ACS Sustainable Chemistry & Engineering

Research Article

pubs.acs.org/journal/ascecg

Kinetics Study of Curing Epoxy Resins with Hydrolyzed Proteins and the Effect of Denaturants Urea and Sodium Dodecyl Sulfate

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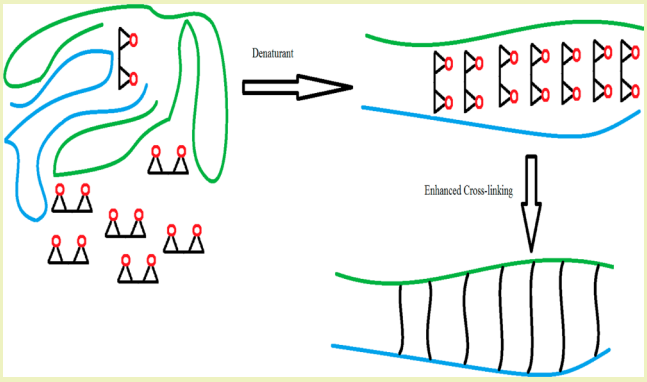
ABSTRACT: The primary goal of this study was to determine the effect of two protein denaturants, urea and sodium dodecyl sulfate (SDS), on the apparent activation energy of cross-linking bisphenol A diglycidyl ether (DGEBA) with hydrolysate of waste animal proteins. Nonisothermal differential scanning calorimetry was used to measure the apparent activation energy of the reactions. The use of SDS resulted in a marked reduction in activation energy, comparable to the reduction in activation energy when a catalyst for epoxy rings, triethylamine (TEA), was used. The addition of urea slightly increased the activation energy. The heat of reaction increased in the presence of SDS because more reactive sites were made available for curing. This work demonstrates the use of SDS as a protein denaturant additive was an energetically efficient alternative to higher degrees of protein hydrolysis for subsequent curing of DGEBA.



KEYWORDS: *Differential scanning calorimetry, Activation energy, Thermosetting polymers*

INTRODUCTION

Cross-linking of proteins with epoxy resins has been studied for well over 20 years. Epoxy resins react by accepting a proton to the epoxy ring to form a hydroxyl group. Therefore, they can react with primary and secondary amines (converting them into secondary and tertiary amines, respectively), hydroxyl groups (converting them into ethers), and carboxylic groups (converting them into esters). Sulfhydryl groups similarly react with epoxy rings.[1] These five groups of reactants are abundantly found in proteins. Because no gas byproducts are released from the reaction, curing exhibits no pressure dependence.

As an alternative to glutaraldehyde, epoxy resins have been proposed in order to improve properties of the final product. Among the cited examples is better resistance to calcification in bioprosthetic materials.[2,3] Collagen cross-linking with 1,4-butanediol diglycidyl ether was reported to reduce degradation by enzymatic activity of collagenase.[4] In a recently published study, we employed differential scanning calorimetry to investigate the curing kinetics of bisphenol A diglycidyl ether (DGEBA) with protein-rich biomass waste materials derived from beef rendering byproducts via hydrolysis and extraction.[1] Hydrolysis of proteins is generally desirable for subsequent reactivity because enzymes are destroyed, thereby avoiding undesirable enzymatic activity in proteins, and the native structure (α-helices and β-sheets) is converted into a denatured state (random coils).[5] Reactive sites are more accessible in denatured proteins than in proteins in their native structure.[6] Hydrolysis is also an important pretreatment to render hazardous protein sources safe to handle prior to value recovery in subsequent modifications. For example, beef byproducts that may contain prions, the causative agent of mad cow disease, must be hydrolyzed in order to inactivate the prions.[7] On the other hand, an increased degree of hydrolysis (at increased temperatures) consumes more energy and produces smaller molecules of hydrolyzed proteins. Reduced molecular size can be detrimental for applications such as adhesion,[6] coagulation,[8] and flocculation,[9] for which larger molecules are more desirable, albeit in their extended state. Even when hydrolysis is sufficient to completely break down α-helices and β-sheets and form random coils, proteins can still coil into structures of reduced surface area in solvents to avoid certain types of interactions, e.g., hydrophobic interactions in aqueous solutions. Therefore, the use of an adequate denaturant is still important to enhance cross-linking reactions involving hydrolyzed proteins.

