

The Modification of Nylon 6 by a Phenol-Formaldehyde Resin

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SYNOPSIS

Modification of nylon 6 by blending with a small amount of a novolac resin has been investigated. Unexpected increases of T_g and tensile modulus and reduction in moisture absorption have been found at levels of novolac incorporation of 1–3 wt %. The small amount of novolac resin also has an effect on the crystallization and nylon 6 crystal structure (α vs. γ form). © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The properties of a semicrystalline polymer are sensitive to the details of molecular organization in both amorphous and crystalline regions. In blends containing crystalline polymers, the presence of a second component may cause changes in the structures of both regions. This report describes preliminary findings of changes in physical, mechanical, and morphological properties of nylon 6 when blended with a small amount of an oligomeric additive. The oligomer chosen for the study was *p*-tertiary butylphenol-formaldehyde resin, simply called novolac in this paper, with a molecular weight of about 950. The molecule was sufficiently large to be excluded from the crystalline lattice but was nevertheless miscible, at least partially, with the amorphous phase by virtue of hydrogen bonding between the hydroxy group of the novolac resin and the amide group of nylon 6.

Experimental observations to be described below indicate changes in morphology and in the properties of the amorphous region at a level of novolac incorporation as low as 1%.

EXPERIMENTAL

Nylon 6 pellets with an average molecular weight of 15000–20000 (intrinsic viscosity 0.5 dL/g in formic

acid) were supplied by Allies-Signal Inc.; *p*-tertiary butyl novolac resin with a number average molecular weight of 950 was synthesized in our laboratory.¹ A CSI-MAX extruder was used for melt blending at 240°C. The materials were pressed in a laboratory compression mold at 250°C and 1,000 psi to obtain films of suitable thickness. These films were stored in a desiccator under controlled humidity conditions.

The glass-transition temperatures and melting points of the samples were measured with a DuPont 9900 Thermal Analyzer under nitrogen atmosphere. The samples were first heated up to 180°C and cooled down to –20°C by dry ice and acetone to avoid the effect of prior thermal history; then thermal scans were conducted at a heating rate of 10°C/min. Only the second scanning curves were used.

A Perkin-Elmer Thermal Analysis Instrument, model 7000, was employed to measure the heats of crystallization and fusion. After the specimens were melted in DSC pans and kept in a desiccator under controlled humidity for 2 weeks at room temperature, they were heated to 240°C and then cooled from the melt under nitrogen at a rate of 5°C/min to determine the crystallization temperature and the heats of crystallization. The heat of fusion was determined from the next heating scan.

Dynamic mechanical moduli were measured by a DuPont instrument, model 982. A heating rate of 5°C/min was used.

Wide angle X-ray spectra were recorded using a Phillips 3100 X-ray spectrophotometer.

Thin films for FT-IR study were cast on KBr plates from 2% solutions using a mixture of formic acid and 2-butanone as solvent. The films, about 5

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μm in thickness, were dried in a vacuum oven at 60°C for 48 h. A Digilab FTS-60 spectrometer was used to record the spectra. Absent in the infrared spectra was the absorption at 1721 cm^{-1} that was characteristic of formic acid dimers; therefore, we believe that these films are essentially free-residual solvent.

For optical microscopy, 0.1% *m*-cresol solutions were used to prepare films on glass slides. The samples were subsequently conditioned isothermally in a vacuum oven at 100°C for 24 h. A magnification of 600 was used throughout. The samples for polarized optical microscopy were prepared from 1% *m*-cresol solutions and were held at 190°C in a vacuum oven for 10 h.

Water and moisture absorption studies were carried out on films between 0.2 and 0.5 mm in thickness. The films were weighed before and after exposure to different humidity conditions or immersion in water for 2 weeks at room temperature.

RESULTS

Glass-Transition Temperatures

The glass-transition temperatures, T_g , of nylon 6-novolac blends are considerably higher than the

Table I Glass Transition Temperatures

Nylon 6 Sample	T_g °C (DSC) ^a	T_{max} °C (DMA) ^b
	43	66
Blend with		
1% Novolac	56	75
2% Novolac	55	77
3% Novolac	56	81
5% Novolac	63	87
10% Novolac	61	

^a The samples were exposed to 64% related humidity for 2 weeks.

^b The samples were dried in a vacuum oven for 24 h at 80°C .

value of 43°C for nylon 6 itself, as can be seen from the data listed in Table I. Even at a level of novolac incorporation of only 1%, the T_g was higher by about 13°C . The increases became progressively larger with increasing novolac content. For a blend containing 5% novolac, the T_g was 63°C . The increase in T_g seemed to have levelled at this composition as the 10% blend had about the same T_g , namely 61°C . The transition temperatures recorded by $(\tan \delta)_{\text{max}}$ in dynamic mechanical measurements (Fig. 1) provided corroborative evidence of increases in T_g .

