Chitin Derivatives. II. Time–Temperature–Transformation Cure Diagrams of the Chitosan Amidization Process

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ABSTRACT: The transformation of the salts of chitosan with acetic and propionic acid, chitosonium acetate and chitosonium propionate, into chitin or the respective homolog of amidized chitosan has been described on the basis of time-temperature-transformation (TTT) cure diagrams. The time to vitrification at various isothermal cure temperatures (T_c) was determined using dynamic mechanical thermal analysis. The time to full cure was derived using a T_g-T_c cure time relationship according to the method of Peng and Gillham, as well as by an extrapolation procedure. Consequently, TTT cure diagrams describing the temperature-driven regeneration process include full cure and vitrification curves. As in thermosets, this transformation displays an Sshaped vitrification curve, and the time to full cure increases with decreasing cure temperature. The time to full cure is very remote from the time to vitrification, and this is attributed to the tendency of vitrification to prevent full cure from being attained. The activation energies for vitrification of chitosonium acetate and chitosonium propionate derived from an Arrhenius equation are similar. This suggests that the same mechanism governs glass formation in the N-acetyl and N-propionyl-glucosamine derivatives. Additionally, the morphology of amidized chitosan and native chitin was examined using X-ray diffraction and FTIR analysis. X-ray diffraction results indicate that amidized chitosan is an amorphous material, whereas native chitin is crystalline. FTIR suggests the existence of hydrogen-bonded amide groups in native chitin but not in amidized chitosan. This difference in morphology between amidized chitosan and native chitin is accounted for in terms of the influence of glass formation in the former. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1879-1889, 1999

Key words: chitin derivatives; time-temperature-transformation cure diagrams; chitosau; thermal analysis; gelation; vitrification

INTRODUCTION

The transformation of a thermosetting resin from the liquid state into the solid state involves polymerization and crosslinking. This is technically referred to as cure.¹ The process of cure is often accompanied by several chemorheological events. These include modulus (stiffness) buildup and T_g increase with isothermal cure time, as well as gelation and vitrification. Both gelation and vitrification give rise to characteristic peaks in the tan δ curve of a typical dynamic mechanical thermal analysis (DMTA) spectrum.² In a previous article we reported on the kinetics of the heat-induced transformation of the ionic salt of chitosan with acetic acid, chitosonium acetate, to chitin.³ An *N*-acetyl derivative (amide) was formed upon exposure of the *N*-acetate salt to isothermal conditions. Also, because this transformation is accompanied by a modulus rise as

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Figure 1 A schematic time-temperature-transformation cure diagram. The diagram depicts the times to vitrification and gelation, as well as the various physical states characteristic of the cure of a thermoset.

well as a T_g increase, it was likened to the process of cure of network-forming resins. However, the amidization curing process differs from crosslinking in terms of chemical and structural changes. Whereas the latter involves chemical reactions between various functional groups that form a three-dimensional network, the former involves thermal dehydration with the formation of a linear polymer closely resembling the starting material. Nonetheless, the chemorheological transformations involved in both processes are similar.

The time-temperature-transformation (TTT) cure diagram has evolved as a useful framework for understanding the cure behavior of thermosetting resins.⁴ It represents the times necessary to achieve gelation and vitrification at various isothermal cure temperatures (Fig. 1). In terms of practical significance, it assists in the selection of time and temperature schedules to achieve a material of certain physical properties. $T_{g,0}$, included in the TTT cure diagram, represents the T_g of the uncured resin and is considered as the safe storage temperature to avoid premature crosslinking. $T_{g,\infty}$ is the ultimate T_g of the network polymer. For polymers that do not show substantial degradation above $T_{g,\infty}$, selection of cure temperatures above $T_{g,\infty}$ represents an effective means of achieving a fully cured polymer.

Palmese and Gillham have studied the conversion of polyamic acid to polyimide using the concept of the TTT cure diagram.⁵ This conversion is referred to as imidization curing of polyamic acid. The process involves thermal dehydration of polyamic acid to the imide (Fig. 2). These authors suggest that the process does not involve gelation because the resulting polyimide is a linear system, closely resembling the starting material.



