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Effect of Adsorbed Salts on the Conductivity of Nylon 66

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ABSTRACT: Films of nylon 66 were immersed in saturated solutions of LiCl, NaBr, NaI, KI, $CuCl_2$, and $ZnCl_2$ until the weight no longer increased. After the films were dried, dielectric data were taken at frequencies from 10^2 to 10^5 Hz and temperatures up to 200 °C. The high-temperature behavior is dominated by conductivity which is increased up to 150-fold by the presence of the absorbed salts. The largest effects were obtained with $CuCl_2$ even though the amount absorbed is less than in the case of $ZnCl_2$. It is suggested that the strong Cu–N interaction facilitates the liberation of amide protons for conduction.

Introduction

Interest in the interaction between nylon and various metal salts goes back many years. Zinc chloride is noted for its ability to cause stress cracking.[1] In 1952, Busse found that $ZnCl_2$ could inhibit or prevent crystallization in nylon 66 as judged by optical transparency, X-ray diffraction, or infrared spectroscopy at a concentration of 1 atom of zinc per 3–5 amide groups (24–40% $ZnCl_2$ added).[2] Kargin and co-workers reported that nylon readily dissolved 1–25% $ZnCl_2$ in the melt and that a composition containing 25% $ZnCl_2$ added was completely amorphous by X-ray.[3] There is infrared evidence that both $ZnCl_2$ and $CuCl_2$ complex with the amide groups.[3,4] The kinetics of the diffusion of $ZnCl_2$ from concentrated solutions has also been studied.[5]

Alkali halides also interact with nylon. Lithium chloride forms a crystalline complex with four molecules of *N*-methylacetamide.[6] When LiCl was melt blended with nylon 66 at the same salt/amide ratio (9.4% LiCl added), the resulting composition was transparent, amorphous by X-ray diffraction, and failed to retain a measurable modulus at temperatures above the glass transition or α-relaxation.[7] Lithium chloride has a strong affinity for water, and the relative humidity above a saturated solution is only 11%. When a molded bar of the blend with nylon was exposed to laboratory humidity, droplets of salt solution appeared on the surface. Thus, LiCl interacts more strongly with water than with nylon.

Kim and Harget reported that several salts including LiCl complex with nylon 6 to increase the glass temperature in the dry state, reduce the melting point, and eliminate crystallinity above a certain concentration.[8] Infrared spectra also provided evidence for complex formation between the salt and the amide groups.

Hansen used lower levels of salts to form void-free nylon monofilaments.[9] In his compositions, the additives retarded but did not prevent crystallization. The most effective salts were LiCl, LiBr, LiI, and NaI at concentrations from 1 to 10%, but usually 2–4%. In addition to retarding crystallization, low levels of LiCl also depress the melting point of nylon 66.[10]

Experimental Section

In the present study, samples of a 4-mil film of nylon 66 were immersed in saturated aqueous solutions of various salts until the weight no longer changed. They were then dried in a vacuum oven at 110 °C until the weight was again constant. To ensure dryness, we emphasize data from second heating cycles after previous heating to 200 °C. An exception was made for the sample containing $ZnCl_2$, which experienced mechanical failure at ca. 186 °C.

Dielectric measurements at frequencies from 10^2 to 10^5 Hz were made in the manner previously described.[11]

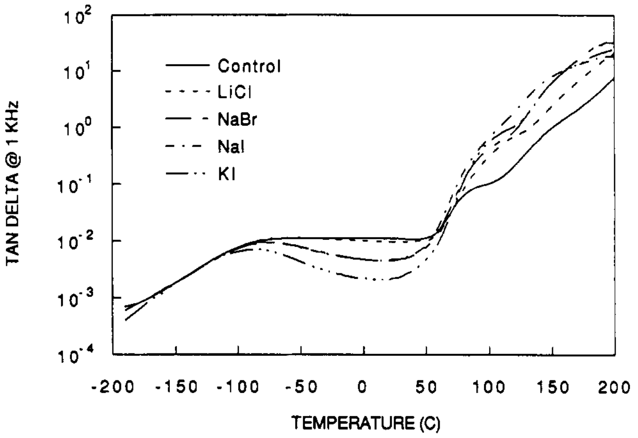

Figure 1. Dissipation factor at 1 kHz of nylon 66 containing alkali halides.

Table I. Properties of Alkali Halides

	salt			
	LiCl	NaBr	NaI	KI
solubility in cold water, g/100 cm^3	63.7	116	184	127.5
relative humidity, %	11	58	38	69
weight gain, wet, %		4.90	4.65	19.54
weight gain, dry, %	0.30	1.46	2.29	12.69

Samples Containing Alkali Halides

Nylon 66 was treated with LiCl, NaBr, NaI, and KI. The properties of these salts are summarized in Table I. Their saturated solutions are used to provide known levels of relative humidity.[12] The difference between the equilibrium weight gains in contact with the saturated solution and after drying corresponds to the amount of water absorbed.

