

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

II. Elastic and Viscoelastic Studies

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SYNOPSIS

The article reports the effect of variation in the concentration of copper chloride on the elastic and viscoelastic properties of nylon-6 films. The elastic modulus for the film is determined using sonic velocity measurement technique. The glass transition temperatures are determined from dynamic mechanical studies with the Rheovibron. It is observed that the glass transition temperature of the doped films increases with increase in the dopant concentration. It is also observed that at low concentrations of doping (up to 1.25%) the salt acts as a plasticizer, whereas for higher concentration of doping (up to 12.5%) it acts as an antiplasticizer.

INTRODUCTION

Polyamides constitute one of the most common polymer systems to which have been added a large variety of metal salts. There exist a number of reports¹⁻⁵ giving an account of the effect of dopant on various properties of nylon-6 such as melting temperature, glass transition temperature, crystallization rates, etc. However, it is found that the results of the measurements of the glass transition temperatures of the doped films, as reported by various authors, differ to a large extent. In earlier works, it was reported that the addition of inorganic salt decreases the crystallization rate³ and hence there is a contraction in the specific volume. This contraction of volume should decrease the free volume of the system and should result in an increase in the glass transition temperature. Yet, it was reported^{1,2,4} that the glass transition temperature, T_g , of nylon-6 is not affected by the type and content of the salt.

The T_g independence of added salt to polycapromide has more recently been shown⁵ to be incorrect because of the effect of water absorption. T_g s of

salted and unsalted nylon-6 are lowered in the presence of moisture. When strict precautions to exclude moisture are taken, the addition of 4% LiCl has been shown to raise the T_g by 25°C.

The study of variation of the glass transition temperature on addition of salts is important because it can be used to determine whether the added salt is a plasticizer for the polymer. A depression in the T_g values indicates that the salt is a plasticizer. Addition of a small quantity of an inorganic salt also improves the flow properties of the polymer if the dopant acts as a plasticizer for the polymer. It was reported by Ghera⁶ that the quantity of added salt is also an important factor to be considered because mechanical properties of a polymer with a small quantity of dopant might be altogether different from those when the quantity of dopant added is large. Jackson and Caldwell⁷ observed that on incorporation of certain types of additives in bisphenol-A polycarbonate the modulus and tensile strength of the films increased. They called this effect "antiplasticization" because opposite results are obtained on plasticization, i.e., decreased modulus and tensile strength. The glass transition temperatures are depressed appreciably less by the antiplasticizers than by conventional plasticizers. Thus, taking into consideration the results of Ghera and

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Jackson and Caldwell, it may be concluded that a certain salt when added in small quantity may act as a plasticizer and the same salt when added in large quantity might act as an antiplasticizer for the polymer or vice versa.

It was, therefore, thought worthwhile to study the effect of CuCl_2 concentration in nylon-6 on its glass transition temperature. These results are used to determine the plasticizing action of the salt on nylon-6. Similar results are also obtained with measurements of other mechanical properties viz. the elastic modulus obtained using sonic velocity measurements and the loss modulus obtained on measurements with a Rheovibron.

EXPERIMENTAL

Sample Preparation

The experimental details of sample preparation are given in part I of this series.⁸ In short, the control and doped films of nylon-6 (0.5, 1.25, 2.5, 5, and 12.5% w/w of CuCl_2) were prepared by dissolving nylon-6 and the dopant in the required ratio in formic acid and then evaporating the solvent. These samples were maintained dry till their use.

Sonic Velocity Measurement

The sonic velocity for control and doped films was determined at room temperature using Sonic Modulus Tester-5R (H. M. Morgan & Co.) at 5 KHz. The instrument measures the time taken by the pulse to travel through the film between the transmitter and receiver kept at a known distance apart. The time required to travel various distances for a sample are thus obtained. The slope of the graph plotted between the distance and the time gives the sonic velocity. The modulus of elasticity, E (Young's or Sonic Modulus), is calculated using the formula $E = \rho C^2$,^{9,10} where ρ is the density (g/cc) of the sample and C is the sonic velocity (cm/sec).

