

Melting and Crystallization of Nylon 6 Containing Copper Chloride

A. SIEGMANN and Z. BARAAM, *Department of Materials Engineering, Technion, Israel Institute of Technology, Haifa, Israel*

Synopsis

The melting and crystallization of nylon 6/copper chloride system has been studied by differential scanning calorimetry. In light of the strong melting temperature depression, above the expected in a polymer-diluent mixture and the strong retardation of the crystallization rate, a high degree of binding, probably even complexing, between the salt and the polymer chain is discussed.

INTRODUCTION

There has been a continuous interest in the effect of inorganic salts on the structure and properties of nylon 6 in aqueous solutions and in the bulk. The interest is mainly in the effect of the interaction between the salts and the polar nylon chain on the polymer melting temperature,¹⁻³ crystallization,⁴ orientation and mechanical properties,⁵ flow and glass transition temperature,⁶ and stress cracking behavior.⁷ It is interesting to note that such systems, including salts of various transition metals, were already put into use as photo- and heat-sensitive materials.^{8,9}

Salts such as LiCl and LiBr were recently reported¹⁻³ to depress effectively the melting temperature (T_m) of nylon 6. The chloride is the more effective salt among the two, depressing T_m up to about 50°C at a molar fraction of 0.16. Correspondingly, crystallinity of melt-crystallized nylon 6, as calculated from differential scanning calorimetry (DSC) data, decreases with increasing salt concentration. At the above-mentioned salt concentration range, the factor mainly affected is the crystallization rate resulting in, at certain crystallization conditions, low degrees of crystallinity. Frasci et al.¹ attribute this behavior to the capacity of the salt to enter into the crystalline region and interact with the amide groups. Valenti et al.³ suggest that binding between the salt and the amorphous polymer phase is the main reason for strong depression of both T_m and crystallization rate.

In the above-mentioned work,¹⁻³ polymer-salt mixtures were always prepared by some way of mixing the two components followed by several hours of annealing at temperatures above the polymer melting temperature, allowing diffusion of salt and homogenization of the mixture. Very careful precautions had to be taken to prevent polymer degradation during such a long period at such elevated temperatures. In the present work, to prevent degradation processes and to use a more practical approach, mixtures were prepared by absorption of the salt from solutions into the bulk polymer. Copper chloride was chosen as the salt because of its high activity⁷ on stressed nylon 6 and its being a divalent metal halide.

In the present work, melting and crystallization of mixtures so prepared were

studied by employing DSC in the heating and cooling modes. The data will be interpreted in terms of the interaction between the salt and the polymer chains in the bulk.

EXPERIMENTAL

Pellets of nylon 6 (manufactured by Höchst, West Germany) with a viscosity-average molecular weight of 25,000 were used as the starting material throughout the work. The polymer was used as received, without any further purifications. Analytical-grade copper chloride (Merck, West Germany) was used.

To prepare mixtures of nylon with salt, the polymer was immersed in a saturated aqueous solution of copper chloride at 80°C ($\sim 30^\circ\text{C}$ above T_g) for various periods of time. To obtain a film made of polymer-salt mixture, the nylon was either first compression molded followed by immersion in the salt solution or first immersed, absorbing salt, followed by compression molding. In the latter route, the mixture goes through melting and crystallization, whereas in the first route, nylon crystallizes from pure melt.

Approximately 80- μm thick films were compression molded at 225°C, in a laboratory Carver press, and quenched by passing tap water through the press hot plates. Such films were immersed in the saturated salt solution for various periods of time (up to 4 hr), resulting in a homogeneous greenish-yellow film, including up to about 17 wt % salt. Control film was immersed in pure water at the same temperature. However, when nylon pellets (2 mm in diameter and 3 mm long) were immersed, a salt concentration gradient had developed, which was observable upon sectioning. Therefore, films molded from such pellets were highly inhomogeneous. To minimize the gradient formation, the polymer particles' dimensions had to be reduced, thus the pellets were ground in a Wiley mill into a fine powder which yielded, after immersion in the salt solution, rather homogeneous films. Later analysis of several specimens proved that these films were indeed homogeneous polymer-salt mixtures.

Salt concentration in the mixture was determined by weight change after immersion of the polymer, which before and after immersion was vacuum dried at 90°C for at least 8 hr (sufficient to attain constant weight). Specimens were always kept in a desiccator at room temperature.