Figure 2 Conversion of polyamic acid to polyimide. The conversion involves removal of water, i.e., a thermal dehydration process.

Consequently, their TTT cure diagram depicted only the vitrification and full-cure curves. Like thermosetting resins, a description of imidization in relation to the TTT cure diagram is useful in so far as it permits selection of time and temperature windows so that vitrification and full cure occurs in a predictable manner. The imidization curing of polyamic acid reported by Palmese and Gillham is similar to the amidization curing of chitosonium acetate, i.e., both processes involve thermal dehydration (Figs. 2 and 3). More importantly, the two processes were found to follow a two-stage transformation scheme; i.e., imidization and amidization; both were observed to proceed by an initial fast reaction followed by a substantially slower reaction.

The usefulness of the TTT cure diagram cannot be overemphasized, yet it has received no atten-



Figure 3 The regeneration of chitin from chitosan. This regeneration process is similar to the conversion of polyamic acid to polyimide, because the two processes involve thermal dehydration.

tion in evaluating the cure behavior of biobased resins. To date, only two reports are found in the literature dealing with a description of the cure behavior of biobased resins on the basis of the TTT cure diagram.^{14,15} These are studies carried out in our laboratory. The close resemblance of amidization to imidization and network formation provides a scenario for understanding amidization on the basis of the TTT cure diagram as well as for extending the concept to biobased polymer research.

During cure, thermosetting resins go through three distinct phases. The precursor material (Astage) is a liquid or solid, and is soluble and fusible.¹ The precursor passes through a B-stage at sufficiently high temperatures. Some resin systems, which are very reactive, can reach this stage at room temperature. The B-stage is characterized by chain extension and prepolymer formation to produce an insoluble but swellable material.¹ The Cstage develops at higher temperatures, and the resulting material is a three-dimensional network that is insoluble and infusible. The ability of thermosets to reach the C-stage depends on gelation and vitrification. For example, at vitrification the polymer chains are completely frozen in position and prevent reactive chain ends from ever reaching each other for chemical crosslinking. Different morphologies develop at each of these phases with implications on the end-use properties. These are influenced by both gelation and vitrification. During the transformation of chitosonium acetate to regenerated chitin vitrification is suspected to occur very early in the process.³ This will likely prevent chain alignment and ordering and thus develop a morphology different from native chitin.

The intent of this article is to describe the amidization curing of the ionic salts of chitosan with acetic and propionic acid, chitosonium acetate and chitosonium propionate, respectively, on the basis of TTT cure diagrams. Also, the influence of vitrification on the phase transition (morphology) of amidized chitosan is investigated.

MATERIALS AND METHODS

Materials

The chitosan used for this study was obtained from Sigma Chemicals, St. Louis, MO. This is derived from crab shells by alkaline hydrolysis (deacetylation). The extent of deacetylation is specified by the manufacturer as 89.3%. Glacial acetic acid and propionic acid were used as solvents for chitosan. Both solvents were obtained from Aldrich Chemicals, Milwaukee, WI. Both chitosan and the acids were used as received from the manufacturer.

Methods

Chitosonium Acetate/Propionate Film Preparation

The preparation of chitosonium acetate and chitosonium propionate films involved dissolution of 57 g of chitosan in 2 L of 10% aqueous acetic acid and propionic acid, respectively, followed by vigorous stirring for 24 h. The resulting solutions were centrifuged to remove suspended matter. About 150–250 mL of each solution was poured into evaporation dishes and left in a laboratory hood for solvent evaporation at room temperature for 2 days. After the second day each evaporation dish was covered with perforated aluminium foil. The aluminium-covered dishes were left for a period of 1 week for further solvent evaporation. This was followed by vacuum drying at room temperature for 24 h. It was necessary to leave the films "glued" to the evaporation dishes to avoid warping of the films during vacuum drying. The films produced had a thickness of 0.2-1.4 mm, depending on the initial volume of solution. Residual solvent content was less than 2%, as measured by thermogravimetry.

