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DSC studies on the curing kinetics of chitosan–alanine using glutaraldehyde as crosslinker

Kamlesh Kumari · K. K. Raina · P. P. Kundu

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Abstract The curing of chitosan–alanine with glutaraldehyde as curing agent in the presence of Chlorpheniramine Maleate (CPM) is carried out with the help of differential scanning calorimeter (DSC). The effect of concentration of chitosan and percentage of crosslinker on the curing is studied at a rate of 5 °C/min. Cure kinetics are measured from 30 to 200 °C at four different heating rates (3, 5, 7 and 10 °C/min). It is observed that the crosslinking of chitosan–alanine is an exothermic process which results in a positive peak in the curves. An increase in activation energy (E_α) is observed with extent of conversion.

Keywords Chitosan · Crosslinker · IPNs · Curing · Thermal analysis

Introduction

Nowadays, natural polymers are used extensively for their rich resources and low costs. Natural polymers find many applications [1–8] due to their unique properties, such as nontoxicity, degradability and good biological compatibility. Chitosan is one of such natural polymer, comprising copolymers of glucosamine and *N*-acetylglucosamine. This is obtained by the partial deacetylation of chitin. Chitin, the second most abundant natural polymer after cellulose, is available in crustaceans, insects and fungi [1, 2]. Chitosan has been widely used in vastly diverse fields, ranging from waste management to food processing, medicine and biotechnology [3, 4]. It becomes an interesting material in pharmaceutical applications [1] due to its biocompatibility, biodegradability [5] and low toxicity [6]. Chitosan has free amine as well as hydroxyl groups, which can be modified to obtain different chitosan derivatives. The application of chitosan based IPNs/semi-IPNs in the field of pharmaceutical applications have received a great deal of attention in recent years as reported in the literature [6–9].

Chemical crosslinking is an important method to control drug release from diffusion-controlled polymeric drug delivery matrices. Modulated drug release rates can be achieved by varying the crosslink density of the matrices. Several hydrogels, proteins and polysaccharides have been crosslinked using a number of crosslinking agents to manipulate the diffusion of an entrapped active agent/drug from such polymeric matrices [10–12]. Crosslinking agents, such as glutaraldehyde, formaldehyde, terephthaloyl chloride, epichlorohydrin, dicyclohexyl carbodiimide, 2,3-butanedione, etc., have been extensively used for crosslinking drug delivery matrices/IPNs derived from proteins and polysaccharides. Many processes have been used for crosslinking of chitosan in the literature [13–15], but the easiest and cheapest way is the formation of Schiff base between the aldehyde functional group of glutaraldehyde (the crosslinking agent) and the amine group of chitosan. The curing reaction results in the formation of imine linkages between chitosan, glutaraldehyde and alanine. Chitosan and amino acids (glycine and alanine) are crosslinked with glutaraldehyde to form semi-IPN for controlled release of Chlorpheniramine Maleate (CPM) drug [16, 17]. Alanine is attached in the form of pendent to

K. Kumari · P. P. Kundu (✉)
Department of Chemical Technology, Sant Longowal Institute of Engineering and Technology, Longowal 148106, India
e-mail: ppk923@yahoo.com

K. K. Raina
Liquid Crystal Group, Material Research Laboratory, School of Physics and Material Science, Thapar University, Patiala 147 004, India

the crosslinked long chitosan chains [17] and acts as spacer in the semi-IPN.

Differential scanning calorimetry (DSC) is widely used for the curing purpose because of its experimental convenience and speed of operation [18, 19]. DSC is a thermal analysis technique for recording the heat necessary to establish a zero temperature difference between a substance and a reference material, which are subjected to identical temperature programs in a heating or cooling environment at a controlled rate. The recorded heat flow gives a measure of the amount of energy absorbed or evolved in a particular physical or chemical transformation. The establishment of cure kinetics provides the scientist or process control engineer with valuable information that can be used to optimize processing conditions or to predict the shelf life of the drug vehicle.

The purpose of present study is to ascertain the mechanism of curing and to find out the activation energy as a function of conversion of the crosslinking process through DSC. This will serve as a useful tool in optimization of drug release through crosslinked chitosan–alanine semi-IPNs.

