

Isoconversional Cure Kinetics of Modified Urea-Formaldehyde Resins with Additives

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Abstract

As a part of abating formaldehyde emission of urea-formaldehyde resin, this study was conducted to investigate thermal cure kinetics of both neat and modified urea-formaldehyde resins using differential scanning calorimetry. Neat urea-formaldehyde resins with three different formaldehyde/urea mol ratios (1.4, 1.2 and 1.0) were modified by adding three different additives (sodium bisulfite, sodium hydrosulfite and acrylamide) at two different levels (1 and 3wt%). An isoconversional method at four different heating rates was employed to characterize thermal cure kinetics of these urea-formaldehyde resins to obtain activation energy (E_a) dependent on the degree of conversion (α). The E_a values of neat urea-formaldehyde resins (formaldehyde/urea = 1.4 and 1.2) consistently changed as the α increased. Neat and modified urea-formaldehyde resins of these two F/U mol ratios did show a decrease of the E_a at the final stage of the conversion while the E_a of neat urea-formaldehyde resin (formaldehyde/urea = 1.0) increased as the α increased, indicating the presence of incomplete cure. However, the change of the E_a values of all urea-formaldehyde resins was consistent to that of the E_a values. The isoconversional method indicated that thermal cure kinetics of neat and modified urea-formaldehyde resins showed a strong dependence on the resin viscosity as well as diffusion control reaction at the final stage of the conversion.

Key words : activation energy, additives, isoconversional method, thermal cure kinetics, urea-formaldehyde resin

Introduction

Urea-formaldehyde (UF) resin forms strong bonds under a wider variety of conditions and cost less than phenol-formaldehyde (PF) resins (Ebewelle *et al.*, 1991). UF resins are based on the manifold reactions of two components, i.e., urea and formaldehyde (Dunky, 1998). By using different reaction conditions and preparation methods, a more or less innumerable variety of condensed structures is possible. In general, UF resin adhesives are prepared at alkaline and then acid condition. The condensations reactions under acid

condition are taking place during the hardening process provide a cross-linked state in order to develop the cohesion strength within the resin adhesive (Conner, 1996). UF resin is a thermosetting polymer and consists of linear or branched oligomeric and polymeric molecules, which also always contain some amount of monomer (Dunky, 1998). The UF resin is regarded as one of the most important type of the so-called amino plastic resins, because it has been widely being used in manufacturing wood composites products such as plywood, fiberboard and particleboard as a binder (Stefke & Dunky, 2006). UF resin possesses some

advantages, such as fast curing, good performance in wood panel, high reactivity, water solubility and lower cost. Disadvantages of using the UF resin include formaldehyde emission (FE) from the panels, lower resistance to water and low durability. Lower resistance to water limits the use of wood-based panels bonded with the UF resin to interior applications (Ebewelle *et al.*, 1994; Park *et al.*, 2006). Lower durability of wood-based panels bonded with UF resin is attributable to hydrolytic degradation of the UF resin (Conner, 1996; Myers, 1984). Whereas, poor durability and the emission of formaldehyde has been recognized as an important drawback in the use of UF resin for wood-based panel product (Kavvouras *et al.*, 1998; Chuang & Maciel, 1993). A limited ability of UF resin to resist moisture is mainly caused by: 1) the brittleness of resin, which allows the cured resin to crack and allow moisture to penetrate into the bonded-wood product and 2) chemical breakdown of the amino bonds within the cured resin (Park *et al.*, 2006). These limitations were evidenced, for example in the strength loss of UF resin-bonded joints, owing to irreversible swelling of UF resin-bonded composite panels and formaldehyde release (Ebewelle *et al.*, 1991).

It was shown that the reversibility of the aminomethylene links and susceptibility to hydrolysis were involved in the process of formaldehyde emission (Dunky, 1998). On the one hand, the FE can occur during the pressing of the board. The FE from panels in service is caused by the residual formaldehyde present in the UF-bonded boards trapped as gas in the structure of the substrate as well as dissolved in the water content of the board. The higher the F/U mol ratio is, the higher the content of free formaldehyde is in the resin (Dunky, 1998). On the other hand the hydrolysis of weakly bound formaldehyde from N-methylol groups, acetals and hemiacetals also contribute the FE. And in more severe cases the hydrolysis of methylene ether bridges also increases the amount of FE (Dunky, 1998). The hydrolysis is often accompanied by the FE, which constitutes a potential health hazard (Kim *et al.*, 2006). The hydrolysis of cured UF resin, resulted from ether