Cure Monitoring by Dynamic Mechanical Thermal Analysis

Amidization curing of chitosonium acetate and propionate was monitored using a Polymer Laboratory DMTA. Samples in the form of circular disks produced from films using a paper puncher were tested in a shear mode under isothermal cure conditions of 80 to 190°C. Rectangular samples of dimensions $8 \times 5 \times 1.1$ mm were also tested using similar isothermal conditions, but in a bending mode. Further, samples in the form of rectangular bars of similar dimensions preheated in an oven at isothermal temperatures of 80 to 190°C for varying cure times were tested under dynamic conditions in a bending mode at a heating rate of 2.5°C/min. Both modes of testing employed oscillation amplitudes of 0.4 mm and frequencies of 1 Hz, as well as a nitrogen purge of 25 cm³/min. Samples tested in bending were oscillated in a single cantilever fashion.

X-ray Diffraction Analysis

The morphology of amidized chitosan, native chitin, chitosan, and chitosonium acetate was ex-

amined using X-ray diffraction analysis. This was carried out using a Scintag PTS XDS 2000 instrument. Measurements were executed from 5 to 60° with irradiation conditions of 30 kV and 25 mA, and a scanning rate of 2°/min of diffraction angle 2θ . Native chitin, chitosan, chitosonium acetate, and amidized chitosan were mounted on the instrument holder with the aid of scotch tape. All samples were in powderous form. The degree of crystallinity of chitosan and native chitin was determined by ratioing the crystalline peak area of the diffractogram and the total peak area (crystalline and diffuse background area).

FTIR Analysis

FTIR measurements were performed at room temperature using a Nicolet FTIR instrument. Native chitin and amidized chitosan were each blended with KBr in a ratio of 1 : 6 (sample : KBr) and pressed into small, clear discs in an FTIR sample holder. Each disc thus obtained was mounted immediately for analysis.

Data Interpretation

The process of cure typically gives rise to gelation, the formation of an infinite polymer network. Gelation precedes vitrification, which corresponds to the point when the rising glass transition temperature of the curing system becomes equal to the isothermal cure temperature. In a typical DMTA spectrum gelation and vitrification are thermal events that give rise to distinctive transitions in the tan δ curve.² Therefore, the construction of the vitrification or gelation curve in a TTT cure diagram involves a series of isothermal cure experiments at several different temperatures (T_c) , where tan δ is recorded as a function of time, and plotted as T_c vs. vitrification or gelation time on a log scale.

Sometimes the TTT cure diagram is constructed to include a full cure curve. This curve aids in the selection of time and temperature paths to achieve full cure.^{5,15} This is particularly important considering that meaningful structure–property relationships of two polymers can be deduced when they are fully cured. Peng and Gillham¹⁶ have related T_g s of epoxy networks to T_c s by a linear equation as follows

$$T_g = A + BT_c \tag{1}$$

where A is a constant influenced by cure time, and B is a constant independent of cure time. Under

the assumption that these networks are fully cured when T_g reaches $T_{g,\infty}$, they obtained the temperatures for full cure to be reached in a specified time, $T_{\infty(t)}$ by recasting eq. (1) as

$$T_{g,\infty} = A + BT_{\infty(t)} \tag{2}$$

Alternatively, the times to full cure can be derived by extrapolation of T_g vs. T_c -curves to $T_{g,\infty}$. The activation energy for vitrification provides

The activation energy for vitrification provides a basis for evaluating the influence of structure on glass formation. Peng and Gillham,¹⁶ as well as Palmese and Gillham,⁵ have described the times to vitrification in an Arrhenius fashion to derive the apparent activation energies for vitrification. The time to achieve a specified extent of cure (p) was reported to be an inverse function of the isothermal cure temperature (T_c) necessary for attaining p,

$$\ln t = (E/R)1/T_c + \ln g(p)$$
 (3)

where E and R are activation energy and universal gas constant, respectively, and g is a constant that depends on p.

