior to scanning, the filled pans were heat treated as for the thin films. Heats of fusion values of 191 J g^{-1} for nylon 6 and 196 J g^{-1} for nylon 66 were used for crystallinity calculations. Such fusion data values represent an average of several measurements[19]. Sample masses were recorded both pre- and post-run in order to determine film water content by mass loss measurements.

The T_g for both treated and untreated films was studied by dynamic mechanical thermal analysis (d.m.t.a.). D.m.t.a. was undertaken with a Mk 2 combined d.m.t.a. machine loaned by Polymer Laboratories. Run in tensile mode, a 0.020 N applied tensile load was used. A frequency of 30 Hz was employed with a heating rate of 3°C min^{-1} for the temperature range of 20–200°C.

RESULTS

D.s.c. measurements for film crystallinity and water contents for untreated, NaCl and $CaCl_2$ treated films are given in *Table 1*. The higher molecular weight nylon 66 is slightly more crystalline than the nylon 6. As has been observed before[4], salt treatment of the films acts to decrease film crystallinity for both the nylon 6 and the nylon 66. Water content after heat treatment is < 1 wt% and typically < 0.5 wt%. D.m.t.a. showed only slight variations in the peak value of dynamic mechanical loss factor (tan δ). Peak values of tan δ were observed to vary between 94°C and 102°C, with similar trends observed for both nylon 6 and nylon 66. For all types of samples

Table 1 Melting temperature (T_m), crystallinity and water content as measured by d.s.c.[a]

	T_m (°C)	Crystallinity (%)	Water content (wt%)
Nylon 6			
Unsalted	263.0	~28	<1.0
Na salted	260.8	~17	<0.4
Ca salted	258.4	~24	<0.1
Nylon 66			
Unsalted	263.3	~30	<0.5
Na salted	260.3	~24	<0.8
Ca salted	261.2	~28	<0.7

[a] Data represent an average of several measurements made for each film type

there was significant scatter within this range, but the average value for $ZnCl_2$ treated nylon was higher than that for $CaCl_2$ treated nylon and this was higher than that for NaCl treated nylon; tan δ for $CaCl_2$ treated nylon was the same as for untreated nylon. The majority of the salted films failed during d.m.t.a. by tearing at ~160°C. Prior to failure a marked increase in film extension was recorded. Whilst the temperature of the tan δ peak is not identical with the T_g for the films, it may be taken as indicative of the T_g. T_g measurements reported for nylon vary, over tens of degrees, with the actual measured value dependent upon the experimental method used[19]. Trends and measured shifts in tan δ, however, will be the same as those in T_g.

Optically the films are seen to comprise a spherulitic microstructure. The spherulites typically range in size from 2 to 5 μm. The onset of localized deformation is apparent in the optical microscope as the development of numerous nearly parallel dark interspherulitic zones some one to two spherulites in length. It is not possible to distinguish optically between shear and craze deformation. Deformed regions develop approximately perpendicular to the principal applied tensile stress.

Recorded SDO values in nylon 6 and 66 films are shown in *Figure 2*. The use of a copper support grid does not allow a direct measurement of stress to craze/shear to be made. The SDO, therefore, is used to provide an indirect indication as to the stress to craze/shear. An initial drop in strain is recorded for both nylon types, followed by a rise in strain for temperatures above reported T_g values for dry nylon (40°C to 52°C for both nylon 6 and nylon 66[19]). The overall level of strain is higher for nylon 66, consistent with the higher level of crystallinity and higher molecular weight. *Figure 3* shows the same data for films soaked in 3 M NaCl for 6 h. *Figure 3a* shows that for nylon 6, at low temperatures, the strain recorded is actually substantially higher after salting than in the untreated material, but the upturn in the SDO beyond T_g is much less pronounced, if present at all. From *Figure 3b* it can be seen that for nylon 66 likewise the SDO after NaCl treatment is higher than for untreated material at all temperatures, with the difference being greatest around 40–60°C. Both nylon 6 and nylon 66 are seen to be affected by NaCl salting, and the temperature dependence of the SDO is much reduced.

For $CaCl_2$ and $ZnCl_2$ treated films it is difficult to obtain reliable data for nylon 6 films, because the recorded strains are very low and catastrophic failure tends to occur rapidly. The nylon 66 is much more resistant and *Figures 4* and *5* show the data for these two salts. The curves are not dissimilar to that of the NaCl salted material, but the overall level of strain is somewhat lower, particularly at the lower temperatures.

