Investigation of Structural and Mechanical Properties of Copper-Chloride-Doped Nylon-6 Films. I. Structure

D. S. KELKAR[1,*] **and N. V. BHAT**[2]

[1]Department of Physics, Institute of Science, Bombay-32, India, and [2]Department of Physics, University Department of Chemical Technology, Matunga, Bombay-19, India

SYNOPSIS

Structural changes in nylon-6 film on doping with various concentrations of copper chloride (0.5, 1.25, 2.5, 5, and 12.5% w/w) have been investigated. Methods such as density measurement, analysis of infrared spectra, and wide-angle X-ray diffraction analysis have been employed to study these structural changes. It is found that doping up to 1.25% of copper chloride increases the crystallization of nylon-6 in the α-crystalline form. Further increase in the dopant concentration, however, gradually changes the crystal structure to hexagonal γ form with reduction in the total crystallization.

INTRODUCTION

Incorporation of inorganic salts in polar polymers changes the structure and hence other physical properties of the polymer. Such changes induced in nylon-6 due to interaction with inorganic salts have been investigated extensively.[1-8]

The α to γ transition in nylon-6 after treatment with (I_2/KI) solution was reported by Abu-Isa.[1] Dunn and Sansom[2-4] investigated stress cracking of nylon-6 due to interaction with various inorganic metal salts. Valenti and others[5] studied the melting behaviour of polycaproamide doped with salts like KCl, LiCl, and LiBr. They observed that LiCl and LiBr favour the γ crystalline form of nylon-6. Wissburn and Hannon[6] reported IR studies of different polymers doped with several nitrate salts. The viscosity and glass transition temperature of nylon-6 doped with KCl, LiCl, and LiBr are reported by Acierno et al.[7] The glass transition temperature of nylon-6–inorganic salt mixtures have been studied by Kim and Harget.[8]

Dunn and Sansom,[3] while studying the stress cracking of polyamides by various inorganic salts, observed that the salts may be classified into two types. Type I metal halide such as zinc, cobalt, copper, and mangenese chloride form complexes in which the metal atom is coordinately bonded to the carbonyl oxygen atom of the amide group, whereas with type II metal halides such as lithium, calcium, and magnesium chlorides the halogen atoms of the salt form complex with $N-H$ replacing the $N-H-O$ hydrogen bond. Similar results are also reported by Kim and Harget[8] while using type II metal halides in nylon-6.

In the present study, nylon-6 has been doped with various concentrations of a single salt viz. copper chloride. This salt belongs to the type I category according to the classification by Dunn and Sansom.[3] These authors have reported a detailed study of the infrared spectra and molecular configuration of doped nylon-6 and our IR results are interpreted on the basis of their work. In this article, we study the effect of salt content on the manner of complex formation using infrared spectra. Other structural changes viz. the crystallinity index and the crystalline form of nylon-6 have also been studied using density measurement and wide-angle X-ray diffraction analysis.

EXPERIMENTAL

Sample Preparation

Nylon-6 obtained from Nirlon Synthetic Fibres and Chemicals (Bombay, India) in the form of beads

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was dissolved completely in formic acid (4% w/v) by continuously stirring for 4 h. The solution was spread on a flat, clean glass plate. The plate was heated at 70°C for about 1 h. The solvent evaporated completely and a film of nylon-6 formed on the glass plate was stripped off. This was considered the control nylon-6 film and was stored in a desiccator until its use.

Hydrated copper(II) chloride, $CuCl_2$, $2H_2O$ reagent grade, was used as received.

Nylon-6 beads (4% w/v) and a known weight of copper(II) chloride in the required ratio was then dissolved in a common solvent viz. formic acid. The solution was stirred well for 4 h and a film was cast in the same manner as described above. Thus, nylon-6 films doped with various amounts of copper chloride (0.5, 1.25, 2.5, 5, and 12.5% w/w) were prepared and stored in a desiccator. The thickness of the films thus formed was about 20 μm.

The percentage of Cu(II) chloride in the cast films was determined by atomic absorption spectroscopy. It was found that the percentage of Cu(II) chloride content in the film was same as that added in the solution.

Density Measurement

The density of the control and doped films of nylon-6 was measured by a flotation method[9] using carbon tetrachloride and benzene (AR grade).