Dynamic Mechanical Measurements

The viscoelastic measurements of the control and doped films were carried out from room temperature to 150°C using a Rheovibron DDV-II that was operated at a frequency of 110 Hz. The experimental sample was a strip of length 3 cm and width 0.2 cm

and was held tightly between the chucks in a temperature-controlled high-temperature chamber. The sample was heated in the chamber at 2°C/min. During the measurements, the temperature of the chamber was maintained constant at a particular value.

The tests were carried out at very low strain levels, where the measurements themselves produced no change in the morphological structure. The measurements of dynamic force and $\tan \delta$ were carried out at increments of 4°C. The temperature at which $(\tan \delta)_{\text{max}}$ occurs gives the glass transition temperature at that frequency. The glass transition temperatures for all the samples were thus obtained.

The values of the storage modulus, E' , were calculated using the formula:

$$E' = E^* \cos \delta$$

where E^* is the complex modulus given by

$$E^* = 2 \times \frac{1}{A(D - K)} \times \frac{L}{S} \times 10^9 \text{ dyne/cm}^2.$$

Here, L = length of specimen in cm, S = cross-sectional area in cm^2 , A = amplitude factor when measuring $\tan \delta$, D = dynamic force dial reading, and K = error displacement constant.

RESULTS AND DISCUSSION

Sonic Velocity Measurement

The experimentally obtained values of the sonic velocity and the values of density, obtained in part I,⁸ have been used to calculate the sonic modulus for the control and doped films of nylon. These values have been tabulated (Table I). From the table, it is obvious that the sonic velocity and modulus increase with increase in the concentration of the salt above 1.25% CuCl_2 . This indicates that copper chloride has an antiplasticizing action on nylon-6 for concentrations more than 1.25%.

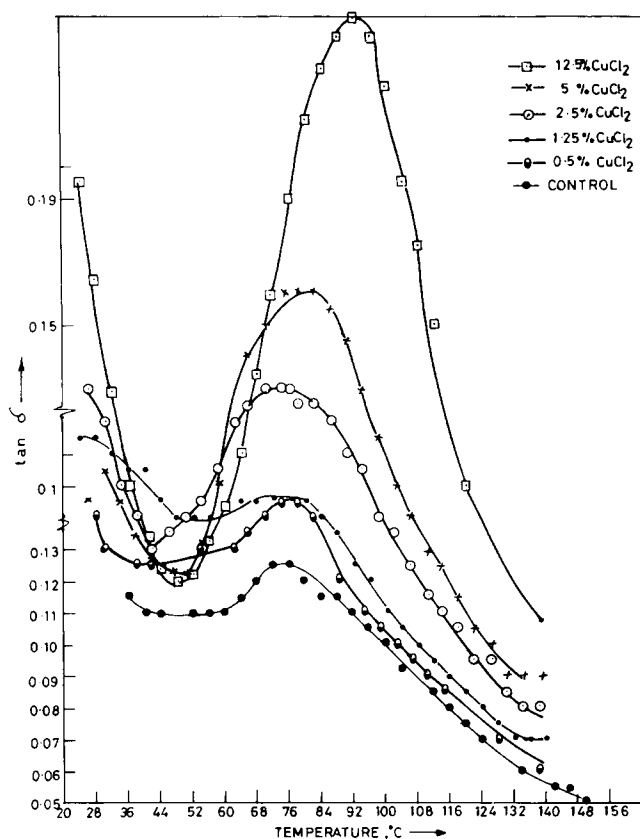
Dynamic Mechanical Measurement

Plots of $\tan \delta$ against temperature for the control, 1.25, 12.5% doped samples are shown in Figure 1. The values of the glass transition temperatures, T_g , for undoped and doped samples of nylon-6 at 110 Hz have also been tabulated (Table I). It may be seen from the table that for concentration of CuCl_2

Table I Values of Density, Sonic Velocity, Sonic Modulus, Storage Modulus, and Glass Transition Temperature for Control and Doped Nylon-6 Films