The utilization of denaturants instead of increased hydrolysis temperatures can offset the impact of increased energy and the larger size of hydrolyzed protein molecules obtained at moderate levels of hydrolysis. The aim of this study was to investigate the effect of denaturing compounds, urea and sodium dodecyl sulfate (SDS), on the kinetics of curing

Received: August 26, 2013
Revised: September 21, 2013
Published: October 2, 2013

DGEBA with hydrolyzed proteins and to compare the results to the effect of triethylamine (TEA), a well-known epoxy ring-opening catalyst. TEA was selected as a catalyst because it lacks functional groups known to be reactive with DGEBA. As a tertiary amine, it is only expected to accelerate the reaction by opening the epoxy ring of DGEBA in the initial stages of curing, which is why TEA is generally considered an initiator.[10] As TEA does not react, its concentration is expected to remain constant for the duration of curing. Additionally, TEA is not expected to compete with hydrolyzed protein molecules, an important factor for the correct analysis of results. Urea and SDS are protein denaturants. As an example of their prior use in value-added applications based on protein-based materials, urea and SDS have been shown to improve adhesive strength and water resistance in wood adhesion applications by uncoiling protein molecules, thereby increasing wood−protein interactions.[6] SDS and urea are known to disrupt protein−protein interactions.[11] As intra- and inter-molecular protein interactions are reduced, more reactive sites may become available for cross-linking with DGEBA. Diffusion of DGEBA molecules can also be expected to increase in the presence of denaturants. This work demonstrated, in quantitative terms, an energy-saving approach to the chemical cross-linking of protein feedstock recovered from waste agricultural streams into value-added polymeric materials.

EPOXY CURING BY DIFFERENTIAL SCANNING CALORIMETRY

The DSC nonisothermal technique was used in this work to obtain the curing thermal data. When cross-linking is studied with a calorimetric instrument, released energy is recorded for the duration of the reaction. The reaction rate, $d\alpha/dt$, can be expressed as $k(T)f(\alpha)h(P)$, where $k(T)$ is the temperature-dependent rate constant, α is the extent of reaction, $f(\alpha)$ is a function of the extent of reaction, and $h(P)$ is the function of pressure dependence of the reaction and is often important for reactions involving gases as reactants and/or byproducts.[12] The term can be dropped for this study because no gases are involved in the reaction. The reaction rate can then be expressed as

$$d\alpha/dt = A_o \exp(-E_a/RT) f(\alpha) \quad (1)$$

where E_a is the activation energy, A_o is the frequency factor, R is the universal gas constant, and T is the temperature. For constant heating rate scans in DSC, $d\alpha/dt$ can be expressed as $\beta_i\, d\alpha/dT$, where is β_i the heating rate. So a plot of $\ln[(\beta_i\, d\alpha/dT)/f(\alpha)]$ vs $1/T$ for constant values of α and an adequate model for $f(\alpha)$ is expected to yield a straight line. The slope is $-E_a/R$ and the y-intercept is $\ln A_o$. The reaction model and its parameters are selected such that the correlation coefficient is maximized.[12,13] Curing epoxy resins generally exhibits autocatalysis, which can be adequately modeled by using the Sestak−Berggren model.[1,12−14] The conversion function, $f(\alpha)$, has the form $\alpha^m(1-\alpha)^n[-\ln(1-\alpha)]^p$. The truncated form, for $p = 0$, can be simplified further by adding a constraint that because reactions rarely have an order exceeding 2, $m + n = 2$, and a plot of $\ln[(\beta_i\, d\alpha/dT)/\alpha^{2-n}(1-\alpha)^n]$ vs $1/T$ yields a straight line.[1,13] The overall order of reaction $(m + n)$ for epoxy−amine reactions is 2, but for epoxy−hydroxyl reactions, the sum is closer to 1.5.[15] Vyazovkin and Sbirrazzuoli have noted that for unconstrained fits, the sum has been found to exceed 2.5 in some cases.[16] For cases where the constraint $(m + n = 2)$ does not lead to a good fit, a multiple linear regression as described by Jubsilp et al. can be used to determine values for m and n.[17]

The isoconversional method is another useful method to probe the progress of the reaction at different conversion rates and provide additional insight into the reaction as the degree of curing increases. Activation energy at different extents of reaction is obtained from the following relationship

$$\ln(\beta_i/T_{\alpha,i}^{\,2}) = \text{Constant} - E_\alpha/\mathrm{RT}_\alpha \quad (2)$$

where $T_{\alpha,i}$ is the temperature at which α is reached for each heating rate, β_i, and E_a is the activation energy at α.[12]

EXPERIMENTAL SECTION

Instrumentation. Thermal Analysis Instruments, DSC 2910, routinely calibrated with indium and zinc standards, was utilized for our work. Aluminum hermetic sample pans and lids were used for experiments. The lid was inverted and sealed on top of the pan. Sample and reference pans were manually placed in the DSC cell. Curing was carried out by heating samples from room temperature to 300 °C at varying rates (5, 10, 15, and 25 °C min^{-1}) under nitrogen. Samples in the mass range of 2−5 mg for curing with the additives urea and TEA were found to be appropriate. For scans where SDS was the additive, samples of no more than 1 mg were found to be appropriate. This is because at a larger sample size, the material expanded outside the sealed pan, and results were not reproducible.

