Mechanical properties of nylon-6 after treatment with metal halides

A. P. More and A. M. Donald*
Cavendish Laboratory, Madingley Road, Cambridge, CB3 0HE, UK
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Conditioning of nylon-6 by immersion in metal chloride solutions modifies the mode of deformation under an applied tensile stress. Infra-red spectroscopy of salt-treated films shows significant modification of the spectrum, indicating changes in the intermolecular bonding. Modulus measurements support the hypothesis that modification of the intermolecular bonding in nylon results in some chain stiffening. This stiffening of the network of chains reduces the mobility that is required for shear deformation. This in turn leads to the onset of scission crazing. NaCl, however, spectroscopically shows no evidence for nylon–salt interactions having occurred. The deformation behaviour of both thin-film and bulk samples of NaCl-treated nylon-6 reflect the absence of any salt–amide interaction.

(Keywords: nylon-6; salt treatment; mechanical properties)

INTRODUCTION

The mechanisms operative during deformation of amorphous polymers are both well documented and well understood through numerous thin-film and macro studies (see reviews by Kramer[1,2]). Such models are described within a framework of the entanglement model[1–4] with two possible routes envisaged for creation of the void–fibril craze microstructure: chain disentanglement or chain scission (breaking of the chain backbone)[1,2].

It has been shown[1,3,5] that the process of disentanglement, which involves the relative motion of one chain past another, is favoured by high temperatures, low molecular weights and low strain rates. On the other hand, chain scission involves the direct breaking of chemical bonds in the backbone, and leads to a substantial energy penalty, which increases in magnitude as the density of entanglement points is increased[1]. Thus scission crazing is less likely to develop in highly entangled polymer networks. The transition to a more brittle response at high temperature, for what is normally a tough polymer, is identified with a switch in deformation from shear yielding to disentanglement-mediated crazing[3]. Shear is always a potential competing mechanism with crazing, and the process that occurs for the lowest stress will develop first.

The nature of crazing in semicrystalline polymers, and the associated mechanisms, are much less well understood than in amorphous polymers. Part of the problem relates to the variability in microstructure in semicrystalline polymers and the subsequent complex interaction between morphology and deformation[6]. Whilst voided craze-like microstructures are not uncommon in semicrystalline polymers, they tend to have a much coarser microstructure (1000 nm fibril spacing) than their amorphous counterparts (e.g. 20 nm fibril spacing for polystyrene)[7,8]. Possible void-generating mechanisms for semicrystalline polymers have been subject to review by Friedrich[7]. Such models tend to be developed at an empirical/phenomenological level and involve a combination of interlamellar slip, chain disentanglement, block rotation and fragmentation processes. Such models lean towards a cold-drawing mode of deformation involving a substantial amount of shear[9–12]. Such models, however, invoke a different framework from that built up for amorphous polymers.

This paper seeks to examine further the deformational behaviour of semicrystalline polymers using nylon-6 conditioned with various salts. Previous studies of salt-conditioned nylons have demonstrated that the mode of deformation is significantly affected by exposure to a variety of metal halides, with the most notable change being from ductile to brittle failure[13,14]. Embrittlement has been shown to relate to a switch in deformation from one that is shear-dominated to one that is craze-dominated[15,16]. This paper investigates the role of the salt in influencing the deformation mechanisms operative, predominantly at room temperature which is below the T_g of the amorphous regions. Infra-red spectroscopy and transmission electron microscopy results are presented for thin-film samples, and correlated with modulus data from bulk samples. Based on these results, explanations are offered for the switch in deformation from ductile to brittle presented in terms of the concepts previously developed for amorphous polymers.

EXPERIMENTAL

Thin films of nylon for infra-red studies were produced in a manner similar to that of Lauterwasser and Kramer[17]. Nylon-6 ($M_w \sim 18\,000$) was supplied by Goodfellows of Cambridge. Produced by drawing glass slides from 3 wt% polymer solutions in a formic acid solvent, the submicron thick films have a slightly

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* To whom correspondence should be addressed

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varying thickness owing to the semicrystalline spherulitic microstructure. The films were floated off the glass slide onto a water bath, after having been conditioned by immersion of the slide in 6 molal solutions of the appropriate metal chloride (Analar grade) for 6 h at 25°C.