bridges as well as terminal methylol groups, appears to contribute the most in subsequent formaldehyde release from UF resin bonded boards (Kavvouras *et al.*, 1998; Zorba *et al.*, 2008). An improvement of the hydrolysis of UF resins catalyzed by acids have been reported as a result of employing materials that are capable of neutralizing the acid catalysts required for UF resin cure. Examples include the addition of glass powder to the adhesive, the post treatment of boards with sodium bicarbonate and the addition of melamine which may act as a buffer (Ebewelle *et al.*, 1991).

Liberated FE can be reduced by lowering the F/U mol ratio, lowering the formaldehyde content and hence distinctly lower the subsequent FE and also lowering the degree of branching and crosslinking in the hardened network, which unavoidably leads to a lower cohesive bonding strength (Dunky, 1998; Park *et al.*, 2006). Adding formaldehyde scavenger materials added directly to the UF resin or treated separately to wood furnish can also reduce the FE. The other ways are treating the panels after their manufacture either with a formaldehyde scavenger or by the application of coatings or laminates. The structural factors responsible for these processes suggest that the stability of UF resin can be enhanced by modifying its structure and more random distribution of cross links (Ebewelle *et al.*, 1991). A significant improvement in the durability of UF resin would broaden the application of UF resins and markets for UF resin-bonded wood products (Ebewelle *et al.*, 1991). A greater moisture resistance has also been reported when additives, such as amines or thermoplastics, were incorporated into the UF resin (Park *et al.*, 2006). The samples with high crosslink density was expected to have lower moisture sorption rates and equilibrium moisture uptake than those with low crosslink density, mainly due to the extra bonds within a given area that would need to be hydrolyzed to allow moisture to penetrate into the sample (Park *et al.*, 2006).

The large variety of structural elements in UF resins, like methylene bridges, ether bridges, methylols, amide groups, or even cyclic derivatives like uron rings and

the variety of possible reactions make their study difficult. The content of these structural elements in the still uncured resins has an obvious influence on their thermal curing kinetics and their structures and subsequently their mechanical properties of the final network. One of the most widely used methods for studying the kinetics of cure reaction is thermal analysis using differential scanning calorimetry (DSC) under isothermal or dynamic modes. Detailed kinetic study has been performed using nonlinear isoconversional analysis (Cai *et al.*, 2008). To characterize a liquid UF resin, several analytical tools have been widely used, namely ^{13}C -NMR spectroscopy and FTIR for investigations of the resin structure (Perez *et al.*, 2009).

There are two categories of cure kinetic models, phenomenological and mechanistic models. Mechanistic models are made from the balance of chemical species taking part in the chemical reaction. Most of the cases, it is difficult to derive this model because of the curing reactions are very complicated. Thus, phenomenological or empirical models are preferred to study the cure kinetics (Cai *et al.*, 2008). Normally, phenomenological rate equations suggested are suitable for analyzing isothermal scanning data. In this study, the cure kinetics is determined from only dynamic scanning data. The rate of conversion was measured for UF resin with different F/U mol ratios and additives compared with results calculated from UF neat resins (Um *et al.*, 2002). The Kissinger-Akahira Sunose (KAS) model has been used to obtain cure kinetic parameters from the curing processes of two novolac-type-L-based phenolic (LPF) resins, differing in L content and a commercial novolac resin that was used as reference (Tejado *et al.*, 2008). Isoconversional models are another type of kinetic model and provide more accurate information as they evaluate the changes in the activation energy throughout the curing process (Perez *et al.*, 2009).

So, this study attempted to investigate thermal cure kinetics of UF resins modified with additives as a part of abating the FE of UF resins. In this work, three additives such as sodium bisulfite, sodium hydrosulfite and acrylamide at different addition levels

has been added to UF resins with different F/U mol ratios in order to modify the chemical structures of UF resins as a way of improving hydrolytic stability of UF resins through possible modification of their chemical structures.

