

# Phase Behavior Study of Chitosan/Polyamide Blends

JO ANN RATTO,<sup>1</sup> CHIEN C. CHEN,<sup>2</sup> and RITA B. BLUMSTEIN<sup>2,\*</sup>

<sup>1</sup>U.S. Army Natick Research, Development & Engineering Center, Natick, Massachusetts 01760;

<sup>2</sup>Polymer Program, University of Massachusetts Lowell, Lowell, Massachusetts 01854

## SYNOPSIS

Blends of chitosan with strongly crystalline polyamides (nylon-4 and nylon-6) and weakly crystalline polyamides (caprolactam/lauro lactam and Zytel®) were investigated. Phase behavior, morphology, interactions with water, mechanical properties, and catalytic reactivity were studied. Films were made from formic acid solutions with the chitosan concentrations ranging from 5% to 95% (w/w). The 80% deacetylated chitosan is in the salt, neutral, or copper chelate form. All the blends have higher relative water contents than does the pure chitosan. Dry neutral chitosan shows a relaxation centered at approximately 90°C which is attributed to local motion. The phase behavior of the blends is influenced by preparation conditions such as the drying temperature. Characterization of blends by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) suggests partial miscibility of chitosan with nylon-4 and lack of miscibility in the remaining cases. Blending with nylon-4 enhances mechanical properties with marked antiplasticization in blends containing 90% chitosan. Catalytic activity of the chitosan is enhanced by blending with nylon-4. Salt and neutral forms of chitosan appear to be equally effective. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Investigation of blends or composites of synthetic polymers with naturally occurring macromolecules is a broad area of materials science that is rich in potential. Use is made of biodegradable, renewable biomass structures which may provide superior properties at relatively low cost. In particular, cellulose with synthetic polymers including polyvinylpyrrolidone, nylon-6, polyacrylonitrile, and poly(vinyl alcohol) have been investigated for compatibility, phase behavior, morphology, mechanical properties, permeation, and adsorption properties.<sup>1-6</sup> There are also studies on multicomponent systems involving chitosan, a derivative of naturally occurring chitin.<sup>7-21</sup> The present study is concerned with investigation of such systems, specifically blends of synthetic polyamides with chitosan.

Chitin is an extremely abundant polysaccharide widely found in crustacean shells and other byprod-

ucts of fishing industries. Chitosan, which contains 1,4-linked 2-amino-2-deoxy- $\beta$ -D-glucan moieties, is prepared by *N*-deacetylation of chitin in aqueous alkaline media as illustrated in Figure 1. Different batches of chitosan vary according to the degree of polymerization and degree of deacetylation. Commercially available materials are generally deacetylated to about 80%, with an ill-defined sequence distribution of acetylamide residues.<sup>22</sup> The amine group endows chitosan with a host of useful properties such as ability to complex metals and biomolecules. Chitosan's affinity for water combined with its chelating potential make it a biomaterial of choice in areas of agricultural, medical, food, and cosmetic industries. One can cite, for instance, applications in food packaging, controlled release of pharmaceuticals, ion transport, blood dialysis, removal of waste, and toxic products via complexation or catalytic degradation.<sup>23-25</sup>

In the present study, we are interested in chitosan's ability to act as a catalyst for the destruction of toxic chemicals via hydrolysis.<sup>26</sup> Blends of chitosan or chitosan-copper chelate with various polyamides are studied. Structure of the polyamides is illustrated in Figure 2. The blends are prepared by

\* To whom correspondence should be addressed.

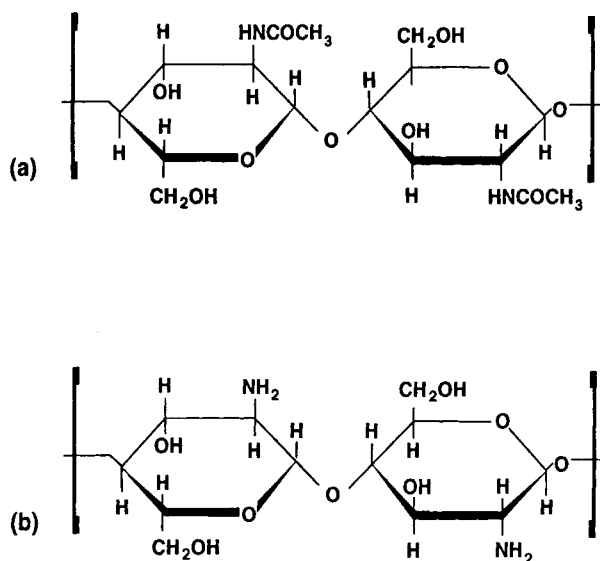


Figure 1 Structure of (a) chitin and (b) chitosan.

casting films from a common solvent. Morphology, phase behavior, mechanical properties, interaction with water, and catalytic reactivity are investigated for various conditions of blend preparation with the goal of providing materials that will combine good mechanical and catalytic properties.