Experimental

Materials and methods

Chitosan (total nitrogen: 7% minimum, percentage of deacetylation 80%; ignition residue (sulfate): <2% and loss on drying <15%) was supplied by Tokyo Kasei Organic Chemicals, Japan and used as received. Chlorpheniramine Maleate (CPM) ($C_{16}H_{19}ClN_2C_4H_4O_4$) was received as a gift sample from Japson Pharmaceuticals Ltd. Sangrur, India. Glutaraldehyde ($C_5H_8O_2$) (MW = 100.11) 25% aqueous, acetic acid and L-alanine ($CH_3CH(NH_2)COOH$) (MW = 89.09) were purchased from CDH (New Delhi, India) and were of analytical grade.

Calorimetric measurements were carried out by differential scanning calorimetry (DSC). The samples were prepared by mixing the known quantities of chitosan, alanine, drug and glutaraldehyde at room temperature. The glutaraldehyde was added just to prepare the uniform mixture of the constituents. The composition and designation of the samples are given in Tables 2, 3 and 4. The prepared samples were transferred immediately to aluminum pan, weighed from 3 to 5 mg and placed in DSC for thermal analysis.

All DSC studies of curing behavior were performed with a DSC L63 LINSEIL differential scanning calorimeter. Prior to DSC runs, the temperature and heat were calibrated using indium and zinc standards. The sealed aluminum pan containing the sample was placed in DSC cell and heated according to the program of constant heating rate. The measurements were conducted under nitrogen atmosphere. Tests were performed in a dynamic mode at various heating rates over a temperature range of 30–200 °C. The heating rates used in the different scans were 3, 5, 7 and 10 °C/min. The heat of cure was determined from the peak area under the cure exotherm.

Experimental design

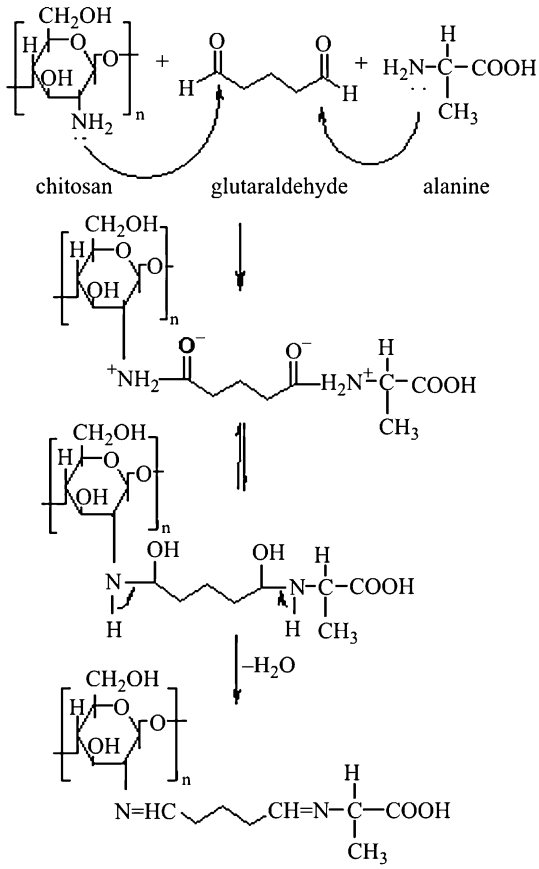
In the first type of scanning, the DSC experiments were carried out to study the effect of concentration of chitosan on the curing of chitosan and alanine at heating rate of 5 °C/min. A second type of scanning run was performed on the samples having equal composition of chitosan and alanine with a varying concentration of crosslinker to study the effect of concentration of crosslinker on curing at a constant heating rate of 5 °C/min. In the third type of scanning, samples having fixed concentration of crosslinker with varying proportions of chitosan/alanine (3/7, 5/5 and 7/3) were cured. The varying heating rates from 3 to 10 °C/min were applied to the samples in order to see the effect of rate of heating on curing and in that process to calculate the activation energy of curing. In all the DSC experiments, a fixed amount of drug (100 mg) was added in order to utilize the resultant information for controlled drug release studies through semi-IPN.