Materials. Bisphenol A diglycidyl ether (Araldite 506, epoxide equivalent weight 172−185 Da), triethylamine (99.5%), and sodium dodecyl sulfate (ReagentPlus 98.5%) were purchased from Sigma Aldrich. Urea (U-15 ACS) was purchased from Fisher Scientific Co. Protein hydrolysate was obtained via thermal hydrolysis (at 220 °C) of SRM obtained from Sanimax Industries, Inc. (Montreal, QC, Canada). Protein hydrolysis and recovery by water extraction were carried out as outlined in our previous work.[1,18] Water-extracted protein hydrolyzed at 220 °C was used for this study (PEP220). Molecular weight was concentrated between 1.4 and 3.5 kDa. As our earlier work demonstrated,[1] curing kinetics with salt-extracted samples were difficult to interpret due to the ionic interactions with reactive groups of protein hydrolysate. Additionally, the higher hydrolysis temperature led to lower molecular weight (<9 kDa), and therefore, improved miscibility with DGEBA.

Sample Preparation. DGEBA was first mixed with the additive (SDS or TEA) and stirred at room temperature to disperse the additive throughout the epoxy resin and ensure homogeneity. Hydrolyzed protein was then added to the DGEBA-additive mixture. For urea, which is not readily soluble in DGEBA, urea was crushed into small particles and then added to DGEBA. The mixture was then heated at 60 °C until urea was dissolved in DGEBA, prior to adding the hydrolyzed protein. For all three sets, the mass ratio of DGEBA to hydrolyzed protein was 3:2. The amount of added TEA was 1% by mass of the final epoxy−protein mass. The amounts of urea and SDS used were the molar equivalent to 1% TEA (2.9% for SDS and 0.6% for urea).

RESULTS AND DISCUSSION

All plots for conversion against time for any heating rate exhibited the autocatalytic model. An example is shown in Figure 1. The truncated Sestak−Berggren model, $f(\alpha) = \alpha^m(1-\alpha)^n$, can adequately model autocatalytic reactions.[1,12−14] The model can be simplified further by adding a constraint that because reactions rarely have an order exceeding 2, $m + n = 2$, and a plot of $\ln[(\beta_i\, d\alpha/dT)/\alpha^{2-n}(1-\alpha)^n]$ vs $1/T$ yields a straight line from which the activation energy and $\ln A_o$ are calculated from the slope and y-intercept, respectively. The reaction order, n, is selected such that the correlation coefficient, r, is at its maximum value.[1,13] An example is shown in Figure 2.

dx.doi.org/10.1021/sc400316v | ACS Sustainable Chem. Eng. 2014, 2, 282−287

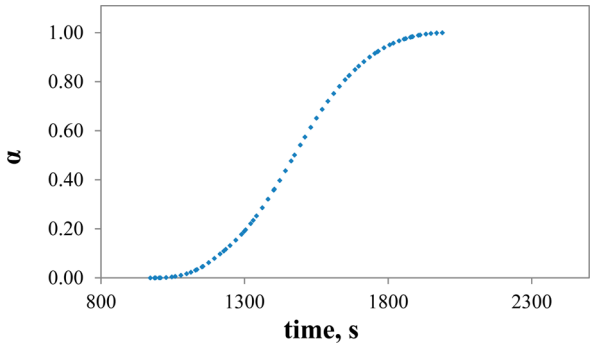


Figure 1. Conversion rate as a function of time for 3:2 DGEBA to PEP220 mass ratio at 5 °C/min in the presence of triethylamine.

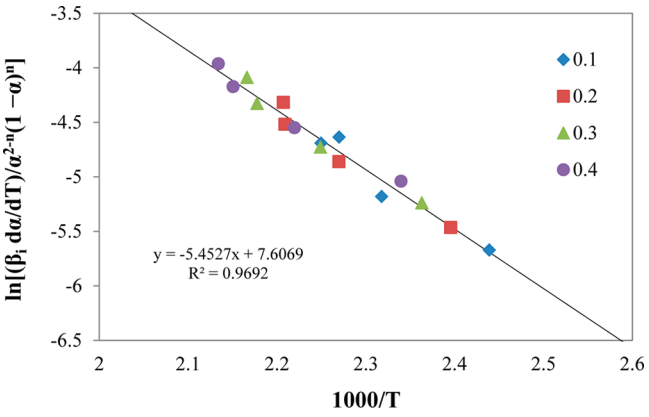


Figure 2. Plot for modified autocatalytic model at different conversions for reaction at 3:2 DGEBA to PEP220 mass ratio in the presence of triethylamine.