The dissipation factor (tan δ) and the dielectric constant (ε′) at 1 kHz are plotted in Figures 1 and 2. At temperatures below the γ-relaxation near −80 °C, the absorbed salts have little effect. However, near 0 °C where the β-relaxation would occur in nylon containing moisture, the dissipation factor is significantly reduced in the samples containing NaBr, NaI, or KI. This effect extends from ca. −120 to +50 °C. In the region of the α-relaxation, which

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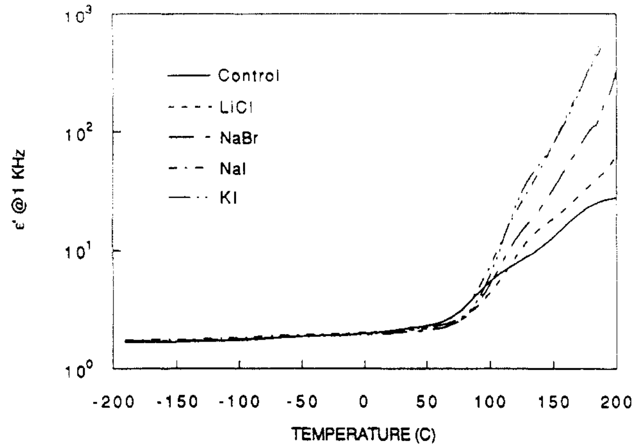

Figure 2. Dielectric constant at 1 kHz of nylon 66 containing alkali halides.

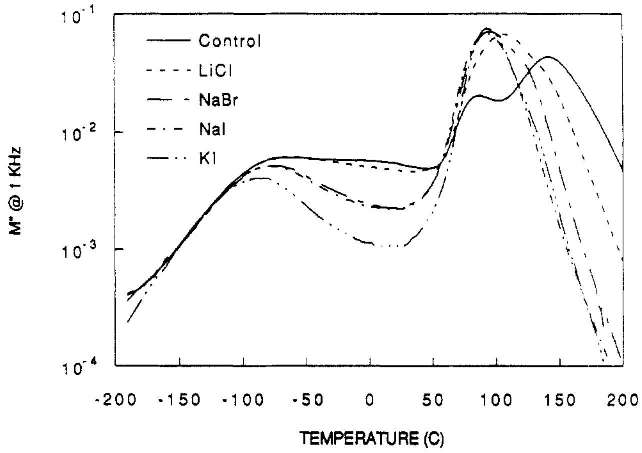

Figure 3. Electric loss modulus at 1 kHz of nylon 66 containing alkali halides.

appears as a shoulder in tan δ near 90 °C, both tan δ and ε′ increase in a major way, especially in the samples containing salts. These effects are attributed to ionic conductivity.[13]

To separate the effects of conductivity and viscoelastic relaxation it can be helpful to express the data in terms of the electric loss modulus.[13] This quantity is given by the equation

$$M'' = \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2} \qquad (1)$$

where ε′ and ε″ are the real and imaginary parts of the complex permittivity. This function is plotted in Figure 3. In the region above room temperature, the curve for the control has two maxima at 88 and 142 °C. The first peak is the α-relaxation, and the second has been called the "conductivity relaxation".[13] For the samples containing salts, there is only one maximum at 108 °C for the sample containing LiCl and 95 ± 1 °C for the other salts. It is thought that the corresponds to a combination of the two peaks for the control.

Further insights come from the frequency–temperature relationships. The lower temperature peak in the control has an apparent activation energy of 145 kcal/mol, a reasonable value for an α-relaxation or glass transition. The activation energy for the upper peak is 26 kcal/mol, which is in line with earlier work on conductivity in nylon.[13] The activation energies for the maxima in M'' for the four samples containing salts range from 31 kcal/mol with LiCl to 53 kcal/mol with KI.

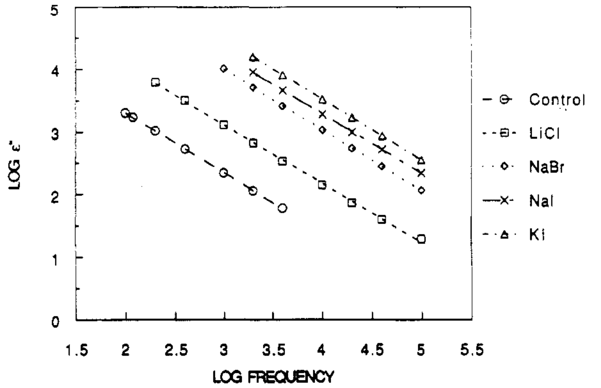

Figure 4. Plot of log ε″ at 200 °C vs log *f* for nylon 66 containing alkali halides.