Infrared Spectra

The infrared spectra of control and doped films of nylon-6 were recorded on Perkin-Elmer model 397 IR Spectrophotometer in the wavelength region 400–4,000 cm^{-1} operating with normal slit in the 10-min scan mode, interposing 20-μm film in the beam.

In nylon-6, it is reported that the band at 1,120 cm^{-1} corresponds to the C—C stretching band.[10] This band is common to both types (A and B) of conformation and hence has been used as a standard band. It is a measure of total amount of polycaprolactam and follows the Lambert–Beer law. The band in the nylon-6 IR spectrum appearing at 930 cm^{-1} corresponds to the CO—NH in plane band.[10] Hence, it is a measure of the conformation A, i.e., α crystal structure of nylon-6.

The (α) crystallinity index (X), therefore, was calculated using the formula.
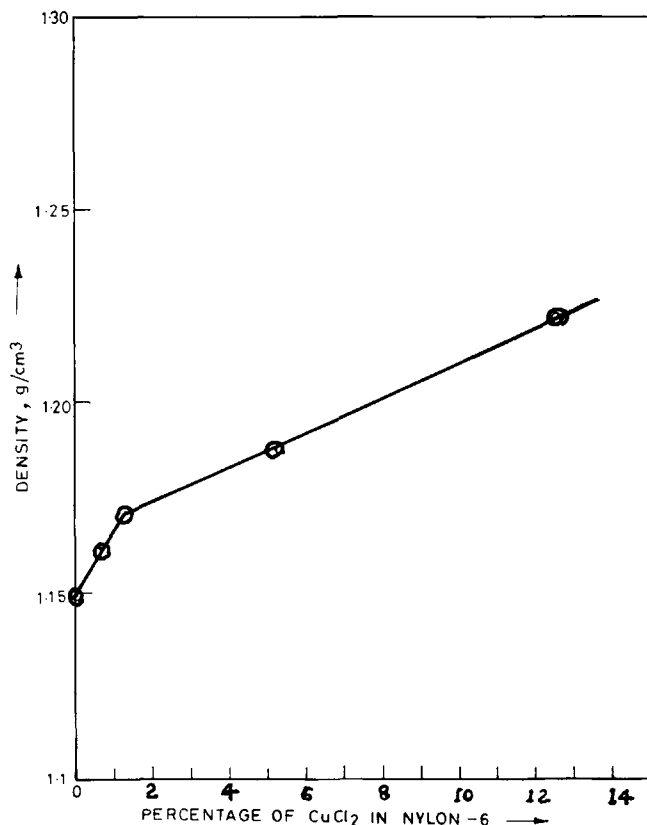

Figure 1 Plot of density vs. percentage of $CuCl_2$ in $CuCl_2$-doped nylon-6 films.

$$X = \frac{OD\,930}{OD\,1120},$$

where OD is the optical density at a particular wavelength and is given by optical density $= \log_{10} I_0/I$, where I_0 and I are the intensities of the incident and transmitted radiation, respectively.

Wide-Angle X-Ray Diffraction

WAXD scans for control and doped films were obtained using a Philips X-ray Diffractometer model PW 1710 unit. Nickel-filtered copper radiation (K_α) was incident on the sample which was scanned at the rate of $1°/\min$ in the reflection mode over a range of 2Θ from 5–35°. From the radial scans of intensity vs. 2Θ, the crystallinity index of the sample was calculated using Manjunath et al.'s formula.[11]

The X-ray order factor or the lateral order (one-resolution factor) gives the measure of crystallinity index for a sample.

RESULTS AND DISCUSSION

Density Measurement

A plot of density of the control and doped films of nylon-6 against the concentration of salt is shown in Figure 1. The plot shows that the density increases continuously with the increase in the dopant con-

centration. The increase is, however, not linear. The plot consists of two straight lines having different slopes. A careful look at the plot indicates that the slope of the line for the low level of doping (up to 1.25%) is more than that for the higher level of doping. The comparison of the observed density values with the calculated density values (by considering it as a physical mixture) shows that the two values differ. This is apparently due to the changes in the density of nylon itself that can possibly occur due to crystallization.

Analysis of Infrared Spectra

The infrared spectra of the control, 1.25, and 12.5% copper-chloride-doped films of nylon-6 are shown in Figure 2.

Dunn and Sansom[3] studied in detail the action of different types of metal halides on nylon-6 and classified these salts into two categories: types I and type II. According to them, copper chloride belongs to the type I category. Accordingly, the complex formation of nylon-6 with type I salt gives a band at 1,595 cm^{-1}.