Mechanism of crosslinking reaction

Crosslinking is the process of chemically joining of two molecules by a covalent bond. Glutaraldehyde has two aldehyde groups, separated by a flexible chain of three methylene bridges (OHC–$(CH_2)_3$–CHO). The mechanism of crosslinking of chitosan and alanine through glutaraldehyde is shown in Scheme 1. The curing reaction among three components, chitosan–glutaraldehyde–alanine can be described by a two step kinetic model. Imine linkages (–C=N–) are formed among chitosan–chitosan and chitosan–alanine molecules through glutaraldehyde.

Results and discussion

Differential scanning calorimeter (DSC) is used to study the kinetics/thermal characteristics of curing of chitosan and alanine by glutaraldehyde. It is observed that the crosslinking of chitosan–alanine is an exothermic process, which results in a positive peak in the DSC curve. These curves are used to calculate the enthalpy of cure by integrating the peak corresponding to a transition. The characteristic points of DSC curves are summarized in Tables 2, 3 and 4.



Scheme1 Mechanism of curing of chitosan and alanine with glutaraldehyde

Effect of presence of bound water in samples

Glutaraldehyde in water solution is used for crosslinking of chitosan and alanine. So, all the samples with glutaraldehyde contain more than 50% of water. Thus, it is required to assess the interaction between water and drug carrier. Thermal analysis is performed to assess the interaction of water with chitosan and alanine at a heating rate of 5 °C/min. DSC scans of the samples as per Table 1 are shown in Fig. 1. DSC analysis of chitosan–water (W1) shows a significant transition band in the range between 30 and 96 °C, which is due to dehydration of loosely bound water molecules. In DSC graph of alanine–water (sample W2), the transition band due to loss of water molecule is towards lower temperature range i.e. 32–65.3 °C. This may be due to the fact that the water molecule is more strongly bound

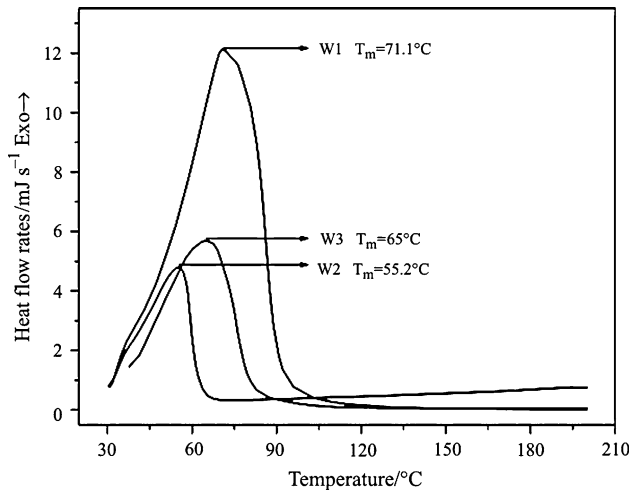


Fig. 1 DSC plots showing the effect of presence of water during curing at a heating rate of 5 °C/min (W1, chitosan–water; W2, alanine–water; and W3, chitosan–alanine–drug–water)

to chitosan in comparison to alanine. The water retention property of chitosan is more due to its hydrophilic nature. This interaction of chitosan–water molecules is reduced in sample W3, due to the presence of equal amount of alanine. More over, alanine is a low molecular mass compound as compared to chitosan and has a higher C:O ratio, as a result of which, the water evaporation peak appeared at 55.2 °C (sample W2). When both of chitosan and alanine along with drug are used (sample W3), the dehydration peak is observed at an intermediate temperature of 65 °C. Although, the same amount of water (3.7 g) is present in all of the samples, the observed variation in peak area is believed to be due to water association with chitosan and alanine. When glutaraldehyde is used for the preparation of semi-IPNs, similar effect of bound water is expected to be present in subsequent DSC runs.