Equation (3) assumes that cure reactions are not influenced by vitrification-related diffusion. However, in most cases reactions are influenced by polymer chain diffusion, particularly beyond vitrification. Nonetheless, a recast of eq. (3) as

$$\ln t_{\rm vit} = (E_{\rm vit}/R) 1/T_c + \ln g(p_{\rm vit}) \tag{4}$$

with $p_{\rm vit}$ as the extent of cure at vitrification produces a linear relationship between the times to vitrification (ln $t_{\rm vit}$) and the cure temperature (T_c). Consequently, the activation energy for vitrification ($E_{\rm vit}$) can be derived by plotting ln $t_{\rm vit}$ vs. T_c .

RESULTS AND DISCUSSION

Phase Transformation of Chitosonium Acetate/Propionate

When chitosonium acetate or chitosonium propionate films are exposed to isothermal cure temperature of 140°C in a DMTA operated in a single cantilever bending mode, two transitions are observed in the loss tangent (Fig. 4). These transitions are within the vicinity of each other, giving a more or less single, broad transition. On the other hand, when similar samples are tested at the same temperature in a shear mode, a single,



Figure 4 Isothermal cure (140°C) monitoring of chitosonium acetate in bending mode using DMTA. Two overlapping peaks are discernible. The first may be due to some structural changes that occur during amidization, and the second peak is related to vitrification. Also, there is an increase in modulus with time. These observations parallel the behavior of thermosetting resins.

well-defined peak is obtained (Fig. 5). In both cases there is an increase of modulus with time. Generally, a network-forming polymer gives two distinctive transitions in the loss tangent under isothermal exposure. These transitions are attributed to gelation and vitrification. This is related to the fact that the reactive polymer exhibits low damping in the liquid phase, but damping rises with time as the material becomes rubbery. This rise becomes limited once the material has gelled on account of restriction on chain mobility, therefore giving a characteristic peak in the loss tangent. The polymer displays a second transition as it transforms from a rubbery phase to a glassy phase, similar to the glass-to-rubber transition.² In the case of chitosonium acetate or chitosonium propionate, no gelation is expected because the final product (amidized chitosan) remains a linear polymer although "physical gelation" is possible by the formation of ordered aggregates (crystalline regions) or physical entanglements. However, because (a) there is no distinct crystallinity (as will be explained in a later section) observed, and (b) there is only a shoulder in the loss tangent, the initial peak in bending is attributed to a phenomenon inherent to clamping rather than a molecular reorganization, and the single loss tangent peak in shear (the peak at log 3.3 s), as well as the second loss tangent peak in bending (the peak at approximately log 3.3 s), are identified as the phase transformation of chitosonium acetate

or chitosonium propionate from the rubbery state to the glassy state, i.e., vitrification. This identification is on the basis that both bending and shear testing are capable of detecting vitrification,^{2,5} and that both peaks are in the vicinity of each other. Presumably, the first peak observed in bending is due to another phenomenon, probably not related to a molecular reorganization that occurs just prior to extensive thermal dehydration. Shear testing may not have been sensitive to such changes. Palmese and Gillham have also observed single peaks at various temperatures in torsional braid analysis of the thermal dehydration of polyamic acid similar to the single peaks observed in shear testing of chitosonium acetate or propionate, and assigned them to vitrification. They have also indicated that no gelation peak is expected.⁵

When unheated chitosonium acetate or chitosonium propionate films are exposed to dynamic conditions in a DMTA operated in a single cantilever bending mode, two transitions are observed in the loss tangent. These occur at 10 and 82°C, and -5 and 77°C for acetate and propionate, respectively (Fig. 6). The high-temperature transition as opposed to the low-temperature transition as opposed to the low-temperature transition is accompanied by an appreciable decline in modulus (not shown). Ratto et al. have observed a subambient transition at -55° C in chitosan films, and have described it as a β -relaxation.¹⁷ The β -transition observed in chitosan films was associated with a limited change in modulus. Therefore, the low-temperature transition in both ace-



Figure 5 Isothermal cure (140°C) monitoring of chitosonium acetate in shear mode using DMTA. A wellresolved peak is discernible, and is assigned to vitrification. Also, there is an increase in modulus with time. These observations parallel the behavior of thermosetting resins.