Salt-conditioned films were picked up from the water bath on a 3 mm copper mesh, previously both annealed and nylon-coated. Films, when dry, were bonded to the grid by brief exposure to solvent vapour (formic acid) for a few seconds. This serves to relieve the stresses in the films in addition to smoothing them out. The films are then vacuum dried for 72 h at 80°C, and stored in a desiccator prior to i.r. examination and deformation.

Infra-red spectroscopy of both salt-treated and untreated films was undertaken with a Mattson 4020 spectrometer equipped with a DGTS detector. Each spectrum was obtained by averaging 200 scans collected with a spectral resolution of $2\,\text{cm}^{-1}$. Scattering losses caused by the copper grids were compensated for by using a similarly oriented uncoated copper grid in the background runs. Spectra were obtained from a circular region of the film ca. 10 mm in diameter. Because the films were typically less than $1\,\mu\text{m}$ thick, channel fringes were not observed. The spectrometer was well purged with dry nitrogen gas to eliminate the effects of atmospheric absorptions. The double-sided interferograms obtained were Fourier-transformed and background-stripped over the range 400 to $4000\,\text{cm}^{-1}$. All spectra were deconvoluted before peak positions were located. The accuracy of the peak positions quoted is about $\pm 1\,\text{cm}^{-1}$.

Films for electron microscopy were prepared and salt-conditioned as for infra-red spectroscopy. Some of the unstrained thin films were stained with a 2% aqueous solution of phosphotungstaic acid (PTA) to allow differentiation of amorphous and crystalline domains — the PTA preferentially enters and stains the amorphous regions. Staining was undertaken by immersion for 30 min at room temperature. Films were strained at a constant strain rate of $\sim 3\times10^{-3}\,\text{s}^{-1}$ in a variable-temperature strain rig mounted on a Carl Zeiss Jenapol optical microscope. The deformation was optically apparent as dark lineations at 160 × magnification. After deformation, individual grid squares were cut from the copper grid for examination. This method allows examination of the film in an as-stressed state as the copper maintains the state of strain. Examination was undertaken with a JEOL 2000 EX transmission electron microscope (TEM) operating at 200 kV.

Modulus measurements were undertaken on thicker films of nylon-6. Melt-cast films of $\sim 160\,\mu\text{m}$ thickness were conditioned by soaking in the 6 molal solutions for 24 h at room temperature. Chemical analysis of cross-sections in a scanning electron microscope indicate development of a metal chloride-rich outer zone and metal chloride-poor core, unlike the micrometre-thick films where a homogeneous salt distribution is apparent. Soak times and immersion temperatures required for complete homogeneous diffusion of the salt through the thicker samples results in significant damage to the nylon, and in the case of zinc chloride–nylon-6 the partial dissolution of the test samples. Thus studies of thick films for which there was complete diffusion of the salts through the films was not possible.

Tensile studies were performed with a Polymer Laboratories Miniature Materials Tester (Minimat) at room temperature with a strain rate of $1\times10^{-3}\,\text{s}^{-1}$. Averaged modulus measurements were made over the interval 0.5 to 1.5% strain.

RESULTS

Infra-red spectroscopy of the salt-conditioned films shows a number of differences between these and the untreated films. Absorbance spectra for thin-film nylon-6, untreated and zinc chloride-conditioned, are presented in *Figure 1*. Of particular interest in the absorbance spectra of polyamide (nylon) are the C–H stretch peaks at 2390 and $2860\,\text{cm}^{-1}$, the C=O stretch (amide I) at $1635\,\text{cm}^{-1}$, the (N–H)(C–N) couple (amide II) at $1540\,\text{cm}^{-1}$, and N–H stretch centred around $3300\,\text{cm}^{-1}$ (see e.g. reviews by Miyazawa[18] and Krimm and Bandekar[19]). Following $ZnCl_2$ treatment, variations in peak intensity and peak position are apparent, with modification of the region around the amide I and II bands particularly clear. $ZnCl_2$ conditioning would appear to give rise to new absorbance bands centred around 1601 and $1570\,\text{cm}^{-1}$ and loss of intensity for the amide I peak at $1635\,\text{cm}^{-1}$. These changes are seen more clearly in *Figure 2*, which expands the region around $1600\,\text{cm}^{-1}$. Also apparent are small shifts in both the amide I peak ($+3\,\text{cm}^{-1}$) and amide II peak ($+8\,\text{cm}^{-1}$). The C–H peak centred at $2938\,\text{cm}^{-1}$ increases in intensity, and shifts a few cm^{-1}. The N–H stretch at $3300\,\text{cm}^{-1}$ broadens with salt conditioning, but no peak shifts are measured.

