

Thermal Cure Kinetics of Modified Cold-Setting Melamine-Urea-Formaldehyde Resins with Liquid Thickeners

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Abstract: Cold-setting melamine-urea-formaldehyde (CS-MUF) resins being used as adhesives for manufacturing laminated wood timber products require to have a proper viscosity using thickener or filler. However, studies on thermal curing kinetics and behavior of the modified CS-MUF resins with liquid thickener are limited. Hence, this study focuses on the thermal cure kinetics of the modified CS-MUF resins with two liquid thickeners at three addition levels to obtain the resin viscosities of 4,000 mPa.s, 8,000 mPa.s and 12,000 mPa.s. Differential scanning calorimetry (DSC) was used to estimate cure kinetics of the modified CS-MUF resins using two analysis methods: 1) model-fitting (MFT) method containing the Kissinger (KSNG) analysis, and 2) model-free (MFK) methods containing Kissinger-Akahira-Sunose (KAS) analysis, and nonlinear isoconversional (VYA) analysis. The KSNG, KAS, and VYA analysis showed that all modified CS-MUF resins followed very similar curing behavior with small difference, except Resin #2 which followed the autocatalytic reaction model based on the Málek method. These results suggest that liquid thickeners increase to a proper viscosity of CS-MUF resins without major impact to their curing behavior.

Keywords: Cure Kinetics, Cold-Setting MUF Resins, Thickener, Reaction Model, Additives.

1. INTRODUCTION

Cold-setting resins such as resorcinol-formaldehyde (RF) resins, phenol-resorcinol-formaldehyde (PRF) resins, phenol-formaldehyde (PF) resins, and melamine-urea-formaldehyde (MUF) resins are being used as adhesives for manufacturing structural timber laminated products such as glued-laminated timber (GLT), cross-laminated timber (CLT), or laminated veneer lumber (LVL). According to the Food and Agriculture Organization of the United Nations (UN FAO 2022), a large portion of wood products depend on adhesives for their bonding performances which resulted in a demand that is estimated up to 18 million tons/y [1]. Due to this colossal quantity of adhesives being sought out, cold-setting melamine-urea-formaldehyde (CS-MUF) resins have advantages of low cost, fast-curing time, and good performance over phenolic resins. Additionally, CS-MUF resins offer advantages such as water resistance, high reactivity and high functionality due to melamine [2]. Alongside the benefits of CS-MUF resins, some additives such as thickener, filler, or extender are added to prepare glue-mix prior to their spread on wood surface [3]. Liquid thickener is frequently added to the glue-mix to obtain a proper viscosity of CS-MUF resins, prior to spreading them on the wood surface. In general, the formulation and preparation method of glue-mix is usually kept under confidentiality in adhesive industry. Therefore the effect of liquid thickener on the curing kinetics and behavior of CS-MUF resins is also unknown.

As a result, differential scanning calorimetry (DSC) has been used to understand an accurate analyses of these thermosetting resins [4-6]. Understanding the thermal curing behavior and cure kinetics of CS-MUF resins are pivotal due to their relationship with cross-linking reaction, reactivity, and consequent adhesion performance [7,8]. The reaction enthalpy (ΔH), activation energy (E_a), and peak temperature (T_p) acquired through DSC enables to understand better cure kinetics of these resins. So, this study investigated the curing kinetics and behavior of modified CS-MUF resins with liquid thickeners to understand these thickeners' impact on the curing of CS-MIUF resins. Hence, this study covered the cure kinetic parameters, reaction order, and pre-exponential factors utilizing two kinetic analysis methods: 1) model-fitting (MFT) method which contains the Kissinger (KSNG) approach, and 2) model-free kinetics (MFK) methods, including the Kissinger-Akahira-Sunose (KAS) analysis which also covers a linear or nonlinear isoconversional method of the Vyazovkin (VYA) method.

2. MATERIALS AND METHODS

CS-MUF resins used in this study are composed of melamine ($C_3H_6N_6$), urea (CH_4N_2O), and formaldehyde (CH_2O). Formalin (37 wt%), melamine (99 wt%), acetic acid (99 wt%), sodium hydroxide from Daejung Chemicals, Korea and urea from SK Geo Centric, Korea was purchased and used without further purification. Two types of thickeners were used: A commercial thickener (CT) (BJ-17, Donghwa Taeyang Chemical Ltd., Incheon, Seoul) with a solid content of 14~16% was purchased and used. Lab thickener (LT)

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was prepared in the laboratory. As additives, both wheat flour and kaolin clay were purchased from Daehan Flour Co., and Takehara Chemical Industrial Co., Ltd., Japan, respectively.