Figure 6 Temperature scan of chitosonium acetate/ propionate. Two transitions are displayed at $10/-5^{\circ}$ C and $82/77^{\circ}$ C. The low temperature transition is described as β -relaxation, and the other corresponds to the glass transition temperature of the uncured acetate/propionate, designated as $T_{g,0}$ in the TTT cure diagram. \blacksquare (acetate), \spadesuit (propionate).

tate and propionate films, which also is accompanied by a negligible change of modulus, corresponds to a β -relaxation. The high-temperature transition is displayed as the uncured films undergo a glass-to-rubber transition. This assignment is supported by the observed decline of modulus typical of the T_g region. Thus, the high temperature transition is described as the T_g of the uncured acetate or propionate designated as $T_{g,0}$ in the TTT cure diagram.

TTT Cure Diagrams for Amidized Chitosan

Glass Transition Temperature of Partially Amidized Salts

After prolonged (12 h) exposure of chitosonium acetate and chitosonium propionate to a temperature of 120°C, the T_g s of the partially amidized chitin increase with cure temperatures (T_c s) (Fig. 7). These T_g s are higher than the T_c s, as depicted by the $T_g = T_c$ line (Fig. 7). The rate of T_g increase with cure temperature is pronounced at low temperatures, but levels off at cure temperatures close to the ultimate T_g ($T_{g,\infty}$) of amidized chitosan (Fig. 7). $T_{g,\infty}$ was determined as 189 and 163°C for chitin regenerated from acetate and propionate, respectively (Fig. 7). As depicted in Figures 4 or 5, vitrification occurs well under 12 h. This implies that the T_g s of the partially amidized chitosan should have been equal to T_c s, i.e., the T_g vs. T_c relationship should have corresponded to the $T_g = T_c$ line. This is because vit-

rification, operationally defined as the point when the T_g of the curing system becomes equal to T_c , freezes all reactions, such that no T_g increase is expected even after prolonged cure beyond vitrification. The fact that the T_g s of the partially amidized chitosan are higher than the T_c s can be accounted for by one of two reasons or both. Either additional amidization occurs even after the material has vitrified, or further amidization is promoted in the course of T_g measurement effectively driving the measured T_g to higher values, or both. The leveling off of T_g s at T_c s close to $T_{g,\infty}$ might be related to the fact that the material may nearly be fully cured.

Vitrification Curves

Isothermal curing was conducted at several temperatures ranging from 80 to 190°C to derive the



Figure 7 Glass transition temperature (T_g) vs. cure temperature (T_c) of isothermally cured chitosonium acetate (top) and propionate (bottom). T_g s are higher than T_c s. This implies that amidization occurs even when the material is vitrified or further amidization is promoted during T_g measurement.



Figure 8 Isothermal cure of chitosonium acetate (top) and propionate (bottom) at 140°C. There is an increase in modulus with time and a corresponding peak in tan δ . The time at which the peak occurs is defined as the time to vitrification.

times to vitrification of chitosonium acetate or chitosonium propionate. The times to vitrification obtained as the maximum in the tan δ curve were used to construct a TTT cure diagram. Representative isothermal spectra are shown (Fig. 8). The time to vitrification of chitosonium acetate and chitosonium propionate shows a decrease with increasing cure temperature between 100 and 150°C, and 80 and 140°C, respectively (Fig. 9). The time to vitrification tends to increase beyond 150 and 140°C for acetate and propionate, respectively. In the case of chitosonium acetate, temperatures between 100 and 150°C constitute the central portion of the S-shaped pattern of the vitrification curve. The corresponding temperatures for chitosonium propionate are 80 and 140°C. Temperatures beyond 150 and 140°C con-

stitute the upper shoulder of the vitrification curve for acetate and propionate, respectively, while temperatures between 100 and 80°C, and their respective $T_{g,0}$ s form the lower shoulder. The S-shaped character of the vitrification curves can be explained on the basis of the following; at low temperatures, the curing system requires a long time to go from the rubbery phase to the glassy phase due to limited molecular motions, resulting in a maximum vitrification time. At sufficiently high cure temperature, the time to vitrification is minimal due to the greater mobility of the polymer chains. However, as $T_{g,\infty}$ is approached, the long times necessary to achieve conversion indicative of vitrification produce a further increase in the time to vitrification.