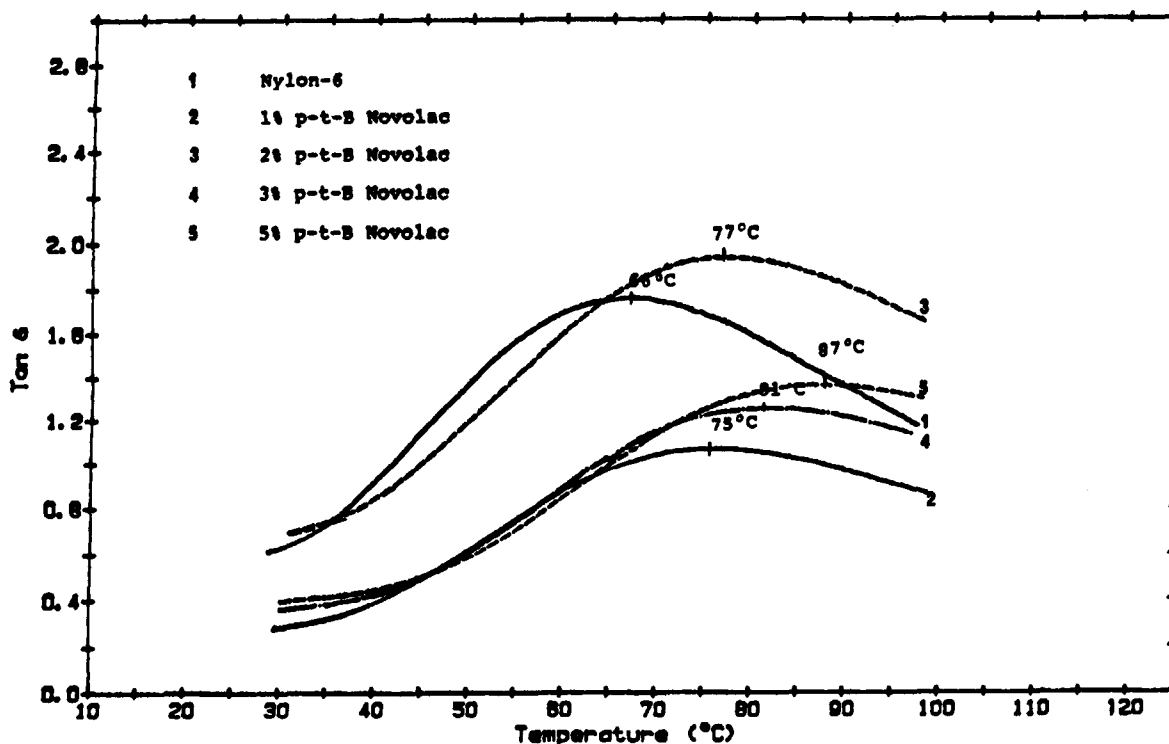


Figure 1 $\tan \delta$ vs. temperature for nylon 6 and its blends. The samples were dried in a vacuum oven at 80°C for 24 h and the heating rate was $5^\circ\text{C}/\text{min}$.

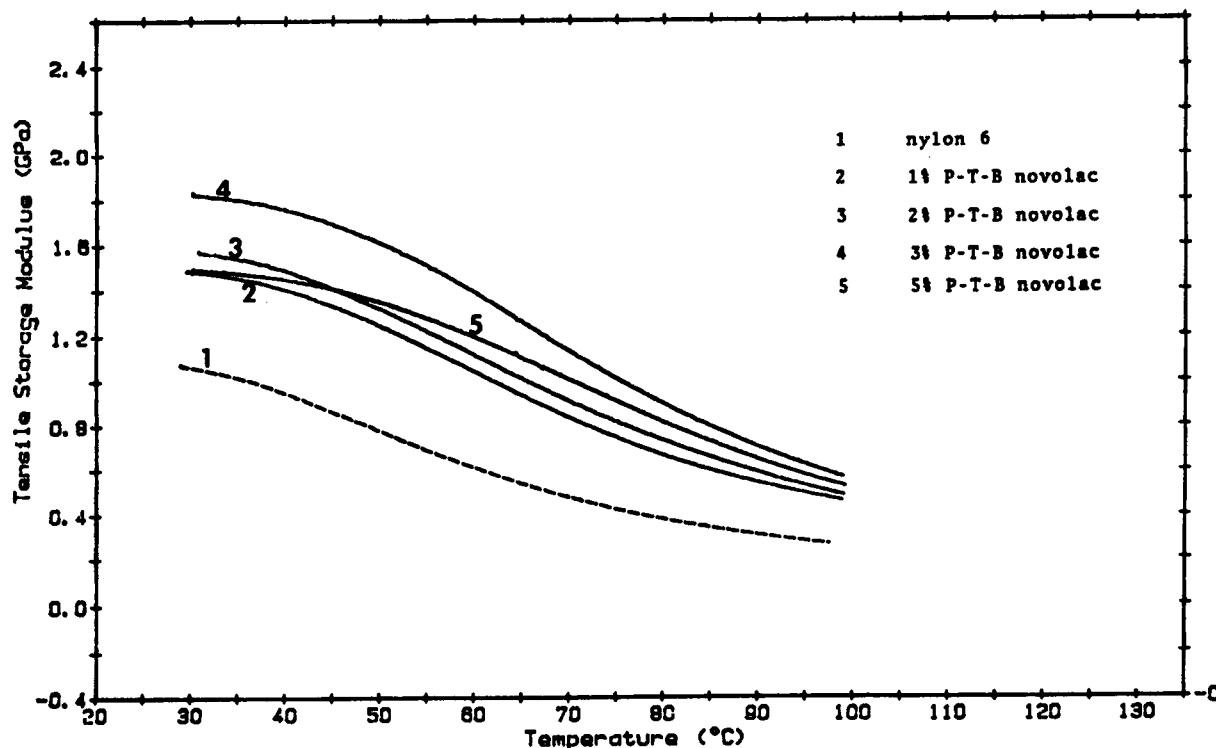


Figure 2 Tensile storage modulus vs. temperature for nylon 6 and its blends. The samples were dried in a vacuum oven at 80°C for 24 h and the heating rate was 5°C/min.

Dynamic Mechanical Moduli

The results of dynamic mechanical measurements are presented in Figure 2 and summarized in Table II. For samples that were dried in an oven at 80°C for 24 h, the dynamic tensile moduli are 40–70% higher in the blends when compared with the host polymer at temperatures below the T_g . The change is manifest even at a level of incorporation at 1%. The maximum modulus value appears at about 3% novolac content.

Table II DMA Measurements

Nylon 6 Sample	Tensile Storage Modulus (Gpa, at 30°C)	Increase (%)
	1.06	
Blend with		
1% Novolac	1.49	40.6
2% Novolac	1.56	47.2
3% Novolac	1.83	72.6
5% Novolac	1.49	40.6

* The samples were dried in a vacuum oven for 24 h at 80°C before testing.