In the curves for deformation onset, the nature of the first deformation to occur is not distinguished. The morphology of the deformation can be examined via TEM. As indicated in the Introduction, three distinct modes of deformation have been observed in unsalted and sodium salted films[15]. For the calcium and zinc treated films, both true shear and fibrillated shear are not particularly well developed, but the incidence of

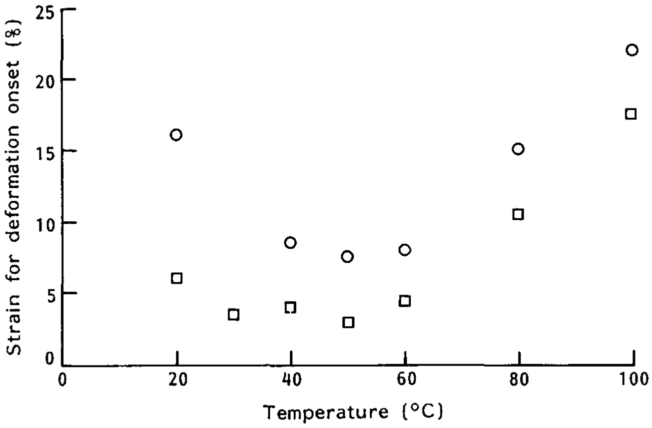

Figure 2 Strain for deformation onset values *versus* temperature for unsalted films of nylon 6 (□) and nylon 66 (○) for a strain rate of ~$1.3 \times 10^{-3} s^{-1}$

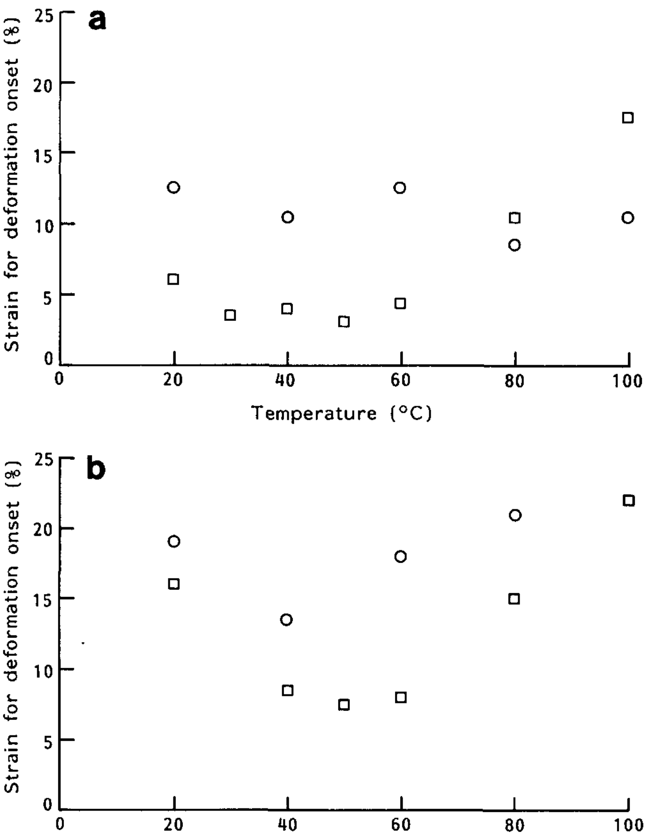

Figure 3 Strain for deformation onset values *versus* temperature for unsalted (□) and NaCl salted (○) films of (a) nylon 6 and (b) nylon 66 for a strain rate of ~$1.3 \times 10^{-3} s^{-1}$