Effect of concentration of chitosan

In Table 2, DSC results regarding the influence of concentration of chitosan for a fixed concentration of glutaraldehyde are reported. Typical non-isothermal DSC spectra of chitosan–alanine samples along with curatives in the temperature range of 30–200 °C are illustrated in Fig. 2. The DSC curves of curing of chitosan and alanine with glutaraldehyde reflect the curing process. The curing peaks

Table 1 DSC results showing the effect of bound water on curing at a constant heating rate of 5 °C/min

Designation	Chitosan/mass %	Alanine/mass %	Drug/g	Distilled water/g	Maxi. peak temp./°C	Enthalpy of transition/J g^{-1}
W1	100	–	–	3.7	71.1 ± 0.1	711.74 ± 0.7
W2	–	100	–		55.2 ± 0.2	190.53 ± 0.3
W3	50	50	0.1		65.0 ± 0.2	325.13 ± 0.5

Table 2 DSC results showing the effect of concentration of chitosan on curing of chitosan–alanine at a constant heating rate of 5 °C/min

Designation	Chitosan/mass %	Alanine/mass %	Drug/g	Glutaraldehyde (25%)/g	Maxi. peak temp./°C	Enthalpy of curing peak/J g^{-1}
A1	100	0.0	0.1	3.7	75.1 ± 0.5	1637.6 ± 0.4
A2	70	30			65.6 ± 0.3	417.34 ± 0.7
A3	50	50			63.8 ± 0.1	344.30 ± 0.3
A4	30	70			58.7 ± 0.2	303.89 ± 0.2

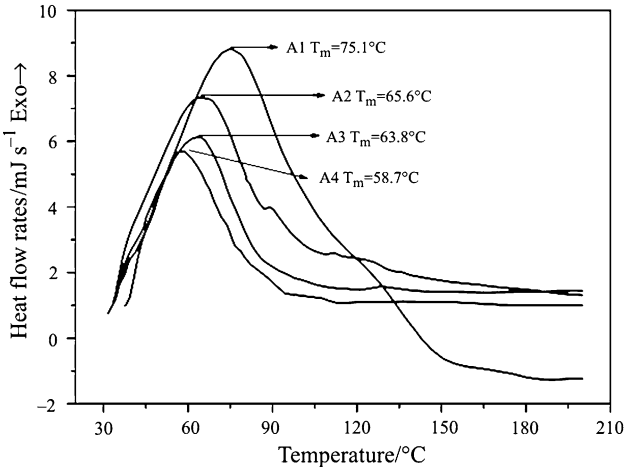


Fig. 2 DSC plots indicating the effect of concentration of chitosan on crosslinking of chitosan and alanine (mass % of chitosan in mixture: 100% (A1); 70% (A2); 50%, (A3); and 30% (A4))

in the curves are also superimposed with the dehydration peaks. As the same concentration of glutaraldehyde is present in these samples, the dehydration peak area will be equal. Thus, one can discuss comparative curing amongst these samples. It is observed that the curing starts from the beginning of the scanning in all of the samples. The curing of chitosan and alanine with glutaraldehyde is a fast reaction, as the process of curing starts immediately after the mixing of the constituents. In case of sample A1, the curve line rises to a maximum peak temperature, 75.1 °C and the subsequent fall shows the completion of curing reaction. As the relative concentration of chitosan decreases, the height and width of curing peak decreases and the maximum peak temperature shifts towards a lower temperature for the given heating rate of 5 °C/min. The reason of this shifting of peak temperature may be due to the fact that as the concentration of chitosan decreases, the effective number of amino groups available to react with the aldehyde group of glutaraldehyde decreases. Due to the decrease in concentration of amino groups, the curing reaction completes at faster rate and thus, the curing peaks are observed at relatively lower temperature as compared to pure chitosan. In other words, as the concentration of chitosan increases, the number of unreacted amino groups increases. The curing reaction takes more time to complete, hence the rate of reaction slows down and forcing the curing peak to shift towards right, a higher end of temperature in the figure. With a decrease in the relative concentration of chitosan, the enthalpy of cure decreases, due to the limited extent of reaction between the amino group of chitosan and aldehyde group of crosslinker.

As the area under the peak decreases with the shifting of curing towards lower temperatures, the enthalpy of curing process decreases with a decrease in chitosan concentration. It is observed that in the absence of alanine as in sample A1, the enthalpy is 1637.56 J g^{-1} which decreases to 303.89 J g^{-1}, for sample A4 having maximum concentration of alanine.