Reaction parameters are summarized in Table 1 and are compared with results obtained in an earlier study in which no additives were used.

Table 1. Summary of Results for Frequency Factor, Activation Energy, and Reaction Order Calculated from the Autocatalytic Model for DGEBA Cured with Hydrolyzed Proteins

additive	ln A_o	E_a (kJ mol^{-1})	n	r
no additive (ref 1)	13.393	65.0	1.31	0.986
triethylamine	6.524	41.5	1.50	0.988
sodium dodecyl sulfate	7.406	43.8	1.67	0.986
urea	15.746	75.0	1.65	0.981

Predictably, the use of the initiator TEA has resulted in a significant reduction in the activation energy compared to the curing reaction without any additives. The results for denaturants SDS and urea were contrasting. The addition of SDS also decreased the activation energy, whereas the presence of urea led to a pronounced increase in activation energy. While the effect of SDS demonstrated that denaturing proteins for cross-linking reactions is as important as targeting the reactive arm of epoxy resins, urea addition was counter-productive. One possible explanation for this is that urea amine groups may interact with the epoxy rings (hydrogen bonding or curing) instead of with the hydrolyzed proteins. Epoxy−urea interactions may therefore offset any benefit from potential protein denaturing. On the other hand, our results showed that SDS was effective in disrupting the hydrophobic interactions among the hydrophobic segments of hydrolyzed proteins[11] and possibly also disrupted such interactions with DGEBA's hydrocarbon backbone. This aspect of SDS may have contributed to increased collisions between reactive groups from the hydrolyzed proteins and epoxide ring of DGEBA.

The reaction order increased for all three reactions in which additives were used compared to the value for epoxy-hydrolyzed protein curing. The use of denaturants, though, caused a more significant increase in the reaction order.

The curing of epoxy resins with materials that contain five different reactive groups (primary and secondary amines, hydroxyls, carboxylic acids, and sulfhydryl groups) is a complex reaction, given the presence of hydroxyl and amine reactive groups that have different reaction orders for curing epoxy rings.[15] Nonetheless, kinetic parameters (Table 1) obtained from the truncated Sestak−Berggren model provided simulations that were in reasonable agreement with experimental data (Figures 3−8).

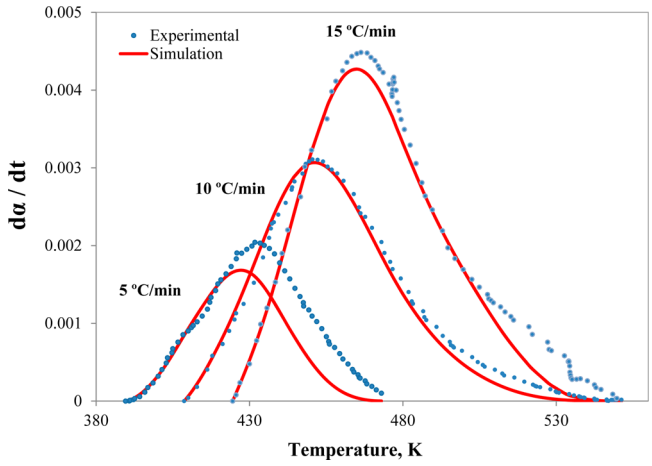


Figure 3. Plot for reaction rate, dα/dt, as a function of temperature for experimental results and model for the reaction of DGEBA−PEP220−TEA at different heating rates.

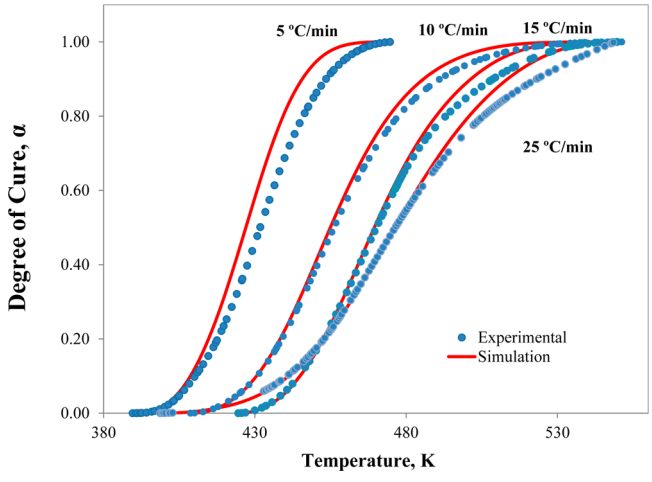


Figure 4. Plot for conversion, α, as a function of temperature for experimental results and model for the reaction of DGEBA−PEP220−TEA at different heating rates.