## EXPERIMENTAL

### Materials

Pronova B-MV chitosan glutamate salt was supplied by Protan Co. Pure neutral chitosan was precipitated from a solution of glutamate salt in distilled water upon addition of 2M sodium hydroxide. The precipitate was washed abundantly with distilled water and freeze-dried. The degree of deacetylation was approximately 80%. The nylon-4 [poly(2-pyrrolidone)] pellets were supplied by Barson Corp. The inherent viscosity in 85% formic acid at 30°C was 3.54 dL/g at a concentration of 0.5 g/dL. Nylon-6 from Aldrich has an inherent viscosity of 0.430 dL/g at a concentration of 0.5 g/dL. The amorphous copolymer, caprolactam/lauro lactam (CLL) was donated by General Motors Research Laboratory. Zytel®, an amorphous polyamide derived from hexamethylene diamine, terephthalic acid, and isophthalic acid was supplied by E. I. Du Pont de Nemours Co. Molecular weights of the polyamides and chitosan are included in Table I.

### Preparation of the Samples

Chitosan, polyamides, and the blend films were cast from clear formic acid solutions (90% formic acid). For the blends, the solutions ranged in concentration from 5% to 95% (w/w) of chitosan. The solutions were allowed to evaporate at room temperature and translucent films were obtained. For some samples, the amine groups on the chitosan were left in the salt form. Other chitosan/polyamide films were converted to the neutral form by immersing the film in a bath of 2M sodium hydroxide. The films were washed with water and dried at 40°C or 100°C under vacuum for several days and kept in a desiccator over anhydrous calcium sulfate. Film thickness ranged from 0.02 to 0.08 mm. The thinner films were used for the Fourier transform infrared spectroscopy (FTIR) experiments while the thicker samples were used for dynamic mechanical analysis (DMA) experiments.

Films for the reactivity tests were prepared using the previous methods and copper was added using the method developed by Andreotti et al.<sup>29</sup> The films were immersed into 0.2M copper acetate solution for approximately 12 h, ammonium hydroxide was added to adjust the pH to 10, and then the films were immersed in a buffer solution for 18 h.

### Measurements

Wide-angle X-ray scattering (WAXS) experiments were performed for the chitosan using a Picker 4

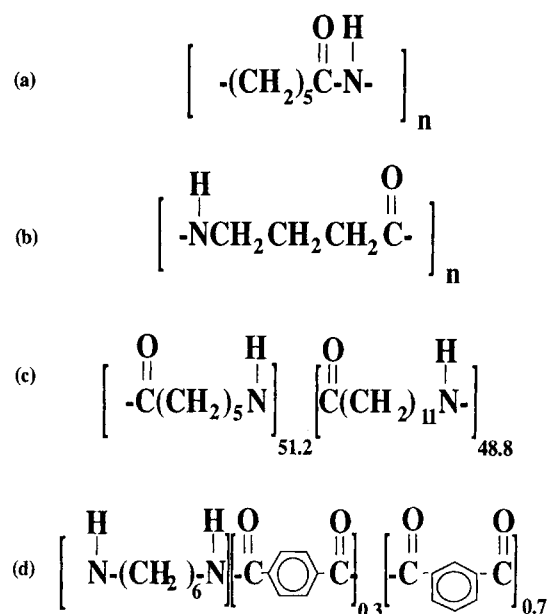


Figure 2 Structure of polyamides: (a) nylon-6; (b) nylon-4; (c) CLL; (d) Zytel.

**Table I** Molecular Weights of Chitosan and Amorphous Polyamides

	Chitosan <sup>a</sup>	CLL <sup>27</sup>	Zytel <sup>28</sup>
$M_n$ (g/mol)	$1.45 \times 10^5$	$24.4 \times 10^4$	$14.0 \times 10^3$
$M_w$ (g/mol)	$2.35 \times 10^5$	$76.8 \times 10^4$	$47.6 \times 10^3$

<sup>a</sup> The molecular weight of chitosan was determined by size exclusion chromatography/light scattering at Worcester Polytechnic Institute in Dr. Rollin's laboratory.

circle Model 210 diffractometer by Technology of Energy Corp. A DuPont 951 thermogravimetric analyzer with a 1091 disk memory thermal analyzer was used to obtain weight vs. temperature graphs at a rate of 20°C/min for the chitosan and chitosan/polyamide blends.

DMA was performed on the neutral films. All films were dried at 40°C under vacuum but were exposed to the air during the loading of the sample. The dynamic storage modulus  $E'$ , loss modulus  $E''$ , and mechanical loss tangent ( $\tan \delta = E''/E'$ ) were analyzed for samples before and after drying the samples at various temperatures (100–180°C) in the DMA chamber. A Seiko DMS-200 instrument was used with a heating rate of 4°C/min and at a frequency of 1 Hz. The samples were cooled using liquid nitrogen and the autocooling accessory.

The FTIR work was performed as a function of temperature using a Perkin-Elmer FTIR 1600 instrument. A heating cell with silver chloride plates were used in the temperature range of 25–180°C.

A Perkin-Elmer differential scanning calorimeter 2-C with the TADS-3600 data station and a subambient mechanical cooler was used. Each sample (5–10 mg) was run under nitrogen atmosphere at a scanning rate of 20°C/min in a temperature range of –40 to 200°C. An indium sample was used as a standard to calibrate the instrument for transition temperatures and enthalpies.

Since there were limitations to the temperature range with the Perkin-Elmer instrument, a TA 2200 DSC was also used to determine phase transition temperatures for the chitosan/polyamide blends in the temperature range –140 to 200°C. Each sample of chitosan/polyamide was heated until the melt temperature of the polyamides and then quenched, and then subsequent heating scans were performed.

For all of the DSC studies, the melting and crystallization transitions are reported as the maximum and minimum peak heights, respectively. Glass transition temperatures ( $T_g$ ) are reported as the midpoint of the base-line discontinuity. DSC blend data are compared by normalizing the data with respect to the sample mass.