Effect of concentration of crosslinker

To know the effect of concentration of crosslinker on curing of chitosan–alanine, the curing experiments are performed with varying concentration of glutaraldehyde (3.13, 6.25, 12.5 and 25%). The composition of samples is reported in Table 3 and the effect of percentage of crosslinker on the curing of chitosan and alanine for the uniform heating rate of 5 °C/min is shown in Fig. 3. The presence of varied concentration of glutaraldehyde solution (aqueous) leads to the presence of varied dehydration peak area. Thus, apparently, comparison of curing peak area with variation in concentration of curative is difficult. But, the higher enthalpy (peak area) of the sample, B1 compared to sample, W3 indicates the effect of curative. So, one can compare the effect of concentration of curative as the total mass of the crosslinker is fixed (i.e. 3.7 g). The curing peak is observed at a temperature of 63.8 °C for the sample B1 having maximum concentration of crosslinker**.** As the concentration of glutaraldehyde decreases, the number of aldehyde groups available for the crosslinking with chitosan and alanine decreases, which reduces the extent of reaction. Thus, more time is taken by the sample to be completely cured and the curing peaks shift towards a higher temperature.

As the concentration of glutaraldehyde increases, the exothermic peak shifts to a lower temperature. In sample B4, having lowest concentration of curing agent, the rate of

Table 3 DSC results showing the effect of concentration of curing agent on curing of chitosan–alanine at a constant heating rate of 5 °C/min

Designation	Chitosan/ mass %	Alanine/ mass %	Drug/g	Glutaraldehyde (3.7 g)/%	Maxi. peak temp./°C	Enthalpy of curing peak/J g^{-1}
B1	50	50	0.1	25	63.8 ± 0.4	344.30 ± 0.8
B2				12.5	66.7 ± 0.6	423.69 ± 0.4
B3				6.25	72.1 ± 0.3	603.57 ± 0.7
B4				3.13	79.1 ± 0.5	1051.5 ± 0.6

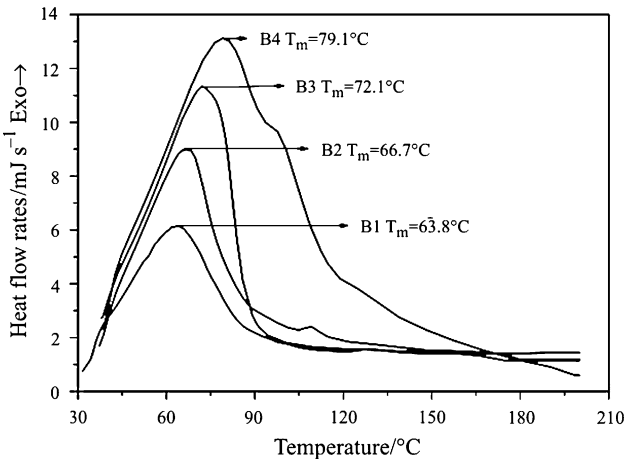


Fig. 3 DSC plots indicating the effect of concentration of crosslinker on curing of chitosan and alanine (mass % of crosslinker in mixture: 25% (B1); 12.5% (B2); 6.25% (B3); and 3.13% (B4))

crosslinking is less or it takes more time to be completely cured and hence, the curing peak shifts towards a higher temperature i.e. 79.1 °C. This shift of peak temperature is also due to the fact that as the concentration of crosslinker decreases the amount of bound water increases in the samples. This increased amount of water results in stronger interaction between chitosan and water molecules and thus shifts the reaction peak towards a higher temperature. The enthalpy of curing increases with the decrease in concentration of crosslinker due to the requirement of higher energy to complete the cure reaction.

Effect of rate of heating

DSC curves are obtained to know the effect of rate of heating on cuing reaction. The composition and the total enthalpy of cure reaction measured as a function of heating rate is reported in Table 4 and DSC plots are illustrated in Figs. 4, 5 and 6. The curing process is influenced by the rate of heating. The reaction maxima shift to a higher temperature with increasing heating rates having the same composition of constituents (samples C, D and E). Further, it is observed that the enthalpy of curing as well as area under the curve increases for all the samples having different composition of chitosan.