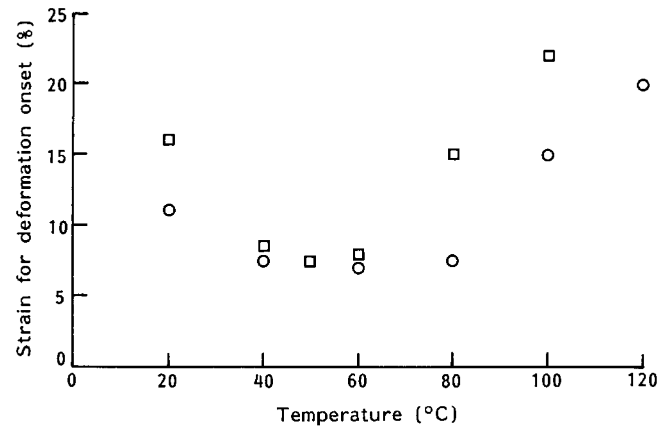

Figure 4 Strain for deformation onset values *versus* temperature for unsalted (□) and $CaCl_2$ salted (○) films of nylon 66 for a strain rate of ~$1.3 \times 10^{-3} s^{-1}$

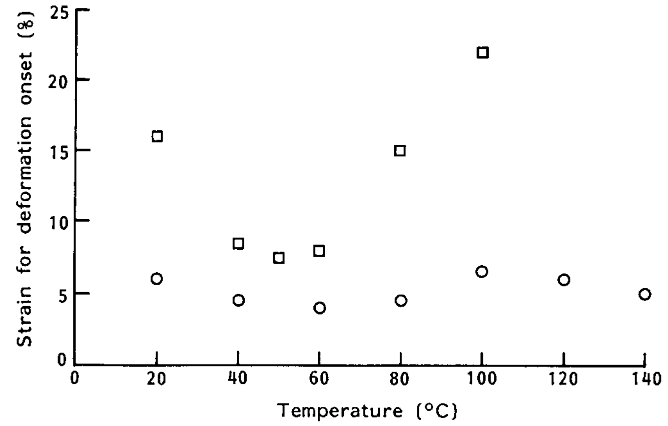

Figure 5 Strain for deformation onset values *versus* temperature for unsalted (□) and $ZnCl_2$ salted (○) films of nylon 66 for a strain rate of ~$1.3 \times 10^{-3} s^{-1}$

crazing is higher than in unsalted films which is consistent with the severe embrittlement reported by others[1,3]. Even in nylon 6 films, for which failure of the films occurs before stable deformation is seen optically, electron microscopic examination of the calcium and zinc films shows the occurrence of some crazing. The coarseness of the fibrils seems to vary with treatment of the films. For nylon 6 a switch is seen from a fine craze structure in NaCl treated films (*Figure 6*) with elongated voids and fine cross tie fibrils to a coarser craze structure with large voids and widely spaced fibrils in the $CaCl_2$ (*Figure 7*) and $ZnCl_2$ treated films. For nylon 66 films less variation in fibril size is apparent for crazes developed in NaCl, $CaCl_2$ and $ZnCl_2$ treated films all showing relatively coarse fibrils with a well developed voided microstructure (*Figures 8* and *9*). Crazes, both coarse and fine structured, are easily distinguished from fibrillated shear on the basis of their void–fibril microstructure (cf. *Figure 10*, where the craze microstructure is rendered more easily visible due to crack development, with *Figure 1*).

Deformation developed in unsalted films comprises a mixture of true and fibrillated shear. Both shear types are seen developed for all temperatures tested (20–100°C). True shear is best observed above 80°C and fibrillated shear between 40°C and 60°C. Crazing is absent in the unsalted films. NaCl induced crazing is seen in both nylon 6 and 66 films. Developed for all temperatures tested (20–100°C), craze fibrils are fine in nylon 6 and coarse in nylon 66 (*Figures 6* and *8*). Crazing is poorly developed in nylon 66. Additionally fibrillated shear is seen for all temperatures and true shear at temperatures above 80°C. $CaCl_2$ and $ZnCl_2$ treated films are craze dominated at

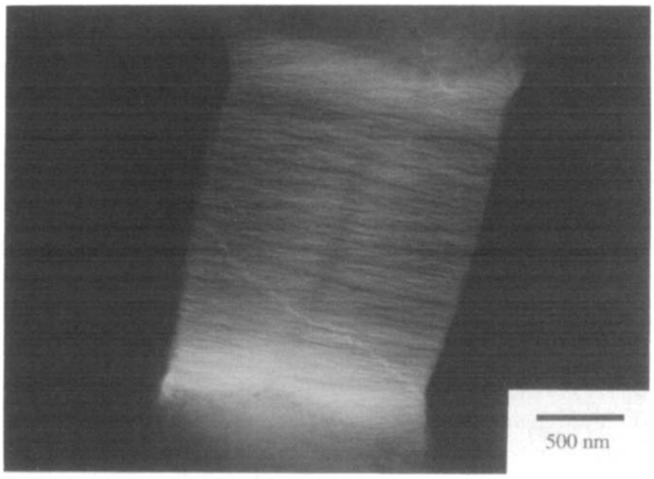

Figure 6 TEM micrograph showing crazing developed in NaCl treated nylon 6. Crazing developed at ~50°C for a strain rate of ~$10^{-3} s^{-1}$