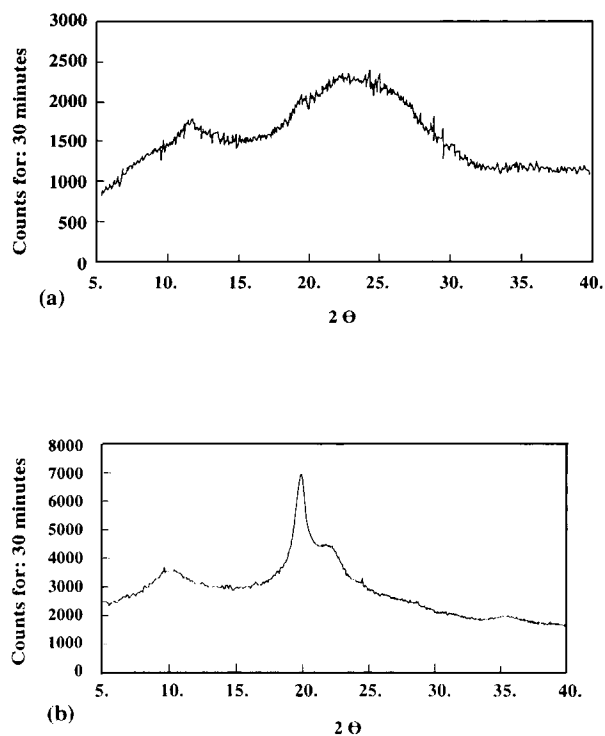
Scanning electron microscopy (SEM) was performed to investigate the morphology of the cross-sectional areas of the films with a JEOL J5M 840A instrument. Samples were prepared by fracturing the samples in liquid nitrogen and coating them with gold.

A Hewlett Packard 598b Direct Insertion Probe ionizer mass spectrometer (MS) was used to analyze the neutral and salt forms of chitosan. The samples were held at 25°C for 2 min, heated at a rate of 10°C/min, and then held at 215°C for 60 min. The samples were also evaluated by MS/gas chromatography (GC) (5996A Hewlett Packard) using a Chemical Data Systems pyro-probe with a quartz-lined interface. The samples were placed in the chamber at 100°C and ramped at 1°C/min to 200°C.

GC experiments for simulant vapor hydrolysis tests were performed on the films. One microliter of neat diisopropyl fluorophosphate (DFP) was allowed to vaporize in a closed vial containing a film of the chitosan/polyamide blends which had been equilibrated for 1 week at 100% relative humidity. A neutral form of chitosan copper chelate film was used as a control. After a specific time, the reaction was stopped by quenching the solution with 3 mL of isopropanol and the mixture analyzed by GC using a Hewlett Packard<sup>TM</sup> 5890 Gas Chromatograph with a 7673A autosampler and a 3392A integrator. Helium was used as the carrier gas.

## RESULTS AND DISCUSSION

Chitosan is a weak polybase with  $pK_a$  equal to 6.5.<sup>30</sup> Samples prepared from formic acid solutions are in the amine salt form and may be neutralized to the free amine by treatment with alkali as described in the Experimental section. X-ray diffraction studies reveal the existence of several polymorphs, depending on the solvent used, preparation method, and annealing history.<sup>31,32</sup> Figure 3 shows the X-ray diffraction of the neutral and salt forms, the former rather strongly crystalline and the latter essentially amorphous, in agreement with a previous report by Samuels.<sup>31</sup>



**Figure 3** WAXS diffraction pattern of chitosan: (a) salt form; (b) neutral form.

### Water Uptake by Chitosan and Blends

In TGA experiments on heating, the neutral film form displays continuous weight loss until 170–180°C (approximately 10% by weight). The salt form and the neutralized copper chelate display continuous weight loss until the onset of thermal decomposition above 250°C (approximately 15% by weight). Mass spectroscopy performed on the copper chelate reveals that only water is lost up to thermal decomposition.<sup>33</sup> Desorption GC/MS experiments performed at 200°C on the neutral and salt-form chitosan films previously dried *in vacuo* at 40°C show no sign of polymer decomposition and only trace residual solvent (formic acid) in addition to water. Thus, we may conclude that weight loss displayed in the TGA experiments is almost exclusively due to loss of water. Thermal cycling may irreversibly change the morphology and permeation properties (one can note, e.g., that tightly bound water is not regained after 24 h at ambient humidity following an isothermal hold at 200°C for 30 min).<sup>34</sup> When water uptake in the blends is measured by TGA, a positive deviation with respect to composition is always observed and this trend is strongest for compositions in the vicinity of 20/80 (chitosan/polyamide).