Moisture and Water Absorption

It is well known that the properties of polyamides are sensitive to the amount of moisture absorbed. Therefore, moisture absorption of the blend is of great interest. The moisture and water absorption of nylon 6 were found to be very sensitive to the presence of novolac (Table III). The decreases in moisture absorption when exposed to 64% relative humidity are significant even at 1% novolac content. Moisture absorption continued to decrease with in-

Table III Water and Moisture Absorption (wt %)

Nylon 6 Sample	64% R.H.	Liquid Water
	7.98	11.3
Blend with		
1% Novolac	6.68	10.8
2% Novolac	4.48	10.6
5% Novolac		10.5
10% Novolac	4.68	10.2

The samples were exposed to 64% R.H. for 2 weeks for moisture absorption measurements, or immersed in liquid water for 1 week for water absorption measurements.

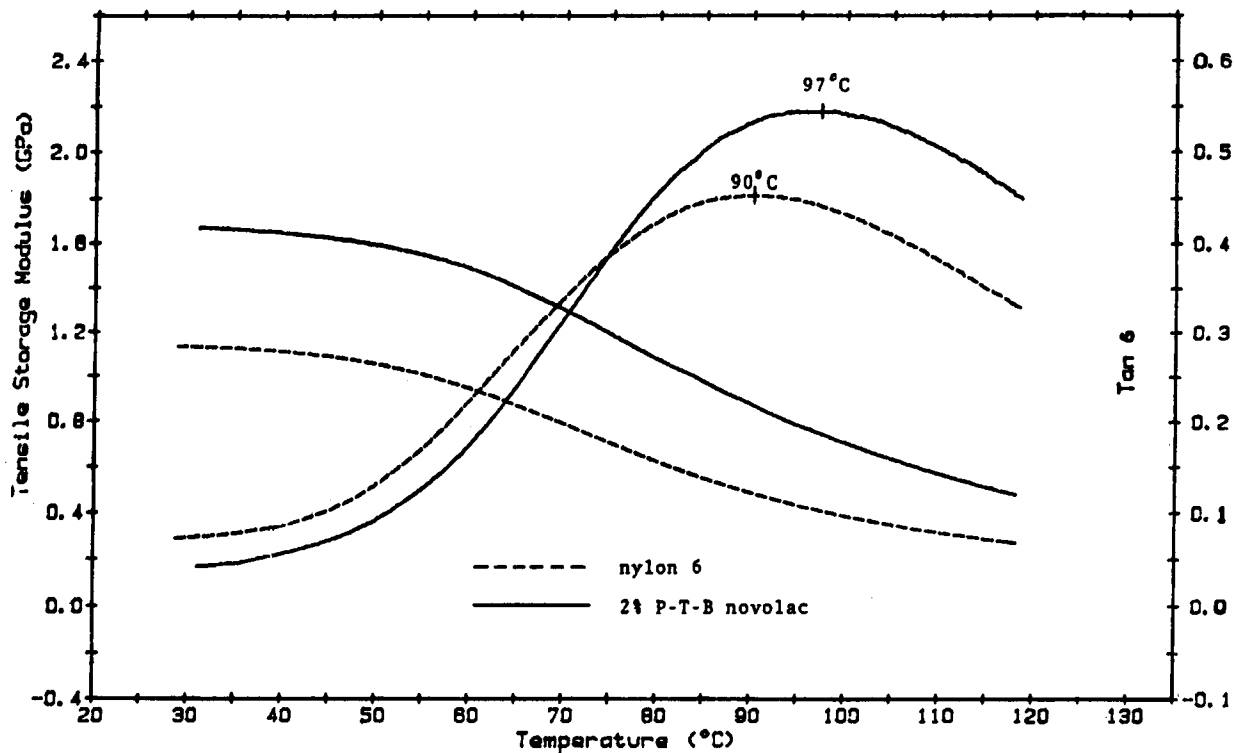


Figure 3 DMA curves of nylon 6 and its blend containing 2% novolac; heating rate was 5°C/min. The samples were treated in boiling water for 1 h, then dried in a vacuum oven at 80°C for 24 h.