Modification to the amide I and amide II peaks is also recorded for $CaCl_2$ treatment of nylon-6 film, as seen in *Figure 2*. Shoulders are observed to develop on the low side of the amide I peak (at $\sim 1614\,\text{cm}^{-1}$), and on the high-wavenumber side of the amide II peak, in addition to slight peak shifts of a few cm^{-1}. NaCl treatment, however, appears to leave the nylon films unchanged spectroscopically. Peak shifts and variations to peak intensity are absent (*Figure 2*).

Electron microscopy of unstrained films confirms the semicrystalline spherulitic microstructure apparent under the optical microscope. Spherulite sizes range from 2 to $6\,\mu\text{m}$ in diameter. Electron microscopy of PTA-stained films (*Figure 3*) allows the identification of the domain

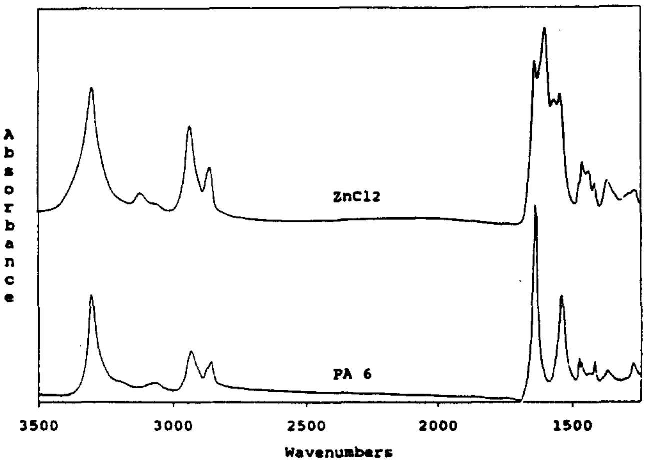

Figure 1 Infra-red absorbance spectra of untreated nylon-6 (PA 6) and aqueous zinc chloride-treated nylon-6 film ($ZnCl_2$). Peaks developed correspond to: the N–H stretch at $\sim 3300\,\text{cm}^{-1}$, a pair of C–H peaks at ~ 2390 and $\sim 2860\,\text{cm}^{-1}$, the C=O stretch (amide I) at $\sim 1635\,\text{cm}^{-1}$ and (N–H)(C–N) couple (amide II) at $\sim 1540\,\text{cm}^{-1}$

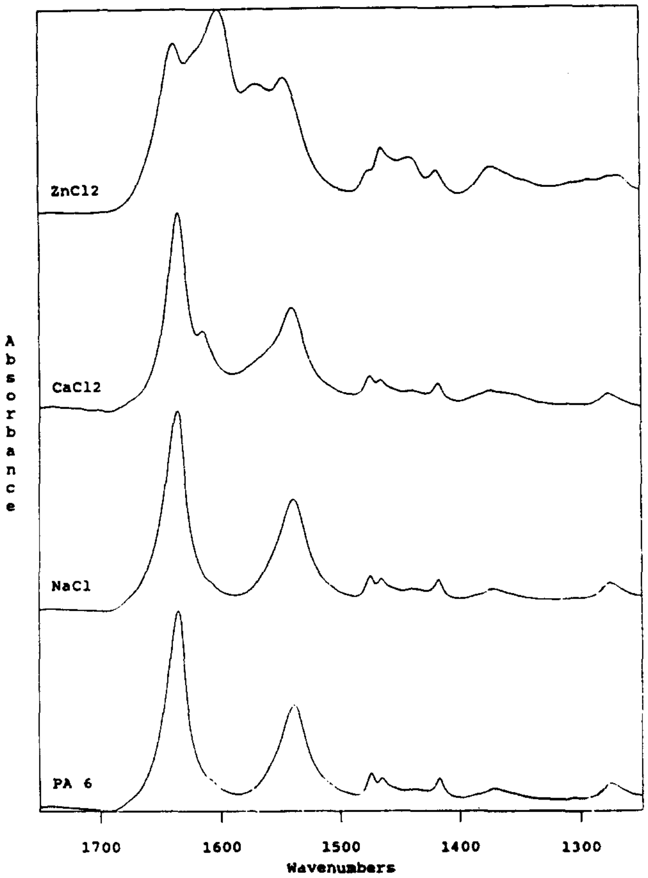

Figure 2 Infra-red absorbance spectra of untreated nylon-6 (PA 6) and NaCl, $CaCl_2$ and $ZnCl_2$ solution-treated nylon-6 films. Peaks at ~1635 and ~1540 cm^{-1} correspond to the amide I or C=O stretch and amide II or (C–N)(N–H) couple respectively