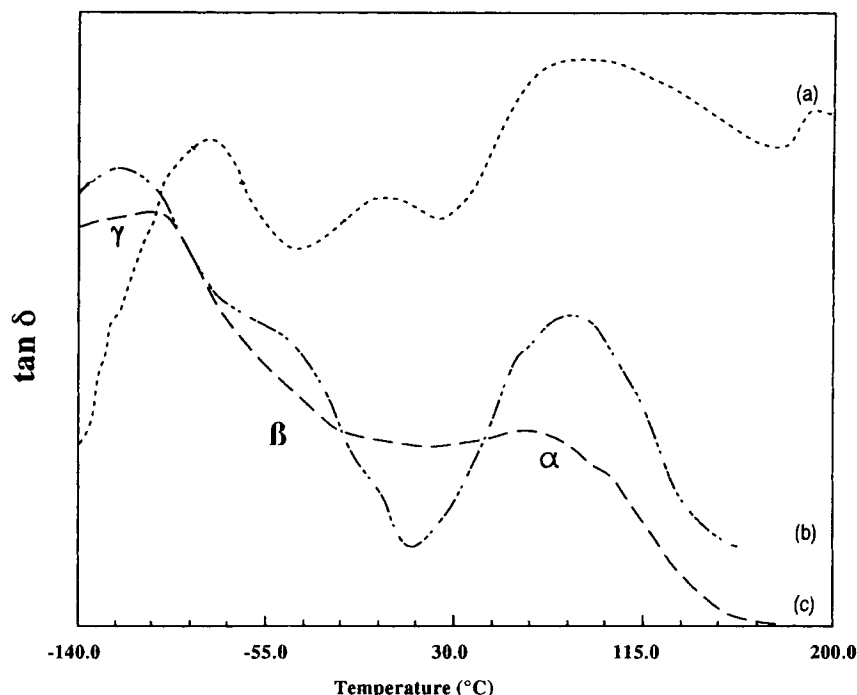
Water is an integral part of the chitosan and blend systems under normal experimental conditions and undoubtedly influences permeation and catalytic reactivity. Indeed, catalytic reactivity may not be envisaged in its absence. Yet, water desorption above ambient temperature perturbs experimental observation of the phase behavior, as discussed below. With this caveat in mind, we shall now discuss the phase behavior of chitosan and of the blends.

### Phase Behavior of Chitosan

Molecular motions and relaxation behavior in the solid state of neutral chitosan (“dry” samples) have been investigated by several authors, with contradictory results.<sup>35–37</sup> A glass transition temperature was reported at 140°C, based on DMA measurements at 1 Hz frequency.<sup>34</sup> Kaymin et al.<sup>36</sup> measured the linear thermal expansion coefficient of neutral chitosan dried at 100°C for 4 h and annealed at 196°C for 5 min. Three discrete expansion steps are observed at –23, 55, and 105°C.<sup>35</sup> In addition, a recrystallization process takes place above 55°C, a temperature which the authors assign as a glass transition to a “leathery” state. The three discrete steps in thermal expansion are attributed to breakdown of systems of H bonds of varying stability. Pizzoli et al., on the other hand, report from dielectric and dynamic mechanical spectra a low amplitude relaxation in the vicinity of 130°C (at 3 Hz).<sup>36</sup> This transition is tentatively attributed to local motion of the dry polysaccharide chain rather than a  $T_g$ -like transition.

The low-temperature gamma relaxation  $\gamma$  peak observed in the vicinity of –100°C (3 Hz) has an activation energy of 47 kJ/mol and is similarly assigned to local motions of the polysaccharide chain, such as small amplitude oscillations of the sugar rings about the glycosidic bonds. A water-induced  $\beta d$  peak develops above the transition as the sample is exposed to moisture, progressively depressing the gamma peak; it is, in fact, the only subambient peak observed for samples stored at room humidity. As moisture content is increased, the position of the  $\beta d$  peak moves to lower temperatures. Pizzoli et al. explained their observations by assuming that small amounts of water at first strengthen the H-bond network, which hinders the motion responsible for the gamma relaxation. As more water is added, however, water–water bridges loosen this network and  $\beta d$  peak moves to progressively lower temperatures.

Figure 4 shows our dynamical mechanical spectra on neutral chitosan films previously dried in the



**Figure 4** Dynamic mechanical spectra of neutral chitosan dried in the DMA chamber at various temperatures: (a) 100°C; (b) 140°C; (c) 180°C.

DMA chamber at various temperatures. Drying at 180°C appears to remove trace moisture, judging by the absence of the  $\beta d$  peak in agreement with TGA results. Our results are similar to that of Pizzoli et al. in the low-temperature region, but instead of a low amplitude transition centered at 130°C, we observe a similar transition centered at 90°C. We do not at present understand the origin of this peak, but assign it tentatively to local chain motion which may originate within the acetamide and amine regions. This conclusion is based on the strong temperature dependence of the FTIR spectrum of chitosan in the 1500–1700  $\text{cm}^{-1}$  region (Fig. 5). This range of frequencies includes the amide I band,  $\text{NH}_2$  deformation, and amide II band.<sup>31</sup> For chitosan at 30°C, the amide I peak is centered at 1663  $\text{cm}^{-1}$  and the amide II band at 1558  $\text{cm}^{-1}$  overlaps with the  $\text{NH}_2$  deformation peak at 1588  $\text{cm}^{-1}$ . As the temperature is increased, a striking decrease in the area encompassing the 1500–1700  $\text{cm}^{-1}$  region is observed together with large shifts in amide peak position. The  $\text{NH}_2$  band becomes clearly resolved in the vicinity of 80°C, as the amide I and II peaks shift to higher and lower frequencies, respectively, in agreement with results reported for other polyamides.<sup>38</sup> The room-temperature spectra are reversibly recovered on cooling. This marked temperature dependence is indicative of bands that reflect conforma-

tional sensitivity and suggests that a significant rearrangement of bond structure may be taking place within the acetamide and amine bond regions (whereas the OH bending mode in the vicinity of 1000  $\text{cm}^{-1}$  appears to be insensitive to temperature in the 30–140°C range).