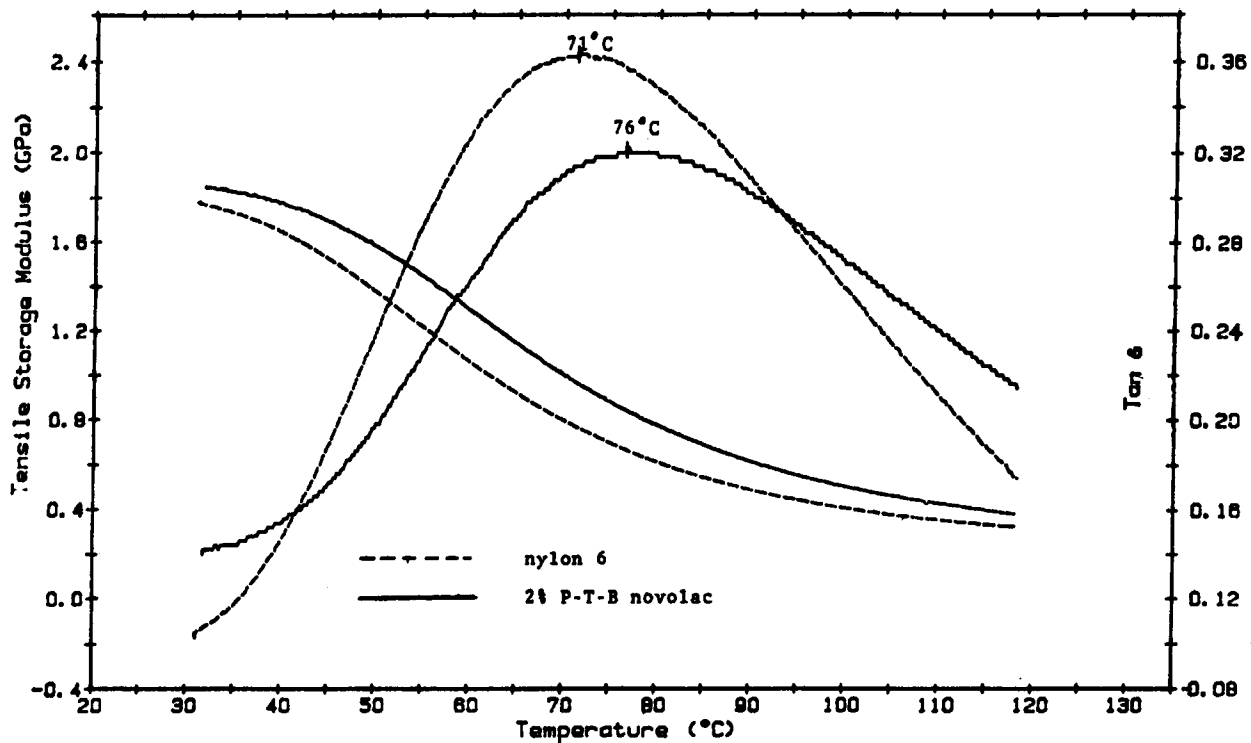


Figure 4 DMA curves of nylon 6 and its blend containing 2% novolac. The samples were treated in boiling water for 1 h, then dried in a vacuum oven at room temperature for 24 h and equilibrium at 3.2% relative humidity for 2 weeks. Heating rate was 5°C/min.

creasing novolac content but novolac content in excess of 2% did not seem to offer additional advantage in the ability to reduce moisture absorption. The reduction in liquid water absorption is less dramatic but nevertheless real.

Immersing the samples in boiling water for 1 h and redrying (80°C in vacuo) again resulted in higher modulus value for the blends (Fig. 3) as in the case of unboiled samples. The maximum in the $\tan \delta$ peak (T_{\max}) occurred at a much higher temperature for each specimen. The temperature of loss maximum for nylon 6 is now 90°C compared with 66°C for the sample before treatment. The value of T_{\max} for the 2% blend becomes 97°C, compared with the original value of 77°C. It was also noted that different drying conditions after boiling water treatment also had an effect on modulus and loss maximum values. For example, when the boiled samples were dried at 25°C in a vacuum oven for 48 h followed by conditioning under 3.2% relative humidity for 2 weeks, there was only a minor difference in the modulus values of nylon 6 and the 2% blend. The T_{\max} now occurred in the same temperature region as before the boiling water treatment (Fig. 4).

Infrared Spectroscopy

In the infrared absorption of the amide I region, a new shoulder at 1664 cm^{-1} appeared in the blend films (Fig. 5). When phenol was used as additive instead of the novolac resin, the same shoulder was seen (Fig. 6). While the assignment of the vibrational mode caused by the 1664 cm^{-1} absorption is uncertain, we would like to believe that band is a

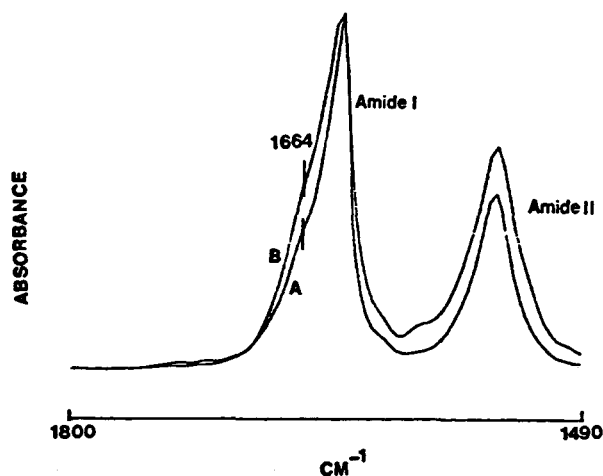


Figure 5 FT-IR spectra of blends of Nylon 6 in the amide I region: (A) containing 5% novolac; (B) containing 10% novolac.

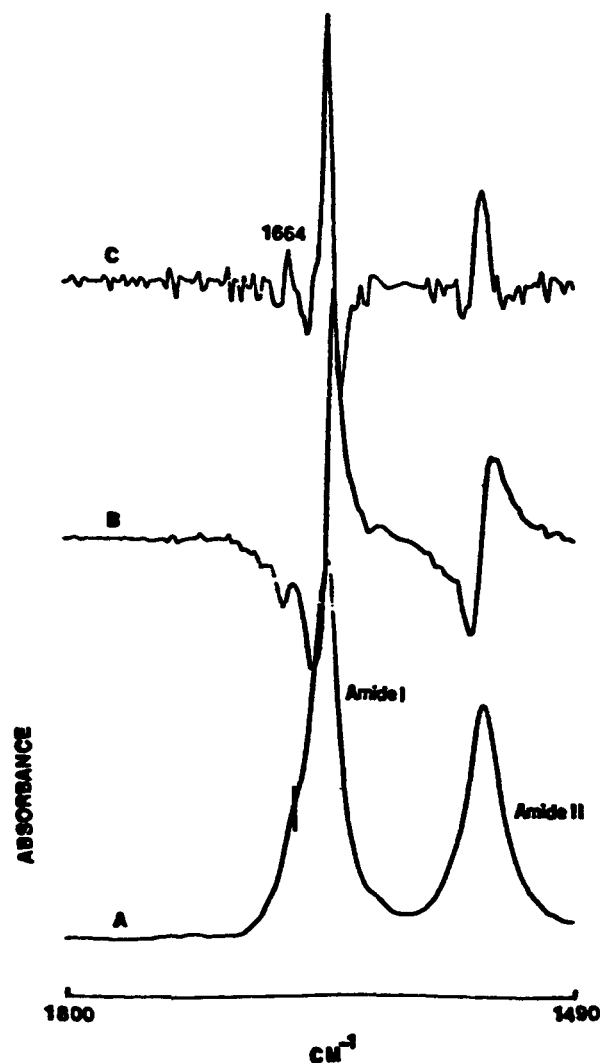


Figure 6 FT-IR spectra of a phenol-nylon 6 blend recorded at room temperature in the amide I region: (A) 5% phenol blend; (B) first derivative curve; (C) second derivative curve.