MATERIALS and METHODS

2.1 Materials

Three additives used in this study were all technical grade reagents. Sodium bisulfate (NaHSO_3) (DC Chemical Co., Ltd., Korea), sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$) (75.0%, Samchun Pure Chemical Co., Ltd., Korea), acrylamide ($\text{H}_2\text{C}=\text{CH}-\text{CO}-\text{NH}_2$) (pH 6.6, 71.08 Mw, Yongsan Mitsui Chemicals, purity 50.2wt%, Korea), were used as received. Formaline (37%) was used for UF resin synthesis as received.

2.2 Methods

2.2.1 Preparation of UF resins and their modification

All UF resins used for this study were prepared in the laboratory, following traditional alkaline-acid two-step reaction. Formaldehyde (37%) was placed in the reactor and then adjusted to pH 7.8 with sodium hydroxide (20 wt%) then heated up to 45°C subsequently a certain amount of urea was added equally at 1-min intervals, and the mixture was heated to 90°C under reflux for 1 hour to allow for methylation reactions. The second stage of UF resin synthesis consisted of the condensation of the methylolureas. The acidic reaction was brought by adding formic acid to obtain a pH of about 4.6, and the condensation reactions were carried out until a target viscosity of JK using a bubble viscometer (VG-9100, Gardner-Holdt Bubble Viscometer, USA). Different amounts of the second urea were added during the condensation step in order to obtain different UF resin with F/U mol ratios of 1.4, 1.2 and 1.0. Then the UF resin was cooled to room temperature by adjusting the final pH to 8.0.

Neat UF resin was physically mixed with two different levels of additives (1 and 3 wt%) immediately

before mixing with 3wt % of NH_4Cl (20% aqueous solution) as hardener. In this study, additives were sodium bisulfite, sodium hydrosulfite, and acrylamide. The mixture was then quickly and vigorously stirred. All additive were easily dissolved at all levels used.

2.2.2 Properties of Modified UF resins

About 1 g of UF resin was poured into a disposable aluminum dish, and then dried in a convective oven at 105°C for 3 hours. Non-volatile solids content was determined by measuring the weight of UF resin before and after drying. An average of three replications was presented.

To compare the reactivity of UF resins synthesized, the gel time of neat and modified UF resins were measured, with 3% NH_4Cl (20 wt%) as a hardener,

at 100°C using a gel time meter (Davis Inotek Instrument, Charlotte, NC). The measurements were done with three replications for each UF resin with different F/U mol ratios. The viscosity of UF resins at 25°C was measured using a cone-plate viscometer (DV-II+, BROOKFIELD, US) with No. 2 spindle at 60 rpm.

The properties of UF resins prepared at different F/U mol ratios were summarized in Table 1. The non-volatile solids contents of UF resins prepared at different F/U mol ratios were ranged from 55 to 59 wt%, and 55 to 61wt% for the modified UF resin with different additives. The resin viscosity showed a large difference between the F/U mol ratios of 1.4 and 1.0. This might be due to greater amount of the second urea for lower F/U mol ratio during the resin synthesis. The addition of the second urea dissolved at later stage of UF resin

Table 1. Properties of UF resins with different F/U mol ratios, additives types, and levels

F/U molratio	Additive type	Additive level (wt%)	Non-volatile solid content (wt%)	Viscosity (25°C , mPa.s)	Gel time (s)
1.0	Control	0	57.95	133.3	237
	Sodium bisulfite	1	57.86	210.0	230
		3	58.28	234.0	236
	Sodium hydrosulfite	1	58.10	230.7	212
		3	58.73	238.7	297
	Acrylamide	1	57.46	226.0	242
		3	57.34	222.0	249
	1.2	Control	0	55.20	225.0
Sodium bisulfite		1	55.47	267.0	207
		3	56.12	294.0	238
Sodium hydrosulfite		1	55.78	284.0	184
		3	56.40	296.0	277
Acrylamide		1	56.38	311.0	237
		3	56.36	328.0	217
1.4		Control	0	58.77	464.0
	Sodium bisulfite	1	59.25	528.0	150
		3	59.81	578.0	239
	Sodium hydrosulfite	1	58.73	534.0	186
		3	58.76	605.0	290
	Acrylamide	1	60.75	578.0	217
		3	60.27	573.0	254

synthesis could reduce the viscosity of UF resin (Park & Lee, 2009). An increase of the F/U mol ratio resulted in an increase in the resin molecular weight. An increase of the sulfur compounds in UF resin also led to increase in its molecular weights (Myers, 1986).