CS-MUF resins with 27 wt% melamine was initially blended with additives and adjusted to appropriate viscosity levels. Both batches of CS-MUF resin were mixed with hardener at the proportion of 100:20 based on the mass of glue-mix to hardener. The mixtures of glue-mix with hardener were spread on the wood surface only within the initial 60 minutes. Table 1 shows the formulations and properties of neat and modified CS-MUF resins used in this study.

2.1. Differential Scanning Calorimetry (DSC) Analysis

DSC thermograms were obtained from an DSC (DSC25, TA Instruments, New Castle, DE, USA) to examine the cure kinetic of the resin samples at four different heating rates of 2.5, 5, 10, and 20 °C/min within a range of 25-200°C. The storage stability of resin samples was also observed over a 14-day period. Each sample, ranging from 19.3-45.3 mg, was then added to a high-pressure pan for scanning. Each sample in the pan was scanned at four heating rates under nitrogen flow of 50-mL/min [3].

3. ANALYSIS METHODS OF CURE KINETICS OF CS-MUF RESINS

Thermal curing parameters from DSC curves obtained using a software (TRIOS v4.3.0, TA Instruments, New Castle, DE, USA) are degree of conversion (α), reaction rate (da/dt), peak temperature (T_p), activation energy (E_a), and isoconversional activation energy (E_c). The activation energies were calculated with the KSNM and KAS method. According to the extrapolated baseline in the scans, the value of α at a specific curing time (t) based on the total heat of reaction (ΔH) are represented in Eq. 1. The reaction rate was calculated by the heat flow (dH/dt) and ΔH according to Eq. 2.

$$\alpha = \frac{\Delta H(t)}{\Delta H_{Total}} \quad \#(1)$$

$$\frac{da}{dt} = \frac{dH}{dt} \frac{1}{\Delta H} \quad \#(2)$$

The conversion rate within curing reaction can be expressed as shown in Eq. (3):

$$\frac{da}{dt} = k(T)f(a) \quad \#(3)$$

As da/dt is the reaction rate, $k(T)$ rate consistent with temperature (T), and $f(a)$ being the function of a reaction model that relies on the extent of conversion. The Arrhenius equation can simplify the reliance on the rate constant with temperature as shown in Eq. (4)

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad \#(4)$$

Therefore, an equation of computing the reaction rate is needed to study the kinetics of the resin. Merging Eq. (3) and (4) has led to Eq. (5) which A clarifies the rate constant with a dependent temperature, and can be expressed as:

$$\frac{da}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(a) \quad \#(5)$$

Furthermore, E_a , A , T , and R are the activation energy (kJ mol^{-1}), pre-exponential factor or Arrhenius frequency factor (s^{-1}), absolute temperature (K) and universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), respectively. Accordingly, if the a remains unchanged the activation energy and pre-exponential factor would be calculated upon the entire completion of the reaction cycle; which $\frac{da}{dt}$ is the rate of non-isothermal reactions at a heating rate (β) expressed in Eq. (6)

$$\frac{da}{dt} = A \frac{1}{\beta} \exp\left(-\frac{E_a}{RT}\right) f(a) \quad \#(6)$$

3.1. Model-Fitting (MFT) Method

Consequently, the Kissinger question was used to calculate the activation energy from the slope, which can be found from the intercept of the plot of $-\ln(\beta/T_p^2)$ against T_p^{-1} , so the calculation can be expressed by the following Eq. (7)

$$-\ln\left(\frac{\beta}{T_p^2}\right) = \frac{E_a}{RT_p} - \ln\left(\frac{AR}{E_a}\right) \quad \#(7)$$

However, the single activation energy from the KSNM method doesn't imply any complete results in regard to the characteristics of the curing process; as many authors believe that model-fitting methods do not provide the most reliable techniques to discover the activation energy of thermally activated resins [9].

3.2. Model Free Kinetics (MFK) Method

As a result, KAS was employed to cross reference Eq. (7) for E_a at α , which is shown by Eq. (8)

$$-\ln\left(\frac{\beta}{T^2}\right) = \frac{E_a}{RT} - \ln\left(\frac{AR}{E_a g(a)}\right) \quad \#(8)$$

The KAS method known as the generalized KSNG method based on Murray and White approximation for the temperature integral [9–11]. Eq. (8) can be converted to Eq. (9)

$$\ln\left(\frac{\beta_i}{T_{ai}^2}\right) = C_K(a) - \frac{E_a}{E_a g(a)} \quad \#(9)$$

as $C_K(a)$ is the constant $\ln\left(\frac{AR}{E_a g(a)}\right)$ and the i denotes different heating rates; each degree of conversion, a , corresponds with T_{ai} and the used heating rate. The E_a can be found according to the linear least square plots from the slope of $\ln\frac{\beta_i}{T_{ai}^2}$ versus $1/T_{ai}$ [9].