manifestation of hydrogen bonding between the phenol group and the amide group. The free amide absorption has been reported to occur at 1670 cm^{-1} ; a shift to 1664 cm^{-1} caused by hydrogen bonding with phenol appeared to be reasonable.² The absence of absorption peak at 1720 cm^{-1} , which is a character of formic acid dimer, is a proof of no existence of solvent residue in the sample.

Crystallization and Fusion

Upon cooling the samples from their melts, the peak temperatures of crystallization (DSC) were found to be near 183°C, which was significantly higher than the value of 172°C for nylon 6 itself. Further-

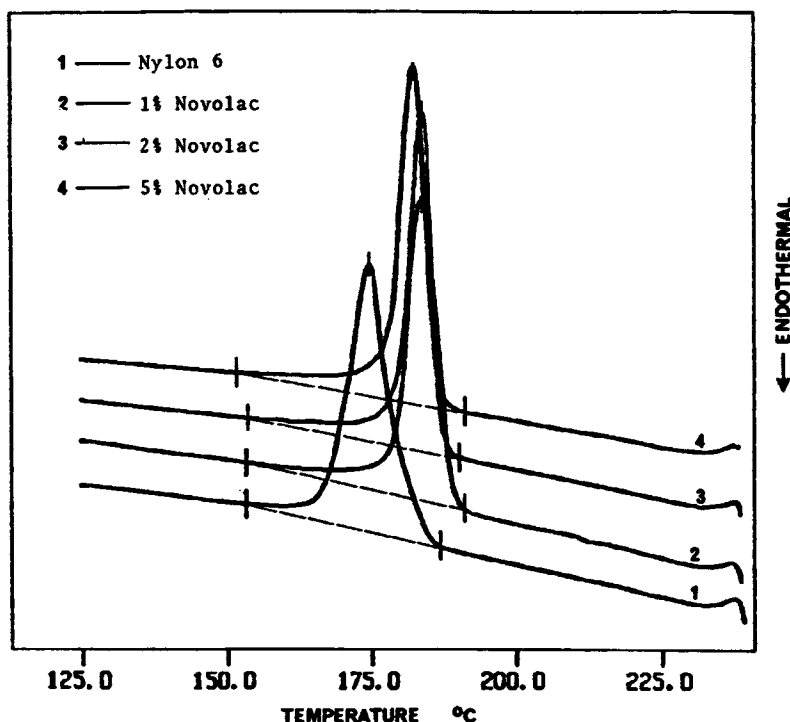


Figure 7 Crystallization temperatures and exotherms of nylon 6 and its blends.

more, the peak for crystallization was narrower and sharper for the blends (see Fig. 7). There was a concomitant increase in the heat of crystallization of each blend. These increases vary from 2–11% (see Table IV). When the samples were reheated, the melting points were found to be about the same in all specimens, namely $215 \pm 1^\circ\text{C}$ (Fig. 8). The difference of about 5 J/g between the magnitudes of

heats of fusion and crystallization is largely due to the uncertainty in drawing baselines.

Morphology

The observation that the crystallization temperatures were about 11°C higher for the blends than the host polymer was highly suggestive of different

Table IV Temperatures and Heats of Crystallization and Fusion

Nylon 6 Sample	T_c °C Onset	T_c °C Peak	ΔH_c (J/g)	T_f °C Onset	T_f °C Peak	ΔH_f (J/g)
	187	172	59	174	216	65
Blend with ^a						
1% novolac	191	183	63			
2% novolac	190	184	65	174	214	71
5% novolac	191	182	67	180	215	72
	187	172	70			
Blend with ^b						
1% novolac	192	183	70			
2% novolac	193	183	70			
5% novolac	191	184	77			

The value of ΔH varied by about ± 5 J/g due to the uncertainty in matching the slopes of the baselines before and after fusion event. (The literature value of heat of fusion for nylon 6 crystal is 188 kJ/kg.¹³)

^a Samples were equilibrated under 64% R.H.

^b Samples were equilibrated under 3.2% R.H.