The gel time of the UF resins prepared increased with a decrease in the F/U molratio. As shown in Table 1, the gel time increased when the F/U mol ratio decreased from 1.4 to 1.0. These results indicate that the reactivity of UF resin decreased with a decrease in the F/U molratio. This might be explained by a decrease in the availability of free formaldehyde at lower F/U mol ratio (Park, 2007).

2.2.3 DSC measurements

All modified UF resins were scanned with a DSC (TA 2910, TA Instruments, Delaware, USA) previously calibrated with indium standard. Experiments were conducted in N₂ atmosphere; using high pressure cells and about 5 mg of the samples were used. All samples were run at four different heating rates (5, 10, 15 and 20°C/min) in a temperature range from 30°C up to 300°C. For each heating rate, two replicated measurements were performed. Measurements of the heat of reaction (ΔH) were made by integrating the area under a exothermic curve with a linear base-line using a thermal analysis software (ver. 4.5A, Universal Analysis 2000, TA Instruments, USA). The values of degree of conversion (α) were also obtained by the integration. The data of runs were fitted to the Kissinger-Akahira-Sunose isoconversional method.

2.2.4 Kinetic methods

The isoconversional method employed in this work is based on dynamic DSC analysis. The equation for the reaction rate employ (da/dt) to study the curing kinetics of UF resin can be expressed, in general as:

$$\frac{d\alpha}{dt} = kf(\alpha) \text{-----(1)}$$

where α is the degree of chemical conversion, or extent of reaction, k is the rate constant, and f(α) is assumed to be independent of temperature. In general, thermoset curing can be divided into several model categories. Two typical models of them are nth-order and autocatalytic reaction. Considering that the rate Eq.(1) is valid for dynamic scan with heating rate, β (K/min). The reaction rate is converted in terms of the β, like da/dt = β (da/dt), the k is the rate constant expressed by the temperature-dependent Arrhenius equation. And then the Eq.(1) can be written as:

$$\beta \frac{d\alpha}{dT} = Ae^{\left[\frac{-Ea}{RT}\right]} f(\alpha) \text{-----(2)}$$

where T is the temperature, A is the pre-exponential factor, E_a is the activation energy, which is independent of the conversion, R is the gas constant and α is the degree of the conversion. The principle of this method states that at a constant extent of conversion, the reaction rate is a function of only the temperature. So, the isoconversional methods require performing a series of experiments at different temperature programs and yield the values of effective activation energy as a function of conversion. This study employed the isoconversional method, which is expressed as follows:

$$-\ln\left(\frac{\beta}{T_\alpha^2}\right) = \frac{E\alpha}{RT_\alpha} - \ln\left(\frac{A_\alpha R}{E\alpha}\right) \text{-----(3)}$$

For a given heating rate, each conversion grade is associated with a single temperature (T_α) and thus the corresponding activation energy (E_α) can be determined from the slope of the straight line obtained by plotting -ln(β/T_α²) vs 1/T_α in the same way as for simple models. The isoconversional methods can be applied to study the curing process of these polymers because it gave low error in conversion degree (Um et al., 2002).

RESULTS AND DISCUSSION

Fig. 1. shows the E_a curves of neat UF resin with the F/U mol ratio of 1.4. It initially increased and then remained constant (53 kJ/mol) almost throughout the entire process, indicating that it is dominated by a single reaction type (Um *et al.*, 2002). The basic cure mechanism in UF resin is based on two main reaction types, namely addition and condensation reactions (Dunky, 1998). The addition of both sodium bisulfite and sodium hydrosulfite decreased the E_a with an increase of α for the entire process (Figs. 1 and 2).

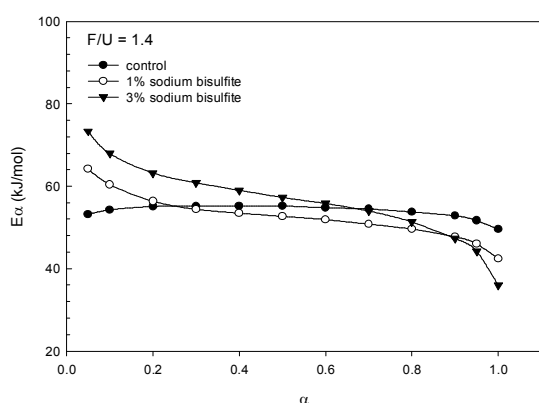


Fig. 1. Exchanges of modified UF resins by sodium bisulfite at the F/U mol ratio of 1.4