### Phase Behavior of the Blends

The following data on the chitosan/nylon-4 systems illustrate the influence of sample preparation on morphology. The salt-form chitosan and blends give mostly transparent films while the neutral-form samples are somewhat scattering. Crystallization of nylon-4 from the melt was not investigated, as the polymer decomposes upon melting. A glass transition temperature is not observed on DSC for pure nylon-4 or chitosan. A broad endotherm was observed around 50°C for the chitosan first heating data, which is in agreement with an endothermic peak that exists for most polysaccharides at low moisture contents.<sup>39</sup> The first heat DSC scans of blends with nylon-4 (salt form) suggest partial miscibility with glass transitions with from the nylon-rich and chitosan-rich regions, but data are distorted by the evaporation of residual water.<sup>40</sup>

Some representative values of  $T_m$  and  $\Delta H_m$  upon first heat are illustrated in Table II for several

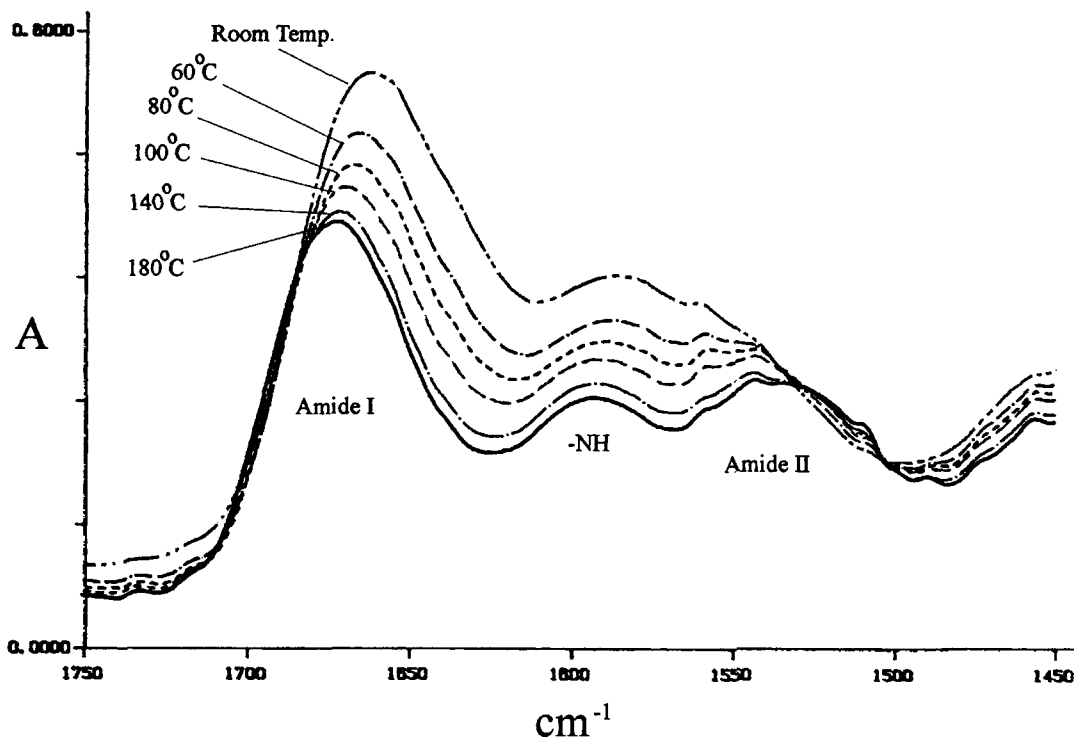


Figure 5 FTIR data of neutral chitosan as a function of temperature.

methods of blend preparation. In general,  $\Delta H_m$  is approximately linear with composition in neutral blends irrespective of drying temperature and mixing time (although  $\Delta H_m$  may be depressed at low nylon-4 contents). The SEM photographs of neutral blends (% chitosan = 0, 40, 50) (Fig. 6) similarly show a smooth evolution of morphology with composition. Similar morphology was also observed in

nylon-4/poly(vinyl alcohol) and nylon-4/hydroxyethyl methacrylate blends.<sup>41,42</sup> The neutral blends display a single melting peak at roughly the same temperature as that of pure nylon-4, irrespective of composition.