dx.doi.org/10.1021/sc400316v | ACS Sustainable Chem. Eng. 2014, 2, 282−287

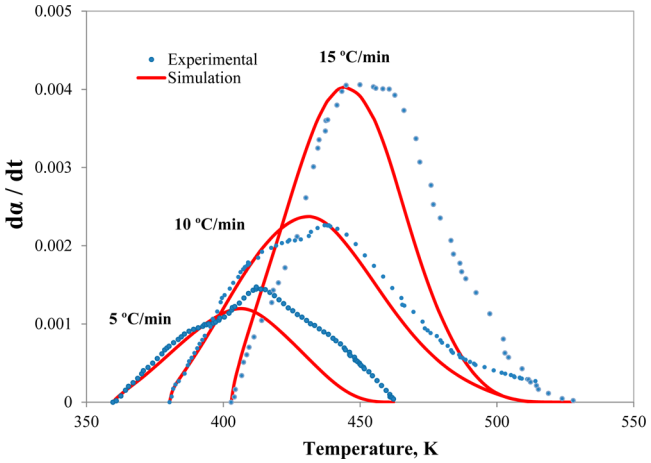


Figure 5. Plot for reaction rate, $d\alpha/dt$, as a function of temperature for experimental results and model for the reaction of DGEBA–PEP220–SDS at different heating rates.

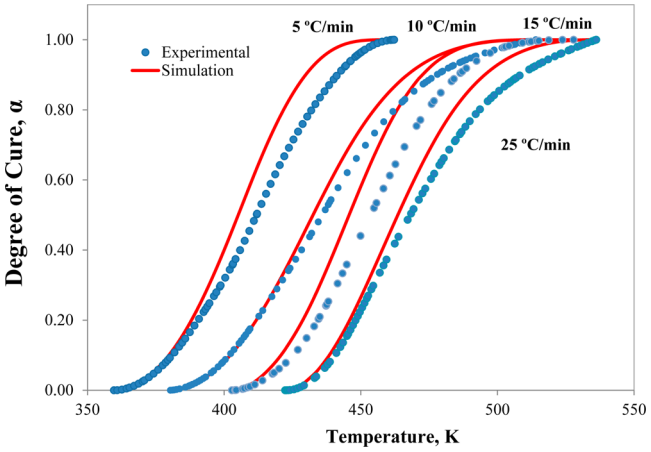


Figure 6. Plot for conversion, α, as a function of temperature for experimental results and model for the reaction of DGEBA–PEP220–SDS at different heating rates.

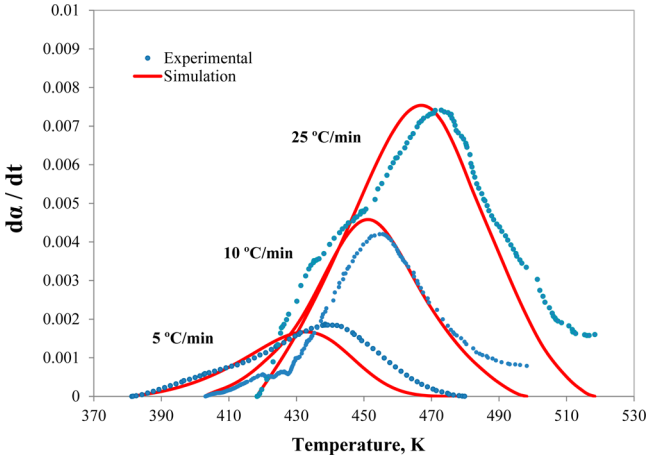


Figure 7. Plot for reaction rate, $d\alpha/dt$, as a function of temperature for experimental results and model for the reaction of DGEBA–PEP220–urea at different heating rates.

The model-free isoconversional method was used to further analyze results. Values for the activation energy and the pre-exponential factor were calculated from eq 2 at increments of 0.05 for degrees of cure in the range from 0.05 to 0.95, and the plots are shown in Figures 9 and 10, respectively.