3.3. Nonlinear Isoconversional Methods

As this study focuses on the cure kinetics of CS-MUF resins during their curing, thermal curing behaviors are estimated by the dependence on the degree of conversion vs. activation energy. These parameters could uncover clues about the curing behavior, complex conversion process, and conversion dynamics. The function $f(\alpha)$ of Eq. (5) is expressed by integration of Eq. (5) as a basis for the evaluation of the Arrhenius parameters (A) in integral form, leading to Eq. (10):

$$\int_0^a [f(a)]^{-1} da \equiv g(a) = A \int_0^t \exp\left[-\frac{E}{RT(t)}\right] dt \quad \#(10)$$

As vital parameters for the integration of Eq. (10), $T(t)$ denotes the temperature through the experiment at the time of t . Eq. (11) is only solved through various approximations that can assess Arrhenius parameters, the most used method is Doyle's approximation. However, as linear heating programs utilize Doyle's approximation, the program can be shown as $T(t) = T_0 + \beta t$. Therefore, a heating program can be represented as an analysis function of $T(t)$.

$$g(a) = \left(\frac{A}{\beta}\right) \int_0^T \exp\left(-\frac{E}{RT}\right) dT = \left(\frac{A}{\beta}\right) I(E, T) \quad \#(11)$$

Ranges of temperature change due to the heat of the reaction, Eq. (10) doesn't consider the thermal lag within the sample, so obtained results of the Arrhenius parameter (A) can be incorrect. Although the linear heating rate is used, it is pivotal to utilize the Vyazovkin method to pursue the process of evaluating the activation energy (E_a) at a degree of conversion (a) [12, 20].

The isoconversional principle states that the reaction rate in the constant extent of conversion is a function of temperature. Utilizing the assumption of the isoconversional principle, the reaction model $g(a)$ is independent of the heating rate. Therefore, at the given conversions and various heating rates (β_i) within the experiment, it can be expressed as:

$$\begin{aligned} \left(\frac{Aa}{\beta_1}\right) I(E_a, T_a, 1) &= \left(\frac{Aa}{\beta_2}\right) I(E_a, T_a, 2) \\ &= \dots = \left(\frac{Aa}{\beta_n}\right) I(E_a, T_a, n) \quad \#(12) \end{aligned}$$

As $T_{a,i}$ ($i = 1, \dots, n$) is temperature during the conversion of β_i . Additionally, removing A_a from both sides, Eq. (12) can be expressed as an equation encasing the minimum value shown in Eq. (13):

$$\sum_{i=1}^n \sum_{j \neq i}^n \frac{[I(E_a, T_{a,i})\beta_j]}{[I(E_a, T_{a,j})\beta_i]} = \min \quad \#(13)$$

i and j denoting the order of experiments at various heating rates (β). If replacing T_a and β in Eq. (13) with obtained values, it is sufficient for a change in the E_a as a function of the degree of conversion if, at the least, the minimum parameter is within its range. Additionally, both Eq. (12) and (13) are the basis of nonlinear isoconversional methods under linear heating programs but has resistance to erratic temperature changes [12-13,20,21].

4. RESULTS AND DISCUSSION

4.1. Properties of CS-MUF Resins

The properties and formulations of neat and modified CS-MUF resins with various amounts of additives and two different liquid thickeners were presented in Table 1. As shown in Table 1, the resin with 5% CT and an adjustment of wheat flour filler yielded a slightly higher non-volatile solids content due to the higher wheat flour mass used. This is due to the wheat flour's protein molecules ability to link well within water and exhibits enhanced viscosity [14]. However, the remaining resin samples were mixed with LTs that had a consistent filler mass level whilst LT values levels were adjusted to achieve appropriate viscosities during their preparation.