Sample	Density (g/cm ³)	Sonic Velocity (km/sec)	Sonic Modulus $E \times 10^{10}$ (dyne/cm ²)	Storage Modulus $E' \times 10^{10}$ (dyne/cm ²) at 30°C	Glass Transition Temperature T_g (°C)
Control	1.149	1.67	3.20	1.92	74
0.5% CuCl ₂	1.160	1.67	3.24	0.95	74
1.25% CuCl ₂	1.17	1.67	3.26	1.08	74
2.5% CuCl ₂	1.173	1.70	3.39	1.82	76
5% CuCl ₂	1.187	1.81	3.89	2.5	78
12.5% CuCl ₂	1.22	2.00	4.88	2.70	92

more than 1.25% T_g increases slowly as the content of the salt is increased. Such an increase in the T_g values has been reported by Kim and Harget¹¹ and Mehta and Andrews.¹² This increase in the T_g values can be explained on the basis of decrease in the free volume of the molecular chain.

**Figure 1** Plot of $\tan \delta$ vs. temperature for control and doped films of nylon-6.

This leads to the stiffening of the nylon chains. The stiffening of chains is one of the effects of antiplasticizing action of salt.⁷

The data on mechanical properties, however, indicate that the behaviour of copper chloride when added in small quantities (up to 1.25%) is different. It is found (Table I) that for the concentration of dopant up to 1.25% the values of the glass transition temperature, as well as the sonic velocity, are the same as for the control sample. These values, however, increase for higher concentration of copper chloride. Values of the sonic modulus and the storage modulus (Table I) for the control and doped samples also show similar behaviour. The results of the maximum values of the mechanical loss given by the height of $(\tan \delta)_{\max}$ show that up to 1.25% of doping the loss is reduced, whereas the loss increases for higher concentrations of CuCl₂. Reduction in the mechanical loss indicates plasticizing action and its increase indicates antiplasticizing action. The increase in the height of $(\tan \delta)_{\max}$ also indicates increase in the amount of amorphous content observed for samples doped with more than 1.25% of CuCl₂. Similar results are obtained with XRD analysis also,⁸ i.e., for doping up to 1.25% CuCl₂ the crystallinity index has increased, but for higher concentrations there is a decrease in the crystallinity index.

All these results point out that the addition of copper chloride up to 1.25% has a plasticizing effect on nylon-6, whereas addition of higher concentrations shows an antiplasticizing action.

True plasticizing action, which is the weakening of the second order (Van der Waal's) attraction forces between polymer chains because of the interposition of the plasticizer molecule and of the

screening of the polar groups, takes place only up to a certain critical concentration, 1.25% in this case.

REFERENCES

1. A. Ciferri, E. Bianchi, F. Marchese, and A. Tealdi, *Makromol. Chem.*, **150**, 265 (1971).
2. B. Valenti, E. Bianchi, G. Greppi, A. Tealdi, and A. Ciferri, *J. Phys. Chem.*, **77**, 389 (1973).
3. E. Bianchi, A. Ciferri, A. Tealdi, R. Torre, and B. Valenti, *Macromolecules*, **7**, 495 (1974).
4. D. Acierno, E. Bianchi, A. Ciferri, B. De Cindio, C. Migliaresi, and L. Nicolais, *J. Polym. Sci., Polym. Symp.*, **54**, 259 (1976).
5. D. Acierno, F. P. La Mantia, G. Titamanlio, and A. Ciferri, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 739 (1980).
6. P. Ghersa, *Modern Plast.*, **36**(2), 135 (1958).
7. W. J. Jackson Jr. and J. R. Caldwell, *J. Appl. Polym. Sci.*, **11**, 211 (1967).
8. D. S. Kelkar and N. V. Bhat, *J. Appl. Polym. Sci.*, communicated.
9. W. H. Church and W. W. Moseley, *Text Res. J.*, **29**, 525 (1959).
10. W. W. Moseley Jr., *J. Appl. Polym. Sci.*, **3**, 266 (1960).
11. Hyo-gun Kim and P. J. Harget, *J. Appl. Phys.*, **50**(10), 6072 (1979).
12. M. J. Mehta and R. D. Andrews, *Polym. Prep.*, **14**, 1260 (1963).

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