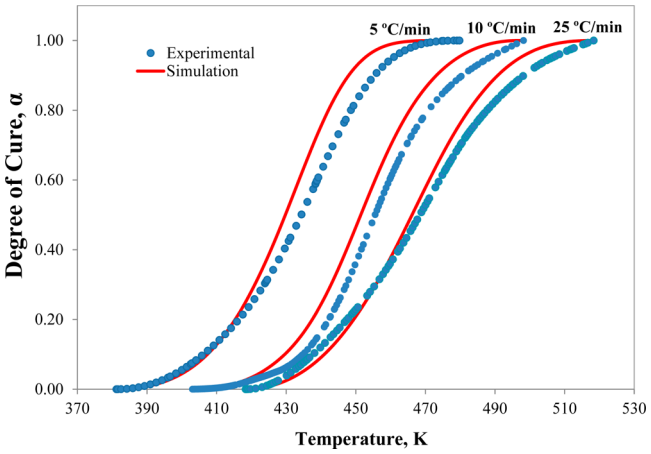


Figure 8. Plot for conversion, α, as a function of temperature for experimental results and model for reaction of DGEBA–PEP220–urea at different heating rates.

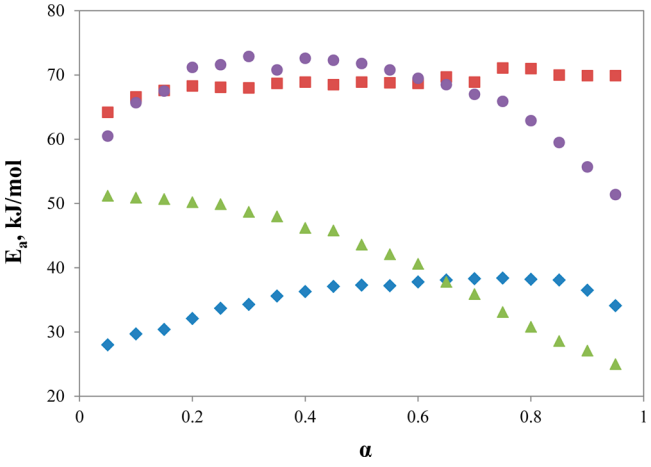


Figure 9. Dependency of activation energy on conversion for DGEBA and PEP220 reaction without additives (red square, ref 1) and in the presence of TEA (green triangle), SDS (blue diamond), and urea (purple circle).

Activation energy values for urea-added curing were slightly higher than values for curing without additives up to conversions of 0.65, remaining nearly constant for the range of 0.1–0.75 and decreasing until reaction completion. Because the amount of urea added to the reaction was rather small (0.6% w/w), had urea reacted with DGEBA, the activation energy should not be consistently higher when compared to the neat system. This result suggests that urea hindered the reaction continuously, making it more likely that there was hydrogen bonding with the epoxy ring oxygen.

SDS-added curing exhibited an activation energy dependency on conversion in contrast to results obtained for curing in the presence of urea. The activation energy slightly increased over the course of the reaction. In fact, activation energy values in the initial stages of the reaction indicated diffusion was the likely rate-determining step. On the basis of this, it may be suggested that hydrolyzed protein denaturing was the predominant process at low degrees of curing. The lack of vitrification as the degree of curing increased for the reaction in

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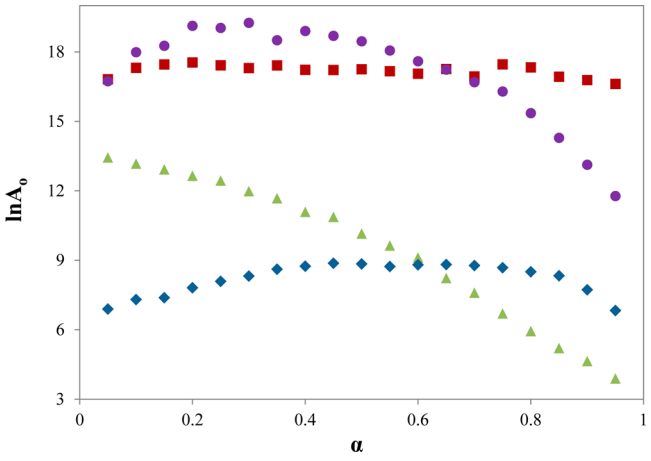

Figure 10. Dependency of ln A_o on conversion for DGEBA and PEP220 reaction without additives (red square, ref 1) and in the presence of TEA (green triangle), SDS (blue diamond), and urea (purple circle).

the presence of SDS may also suggest that the formed gel remained in the rubbery state, not the glassy state in which vitrification is expected to occur,[16] further confirming the role of SDS as a denaturant.