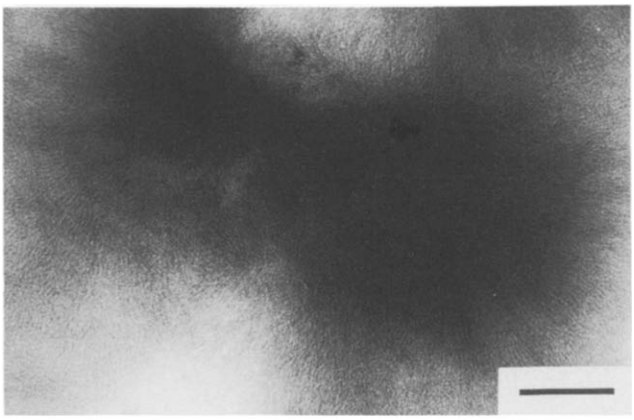

Figure 3 Transmission electron micrograph of a PTA-stained sample of untreated PA 6. The sample was exposed to a 2% solution of PTA for 10 min. Scale bar 200 nm

structure previously reported for bulk nylon[20]. These domains are made up of crystalline lamellae interspersed with amorphous regions; lamellae thicknesses vary between 10 and 20 nm and are spaced ~10 nm apart.

TEM of unstrained films that have been treated with any of the metal halides reveals the same stained spherulitic structure confirming that the metal ions, which are of comparatively high atomic number and therefore scatter electrons more strongly than the nylon itself, enter the amorphous regions separating the crystalline lamellae. This staining can also be used to follow the deformation of the lamellae after straining (see below).

Transmission electron microscopy of both salted and untreated films after straining shows a variety of deformation microstructures to be operative. In all samples deformation is principally confined to interspherulitic regions, and develops in zones running approximately perpendicular to the applied tensile stress. These interspherulitic regions are slightly thinner than the majority of the film and are therefore subjected to higher stresses. Regions of deformation, both shear- and craze-dominated, tend to be short, extending for a few spherulites in length, and vary in width from 0.5 to 2 μm. *Figure 4* shows how metal ion staining (Zn in this case) allows observation of the spherulitic material being drawn into deforming interspherulitic regions.

Both crazing and shear processes are observed in the deformed films. Crazing is restricted in development to salt-conditioned films; most particularly in $ZnCl_2$- and $CaCl_2$-treated films, but to a lesser extent also in those exposed to NaCl. Such NaCl crazes, however, are patchy and poorly developed. For all film types examined, crazing is developed for all temperatures employed (25 to 90°C), and best developed between 40 and 60°C[16]. Deformation in unconditioned and NaCl-conditioned films is shear-dominated.

Shear deformation comprises a mixture of localized uniform thinning, similar to the deformation zones described for amorphous polymer films[21], and non-uniform or inhomogeneous thinning accompanied by micro-voiding and the incorporation of semicrystalline material within the deformation zone. The development of microvoids and incorporation of semicrystalline material gives a fibrillated appearance to the deformed region similar to that observed in semicrystalline polyethylene and polypropylene films[7]. Similar microstructures have been recorded in deformed poly(ether ether ketone) (PEEK)[22] and previously described by us for nylon[16]. *Figure 5* illustrates such an area of fibrillated shear.