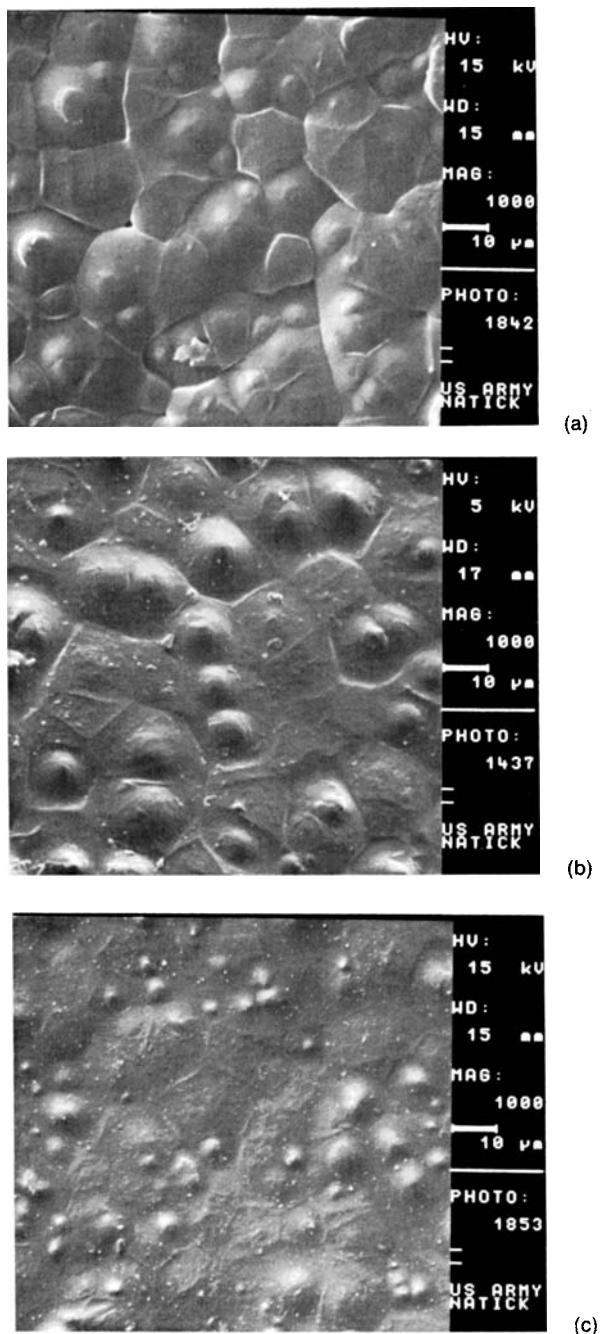
In the salt form, on the other hand, blending with chitosan may strongly depress crystallization of nylon-4, especially for drying at temperatures below

Table II Phase Behavior in Blends of Chitosan/Nylon-4 (First Heat Scans)

Composition (% Chitosan)	$T_m$ (°C)				$\Delta H_m$ (cal/g)		
	A <sup>a</sup>		B	C	A <sup>a</sup>		
	Low	High			A <sup>a</sup>	B	C
95	251	264	—	—	0.5	—	—
90	252	264	—	—	1.0	—	—
80	252	264	251	265	3.4	0.3	1.8
60	255	263	256	261	6.4	0.8	6.4
40	256	265	260	261	9.9	7.6	8.8
20	—	265	265	265	14.7	13.8	13.5
10	—	—	265	—	—	16.9	—
0	—	272	267	268	23.3	18.8	17.5

A: salt form, mixed overnight and dried at 100°C. B: salt form, mixed 3 weeks and dried at 100°C. C: neutral form, mixed overnight and dried at 40°C.

<sup>a</sup> Double melting peaks;  $\Delta H_m$  reported as the sum of low- and high-temperature melting enthalpies.



**Figure 6** SEM photographs of the chitosan/nylon-4 surface (magnification 1000 $\times$ ): (a) 0/100; (b) 50/50; (c) 60/40.

the  $T_g$  of amorphous nylon. This is also illustrated in Table II. Double melting peaks are observed for samples mixed overnight and dried at 100 $^{\circ}$ C. When mixing time is extended to 3 weeks, a single melting peak (with a shoulder at higher nylon contents) and a depressed value of  $\Delta H_m$  and  $T_m$  with decreasing nylon content are observed. This suggests interac-

tion between the two blend components upon extended mixing time. Values of  $T_g$  measured from second heating scans are summarized in Table III for the other neutral blend systems (first heating to 200 $^{\circ}$ C, followed by quench cooling to -40 $^{\circ}$ C). These data suggest lack of miscibility with chitosan, a result which was confirmed by DMA in the case of chitosan/Zytel blends. Nylon-6 was also shown to be immiscible with cellulose.<sup>3</sup>

Representative DSC results are shown in Table IV for the CLL system. The results shown are for mixing times of 1-2 days followed by drying in vacuum at 40 $^{\circ}$ C. The data for pure CLL are in agreement with values reported by Ellis.<sup>28</sup> (e.g., weak crystallization from solution as seen on first heating, and little or no crystallization from the melt, as seen from the second heating scan). The CLL melting peak observed on the first heating scan can be reliably separated from the water loss endotherm at higher CLL contents, but the glass transition is buried under the water loss peak upon first heating. It is, however, clearly detected upon the second heating. The value of  $T_g$  appears to decrease with increasing chitosan content, except for the 90/10 composition. These data suggest lack of miscibility as well as some plasticization by residual water. While CLL itself does not cold-crystallize, cold crystallization (presumably occurring in the interfacial zone) appears to be facilitated in the blends, where the presence of residual water may impart the required translational chain mobility. Cold crystallization temperature increases with increasing  $T_g$ , as expected. The value of  $\Delta H_m$  is very close to  $\Delta H_{cc}$  and displays a maximum (on a normalized basis) for minimum value of  $T_g$ .

DMA analysis on the Zytel blends simply confirms lack of miscibility observed by DSC; however, DMA results on the nylon-4 blends are more informative and are illustrated below. Figure 7 shows DMA data ( $E''$  vs. temperature) for neutral samples preheated at 180 $^{\circ}$ C for 30 min in the DMA chamber, to remove trace water as confirmed by the absence of  $\beta d$  peaks. The data for pure chitosan were previously discussed. For pure nylon-4, a transition centered at -100 $^{\circ}$ C (from  $E''$ ) is probably associated with the onset of cooperative motion between  $\text{CH}_2$  groups in the amorphous regions. The glass transition temperature region of nylon-4 is rather broad with a shoulder on the main transition observed reproducibly at 84 $^{\circ}$ C on  $E''$ . This may reflect a heterogeneity within the amorphous regions and suggests the possibility of a rigid amorphous region at the crystalline interface.