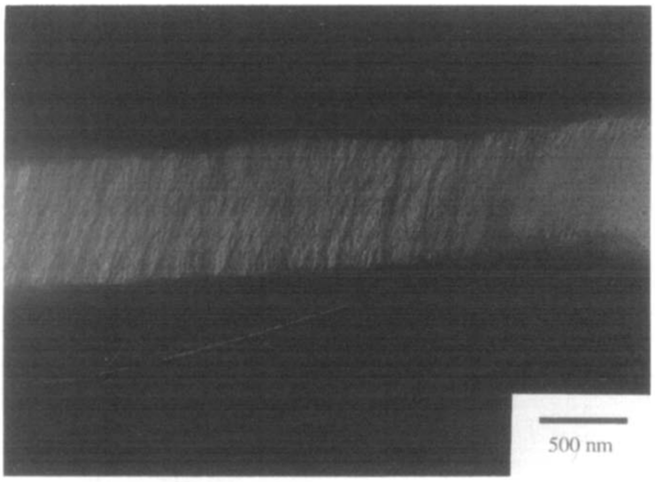

Figure 7 TEM micrograph of crazing developed in $CaCl_2$ treated nylon 6. Note relatively coarse fibrils compared to NaCl treated nylon 6 (*Figure 6*). Crazed at ~20°C for a strain rate of ~$10^{-3} s^{-1}$

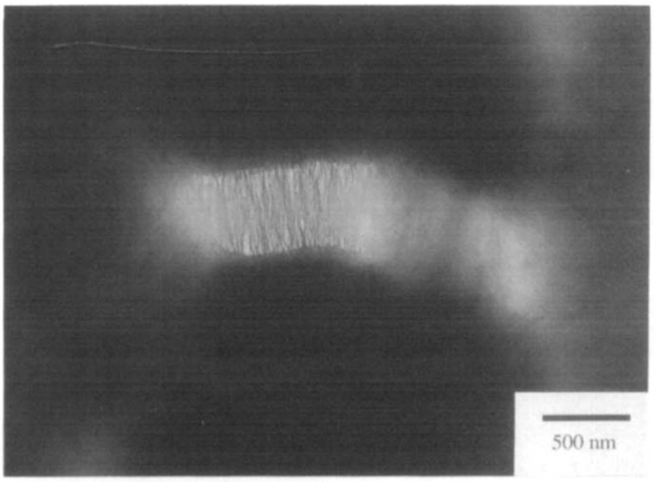

Figure 8 TEM micrograph of crazing in NaCl treated nylon 66. Crazed at ~20°C for a strain rate of ~$10^{-3} s^{-1}$

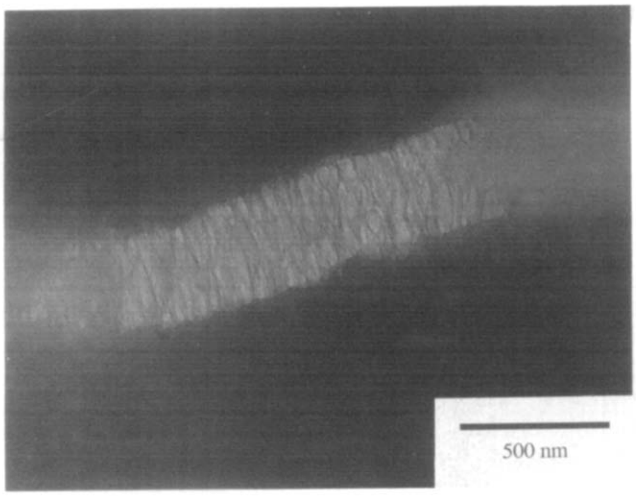

Figure 9 TEM micrograph of crazing in $ZnCl_2$ treated nylon 66. Crazed at ~60°C for a strain rate of $\sim10^{-3}\,s^{-1}$