Figure 9 Time-temperature-transformation (TTT) cure diagrams for *N*-acetyl (top) and *N*-propyl (bottom) analogs of chitosan. The vitrification curve has an S-shaped upper shoulder, typical of thermosetting resins. Also included in the TTT cure diagram is the ultimate glass transition temperature, $T_{g,\infty}$, and initial glass transition temperature, $T_{g,0}$, of *N*-acetyl or *N*-propyl analog of chitosan. The dashed line is hand drawn to illustrate the lower shoulder of the S-shape of the vitrification curve.



Figure 10 Glass transition temperature, T_g , vs. cure temperature, T_c . The data points represent the T_g vs. T_c relationship for various cure times in hrs. indicated as subscripts within the figure. The time to full cure can be determined by extrapolation of the curve fit line to $T_{g,\infty}$ or by the method of Peng and Gillham.

Time to Full Cure

The experimental data of T_g for both N-acetyl and N-propionyl homologs of amidized chitosan plot-

ted as T_g vs. T_c for several cure times shows an increase with cure time as well as with cure temperature (Fig. 10). Values of B calculated according to eq. (2) are nearly constant with an average value of 1.0 and 0.892 for acetate and propionate, respectively (Table I). On the other hand, the constant A varies with cure time. Times to full cure calculated according to eq. (2) and incorporated into the TTT cure diagrams decrease with increasing cure temperature (Fig. 11). Likewise, the values of the times to full cure calculated by the extrapolation procedure also decrease with increasing cure temperature. There is close correlation of the full cure curves derived by the method of Peng and Gillham and the extrapolation procedure (Fig. 11). These results suggest that the two procedures for constructing the full cure curve of a typical TTT cure are applicable to amidization. It must be emphasized that full cure asused here does not imply a completely amidized chitosan; it merely implies that amidized chitosan has attained the maximum $T_{\sigma}(T_{\sigma,\infty}).$

The time required to achieve full cure (Fig. 11) is much delayed beyond vitrification. This is not a surprising observation. Vitrification of chitosonium acetate or propionate occurs very early in the amidization process, so the tendency of the material to achieve full cure is opposed by the tendency of vitrification to freeze all reactions. The large time difference between full cure and vitrification indicates that the influence of vitrification dominates the tendency to reach full cure.

A schematic TTT cure diagram constructed for the amidization curing of chitosonium acetate and chitosonium propionate using experimentally determined times to vitrification and full cure suggests an S-shaped vitrification curve (Fig. 12).

Table IValues for Parameters A and B in Equation (1) for Chitosonium Acetate (CA) andChitosonium Propionate (CP)

	Cure Time (h)					
	0.5	1	2	4	6	
	CA/CP	CA/CP	CA/CP	CA/CP	CA/CP	
A	37/21	ª/14.8	19.4/11.6	3.4/1.4	4.0/8.8	
В	0.64/0.6	ª/0.73	0.97/1.01	1.16/1.06	1.25/1.06	
r^2	0.93/0.99	ª/0.97	0.99/0.97	0.97/0.98	0.99/0.99	

 r^2 is the correlation coefficient.

^a Not determined.