Texturally, true crazes differ from fibrillated shear by the development of a regular void–fibril microstructure similar to that characteristic of crazing in amorphous polymer films[1]. Crazes developed in NaCl-conditioned films (*Figure 6*) appear to possess a much finer microstructure than their counterparts in $ZnCl_2$- and $CaCl_2$-conditioned films. For these, a coarse fibrillar microstructure is seen (*Figures 7* and *8*). One-dimensional fast Fourier transforms of digitized craze images can be

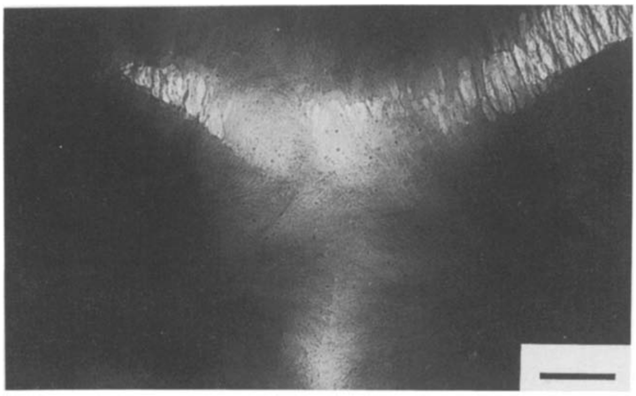

Figure 4 Transmission electron micrograph of a $ZnCl_2$-treated sample after straining. The lamellae, which are highlighted by the intervening stained amorphous regions, can be seen being drawn into the deforming interspherulitic regions. Scale bar 0.25 μm

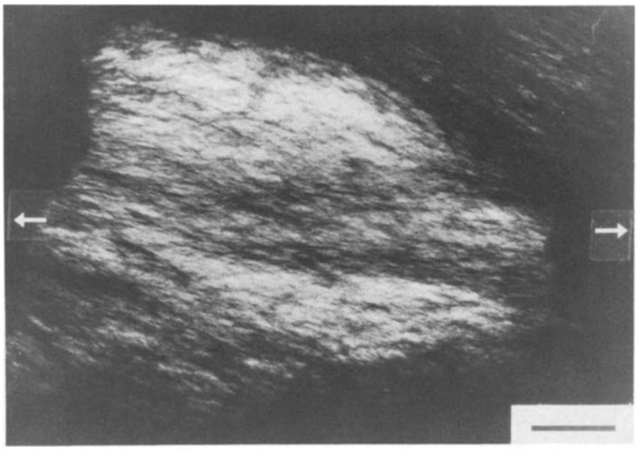

Figure 5 Transmission electron micrograph showing region of inhomogeneous or fibrillated shear developed in untreated nylon-6 film. The sheared region has a fibrillated microstructure due to incorporation of crystalline spherulite material. Draw direction arrowed. Scale bar ~0.5 μm

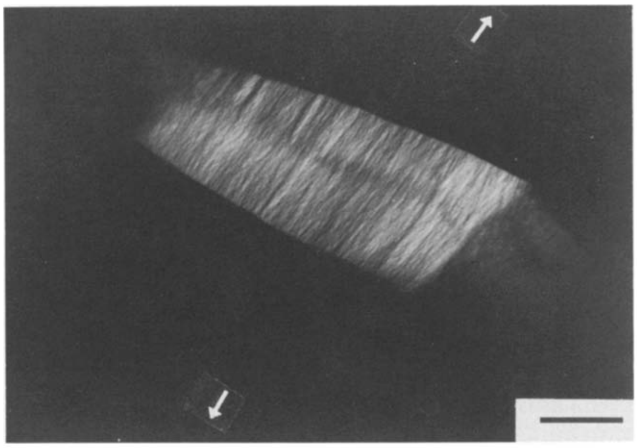

Figure 6 Transmission electron micrograph of interspherulitic craze developed in sodium chloride solution-treated nylon-6 film. Craze exhibits dark mid-line. Draw direction arrowed. Scale bar ~1 μm

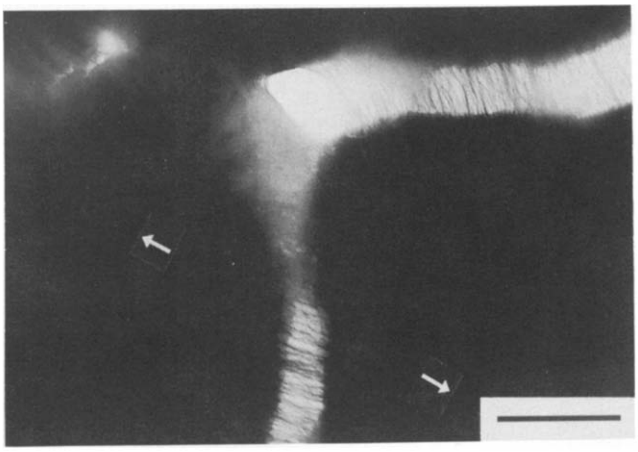

Figure 7 Interspherulitic crazing developed in calcium chloride-conditioned nylon-6 film. Localized shear thinning develops where the craze changes direction. Draw direction arrowed. Scale bar ~1 μm