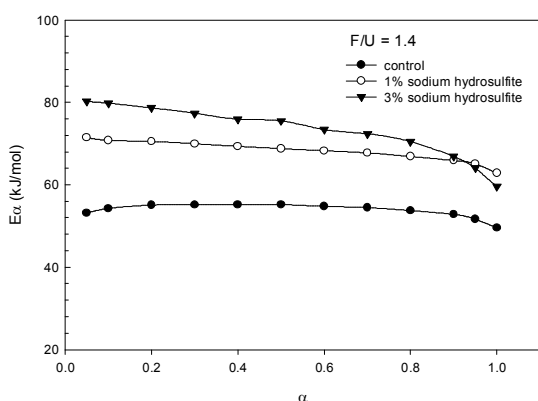


Fig. 2. E_a changes of modified UF resins by sodium hydrosulfite at the F/U mol ratio of 1.4

This has been traditionally assigned to a change in the final stage of the resin cure from a kinetic to a diffusion regime in these modified UF resins due to

the increase in viscosity caused by the additives (Perez *et al.*, 2009; Um *et al.*, 2002). Fig. 3. shows that the E_a of modified UF resin with 3 wt% acrylamide slightly increased in the E_a at the beginning and then was constant until it reached a 0.5. And then it started to decrease for the whole process. 1 wt% level of acrylamide also showed a similar behavior to neat UF resin where the E_a was constant from the initial stage to the end of the process. Not only acrylamide but also the sodium bisulfite and sodium hydrosulfite at 1 wt% level showed a similar behavior to the neat UF resin. It indicated that 1 wt% of additives did not much influence to control resin with the F/U mol ratio of 1.4. From these three additives, the acrylamide with 3 wt% level gave the lowest E_a at the F/U mol ratio of 1.4. It indicated that acrylamide did react with the free formaldehyde in UF resin and created cross-links with methylolureas during the cure process (Kavvouras *et al.*, 1998).

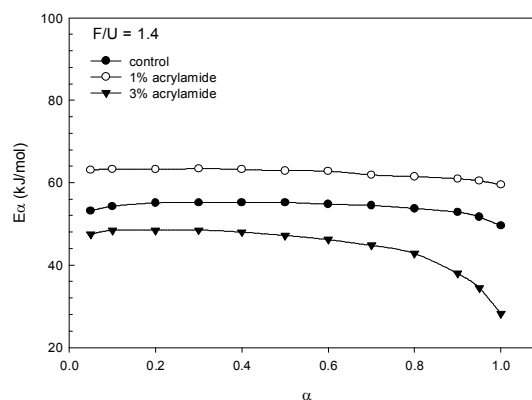


Fig. 3. Exchanges of modified UF resins by acrylamide at the F/U mol ratio of 1.4

Fig. 4. shows that the E_a values of neat UF resin with the F/U mol ratio of 1.2 decreases with an increase of α . Both sodium bisulfite and acrylamide at 1 wt% (Figs. 4 and 6) showed a similar trend of E_a curves to that of neat UF resin. The effect of viscosity might be one of the reasons in influencing the downward E_a curves (Um *et al.*, 2002). The other reason might be an optimum stoichiometric combination between the amount of free formaldehyde and the additive levels. The E_a of the

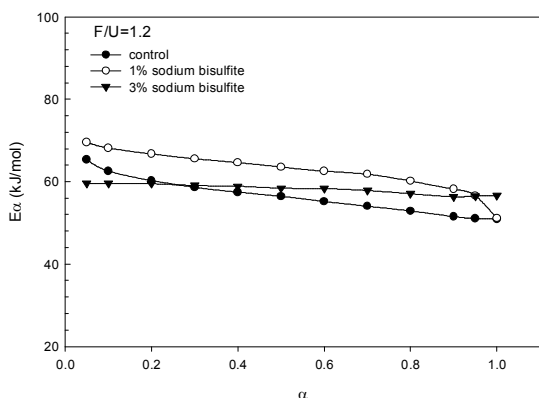


Fig. 4. E_{α} changes of modified UF resins by sodium bisulfite at the F/U mol ratio of 1.2