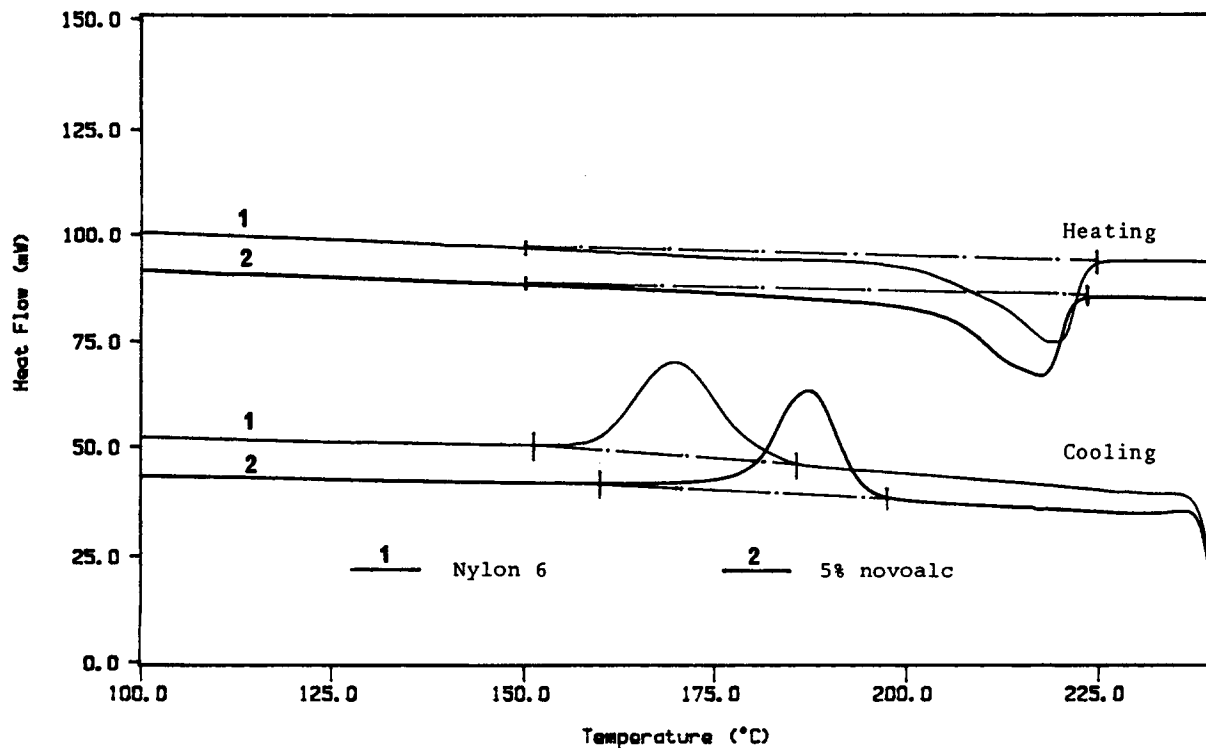


Figure 8 Melting and fusion temperatures of nylon 6 and its blend.

crystal growth parameters. A series of photomicrographs were therefore taken for films cast from 1% *m*-cresol solutions and conditioned at 190°C for 10 h in a vacuum oven. The three micrographs in Figure 9 clearly show an increase on the size of spherulite in the blends.

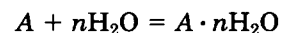
Films prepared from somewhat different conditions revealed additional features. In Figure 10, the photomicrographs of films conditioned at 100°C are shown. As in the previous figure, nucleation densities have been reduced in the blends and the sizes of spherulites are notably larger. The blend containing 2% novolac has the largest spherulite size, about four times that of nylon 6 itself. Upon further increase in the quantity of novolac, annulus formation becomes easily recognizable. These results are similar to the findings of Keith et al.³ on morphological changes induced by small concentrations of polymeric diluents in several crystalline polymers, when the blends were cooled from the molten state. Similar morphological changes have been reported earlier by A. V. Yermolina et al.⁴ for the solution cast films.

Wide angle X-ray scattering data recorded for nylon 6 and its blends at room temperature are given in Figure 11. Three peaks were observed at 2θ , 20.1°,

21.4°, and 23.5°, respectively. Whereas the peaks occurring at 2θ of 20.1° and 23.5° represent α crystals, the 21.4° peak represents γ crystals. For blends containing 1, 2, and 3% novolac, the intensities at 2θ of 20.1° and 23.5° increased but the peak at 21.4° could not be seen. For the 5% blend, the peak at 21.4° reappeared while the other two became less distinct. Finally, only a broad peak was seen for the 10% blend.

DISCUSSION

The sorption of moisture by nylon 6 in the fiber, fabric, or bulk form has been studied extensively.⁵ The experimental results were often analyzed by modified "localized sorption sites" models. For the purpose of this discussion, however, a more simplistic treatment will be used. In the treatment, the sorption equilibrium is expressed as:



where A denotes the concentration of free amide groups and $(A \cdot n\text{H}_2\text{O})$, the concentration of amide groups that has, on the average, n bound water mol-