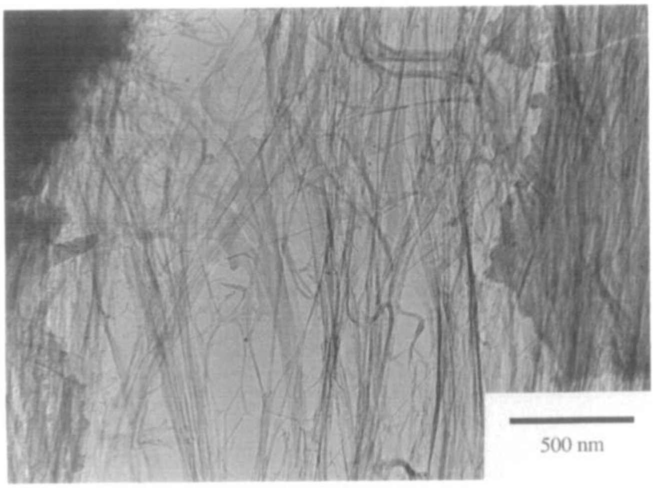

Figure 10 TEM micrograph showing well developed fibril–void structure of crazes in NaCl treated nylon 6. Craze structure is accentuated as the craze has started to fail by fibril breakdown. Crazed at ~50°C for a strain rate of $\sim10^{-3}\,s^{-1}$

all temperatures (20–100°C). For temperatures up to 60°C fibrillated shear, poorly developed, may additionally be seen, as may be true shear for temperatures above 80°C. Composite deformation zones are common for all film types and treatments, especially at high temperatures. Where crazes terminate abruptly, usually at high angle boundaries with adjacent spherulites, they tend to terminate in shear dominated zones (*Figures 8* and *9*).

DISCUSSION

Thin film studies of nylon have shown a range of deformation mechanisms to be operative; namely crazing, true shear and fibrillated shear, with crazing only seen in salt treated films[15]. Texturally similar deformation microstructures have been seen in poly(ether ether ketone)[20]. The mechanisms involved in fibrillated shear follow that originally ascribed to the early stages of craze development in semicrystalline polypropylene films[16]. In the model proposed by Friedrich three stages involving a combination of shear and chain disentanglement processes are described (although the model was not originally presented in these terms). For the nylon thin films only the first two stages of this model in the evolution of fibrillated shear are apparent; namely (1) the strain being taken up by deformation of interlamellar regions by a mixture of shear and chain disentanglement, followed by (2) the drawing out of small blocks of crystalline material into the deformed region. Such drawing out is accompanied by microvoid formation. Larger scale voiding corresponding to the third stage, which would be required to generate a craze, does not occur for fibrillated shear.

Whilst both fibrillated shear (in which blocks of crystalline material are preserved intact within the deformed regions[15]) and crazing are seen in the salt treated films, no evidence for fibrillated shear being a precursor to crazing is apparent; rather it is a deformation mechanism in its own right. Composite deformation zones, i.e. zones comprising both shear and crazing, have been reported for amorphous polymer films[21]. Such zones seen developed in the salt treated nylons cannot, therefore, be taken as evidence for fibrillated shear being a precursor stage in craze development. Crazing is restricted to salt treated films, unlike fibrillated shear, which is developed in both untreated and salt treated films.

Turning to possible roles of salt in film deformation, previous i.r. spectroscopic studies of salted nylon thin films suggest that the salt cations form adducts with the amide group[4,22]. Spectroscopically NaCl would appear to leave the films unchanged, whilst other salts vary in their action from moderate ($CaCl_2$) to severe ($ZnCl_2$)[22]. I.r. spectroscopy indicates salt complexing of the amide bonding, with the polymer chains behaving more as rigid rods than flexible chains[22]. Such salt–nylon interactions are cited as having a two-fold effect on polymer deformation: (1) chain stiffening leads to a reduction in shear capacity, as straightening and uncoiling of the nylon chains is now much more difficult; and (2) strengthening of the intermolecular bonding[22] reduces the tendency for chain disentanglement during deformation. I.r. studies undertaken on the films of this study confirm the presence of salt–amide interactions; the consequences of these are reflected in measured changes to the elastic moduli of similarly treated macrosamples[23].