**Table III DSC Second Heat Data of Glass Transition Temperatures for Nylon-6, CLL, and Zytel in the Chitosan/Polyamide Blends**

Composition (% Chitosan)	$T_g$ of Nylon-6 (°C)	$T_g$ of CLL (°C)	$T_g$ of Zytel (°C)
90	—	24	—
80	—	25	—
60	—	21	132
50	49	26	131
40	47	29	136
20	40	22	136
10	47	37	137
0	46	32	132

—, not observed.

Both  $T_g$  and moduli values vary with chitosan content, confirming partial miscibility within the amorphous regions, although this variation shows no discernible quantitative trend. Figure 8 shows the evolution of  $E'$  with composition, illustrating a strong antiplastisizing effect in the case of the 90/10 composition (a similar behavior is observed in the "wet" samples as well).

Several observations may be made from the DMA data: The  $E'$  values indicate that blending improves mechanical properties. The glass transition region is broadened, suggesting heterogeneity, possibly with some nylon-rich and some chitosan-rich regions. This is especially striking for the 90/10 composition. The 90/10 composition reproducibly shows unusual behavior, even in "wet" samples. The value of  $E'$  is increased severalfold with respect to the pure components, suggesting some antiplasticizing interaction. This is to be compared with the apparent suppression of the  $\beta d$  peak in the salt-form 90/10 composition, even for "wet" samples.

### Reactivity

While DMA was carried out on dry samples, reactivity measurements involving the hydrolysis of diisopropyl fluorophosphate were performed in samples equilibrated at 100% humidity. All data represent the average of four replicates at each composition.

Figure 9 shows percent hydrolytic reactivity in the salt and neutral forms of chitosan copper chelates/nylon-4 blends (copper content as shown) and the neutral form of chitosan copper chelates/Zytel. Reactivity is clearly higher in the blends than in the pure chitosan, especially in the vicinity of the 80/20 chitosan/polyamide composition.

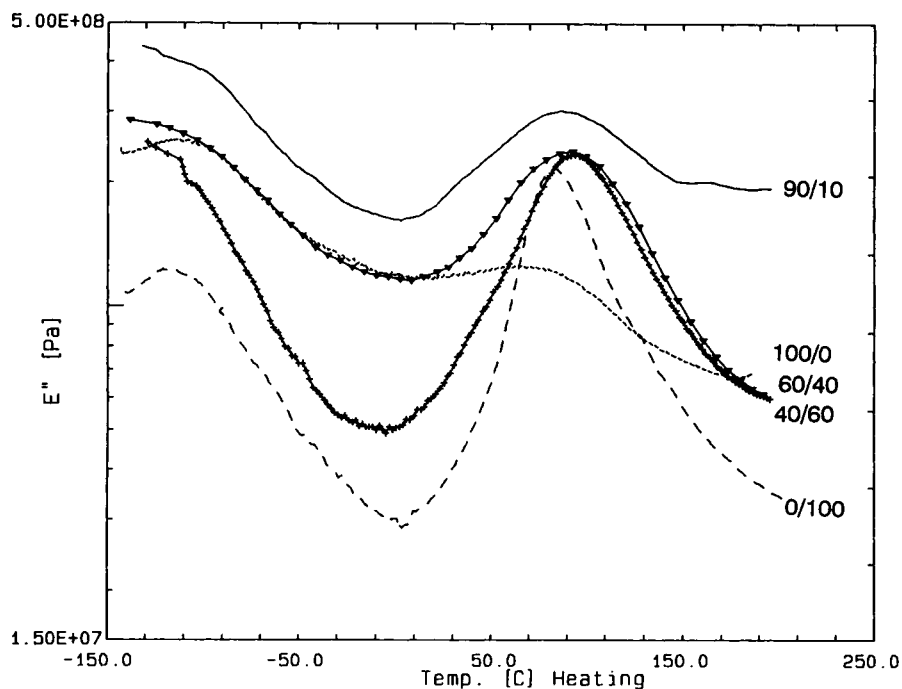
There seems to be no significant difference in reactivity between the salt and neutral forms, suggesting that the neutralization step may not be required in film preparation, if chelating activity is of interest. While blending with nylon-4 significantly enhances reactivity, reactivity in the presence of

**Table IV Phase Behavior in Salt-form Blends of Chitosan/CLL**

Composition (% Chitosan)	A					B	
	$T_g$ (°C)	$T_{cc}$ (°C)	$\Delta H_{cc}$ (cal/g)	$T_m$ (°C)	$\Delta H_m$ (cal/g)	$T_m$ (°C)	$\Delta H_m$ (cal/g)
100	—	—	—	—	—	—	—
90	28	?	?	124	0.1	—	—
80	15	65	1.0	124	1.2	—	—
60	18	76	1.2	125	1.3	—	—
50	18	71	1.9	124	2.2	—	—
40	31	?	?	124	0.2	147	3.4
20	30	95	0.2	125	0.2	147	5.8
0	35	—	—	126	0.1	148	7.5

—, not observed; ?, difficult to estimate; A, second heat, mixing 1 day; B, first heat, mixing 1 week, 0.5% solution.