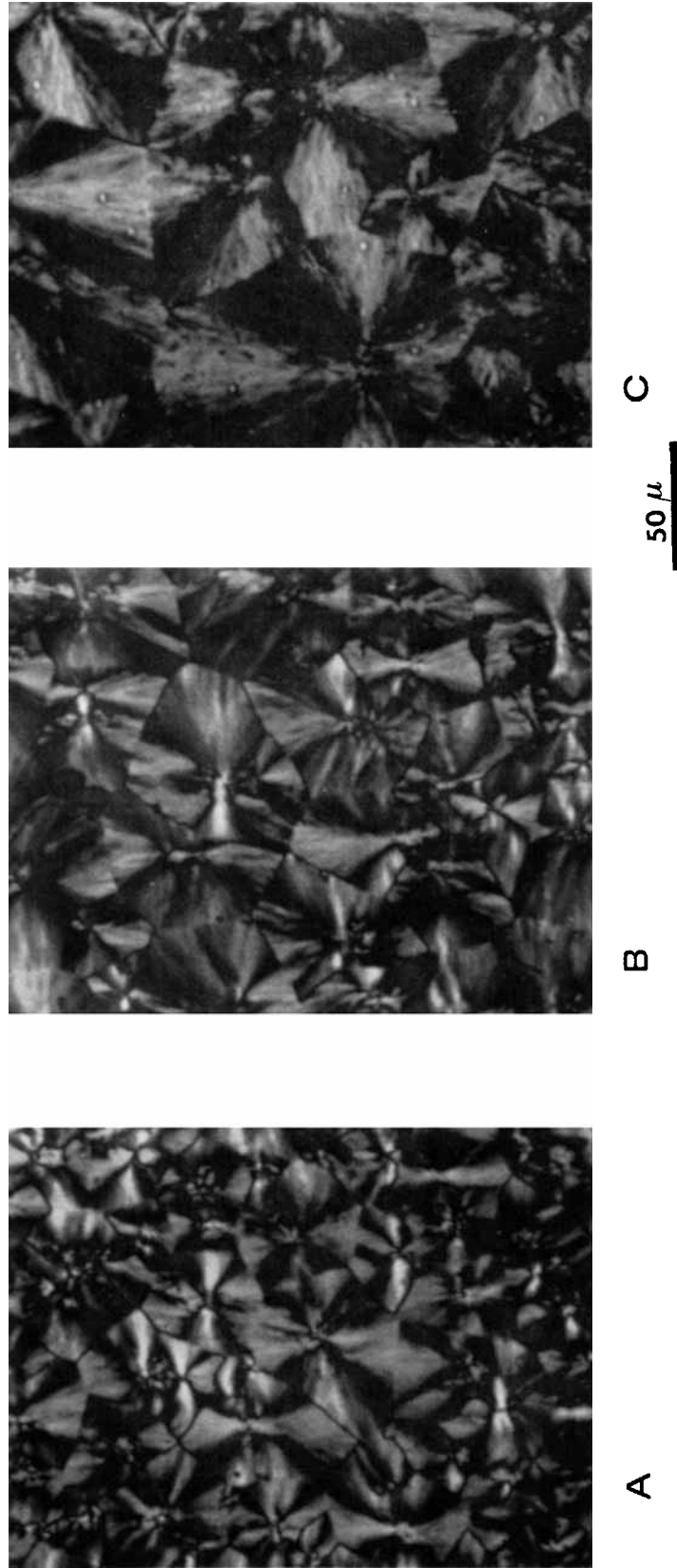


Figure 9 Comparison of spherulites formed at 190°C from nylon 6 and its blends photographed between cross polarizers at the same magnification: (A) nylon 6; (B) 2% novolac; (C) 10% novolac.

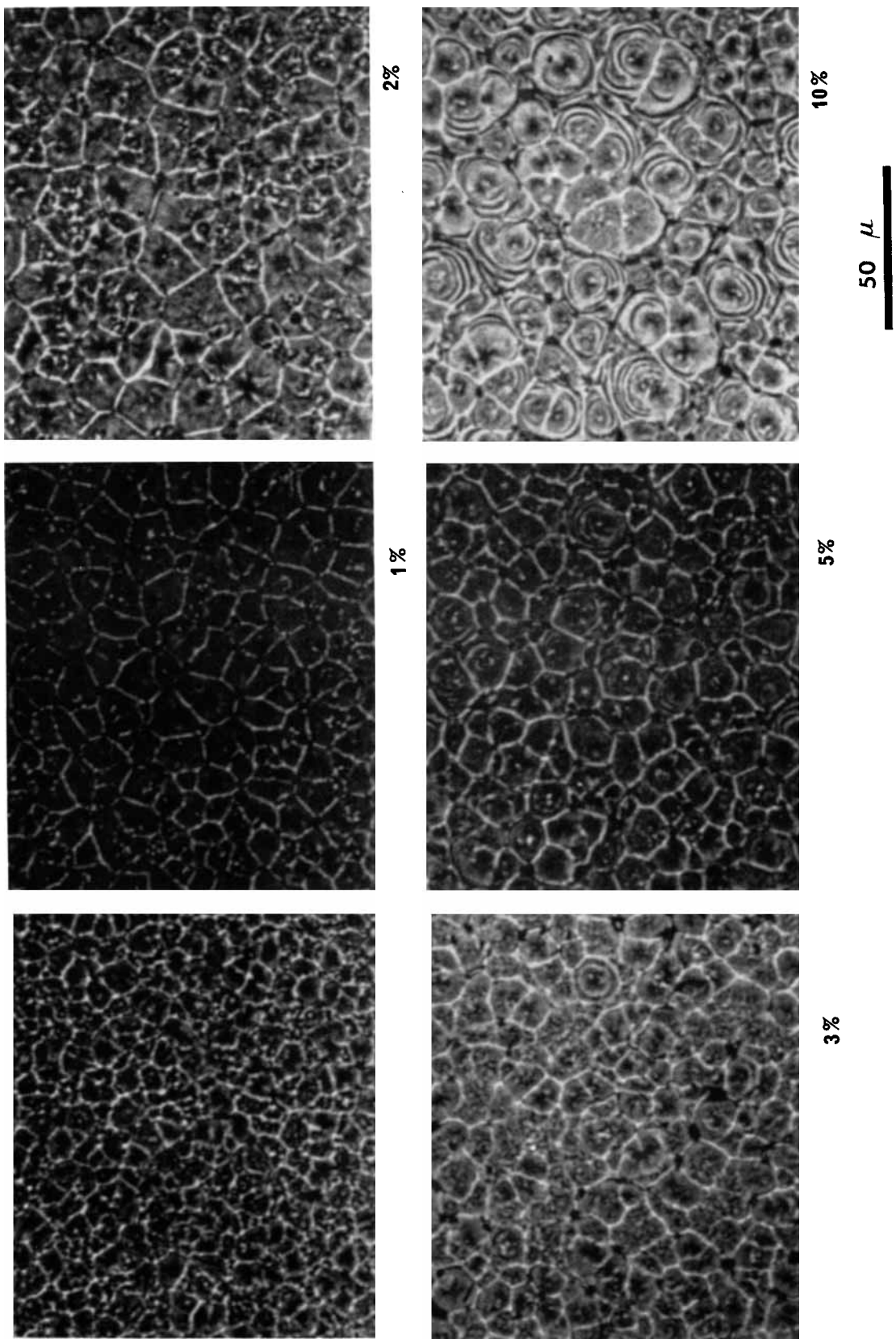


Figure 10 Optical micrographs of nylon 6 and its novolac blends. Weight fractions of novolac are labelled under each graph. The films were cast from *m*-cresol solvent and then conditioned at 100°C for 24 h under vacuum.