used to give an estimate of mean fibril separation[23]. For crazes in NaCl-conditioned films, a mean fibril separation of ~60 nm is measured. Crazes in $CaCl_2$-conditioned films have a measured mean fibril spacing of ~105 nm, and ~140 nm for $ZnCl_2$-conditioned films. Fibril widths appear in the micrographs to show similar variations with conditioning.

Macroscopic stress–strain measurements were made at room temperature for a strain rate of $1 \times 10^{-3}\,s^{-1}$ on the thick-film nylon-6. Averaged moduli values are calculated over the strain interval 0.5 to 1.5%. Stress–strain curves show evidence for plastic behaviour, especially at large percentage strains. In addition to modulus measurements, elongation at fail was recorded. Samples showed too wide a scatter in their failure strains, however, for any meaningful values to be measured. Failure occurs via formation of a necked region exhibiting ductile tearing. Occasionally, for some $ZnCl_2$-treated samples, a sharp brittle-like failure occurred, with little evidence for neck formation or ductile drawing.

Typical stress–strain curves for unconditioned and salt-conditioned nylon-6 films are presented in *Figure 9*, with the $ZnCl_2$-conditioned sample exhibiting brittle-like failure after only a few tens of per cent. Yielding of both NaCl-conditioned and the unconditioned-film is more gradual, with extensive plastic deformation occurring.

Averaged moduli values presented in *Table 1* give a measure of changes in the elastic modulus due to salt

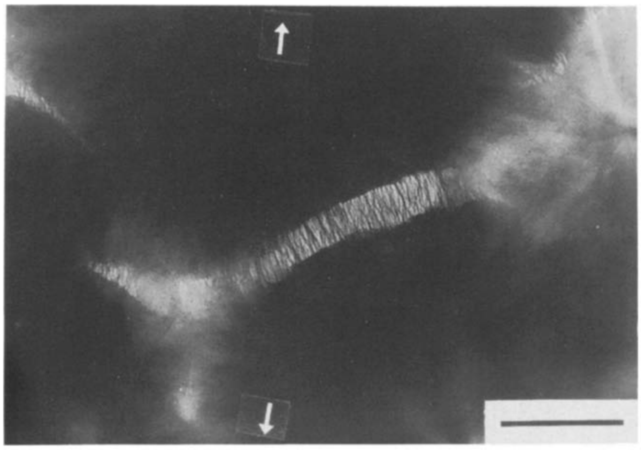

Figure 8 Interspherulitic crazing developed in zinc chloride-conditioned nylon-6 film with a narrow tapering termination at one end and blunted shear-dominated termination at the other. Draw direction arrowed. *Figure 4* is an enlarged region of part of this micrograph. Scale bar ~1 μm

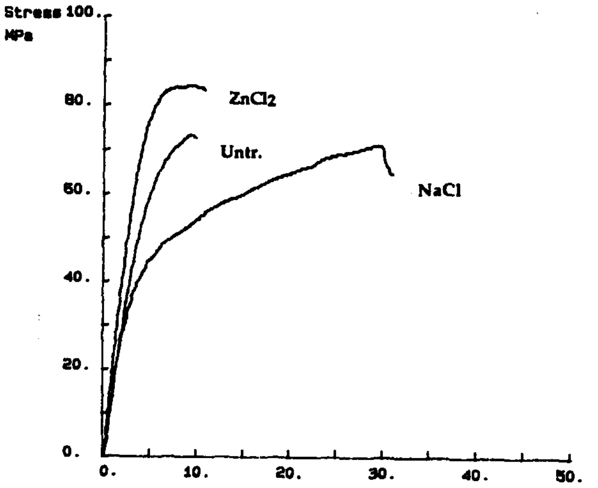

Figure 9 Typical stress–strain curves for unconditioned, NaCl-conditioned and $ZnCl_2$-conditioned nylon-6 macro samples. Strain rate of $\sim 1 \times 10^{-3}\,s^{-1}$