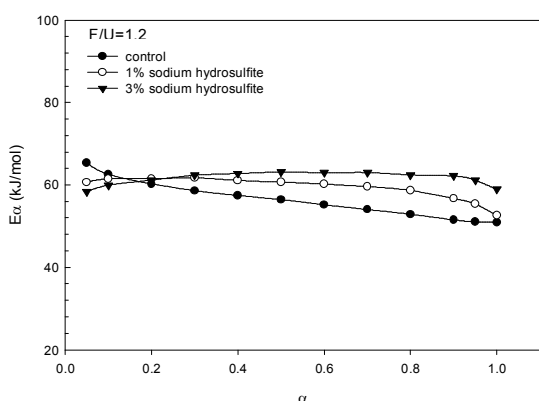


Fig. 5. E_{α} changes of modified UF resins by sodium hydrosulfite at the F/U mol ratio of 1.2

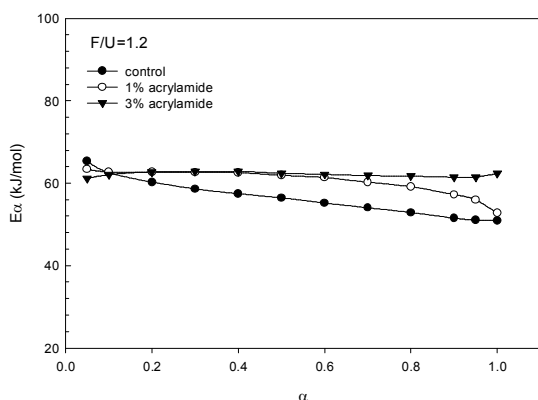


Fig. 6. E_{α} changes of modified UF resins by acrylamide at the F/U mol ratio of 1.2

1 wt% of sodium hydrosulfite (Fig. 5.) initially increased and then later started to decrease at $\alpha = 0.4$. Compared to the F/U mol ratio of 1.4, those of UF resins with

the F/U mol ratio of 1.2 was much affected by additives even at 1 wt%. It might be due to the lower viscosity and molecular weight of UF resin with 1.2 F/U mol ratio compared to the UF resin of 1.4 F/U mol ratio. So, the additives were easily reacted with UF resin and resulted in lower E_{α} . Also, it indicates that there are different kinds of individual reactions related to urea components that had been taken place in modified UF resins and resulted in low E_{α} value (He & Riedl, 2003). The 3 wt% levels of sodium bisulfite and acrylamide (Figs. 4 and 6) also shows a quite similar trend of the E_{α} curves which remain constant throughout the process except for the initial stage. This result indicated that its rate was determined by a single step. And an increase of the E_{α} at $\alpha = 0.9$ could be associated with a chemical process that was initiated at higher temperature. A similar trend at 1 wt% of sodium hydrosulfite (Fig. 5) and acrylamide (Fig. 6) was obtained where the E_{α} started to decrease at $\alpha = 0.4$ and $\alpha = 0.5$, respectively, due to diffusion controlled reaction. The E_{α} decreased throughout the entire process for the sodium bisulfite (Fig. 4), which could be explained by diffusion control that was associated with vitrification.

Fig. 7. shows an initial increase in the E_{α} of UF resin with the F/U mol ratio of 1.0. This effect may indicate that in some incompletely cured systems the rate of cross-linking can be limited not by diffusion of small molecules, but by the mobility of longer polymer chains (Vyazovkin & Sbirazuoli, 2006). Therefore, an increase

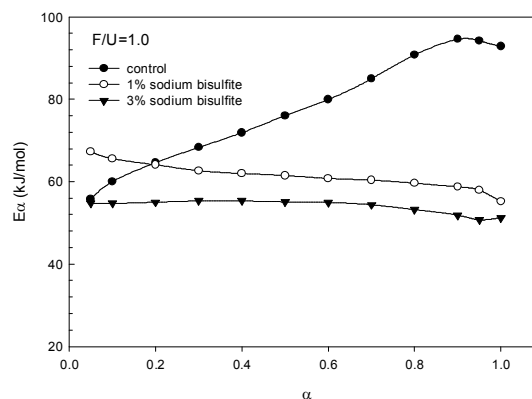


Fig. 7. E_{α} changes of modified UF resins by sodium bisulfite at the F/U mol ratio of 1.0