Activation Energy for Vitrification

The times to vitrification of chitosonium acetate and propionate, determined by DMTA for isothermal cure experiments conducted at several cure temperatures (T_c) , show a linear relationship with T_c when plotted in an Arrhenius fashion according to eq. (4) (Fig. 13). $E_{\rm vit}$ values determined from the slopes of Figure 13 are lower than the apparent activation energies for full cure (Table II). The activation energies for vitrification of chitosonium acetate and chitosonium propionate are similar (Table II). This similarity suggests that the same mechanism is responsible for glass formation in the two materials. The activation energy for full cure is expected to be higher than $E_{\rm vit}$. This is because the material vitrifies very



Figure 11 TTT cure diagram showing the times to vitrification and full cure of chitosonium-acetate (top) and propionate (bottom). The times to full cure are determined by an extrapolation method (solid line) and the theoretical method after Peng and Gillham (data points).



Figure 12 A schematic TTT cure diagram describing the regeneration of chitin from the ionic salts of chitosan with acetic and propionic acids. The diagram depicts the various physical states during the regeneration. Also included are the times to vitrification and full cure.

early in the process, such that the tendency of the material to achieve full cure is opposed by the tendency of vitrification to freeze all reactions; consequently, there is a higher energy barrier to the progress of amidization. This effect is well demonstrated by the large time difference between the vitrification and full-cure curves in the TTT cure diagram (Fig. 11).

Influence of Vitrification on the Morphology of Amidized Chitosan

When amidized chitosan is exposed to X-ray diffraction analysis, it gives a diffuse type of diffractogram with no peaks characteristic of crystalline regions. On the other hand, native chitin gives an intense peak identifiable with crystalline materials (Fig. 14). Chitosan exhibits a similar diffractogram pattern as native chitin. Chitin and chitosan have 39 and 18% degrees of crystallinity, respectively. Chitosonium acetate gives a characteristic diffuse diffractogram as in amidized chitosan (Fig. 14).

When native chitin and amidized chitosan are examined by FTIR, the former displays bands at 3439, 3263, and 3103 cm⁻¹ (not shown). On the other hand, amidized chitosan reveals only a single band at 3439 cm⁻¹ (not shown). These bands can be described as nonhydrogen-bonded NH groups, hydrogen-bonded NH groups, and neighboring hydrogen-bonded amide groups, respectively, according to the work of Miyake,¹⁸ as well as Trifan and Terenzi.¹⁹ Extensive hydrogen bonding is responsible for the crystalline morphology of chitin. Miyake,¹⁸ as well as Trifan and Terenzi,¹⁹ have reported that the amide groups in polyamides are hydrogen bonded and provide the



Figure 13 Arrhenius plot of time to vitrification (t_{vit}) vs. cure temperature. The slope of the curve is used to determine the activation energy for vitrification. *N*-acetyl (top) and *N*-propyl (bottom).

polymer chains an ordered alignment such that a crystalline morphology is produced. Additionally, these authors have observed an increasing extent

Table II A Comparison of Activation Energy for Vitrification $(E_{A,vit})$ and Full Cure $(E_{A,full cure})$ of Chitosonium Acetate and Propionate

Material Type	$E_{A,\mathrm{vit}}$ (kcal/mol)	$E_{A,{ m full\ cure}}\ ({ m kcal/mol})$
Acetate	13	36
Propionate	11	37

 $E_{A,{\rm full\,cure}}$ derived from addition of the activation energies of the first and second phases of amidization reported in this series.



Figure 14 X-ray diffractograms of native chitin (A), chitosan (B), chitosonium acetate (C), and amidized chitosan (D). Both A and B display peaks typical of a crystalline morphology. There are no such peaks in C and D.

of hydrogen bonding with increasing concentration of amide groups. On this basis it is reasonable to expect that increasing the severity of heat treatment for producing amidized chitosan should lead to more hydrogen bond formation; this is because more amide groups are produced. The fact that no hydrogen bonding occurs with the amide groups of amidized chitosan may suggest that the groups are not within the vicinity of each other. The concept of a TTT cure diagram has shown that vitrification occurs very early in the transformation of chitosonium acetate to chitin. Presumably, once vitrification occurs, the resulting immobilization of the polymer chains prevents the chains to move into environments favorable for hydrogen bonds to form, let alone alignment of chains for formation of an ordered morphology. Beside amide groups, the presence of hydroxyl groups should give rise to extensive hydrogen bonding, and consequently, a crystalline morphology, provided suitable alignment of polymer chains is present. The diffractogram of chitosonium acetate indicates that it is amorphous. It is suspected that solvation of chitosan by acetic acid/water disrupts hydrogen bonds present in chitosan. Possibly hydrogen bonds, due to hydroxyl group interactions, are not reformed during the transformation of chitosonium acetate to amidized chitosan. This may be related to the influence of vitrification as well. Based on this discussion, we suspect that vitrification prevents amidized chitosan from achieving a crystalline morphology.