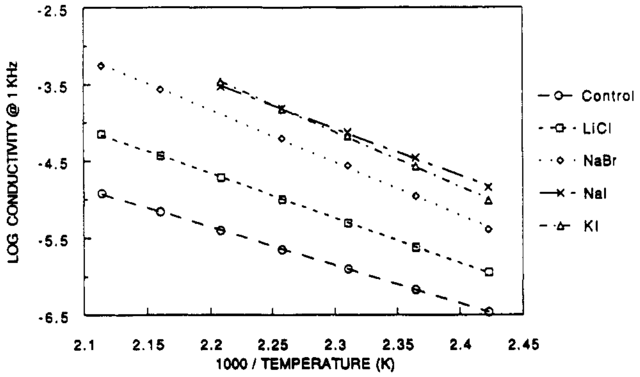

Figure 5. Arrhenius plot of the apparent conductivity at 1 kHz for nylon 66 containing alkali halides.

The apparent electrical conductivity is given by

$$\sigma = \epsilon''\omega\epsilon_0 \qquad (2)$$

where $\omega = 2\pi f$ and ϵ_0 is the absolute permittivity of free space (8.354×10^{-12} F/m). Thus, if the response is purely conductive, ε″ should be inversely proportional to the frequency. This is tested in Figure 4 in which log ε″ is plotted against log *f* for data taken at 200 °C, the highest temperature of these experiments. The slopes are −0.964 ± 0.0112. This indicates that conductivity is the dominant but not the only contributor to the dielectric loss.

Figure 5 is an Arrhenius plot for the apparent conductivity at 1 kHz. The activation energies are 25 kcal/mol for the control and 31.5 ± 3.3 kcal/mol for the samples containing salts. In the case of KI, the conductivity at 180 °C is increased over that of the control by a factor of almost 90.

Samples Containing $ZnCl_2$ or $CuCl_2$

Infrared studies have shown that $ZnCl_2$ and $CuCl_2$ cause shifts in both the CO an NH bands.[1,3] This has been interpreted as evidence for complex formation with amide groups. Of the two salts, $ZnCl_2$ seems to be more active although copper salts are useful in stabilizer formulations. The solubilities in cold water are 432 g/100 cm³ for $ZnCl_2$ and 70.6 g/100 cm³ for $CuCl_2$. The gains in weight of nylon films after equlibration in saturated solutions followed by drying at 110 °C were 37.1% for $ZnCl_2$ and 2.92% for $CuCl_2$.

Figure 6 is a plot of M'' at 1 kHz vs temperature for the samples containing these salts and the control. Near 0 °C, M'' is largest for the control and smallest for the sample containing $CuCl_2$. Since the sample containing $ZnCl_2$ has not previously been cycled to 200 °C, it is not surprising that the loss is somewhat higher near room temperature. This is the region where the β-relaxation would occur in

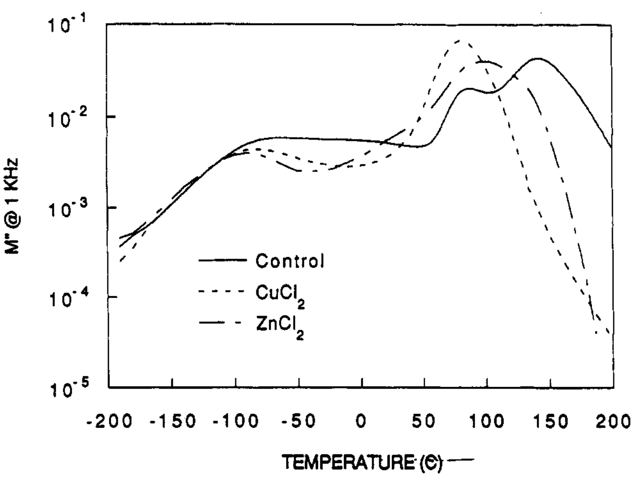

Figure 6. Electric loss modulus at 1 kHz of nylon 66 containing $ZnCl_2$ or $CuCl_2$.

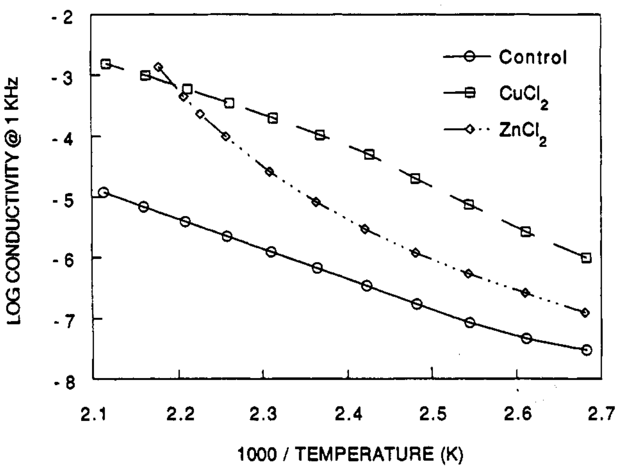

Figure 7. Apparent conductivity at 1 kHz for nylon 66 containing $ZnCl_2$ or $CuCl_2$.

nylon containing moisture. The major peak in M'' occurs at 100 °C for the sample containing $ZnCl_2$ and 82 °C for the sample containing $CuCl_2$.