Activation energy of chemical curing

Crosslinking of chitosan–glutaraldehyde–alanine is a complex phenomenon due to simultaneously occurrence of multiple-step curing. It is generally believed that the activation energy (E) and frequency factor (A) remain same for

Table 4 DSC results showing maximum exothermic peak temperatures of different samples of chitosan–alanine at various heating rates

Designation	Chitosan/mass %	Alanine/mass %	Drug/g	Glutaraldehyde (25%)/g	Maxi. peak temp./°C	Rate of heating/°C/min	Enthalpy of curing peak/J g^{-1}
C1	30	70	0.1	3.7	44.5 ± 0.7	3	169.36 ± 0.9
C2					58.7 ± 0.8	5	303.89 ± 0.3
C3					68.8 ± 0.4	7	525.40 ± 0.6
C4					78.9 ± 0.3	10	590.23 ± 0.5
D1	50	50	0.1	3.7	50.4 ± 0.2	3	187.68 ± 0.6
D2					63.8 ± 0.9	5	344.30 ± 0.2
D3					71.6 ± 0.6	7	535.93 ± 0.3
D4					79.6 ± 0.5	10	632.87 ± 0.5
E1	70	30	0.1	3.7	52.9 ± 0.3	3	192.25 ± 0.4
E2					65.6 ± 0.5	5	417.34 ± 0.7
E3					72.7 ± 0.2	7	611.96 ± 0.3
E4					81.1 ± 0.8	10	837.92 ± 0.5

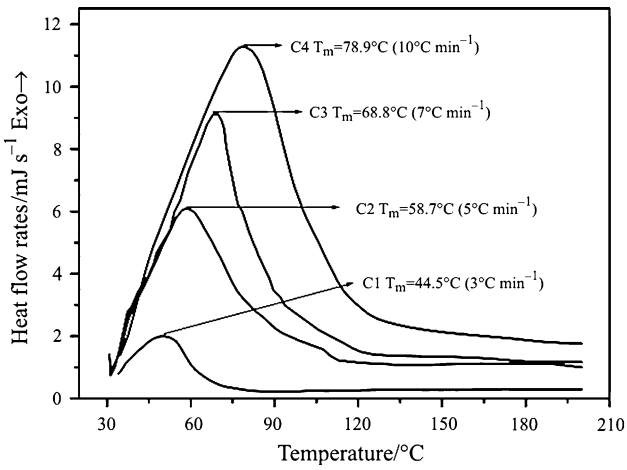


Fig. 4 DSC plots of cross linking of chitosan and alanine (3/7 mass ratio) at various heating rates: (C1) 3 °C/min, (C2) 5 °C/min, (C3) 7 °C/min and (C4) 10 °C/min

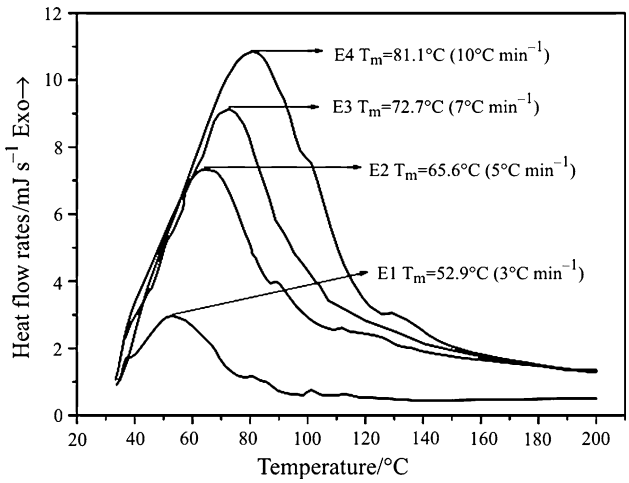


Fig. 6 DSC plots of cross linking of chitosan and alanine (7/3 mass ratio) at various heating rates: (E1) 3 °C/min, (E2) 5 °C/min, (E3) 7 °C/min and (E4) 10 °C/min