In the present work, we observed an additional band at 1,570 cm^{-1} for all doped samples. This band increases in intensity with increase in the concentration of copper chloride. It is also reported[3] that the amides I and II bands at 1,640 and 1,530 cm^{-1},

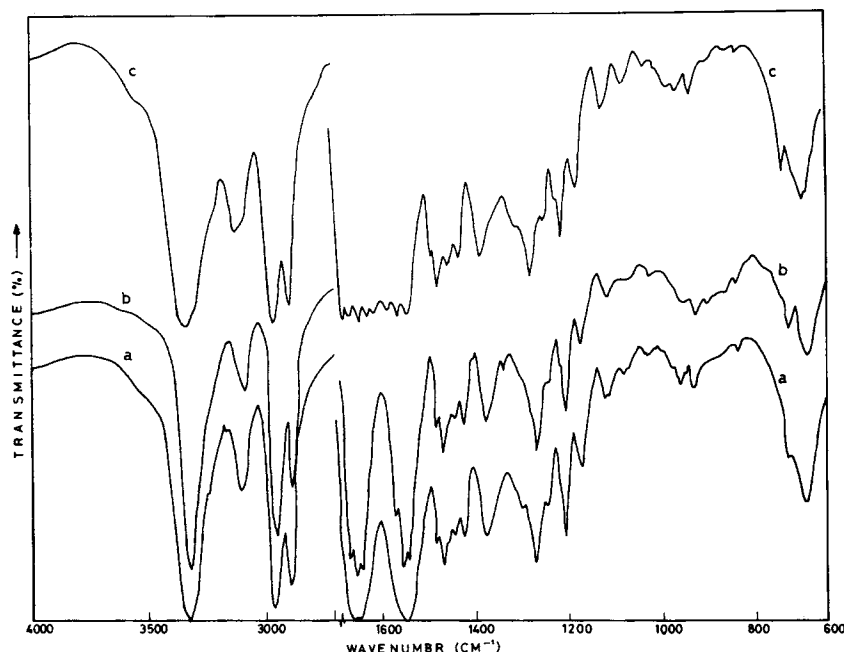**Figure 2**   Infrared spectra of control, 1.25, and 12.5% CuCl$_2$-doped films of nylon-6.

Table I α-Crystallinity Index for Control and Doped Films of Nylon-6 (IR Spectra)

Sample	Crystallinity Index
Control	0.75
0.5% CuCl₂ doped	0.76
1.25% CuCl₂ doped	0.84
2.5% CuCl₂ doped	0.73
5% CuCl₂ doped	0.71
12.5% CuCl₂ doped	0.34

respectively, show shifts toward each other simultaneously. Similar shifts are observed for the samples doped up to 5% $CuCl_2$. For the 12.5% doped sample, these bands do not remain separated but merge into a single broad band.

According to Dunn and Sansom,[3] the appearance of a new band (at 1,570 cm^{-1}) together with the shifts of amides I and II bands show trans to cis transformation. In addition, the shift of the carbonyl stretching frequency at 1,640 cm^{-1} to a lower value indicates the formation of carbonyl–metal coordinate link.

Major changes are also observed in the N—H stretching band at about 3,300 cm^{-1}. Initially, for the films doped with concentration up to 1.25% $CuCl_2$, the N—H stretching band at 3,300 cm^{-1} becomes sharp and its height increases. Above this concentration, the band becomes broader and a continuous reduction in intensity is also observed as the concentration of salt is increased. The N—H stretching band is a composite band consisting of a higher frequency trans-form contribution and a

lower frequency cis-form contribution.[3] The non-symmetry of the band with a low-frequency shoulder and the subsequent changes on treatment with metal halides can be explained as due to the change in the structure of nylon-6 from trans to cis form. It has been observed during this study that for low-level of doping (up to 1.25%) the structure is more in the trans-form, as indicated by the sharp and symmetrical band at 3,300 cm^{-1}.

Shifts are also observed in the small absorption band at 3,080 cm^{-1} for doped nylon-6 films. For low concentrations of doping, the shift is to the low wavenumber side, whereas for higher concentrations it is to the high wavenumber side of 3,080 cm^{-1}. Other changes are also observed in the IR spectra of the doped nylon-6 film such as the appearance of only three bands at 1,420, 1,460, and 1,480 cm^{-1} instead of the four C—H deformation bands at 1,420, 1,440, 1,460, and 1,480 cm^{-1} in control nylon-6 spectrum.