A du Pont 990 differential scanning calorimeter was employed for the thermal analysis. Each specimen was heated at a rate of 10°C/min to a temperature just beyond the melting completion; the heater was then turned off and the DSC was allowed to cool at its natural rate ($\sim 10^\circ\text{C}/\text{min}$). This heating cycle enables to follow both melting and crystallization processes. Specimens for DSC were kept carefully in the range of 9–11 mg and in the dry state. The DSC was calibrated using standard materials having melting points in the temperature range of interest. Reported melting or crystallization temperatures are those at the endotherm and exotherm peak tips, respectively.

RESULTS AND DISCUSSION

Typical DSC thermograms of the melting range of nylon 6 containing various amounts of CuCl_2 are shown in Figure 1. The curves in this figure were vertically shifted freely for better presentation. It is clearly seen that with increasing salt

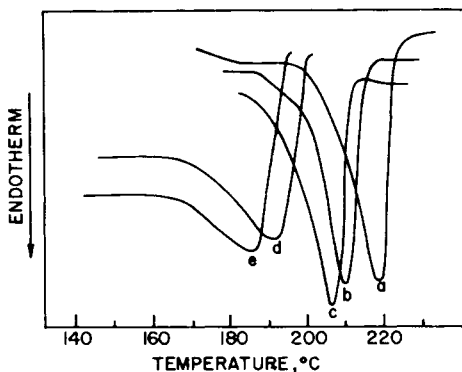


Fig. 1. DSC thermograms, in the melting region, of nylon 6 containing 0 (a), 5.6 (b), 10 (c), 13 (d), 15 wt % (e) CuCl₂ (heating rate 10°C/min).

concentration, from none in curve a to 15% in curve e, the melting temperature decreases gradually and the peaks broaden, especially at concentrations above 10%. The latter is expected for any polymer-diluent mixtures; the breadth of the melting process depends on the amount and type of diluent added, becoming more expanded as the concentration of diluent is increased.^{10,11} The thermograms of pure nylon samples, which were treated similarly to the mixtures, did not change appreciably.

When plotting T_m as a function of salt content (see Fig. 2), a linear fit represents very well the data obtained for immersed films and powders. However, data obtained for films molded from immersed powder are just on the lower side of the linear line. Nevertheless, T_m depression appears almost independent on the sample preparation procedure. The largest T_m depression of 35°C was observed for a mixture containing 16% CuCl₂. It should be noted here that T_m of various pure nylon samples having different thermal histories (similar to those used in the present work) did not change more than ±1°C. Hence, the nylon by itself did not undergo appreciable degradation, and thus the melting temperature depression observed is not a result of having degradation products, except for probably an expected minor effect.

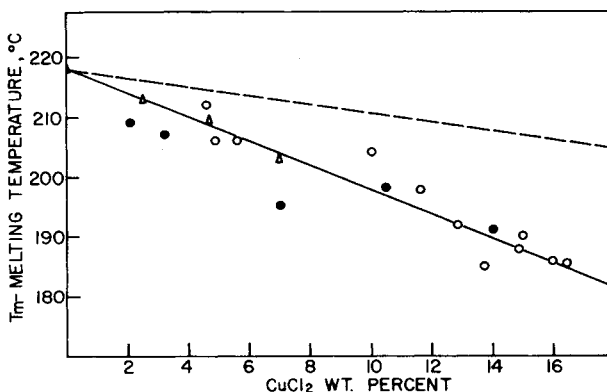


Fig. 2. Dependence of nylon 6 melting temperature on CuCl₂ concentration: (—) measured values; (---) calculated values according to eq. (1): (O) immersed film, (Δ) immersed powder, (●) film molded from powder.

To understand the polymer-salt relations better, the observed T_m depression should be compared with that predicted by the well-known equation for a polymer-diluent mixture, in which only one of the components crystallizes over the complete composition range²:

$$\frac{1}{T_m} - \frac{1}{T_m^o} = \frac{R}{\Delta H_u} \frac{V_u}{V_i} (v_1 - \chi_1 v_1^2) \quad (1)$$

where T_m^o and T_m are the melting temperatures of pure polymer and of polymer in mixture, respectively; V_u and V_i are the molar volumes of the repeating unit and diluent, respectively; ΔH_u is the heat of fusion per mole of repeating unit; v_1 and v_2 are the volume fraction of diluent and polymer, respectively; and χ_1 is a polymer-diluent interaction parameter. This equation is plotted in Figure 2 using a value of $V_u/V_i = 2.32$, $\chi_1 = 0.2$ (reasonable value for a "good" diluent,¹²) and $\Delta H_u = 5100$ cal/mole.¹³ This equation predicts a much smaller T_m depression than the observed values; thus, the observations cannot be explained by this theory alone, unless a high negative value of the interaction parameter is used. Hence, eq. (1) takes care of only part of the T_m depression.