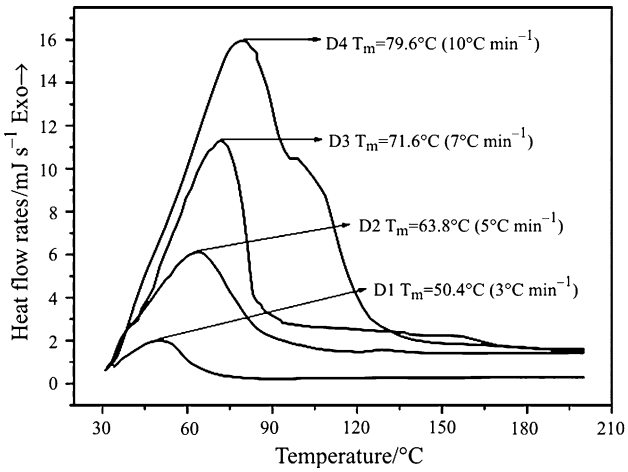


Fig. 5 DSC plots of cross linking of chitosan and alanine (5/5 mass ratio) at various heating rates: (D1) 3 °C/min, (D2) 5 °C/min, (D3) 7 °C/min and (D4) 10 °C/min

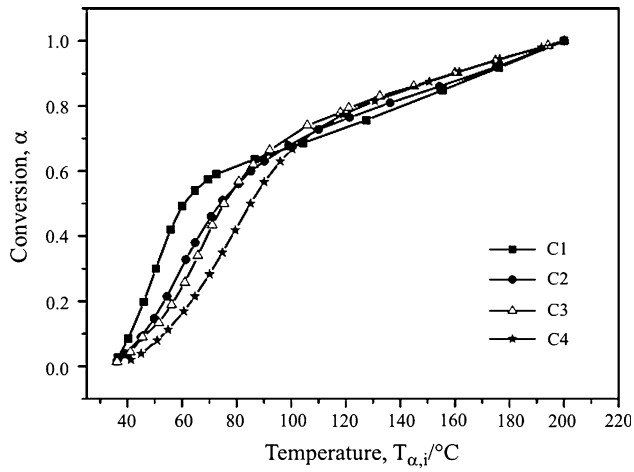


Fig. 7 The conversion-temperature curves for curing of chitosan–alanine (3/7 mass ratio) by glutaraldehyde, obtained at various heating rates. For the details of the heating rates see Fig. 4

one step reaction; however, it is reported [20–22] that in multistep reactions, these kinetic parameters may vary with the progress of the reaction (α). If the process involves several steps with different activation energies, the relative contribution of these steps to over all reaction rates will vary with both temperature and extent of conversion [23]. This variation can be determined by isoconversional methods. Vyazovkin and Sbirrazzuoli [24] explained the application of isoconversional methods to the curing reactions involving complex kinetics. The isoconversional methods employ multiple temperature programs (i.e. different heating rates and temperatures) to obtain data for varying heating rates at a constant extent of conversion [23].

For non-isothermal conditions when the temperature is raised at a constant heating rate β, Doyle [25] gives the following relation;

$$\ln(\beta i) = \text{Const.} - \frac{1.05E\alpha}{\text{RT}\alpha, i} \quad (1)$$

which is used in most popular isoconversional methods of Flynn and Wall [26] and Ozawa [27]. It involves measuring temperatures corresponding to fixed values of conversion, α from experiments at different heating rates, β and plotting ln (β_i) against $1/T_i$. The slopes of such plots give $-E_\alpha/R$, where R; is the gas constant and E_α; is the activation energy at a particular value of extent of conversion, α.

The relationships between the extent of conversion and temperature for different heating rates and with varying

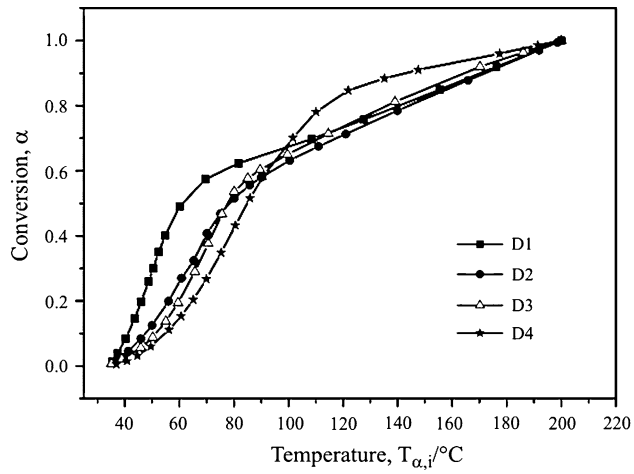


Fig. 8 The conversion-temperature curves for curing of chitosan–alanine (5/5 mass ratio) by glutaraldehyde, obtained at various heating rates. For the details of the heating rates see Fig. 5