In the presence of an initiator that opens the epoxy ring, the curing of DGEBA proceeded to completion at a high rate up to conversions of 0.5 and then exhibited vitrification at higher conversions as the rate-determining step changes from a chemical-controlled process to a diffusion-controlled process.[12] The activation energy underwent a small decrease as conversion increased up to 0.5, and then a higher rate of activation energy decrease occurred until completion of the curing. The average values for the activation energy obtained from the model-free method were 66.7 ± 6.2 kJ/mol for urea-added curing, 41.4 ± 8.9 kJ/mol for TEA-added curing, and 35.3 ± 3.2 kJ/mol for SDS-added curing. The correlation coefficient, *r*, for isoconversional plots exceeded 0.98 in the conversions range of 0.05−0.65 for urea, 0.2−0.95 for TEA, and 0.05−0.85 for SDS. In agreement with results obtained from the truncated Sestak−Berggren model, addition of the denaturant SDS, but not urea, resulted in a significant reduction in activation energy. This decrease in activation energy was more than obtained by reducing the molecular size of proteins by carrying out hydrolysis at higher temperatures,[1] thereby demonstrating that utilization of a suitable denaturant is a cost-saving alternative to an energy-intensive hydrolysis process in which proteins are subjected to a higher degree of hydrolysis without significantly improving reactivity in subsequent reactions.

Dependencies of ln A_o on conversion (Figure 10) had trends similar to dependencies of activation energy on conversion. The average values for ln A_o obtained from the model-free method were 17.1 ± 2.1 for urea-added curing, 9.5 ± 3.1 kJ/mol for TEA-added curing, and 8.2 ± 0.69 kJ/mol for SDS-added curing.

Heats of reaction, ΔH, were obtained by integrating the exothermic peaks. Values for the three reactions investigated in this work, expressed in terms of 1 mol of oxirane, are listed in Table 2. Heats of reaction in the presence of urea and triethylamine were comparable to results obtained earlier for the curing of DGEBA with hydrolyzed proteins without any additives. When SDS was used, the heat of reaction has increased. Typical heats of reaction for 1 mol of epoxy rings with primary and secondary amines are 83 and 131 kJ/mol, respectively, and 65 kJ/mol with hydroxyl groups.[19] The increase in reaction heat in the presence of SDS further supports earlier findings that denaturation has the potential to allow DGEBA molecules increased access to reactive sites of the hydrolyzed protein. This increase in reaction heat is an indication that more primary and secondary amines cured the epoxy rings instead of the hydroxyl group. When DGEBA has limited reactive sites, subsequent reactions may occur between unreacted epoxy rings and hydroxyl groups that were formed from the curing of epoxy rings. The presence of SDS enhanced DGEBA−protein reactions at the expense of DGEBA−DGEBA reactions.

Table 2. Heats of Reaction for DGEBA Curing Expressed in Terms of 1 mol of Oxirane

additive	ΔH (kJ/mol)
no additive (ref 1)	55.0 ± 9.9
triethylamine	64.3 ± 15.7
sodium dodecyl sulfate	97.5 ± 20.9
urea	60.9 ± 17.7

CONCLUSION

DSC was used to investigate DGEBA curing with hydrolyzed proteins in the presence of two protein denaturants and an epoxy ring-opening catalyst (TEA). The addition of either TEA or SDS lowered the activation energy, whereas urea addition led to a slight increase in activation energy. Additionally, SDS increased the heat of reaction by increasing the availability of primary and secondary amines for curing DGEBA. The heat of reaction in the presence of urea and TEA remained the same compared to the neat epoxy−protein reaction. This work demonstrated the use of SDS as an energetically efficient alternative to provide uncoiled proteins for curing DGEBA rather than producing lower molecular weight protein hydrolysate by increasing the degree of hydrolysis. Cure kinetics in the presence of urea illustrate the importance of selecting an adequate denaturant, such that it interacts with protein molecules instead of the cross-linking reagent.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The financial support of the Alberta Livestock and Meat Agency (ALMA) is greatly appreciated. SRM was supplied by Sanimax Ltd. (Montreal, Quebec, Canada). We are thankful to Mr. Tizazu Mekonnen in the Biorefining Conversions and Fermentations Laboratory for kindly providing the hydrolyzed protein samples used in this study.

REFERENCES

(1) El-Thaher, N.; Mekonnen, T.; Mussone, P.; Bressler, D.; Choi, P. Nonisothermal DSC study of epoxy resins cured with hydrolyzed specified risk material. *Ind. Eng. Chem. Res.* **2013**, *52* (24), 8189−8199.