For systems showing a continuous depression of T_m with increasing diluent concentration, it has been suggested a more direct comparison with eq. (1) be made. Equation (1) can be rewritten as follows:

$$\frac{1/T_m - 1/T_m^o}{v_1} = \frac{R}{\Delta H_u} \frac{V_u}{V_i} \left(1 - \frac{BV_1 v_1}{R T_m} \right) \quad (2)$$

where $B = \chi_1 R T_m / V_1$ represents the interaction energy density characteristic of polymer-diluent pair.¹² Plotting $(1/T_m - 1/T_m^o)/v_1$ against v_1/T_m should yield a straight line, and indeed the experimental data, shown in Figure 3, are in accordance with eq. (2). From the intercept in Figure 3 a value of 4800 cal/mole for ΔH_u can be deduced, which is in good agreement with literature.¹³ Furthermore, Mandelkern¹⁴ suggests that since the quantity ΔH_u is independent of the diluent used and is a property of the crystallizing chain repeating unit, equilibrium between the pure crystalline polymeric phase and two-component liquid phase is established at T_m .

As has been shown above, eq. (1), which takes into account only thermodynamic interactions in the polymer-salt system presented by χ_1 , does not predict such large T_m depression as experimentally observed. Melting temperature will be depressed further if complexing between the salt and specific groups along the polymer chain occurs in the amorphous phase. Therefore, an increase in the extent of complexing would shift the crystal-liquid equilibrium to lower temperatures. In such a case the melting point equation becomes¹⁵:

$$\frac{1}{T_m} - \frac{1}{T_m^o} = \frac{R}{\Delta H_u} \frac{V_u}{V_i} (v_1 - \chi_1 v_1^2) + \frac{RN_a}{\Delta H_u} \ln(1 + Ka_c) \quad (3)$$

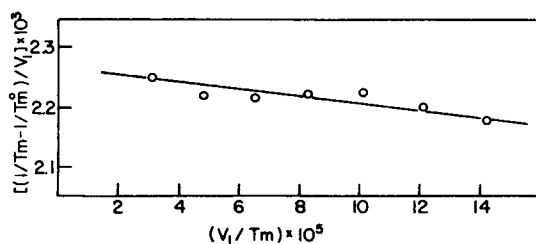


Fig. 3. Plot of $(1/T_m - 1/T_m^o)/v_1$ vs. v_1/T_m for nylon 6 mixed with CuCl_2 .

TABLE I
Energy of Binding and Melting Temperatures for Several CuCl₂-Nylon 6 Systems

Volume fraction V_1	$-\Delta F$, cal/mole	T_m , °C
0.015	49.8	210
0.031	98.2	208
0.047	146.0	194
0.067	185.0	186

where N_a is the number of reacting sites per repeat unit, K is a binding constant, and a_c is the salt activity. The last term on the right in eq. (3) represents the T_m depression, at a given composition, due to the polymer-salt complex formation.

The free energy of binding,^{13,16} $\Delta F = N_aRT \ln(1 + Ka_c)$, has been calculated in accordance with eq. (3). Calculated values using the experimental data presented in Figure 2 for several salt-nylon systems having different salt concentrations are summarized in Table I. As expected, the free energy of binding so obtained is directly proportional to the salt concentration. Consequently, the present data appears to show that all CuCl₂ (in the studied concentration range) forms a complex with the polar groups of the nylon chains in the amorphous phase. The free energy of binding is expected to increase linearly with salt concentration, attaining an ultimate value at saturation; above the saturation concentration, no further binding will occur. Saturation should depend on such factors as experimental procedures, polymer degree of crystallinity, and so on.

When a crystallizable polymer is heated above its melting temperature, followed by cooling in the DSC, some crystallization kinetics information can be obtained. Figure 4 shows several DSC thermograms in the crystallization region obtained upon cooling nylon-salt systems in the DSC cell (estimated cooling rate of 10°C/min). The crystallization exotherms shift to a lower temperature and broaden with increasing salt concentration. The crystallization temperature (taken at the peak tip), at the present experimental cooling rate, decreased linearly from 186°C for pure nylon, to 115°C for nylon containing 16% salt (see Fig.