Suppression of chain disentanglement in either semicrystalline or amorphous polymers can cause a switch from chain disentanglement to chain scission, as the energy necessary for chain disentanglement becomes greater than that required for chain scission (which translates into a higher stress required for chain disentanglement[7]). Thus the observed switch from shear dominated deformation for unsalted films (both true and fibrillated) to craze dominated deformation in salted films is not unexpected. Shear and disentanglement processes appear to be operative again for higher temperatures (as the temperature approaches measured peak tan δ values) as an increase in fibrillated and true shear is seen for all types of salted films—the mobility of the chains increases as T_g is approached and passed. Crazing, however, still persists at such temperatures. Previous studies of salt treated nylon macrosamples relate the development of stress cracking (crazing) to possible shifts in T_g with salting[4]. Measurements of peak tan δ values for these salt treated macrosamples showed large increases in T_g (ΔT_g up to +100°C) with high temperature treatment (soak temperature of 100°C) along with a rise in both the salt and water contents. NaCl was noted as leaving the samples relatively unchanged, with no susceptibility to stress cracking apparent[4].

For the nylon films investigated here both similarities and differences between macrosample and thin film behaviour are apparent. Shifts in $\tan\delta$ values, and hence in T_g, measured for the salt treated films are much smaller than those recorded for the salted macrosamples ($\Delta\tan\delta$ a maximum of $+6°C$ for $ZnCl_2$), probably due to the lower temperature of treatment of the thin films being studied here. However, for the thin films no relationship between T_g (or correspondingly the peak in $\tan\delta$) and the temperature for crazing onset is apparent. Crazing is observed for all test temperatures below measured peak $\tan\delta$ values, though as deformation temperatures approach that of the peak in $\tan\delta$, shear processes become more dominant.

Stress states in thin films differ from those developed in macrosamples due to the approach of plane stress conditions. In addition, these films possess a non-uniform thickness due to the spherulitic morphology, with the interspherulitic regions being significantly thinner than the spherulites themselves (the films are approximately one spherulite thick) resulting in a non-uniform stress field across the film. Stresses will be greatest in the amorphous interspherulitic regions (which correspondingly leads to the deformation being concentrated in these regions), and locally are likely to be substantially higher than those in the corresponding macrosamples for any given degree of applied strain.

Both $CaCl_2$ and $ZnCl_2$ treated thin films, like their macroscopic counterparts, are embrittled relative to the NaCl and untreated nylons; this is especially the case for the shorter chained nylon 6. $CaCl_2$ and $ZnCl_2$ are cited as being more aggressive than NaCl and are known to damage the nylon chains in addition to complexing, whereas NaCl does not[4]. The crazes which form are due to the suppression of shear and disentanglement processes by the salting and are scission crazes. Unlike the NaCl treated macrosamples of Wyzgoski and Novak[4], NaCl would appear capable of inducing crazing in thin film nylon. The reduction in chain mobility due to complexing, coupled with the low level of chain damage[4], results in this appearance of crazing being coupled with a rise in SDO over that for untreated, $CaCl_2$ or $ZnCl_2$ treated films (i.e. the NaCl films are not embrittled).

CONCLUSIONS

Conditioning of thin nylon 6 and 66 films, by soaking the films in saline solutions at room temperature, is seen to affect the deformation of the films. Salting has been claimed both to stiffen the nylon chains, making them more rod-like, and modify intermolecular bonding, strengthening it in the process. The effect of such modifications is to cause a switch from shear dominated deformation to crazing. Unsalted films, at temperatures below T_g, deform by a mixture of true and fibrillated shear. Fibrillated shear, a consequence of the spherulitic and semicrystalline film microstructure, develops via a mixture of shear and chain disentanglement processes.

Suppression of shear and disentanglement processes by the salting results in the observed switch from shear to (scission) crazing, as the stress for crazing drops below that for shear. Films treated at room temperatures show only slight variations in T_g with salting. Films craze for all temperatures below T_g. $CaCl_2$ and $ZnCl_2$ act as aggressive crazing agents, and for the shorter chained nylon 6 are also severely embrittling. For nylon 66 embrittlement is less pronounced though still apparent. NaCl is seen to act as a weak crazing agent and does not embrittle in the manner of the other salts. All salts are seen to reduce the temperature dependence of the strain for deformation onset.

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