in the E_a is observed up to $\alpha = 0.9$. Later, the E_a curve takes downward dependence as a result of the transition in the control of kinetics from chemical reaction to diffusion control (Alonso *et al.*, 2006). Once additives have been added to neat UF resin, all E_a curves were below that of the control resin. These results indicated that all additives reduced the E_a of UF resins with the F/U mol ratio of 1.0 (Figs. 7-9). As shown in Figs. 7 and 8, the E_a values of modified UF resins at 1 wt% of sodium bisulfite and sodium hydrosulfite resulted in a continuous decrease and increase, which could be attributed to diffusion controlled reaction or incompletely cure system (Vyazovkin & Sbirrazuoli, 2006). And the 1 wt% acrylamide showed a slight increase in the E_a values at the beginning, which could be explained by higher viscosity of the modified UF

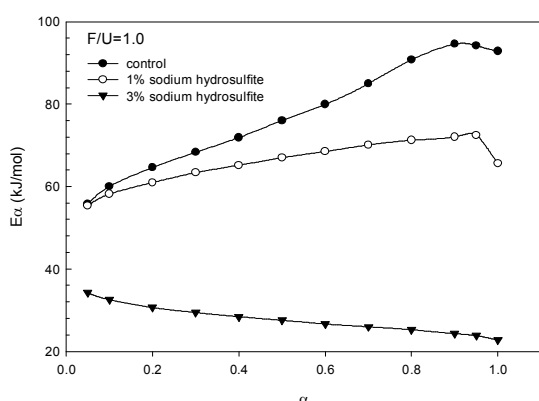


Fig. 8. E_a changes of modified UF resin by sodium hydrosulfite at the F/U mol ratio of 1.0

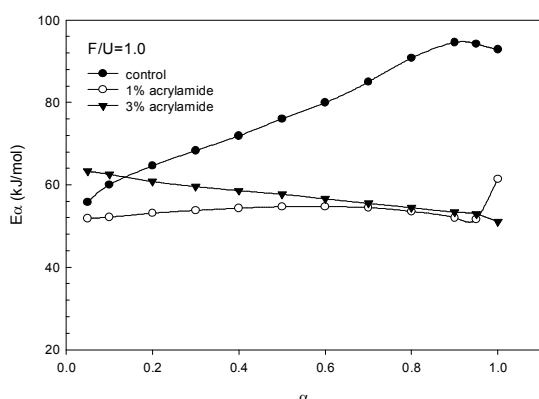


Fig. 9. Echanges of modified UF resins by acrylamide at the F/U mol ratio of 1.0

resin. Then it decreased at $\alpha = 0.8$ before an increase again at $\alpha = 0.9$, which might be due to an autocatalytic mechanism as well as the mechanism of viscosity related diffusion as reported in the epoxy resin (Vyazovkin & Sbirrazuoli, 2006). Three additives at 3 wt% level showed a similar trend, where the E_a values continuously decreased, which could be due to the viscosity control. Except for the sodium bisulfite where the E_a increased again at final stage of the resin curing, this phenomenon could be explained by a change in the curing process from noncatalyzed to an autocatalytic mode (Vyazovkin & Sbirrazuoli, 2006). From these three additives, the sodium hydrosulfite at 3 wt% (Fig. 8) gave the lowest E_a value for UF resin with the F/U mol ratio of 1.0. It shows that the sodium hydrosulfite reacts readily with formaldehyde solution (Pasch *et al.*, 1990). As a result, it needs low energy in order for the modified UF resin to cure.

CONCLUSIONS

This study was undertaken to investigate the effects of additive types and levels on the thermal cure kinetics of neat and modified UF resins using isoconversional method, resulting in the determination of E_a . The following conclusions were made from this study:

1. The E_a values of neat UF resins (F/U = 1.4 and 1.2) consistently changed as α increased. Neat and modified UF resins of these two F/U mol ratios did not show a decrease of the E_a at the final stage of the conversion while the E_a of neat UF resin (F/U = 1.0) increased as α increased, indicating the presence of incomplete cure as well as strong diffusion control reaction.
2. The isoconversional method indicated that thermal cure kinetics of neat and modified UF resins showed a strong dependence on the resin viscosity as well as diffusion control reaction at the final stage of the conversion, which was typical at the F/U mol ratio (F/U = 1.0).

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