CONCLUSIONS

- 1. The transformation of chitosonium acetate and chitosonium propionate to *N*-acyl homologs of chitin gives rise to characteristic tan δ peaks, and these are typical of vitrification.
- 2. The glass transition temperatures of partially amidized and vitrified chitin are always higher than the cure temperatures. This suggests that amidization occurs even after the material has vitrified or that further amidization is promoted during T_g measurement.
- 3. Isothermal cure monitoring at several temperatures can be used to describe the vitrification behavior of chitosonium acetate and chitosonium propionate on the basis of the TTT cure diagrams. As in thermosets, the vitrification curves of the TTT cure diagrams describing the amidization curing of these ionic salts of chitosan are S-shaped. $E_{\rm vit}$ is the same during amidization of chitosonium acetate and chitosonium propionate. This similarity suggests that the same mechanism governs glass formation in the two materials.
- 4. An extrapolation method, and also the theoretical method of Peng and Gillham, can be used to determine the time to full cure. The time to full cure increases with decreasing cure temperature. Full cure takes much longer than vitrification, and this is due to the tendency of vitrification to prevent full cure from being attained.
- 5. Native chitin and chitosan are crystalline. Chitosonium acetate and amidized chitosan have amorphous morphologies. The amorphous character of amidized chitosan is related to the influence of vitrification.

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REFERENCES

- Turi, E. A. Thermal Characterization of Polymeric Materials; Academic Press, Inc.: New York, 1981.
- Hofmann, K.; Glasser, W. Thermochim Acta 1990, 166, 169.
- 3. Toffey, A.; Samaranayake, G.; Frazier, C. E.; Glasser, W. J Appl Polym Sci 1996, 60, 75.
- Aronhime, M. T.; Gillham, J. K. Adv Polym Sci 1986, 78, 83.
- Palmese, G. R.; Gillham, J. K. J Appl Polym Sci 1987, 34, 1925.
- Enns, J. B.; Gillham, J. K. J Appl Polym Sci 1983, 28, 2567.
- Aronhime, M. T.; Gillham, J. K. Adv Polym Sci 1984, 56, 35.
- Babayevsky, P. G.; Gillham, J. K. J Appl Polym 1973, 17, 2067.
- Schneider, N. S.; Sproise, J. F.; Hagnauer, G. L.; Gillham, J. K. Polym Eng Sci 1979, 19, 304.
- Wisanrakkit, G.; Gillham, J. K. ACS Polym Mater Sci Eng Prep 1987, 56, 87.
- 11. Gillham, J. K. Br Polym J 1985 17, 224.
- Gillham, J. K.; Enns, J. B. ACS Polym Mater Sci Eng Prep 1988, 59, 851.
- Wisanrakkit, G.; Gillham, J. K. ACS Polym Mater Sci Eng Prep 1988, 59, 969.
- 14. Hofmann, K.; Glasser, W. Macromol Chem Phys 1994, 195, 65.
- 15. Toffey, A.; Glasser, W. G. Holzforschung 1997, 5, 71.
- Peng, X.; Gillham, J. K. J Appl Polym Sci 1985, 30, 4685.
- Ratto, J. N.; Chen, C. C.; Blumstein, R. B. J Appl Polym Sci 1996, 59, 1451.
- 18. Miyake, A.; J Polym Sci 1960, 64, 223.
- Trifan, D. S.; Terenzi, J. F.; J Polym Sci 1958, 28, 443.