It is shown in Figure 7 that the sample containing $CuCl_2$ has the highest conductivity except at the temperatures where the sample containing $ZnCl_2$ is about to break up. This contrast is especially striking considering how much more $ZnCl_2$ was absorbed (0.3 $ZnCl_2$/amide vs 0.025 $CuCl_2$/amide). With $CuCl_2$, the conductivity is ca. 150 times that of the control. Figure 8 is an Arrhenius plot of the apparent conductivity for the sample containing $CuCl_2$ showing data taken at 10 °C intervals from 100 to 200 °C for all of the frequencies investigated. The divergence of the points at the lower temperatures is indicative of the role of viscoelastic relaxation. The high degree of superposition of the points for the various frequencies at the highest temperatures shows the dominance of conductivity in this region. The activation energy for conduction was 22 kcal/mol, the lowest observed in this study.

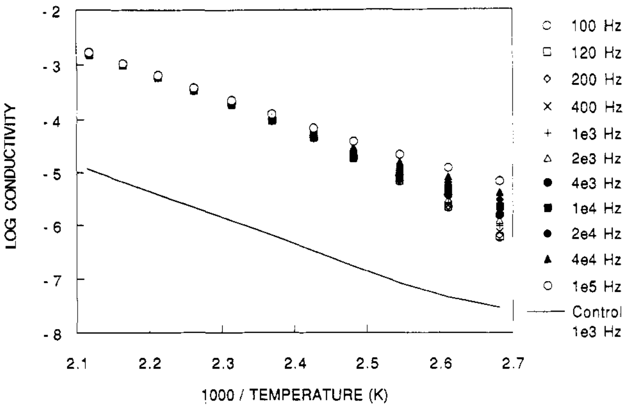

Figure 8. Arrhenius plot of the apparent conductivity at various frequencies for nylon 66 containing $CuCl_2$. Solid line: apparent conductivity of the control at 1 kHz.

Cupric chloride gave the highest and purest conductivity of all the salts investigated even though its concentration was not extremely high. We believe that the charge carriers in nylon at high temperatures are protons. Perhaps the strong Cu–N interaction facilitates the liberation of the amide protons for conduction.

Conclusions

When nylon 66 is equilibrated with saturated salt solutions followed by drying, there are major increases in the conductivity at elevated temperatures. With alkali halides, the effect scales with the weight of salt absorbed. Even larger increases in conductivity were observed with $ZnCl_2$ and $CuCl_2$. The effect is particularly dramatic with $CuCl_2$, where the weight gain was only 2.92%. It is suggested that strong Cu–N interactions result in the release of protons for conduction.

References and Notes

(1) Dunn, P.; Sansom, G. F. *J. Appl. Polym. Sci.* **1969**, *13*, 1641.
(2) Busse, W. F., unpublished research, 1952.
(3) Kargin, V. A.; Sogolov, T. I.; Rapoport, N. Ya.; Vorotnikova, V. A.; Slovokhotova, N. A. *Vysokomol. Soedin., Ser. A* **1971**, *A13*, 1997.
(4) Dunn, P.; Sansom, G. F. *J. Appl. Polym. Sci.* **1969**, *13*, 1657.
(5) Barford, R. P.; Harrauer, E. *Polymer* **1983**, *24*, 1001.
(6) Bello, J.; Haas, D.; Bello, H. R. *Biochemistry* **1966**, *5*, 2539.
(7) Starkweather, H. W., unpublished research, 1971.
(8) Kim, H.; Harget, P. J. *J. Appl. Phys.* **1979**, *50*, 6072.
(9) Hansen, J. E. Canadian Patent 829,974, Dec 16, 1969.
(10) Valenti, B.; Bianchi, E.; Tealdi, A.; Russo, S.; Ciferri, A. *Macromolecules* **1976**, *9*, 117.
(11) Starkweather, H. W.; Avakian, P. *Macromolecules* **1989**, *22*, 4060.
(12) Greenspan, L. *J. Res. Natl. Bur. Stand.* **1977**, *81A*, 89.
(13) Starkweather, H. W.; Avakian, P. *J. Polym. Sci., Polym. Phys. Ed.* **1992**, *30*, 637.