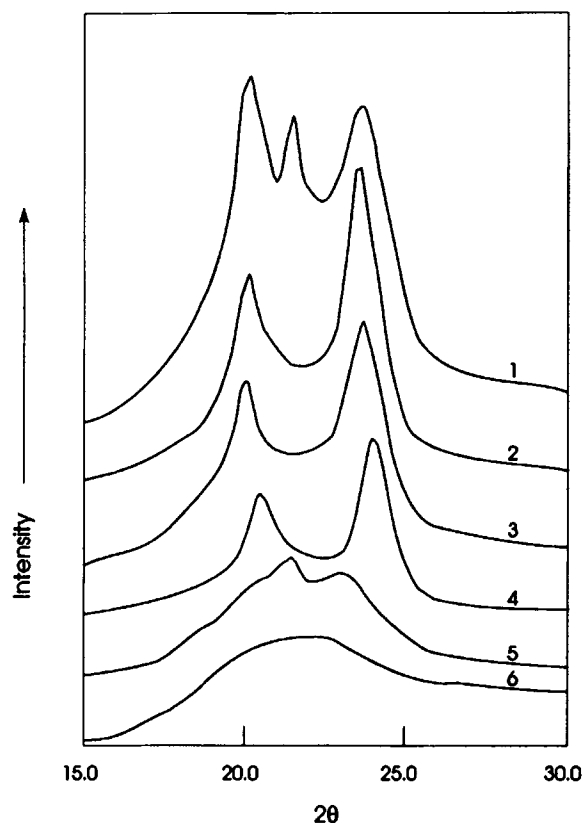


Figure 11 X-ray diffraction spectra of nylon 6 and its blends. (1) nylon 6; (2) 1% novolac; (3) 2% novolac; (4) 3% novolac; (5) 5% novolac; (6) 10% novolac.

ecules per group. The equilibrium constant can then be written as:

$$K = \frac{A_b}{A_f(\alpha_{\text{water}})^n} \quad (1)$$

In eq. (1), the subscripts *b* and *f* represent bound and free species respectively and α is the activity of water. At a given relative humidity and temperature, eq. (1) reduces to

$$K' = \frac{A_b}{A_f}$$

or

$$\frac{A_b}{A_f} = \frac{K'}{K' + 1} \quad (2)$$

phenolic resin is incorporated in nylon 6, can then be interpreted as the result of a corresponding decrease in the available total amide groups. The amount of unavailable amide groups is then 0.1 mol/100 g. When this value is compared with the concentration of phenol group, 0.006*M*/100 g, in the

blend, it is clear that the decrease of available amide groups cannot be accounted for by simply assuming the occupation of amide sites by phenol groups. For the blend containing 2% novolac resin, sorption decreases by 44%. The concentration of unavailable amide groups is 0.27*M*/100 g, in comparison with phenol concentration of 0.012*M*/100 g.

The equilibrium sorption of liquid water is about 1.0 mole per mole amide. The effect of novolac resin on absorption is much less pronounced; the decrease is 4.4% for the blend containing 1% novolac and 6.2% for the 2% blend. These values correspond to decreases in the available amide groups of 0.027 and 0.038*M*/100 g, which are still two- to threefold larger than the number of phenol groups. Thus the effect of the novolac resin is out of proportion to its amount; it seems that the presence of novolac results in a change in the equilibrium constant of sorption.

Although the decrease in moisture sorption upon incorporation of a phenolic resin has been reported in the patent literature,⁶ the increase in T_g and elastic modulus are believed to be new observations. We do not know whether the T_g and modulus increases are attributable solely to the effect of reduced moisture content.⁷ However, together with the observation of a new infrared absorption peak at 1664 cm^{-1} , the T_g and modulus results suggest that the novolac resin reinforces the interlamellar structure of nylon 6 via hydrogen bonding interaction between the phenol and amide groups. The physical crosslinks that result from interpolymer hydrogen bonding can also conceivably alter the sorption equilibrium constant itself or by decreasing the number *n*.

An increase of approximately 10°C in the crystallization temperature was found for all blends. At first thought, the increase in T_c suggests nucleation activity of the novolac resin. However, unlike other nucleating agents, the spherulite diameter increases and the nucleation density decreases as novolac content increases. Therefore, it seems that the addition of novolac resin enhances the rate of crystallite growth rather than the nucleation density. At about 3% novolac in the blend, banded spherulites can be seen. The regularity of banding becomes more pronounced in the 10% blend. The decrease in nucleation density and the appearance of banded structure has been reported earlier by Keith and Padden³ for nylon 66 or 610 containing 5% poly(vinylpyrrolidone).

Two crystal forms, α and γ , are commonly observed in nylon 6 fibers.⁸⁻¹¹ The α to γ conversion depends on the condition of spinning or moisture. In this study, we noticed a change in the crystal forms in the compression-molded films (Fig. 11). In the nylon 6 sample there is a mixture of α and γ

crystal forms. The peak intensities for the α form ($2\theta = 20.1^\circ$ and 23.5°) increase in the blends containing 1, 2, and 3% novolac, while the peak at 2θ of 21.4° for the γ form almost disappears. The γ form reappears at 5% novolac content. In the 10% blend, the peaks broaden and become unresolvable. The underlying reasons for the change in crystal forms are not understood at present. However, the melting points observed in DSC scans remain the same for all samples. This might be caused by the crystalline relaxation when the samples are slowly heated up at the rate of $5^\circ\text{C}/\text{min}$. A similar relaxation has been discussed by Murthy for the nylon 6 fiber.¹²

In tabulating the experimental data on T_g , T_c , moisture sorption, elastic modulus, and crystal structure, we notice that by far the largest property changes occur when the first 2–3% novolac resin is blended with nylon 6. The incorporation of larger amounts of novolac seems to cause smaller incremental changes in properties. It is tempting to speculate that the miscibility limit of novolac in nylon 6 is around 3%.

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