Table 1 Elastic moduli values for unconditioned and salt-conditioned macro samples averaged over the strain interval 0.5 to 2.0%

Treatment	Averaged modulus (MPa)	Standard deviation (MPa)	Change (%)	Failure mode[a]
$ZnCl_2$	2040	92	+11	B+D
$CaCl_2$	1980	116	+8	D
NaCl	1628	104	−12	D
Untreated	1840	103	-	D

[a] Failure mode: B, brittle; D, necking and ductile tear

conditioning. Owing to the non-uniform nature of the salt ingression, absolute values may not be measured. Both $CaCl_2$- and $ZnCl_2$-conditioned samples show a moderate degree of stiffening, with an increase in modulus apparent, whereas NaCl-conditioned samples would appear to be plasticized, with a decrease in modulus measured. Although the shifts are small, the qualitative trends seems clear from the table; quantitative data cannot be obtained because of the non-uniform penetration of the salts through the samples referred to above.

DISCUSSION

The different types of deformation observed in thin nylon films after salt treatment, and the strains at which deformation first occurs, have been described previously[16]. With the additional data from i.r. and modulus measurements, coupled with the results of other workers, a framework for understanding the embrittling effect of the various salt solutions can now be proposed, which can be correlated with what is already known for amorphous polymers.

The i.r. results show that the most drastic spectral modifications occur following treatment with $ZnCl_2$, with less marked changes occurring for $CaCl_2$-treated samples. These results are similar to those reported by Dunn and Sansom[24], who considered the i.r. spectrum of nylon-6 with and without $ZnCl_2$ treatment, and compared the changes observed with model compounds to aid interpretation. These workers likewise observed the appearance of a strong new peak at around $1600\,cm^{-1}$ (they actually locate it at $1595\,cm^{-1}$ compared with the $1601\,cm^{-1}$ of the present study), together with small shifts in position of the amide I and amide II bands. The spectra shown in *Figure 2* actually have better resolution than the traces shown by Dunn and Sansom. The peak at $1601\,cm^{-1}$ appears to have a shoulder on its upper side and this shoulder appears to correspond to the downward-shifted amide I peak identified by Dunn and Sansom; the peak shifted slightly up, which we assign to amide I, does not seem to have been resolved in the earlier paper, nor does the peak at $1570\,cm^{-1}$. The total effect of these changes is that the weight of the amide I band moves down, and the amide II band moves up.

On the assumption that the Dunn and Sansom comparative study of the effect of $ZnCl_2$ on model compounds is still pertinent, even though modern spectrometers may provide additional resolution and therefore the identification of more peaks, we will use their analysis of the spectral shifts to aid in our interpretation of the effect of salt on the mechanical properties of nylon. The changes in the amide I and II region were attributed to the formation of a coordination complex, with the amide group acting as a ligand. It was suggested that the amide group is linked to the metal ion through the oxygen atom. The broadening of the N–H stretching band at around $3300\,cm^{-1}$ seen in *Figure 1* was likewise reported by Dunn and Sansom. This broadening was attributed by them to the formation of a *cis*-form complex. The net effect of these two changes in structure is a shift from there being significant interchain hydrogen bonding in favour of intrachain hydrogen bonding through the *cis*-form complex.

Other workers have suggested that the formation of these amide–salt complexes (formed with a variety of salts including $ZnCl_2$ and $CaCl_2$) affect properties other than the i.r. spectrum. For instance Kim and Harget[25] report significant shifts in T_g with salt content, as did Siegmann and Baraam[26] with some rather different salts. Wyzgowski and Novak[27] report changes in d.m.t.a. spectra. All groups attributed the T_g shifts to the amide complexes leading to a stiffening of the flexible polymer chains. This leads to a greater barrier to rotation of the chains, as demonstrated by calculations (with a lithium ion) by Balasubramanian *et al.*[28]. This reduction in chain mobility may be expected to have consequences for the ease with which deformation can take place. In addition, the fact that thick films soaked for long times in $ZnCl_2$ often disintegrate before complete permeation of the salt occurs indicates that this salt solution at least can also lead to substantial chemical damage, presumably via actual breaking of the chain backbone bonds.