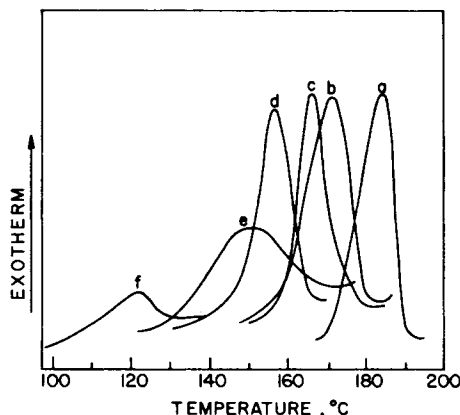


Fig. 4. DSC thermograms, region of crystallization upon cooling from the melt, of nylon 6 containing 0 (a), 2.5 (b), 5.6 (c), 7 (d), 12 (e), 15 wt % (f) CuCl₂ (cooling in the DSC cell at an estimated rate of 10°C/min).

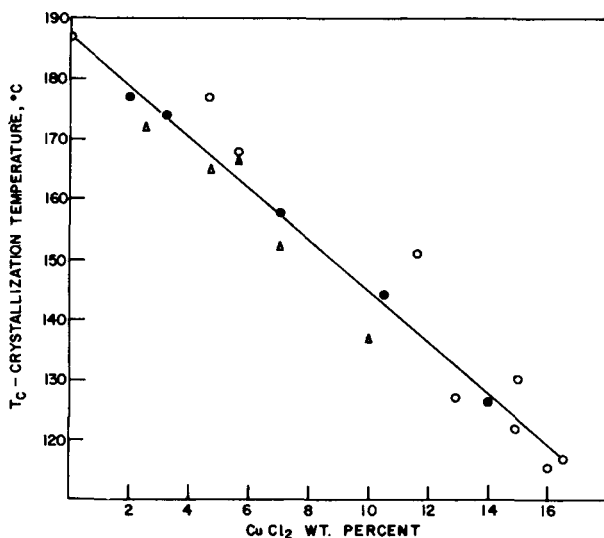


Fig. 5. Variation of the crystallization temperature, as obtained by DSC, of nylon 6 containing various amounts of CuCl_2 : See Fig. 2 for legend.

5). In addition, the degree of supercooling required for crystallization to occur at the present experimental cooling rate increases linearly with salt content (see Fig. 6). Hence, the presence of salt also affects the crystallization kinetics of nylon 6, namely, it reduces its rate markedly. This effect resembles the crystallization hindrance reported^{3,4} for nylon-LiCl mixtures. In the latter system, crystallization time had to be very prolonged relative to pure nylon, and above a certain salt content no crystallization could be detected. In polymer-diluent mixtures, not only the temperature of equilibrium between the crystalline and liquid phases decreases, but in addition the supercooling is lowered and an attenuation in the nucleation rate occurs. Subsequently, the overall rate of crystallization is retarded.¹⁷

In the present system, the melting temperature depression and the crystallization data presented above indicate strongly the existence of a high degree of binding between CuCl_2 and nylon. This conclusion is supported by Dunn and Samson,⁷ who have studied the mechanism of polyamide stress cracking by metal

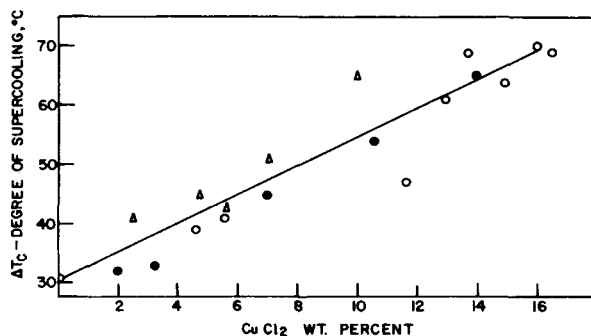


Fig. 6. Variation of the degree of supercooling, as obtained by DSC, of nylon 6 containing various amounts of CuCl_2 : See Fig. 2 for legend.

salts, employing IR spectroscopy. They have suggested that metal halides, including CuCl_2 , form a coordination complex having nitrogen atom-metal ion coordinate bond. Also, Ancierno et al.⁶ have recently reported that although the mixing of various salts with nylon did not affect its glass transition temperature, it did increase significantly its melt viscosity. The latter has been suggested to result from the flow of segments carrying bound ions and probably strong multimolecular interactions giving rise to pseudo-crosslinked structure.

Presently, we continue our work studying the effect of salts on some bulk properties of nylon 6.

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