Thus, the analysis of the infrared spectra of doped films clearly indicates that complex formation does take place due to doping. Further, the manner in which nylon-6 chain turns due to the complex formation (cis or trans) depends upon the concentration of the dopant.

The crystallinity index (α) for the doped samples of nylon-6 has been estimated using their IR spectra. The infrared spectra of the control and doped samples show a variation in the height of 930 cm^{-1} band. This band is assigned to the CO—NH in plane vibrations.[10] Doskocilova et al.[12] showed that in nylon-6 the differences in infrared spectra do not correspond to differences in crystal lattice but to two
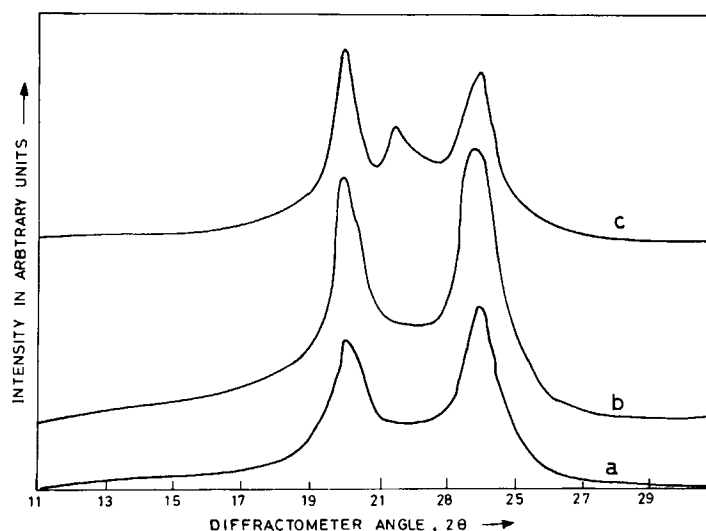

Figure 3 XRD scans of control, 1.25, and 12.5% CuCl₂-doped nylon-6 films.

Table II   Crystallinity Index for Control and Doped Films of Nylon-6 Using XRD Analysis

Sample	Crystallinity Index
Control	0.56
0.5% $CuCl_2$ doped	0.63
1.25% $CuCl_2$ doped	0.64
2.5% $CuCl_2$ doped	0.62
5% $CuCl_2$ doped	0.55
12.5% $CuCl_2$ doped	0.52

possible conformations of the polyamide chain, A and B. It is observed that the conformation A in nylon-6 exists exclusively in the monoclinic α crystalline form, whereas the conformation B usually occurs in an amorphous or mesomorphous state. The amorphous and the crystalline form of conformation B that is the hexagonal γ form exhibit identical spectra. Hence, from the infrared spectra, direct measurement of γ crystalline content is not possible. For conformation A, i.e., α crystal structure, CO—NH groups lie in-plane with polymethylene chains and hence intensity of the 930 cm^{-1} band, which is assigned to CO—NH in-plane vibration, gives directly a measure of α crystalline phase.

The α crystallinity indices calculated for the control and doped samples are given in Table I. From the table, it is clear that the α crystallinity index increases for the samples doped up to 1.25% of salt. Above this concentration, the α crystallinity index decreases.

Analysis of Wide-Angle X-Ray Diffraction

The XRD scans for the control and 1.25 and 12.5% doped films of nylon-6 are depicted in Figure 3. The XRD scans of the control and doped films up to 1.25% show two peaks corresponding to the α crystal form. For higher concentrations, a third peak at 2Θ = 22°, corresponding to the γ form, starts appearing. The intensity of this peak increases with the increase in salt concentration. The crystallinity index of the control and the doped nylon-6 films are tabulated (Table II). It can be observed that the crystallinity increased for low concentrations of doping and de-

creased for high concentrations of doping. But, on the whole, the crystallinity index has not reduced much from that for the control sample.

CONCLUSION

The results of the density measurement, infrared analysis, and X-ray diffraction analysis point out that the structure of nylon-6 changes on doping with copper (II) chloride. Further, these changes depend upon the dopant concentration. The dopant concentration not only changes the total crystallinity index of the sample but also has an effect on the manner in which the nylon-6 chain is turned due to complex formation and also the crystalline form of the sample.

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