(2) Imamura, E.; Noishiki, Y.; Koyanagi, H.; Miyata, T.; Furuse, M. Bioprosthetic Valve. U.S. Patent 5,080,670, Koken Co., Ltd., 1992.

(3) Imamura, E.; Sawatani, O.; Koyanagi, H.; Noishiki, Y.; Miyata, T. Epoxy compounds as a new cross-linking agent for porcine aortic leaflets: Subcutaneous implant studies in rats. *J. Card. Surg.* **1989**, *4* (1), 50−57.
(4) Zeeman, R.; Dijkstra, P. J.; van Wachem, P. B.; van Luyn, M. J. A.; Marc Hendriks, M.; Cahalan, P. T.; Feijen, J. Successive epoxy and carbodiimide cross-linking of dermal sheep collagen. *Biomaterials* **1999**, *20* (10), 921−931.
(5) Sunphorka, S.; Chavasiri, W.; Oshima, Y.; Ngamprasertsith, S. Kinetic studies on rice bran protein hydrolysis in subcritical water. *J. Supercrit. Fluids* **2012**, *65*, 54−60.
(6) Kumar, R.; Choudhary, V.; Mishra, S.; Varma, I. K.; Mattiason, B. Adhesives and plastics based on soy protein products. *Ind. Crop. Prod.* **2002**, *16* (3), 155−172.
(7) Somerville, R. A.; Fernie, K.; Smith, A.; Andrews, R.; Schmidt, E.; Taylor, D. M. Inactivation of a TSE agent by a novel biorefinement system. *Process Biochem.* **2009**, *44* (9), 1060−1062.
(8) Walles, W. E. Role of flocculant molecular weight in the coagulation of suspensions. *J. Colloid Interface Sci.* **1968**, *27* (4), 797−803.
(9) Hunter, R. J. *Foundations of Colloids*, 2nd ed.; Oxford University Press: Oxford, 2001.
(10) Samios, D.; Castiglia, S.; Pesce da Silveira, N.; Stassen, H. Network formation studied by temperature scanning brillouin scattering and differential scanning calorimetry techniques. I. The cure of 1,4=butanediol diglycidyl ether with cis=1,2=cyclohexanedicarboxylic anhydride initiated by triethylamine. *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *33* (13), 1857−1866.
(11) Verbeek, C. J. R.; van den Berg, L. E. Development of proteinous bioplastics using bloodmeal. *J. Polym. Environ.* **2011**, *19* (1), 1−10.
(12) Vyazovkin, S.; Burnham, A. K.; Criado, J. M.; Perez-Maqueda, L. A.; Popescu, C.; Sbirrazzuoli, N. ICTAC kinetics committee recommendations for performing kinetic computations on thermal analysis data. *Thermochim. Acta* **2011**, *520* (1−2), 1−19.
(13) Hong, I.; Lee, S. Cure kinetics and modeling the reaction of silicone rubber. *J. Ind. Eng. Chem.* **2013**, *19* (1), 42−47.
(14) Roşu, D.; Caşcaval, C. N.; Mustaţă, F.; Ciobanu, C. Cure kinetics of epoxy resins studied by non-isothermal DSC data. *Thermochim. Acta* **2002**, *383* (1−2), 119−127.
(15) Oh, J. H.; Jang, J.; Lee, S. H. Curing behavior of tetrafunctional epoxy resin/hyperbranched polymer system. *Polymer* **2001**, *42* (20), 8339−8347.
(16) Vyazovkin, S.; Sbirrazzuoli, N. Kinetic methods to study isothermal and nonisothermal epoxy-anhydride cure. *Macromol. Chem. Phys.* **1999**, *200* (10), 2294−2303.
(17) Jubsilp, C.; Punson, K.; Takeichi, T.; Rimdusit, S. Curing kinetics of benzoxazine-epoxy copolymer investigated by non−isothermal differential scanning calorimetry. *Polym. Degrad. Stab.* **2010**, *95* (6), 918−924.
(18) Mekonnen, T.; Mussone, P.; Stashko, N.; Choi, P.; Bressler, D. Recovery and characterization of proteinacious material recovered from thermal and alkaline hydrolyzed specified risk materials. *Process Biochem.* **2013**, *48* (5−6), 885−892.
(19) Langmaier, F.; Mokrejs, P.; Kolomazník, K.; Mládek, M.; Karnas, R. Cross-linking epoxide resins with hydrolysates of chrome-tanned leather waste. *J. Therm. Anal. Calorim.* **2007**, *88* (3), 857−862.