The spectral evidence therefore points to changes in bonding leading to chain stiffening, certainly for $ZnCl_2$, and to a lesser extent for $CaCl_2$. No changes in the i.r. spectrum were evident for NaCl-treated films, and it has previously been stated that NaCl treatment does not affect the mechanical properties of nylon-6[29], although this does not agree with our own previous work[16]. For the moment, discussion of the NaCl case will be deferred and we will concentrate on $ZnCl_2$ and $CaCl_2$. It is seen that these salts lead to a reduction in processes involving shear, either simple shear leading to the formation of interspherulitic shear deformation zones or fibrillar shear (seen in *Figure 5*). Crazing instead becomes dominant. In addition, we have previously shown[16] that the strain for deformation onset is markedly decreased upon salting — by a factor of 3 for $ZnCl_2$-treated thin films at room temperature — as the switch from shear-only processes to crazing-dominated takes place. The modulus measurements on thick samples show that the effect of these two salts is to increase the modulus (*Table 1*). In other words the stiffening of the chains revealed by the spectroscopy is accompanied by a macroscopic stiffening of the material.

Using the picture built up for amorphous polymers of competing shear and crazing, with the possibility of two routes to crazing — via scission or disentanglement processes — it is now possible to reconcile these various results. In untreated films it is clear that shear processes can occur readily, leading to a typical ductile response: nylon-6 is normally a tough material. Either pure shear or fibrillar shear[15,16] may occur. Both processes require the possibility of neighbouring chains sliding over one another. The chain stiffening that occurs upon salting, however, makes this type of motion very difficult — the chains cannot move independently of one another. Clearly this rules out not only shear and fibrillar shear, but also the possibility of disentanglement crazing. However, the reduction in chain mobility now leads to increased build-up of stress on individual chains as the external stress is applied, and the stress for chain scission can therefore be attained before the intervention of shear. Chain scission may also be occurring (particularly for $ZnCl_2$) by virtue of chemical damage to the chains. The net effect is that scission crazing now becomes dominant. Since the initial molecular weight of the nylon is comparatively low, few scission events per chain are required before craze breakdown occurs. Thus the polymer has become severely embrittled due to the complex formation and consequent reduction in chain mobility. This conclusion, based predominantly on results obtained on thin films, can equally well explain the results of Wyzgowski and Novak[14,27,29] on bulk samples.

The case for NaCl treatment is less easily explained. The i.r. spectrum shows no evidence for modifications to bonding by complex formation. There is therefore no reason to expect chain stiffening to occur. Furthermore *Table 1* shows that the bulk modulus actually drops after treatment with NaCl, suggesting a plasticization effect. This could explain why in our earlier work we detected an increase in the strain at which deformation first sets in at room temperature of a few per cent, so that the stresses for deformation onset before and after treatment are very similar. Nevertheless, although the NaCl treatment does not appear to be embrittling, there is nevertheless a shift towards crazing (crazes were never seen in our TEM observations of untreated nylon-6). One speculative possibility is that the plasticization without any concomitant complex formation actually leads to enhanced chain mobility. A sufficient increase in chain motion could lead to the onset of disentanglement crazing, just as may occur in some amorphous polymers upon raising the temperature[3]. Disentanglement crazes will be much less susceptible to craze breakdown, since their molecular weight is undegraded, and thus the appearance of such crazes will not necessarily be accompanied by bulk embrittlement.

CONCLUSIONS

Infra-red spectroscopy shows significant changes in the amide I, amide II and C–H stretch regions of the spectrum of nylon-6 after treatment with $ZnCl_2$ and $CaCl_2$. The changes are thought to be due to complex formation of the amide group with the metal ions and lead to significant stiffening of the nylon chains. Accompanying this stiffening is a consequent reduction in chain mobility. This reduction in mobility has a marked effect on the mechanical properties of the nylon. The macroscopic modulus is seen to increase, corresponding to an overall stiffening of the material. Simultaneously there is a shift in the mode of deformation (as revealed by TEM of thin films) from one that is shear-dominated to one that is primarily crazing. The occurrence of crazing is due to the possibility of scission as the chain mobility drops. These scission crazes are inherently weak and the material is embrittled.

The effect of NaCl treatment is rather different. The i.r. spectrum shows no evidence for complex formation, and the macroscopic modulus drops relative to the untreated nylon. Nevertheless TEM observations show that there is a switch towards crazing. It is speculated that this is due to the onset of disentanglement crazing, which is much less damaging than scission crazing. The embrittlement brought on by $ZnCl_2$ and $CaCl_2$ does not therefore occur.

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