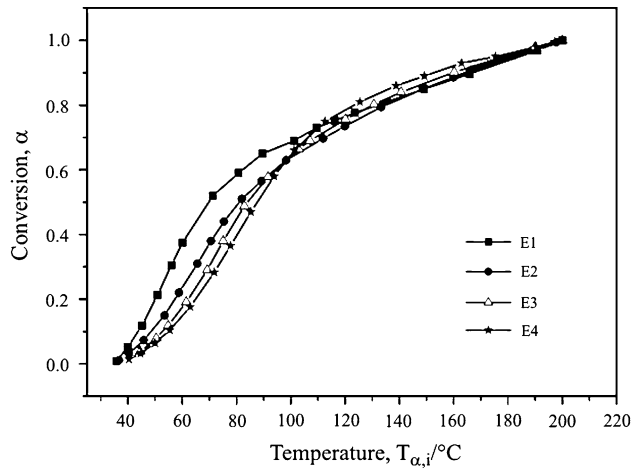


Fig. 9 The conversion-temperature curves for curing of chitosan–alanine (7/3 mass ratio) by glutaraldehyde, obtained at various heating rates. For the details of the heating rates see Fig. 6

composition of chitosan are obtained from Figs. 4, 5 and 6 and are shown in Figs. 7, 8, 9. The dependence of activation energy on the extent of conversion is determined by Eq. 1 and is reported in Fig. 10. It is observed that the activation energy, E_α increases with extent of conversion, α. As the reaction progresses the molecular mass of the crosslinked polymer increases. The stepwise crosslinking process results in a decrease in molecular mobility and hence the curing kinetics is controlled by diffusion of reactants at latter stage. Due to the decrease in the mobility of the crosslinked chains, the penetration of the crosslinker becomes difficult and therefore, higher amount of energy is required for further curing of the reactants. However, the increase in activation energy is moderate up to the conversion, $\alpha = 0.4$, followed by a fast increase for all cases as depicted in Fig. 10.

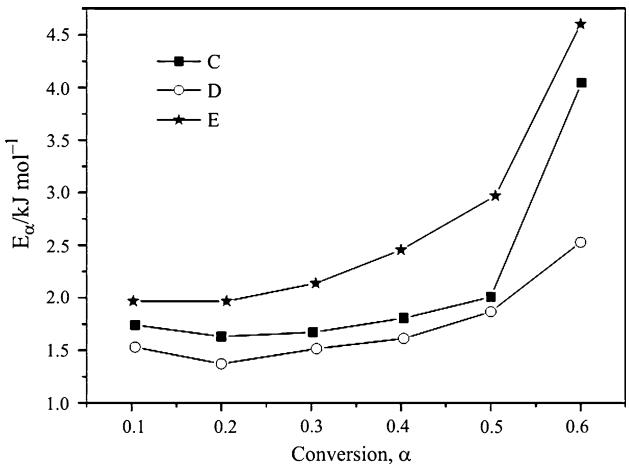


Fig. 10 The E_α dependencies obtained for curing of chitosan–alanine by glutaraldehyde for different compositions of chitosan/alanine (C: 3/7, D: 5/5 and E: 7/3) by isoconversional method (Eq. 1)

Conclusions

Thermodynamic properties of crosslinking of chitosan and alanine with glutaraldehyde having various proportionate mixtures are studied using the technique of differential scanning calorimetry (DSC). The concentration of chitosan and crosslinker has enormous effect on the cure kinetics. The total enthalpy of cure reaction increases with an increase in the concentration of chitosan and a decrease in the concentration of glutaraldehyde. Experiments are performed to check the effect of rate of heating on cure kinetics at four different heating rates (3, 5, 7 and 10 °C/min). The increasing rate of heating causes the enthalpy of curing (peak area) to increase. Flynn, Wall and Ozawa analysis of non-isothermal measurements, are used to determine the activation energy for multistep crosslinking. The use of an isoconversional method for the calculation of activation energy results in an increase in activation energy with the extent of conversion.

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