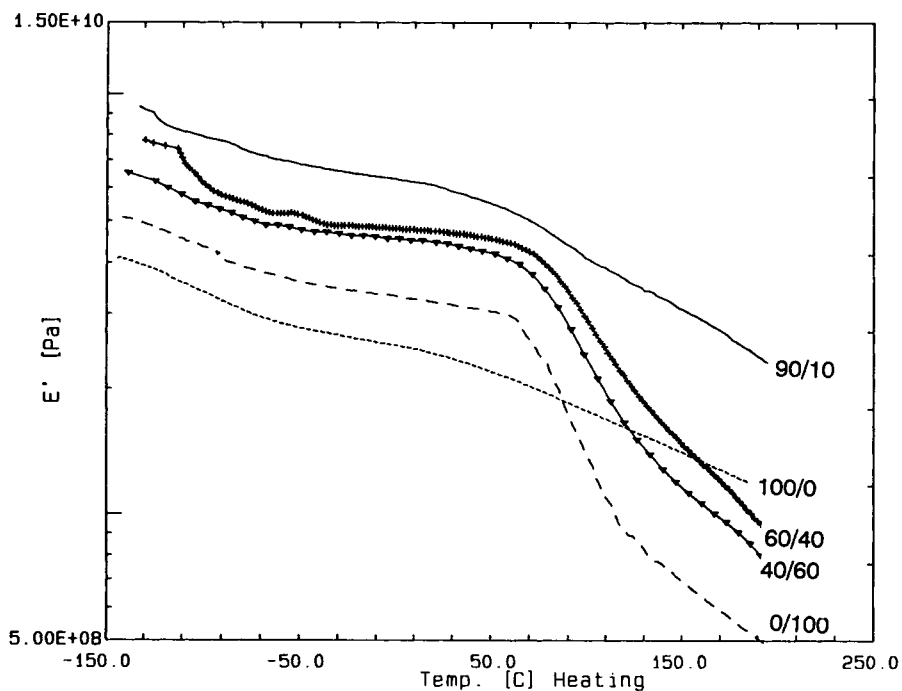




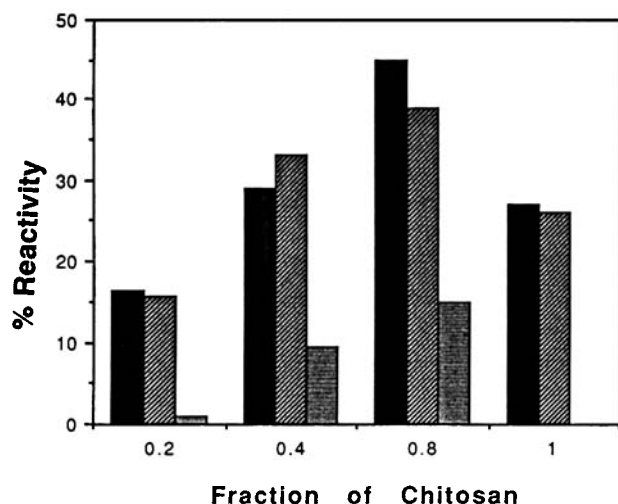
**Figure 7** DMA data ( $E''$ ) of neutral chitosan/nylon-4 blends dried at 180°C in the DMA chamber: (-----) 100/0; (——) 90/10; (+++++) 60/40; (▶▶▶▶) 40/60; (-----) 0/100.

Zytel decreases with chitosan content in roughly linear fashion, suggesting that Zytel acts essentially as a diluent that neither hinders nor enhances hy-

drolysis. Blending with nylon-4, on the other hand, results in both partial miscibility and enhanced catalytic reactivity although there are no significant



**Figure 8** DMA data ( $E'$ ) of neutral chitosan/nylon-4 blends dried at 180°C in the DMA chamber: (-----) 100/0; (——) 90/10; (+++++) 60/40; (▶▶▶▶) 40/60; (-----) 0/100.



**Figure 9** Hydrolytic reactivity of salt and neutral forms of chitosan/nylon-4 and chitosan/Zytel blends: (■) chitosan/nylon-4 (neutral form of chitosan); (▨) chitosan/nylon-4 (salt form of chitosan); (▩) chitosan/Zytel. Percent copper for the blends is 8, 7, 4, and 1% for the chitosan fractions 1, 0.8, 0.4 and 0.2, respectively.

differences in the overall water affinity between the Zytel and nylon-4 blends.

## CONCLUSIONS

We have described the preparation of catalytic blends with hydrolytic reactivity. In fact, films based on blends of chitosan with nylon-4 have a higher reactivity than does chitosan itself. The salt and neutralized forms of chitosan appear to be equally effective in this respect. Strong interactions between chitosan and the polyamide appear to be required, rather than the absence of polyamide self-association (lack of crystallinity). Indeed, the amorphous polyamides CLL and Zytel are immiscible with chitosan just as the semicrystalline nylon-6. Semicrystalline nylon-4, on the other hand, is partially miscible as illustrated by the DMA results. This is not surprising in view of the high density of amide linkages along the nylon-4 backbone with concomitantly high potential to form associations via hydrogen bonding. The 90/10 (chitosan/nylon-4) composition displays antiplasticization as well as the absence of water-induced relaxation in dry samples and in samples subjected to ambient humidity. This suggests strong chitosan-nylon-4 hydrogen bonding, displacing hydrogen bonding to water for this composition. Maximum catalytic reactivity is observed for approximately 80/20 compositions.

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