4.2. Curing Behavior of CS-MUF Resins

The modified CS-MUF resins with two liquid thickeners were analyzed with DSC at heating rates of 2.5 °C/min, 5 °C/min, 10 °C/min, and 20 °C/min. Figure 2 shows DSC thermograms of neat (CTRL) and modified

Table 1: Formulations and Properties of Neat and Modified CS-MUF Resins with Liquid Thickeners in this Study

Resin No.	Kaolin Clay (wt%)	Wheat Flour (wt%)	Thickener Type ²	Thickener (wt%)	Non-volatile Solids Content (wt%)	Viscosity (mPa.s)
CTRL ¹	0	0	—	0	100	193
#1	1	8	CT	5	61.75	4,000
#2	1	10	"	5	65.75	8,000
#3	1	12	"	5	68.67	12,000
#4	1	5	LT	3	64.05	4,000
#5	1	5	"	11	60.20	8,000
#6	1	5	"	17.5	56.51	12,000
#7	1	5	"	14	55.79	4,000
#8	1	5	"	24	51.98	8,000
#9	1	5	"	33	48.80	12,000

¹CTRL: neat CS-MUF resin, ²CT: Commercial thickener, LT: Laboratory thickener.

CS-MUF resins with different liquid thickeners and their addition levels under four different heating rates. As shown, all DSC thermograms have a single exothermic reaction peak temperature (T_p) which depends on the heating rate used. The T_p values between 50 and 150 °C indicate that the condensation or curing reactions of CS-MUF resins occurs due to the primary amino groups and the hydroxymethyl groups whilst various species of oligomers are produced. As presented in Figure 2, T_p increases with heating rate due to the prolonged thermal lag in the sample; therefore, the lower the heating rate the more completeness of curing reaction. This concept can also be understood with a higher heating rate influencing a great thermal lag in the sample and causing a higher T_p [14, 25].

As shown in Figure 3, T_p of all resins generally increased with an increase in heating rate. This could be due to the fact that the oligomers were cured through exothermic condensation reactions presented in Figure 1. Formaldehyde is reacted either with melamine or urea in the addition reaction under alkaline pH to form hydroxymethylated-melamine or -urea. Under acidic pH, the hydroxymethylated-melamine and -urea are reacted by the condensation reaction by splitting off water molecules as by-product. The condensation reaction continued to form three-dimensional network until the end of curing [18]. Figure 4 shows the degree of conversion of the resins as a functions of curing temperature, and proves that the curing reaction expressed as the degree of conversion

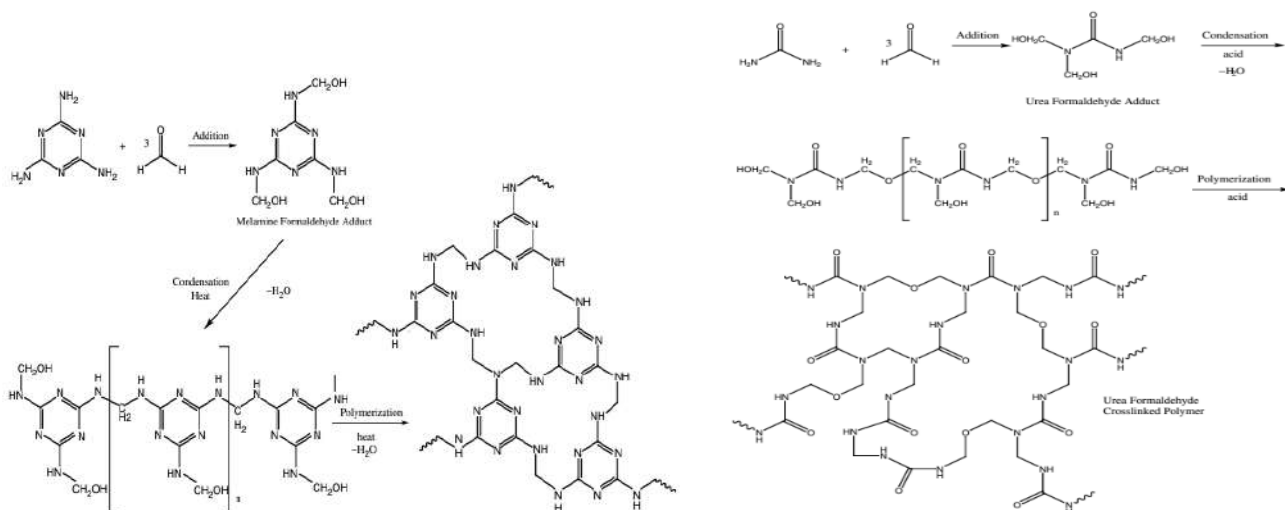


Figure 1: Schematic diagram of the addition and condensation reaction in CS-MUF resins [26].

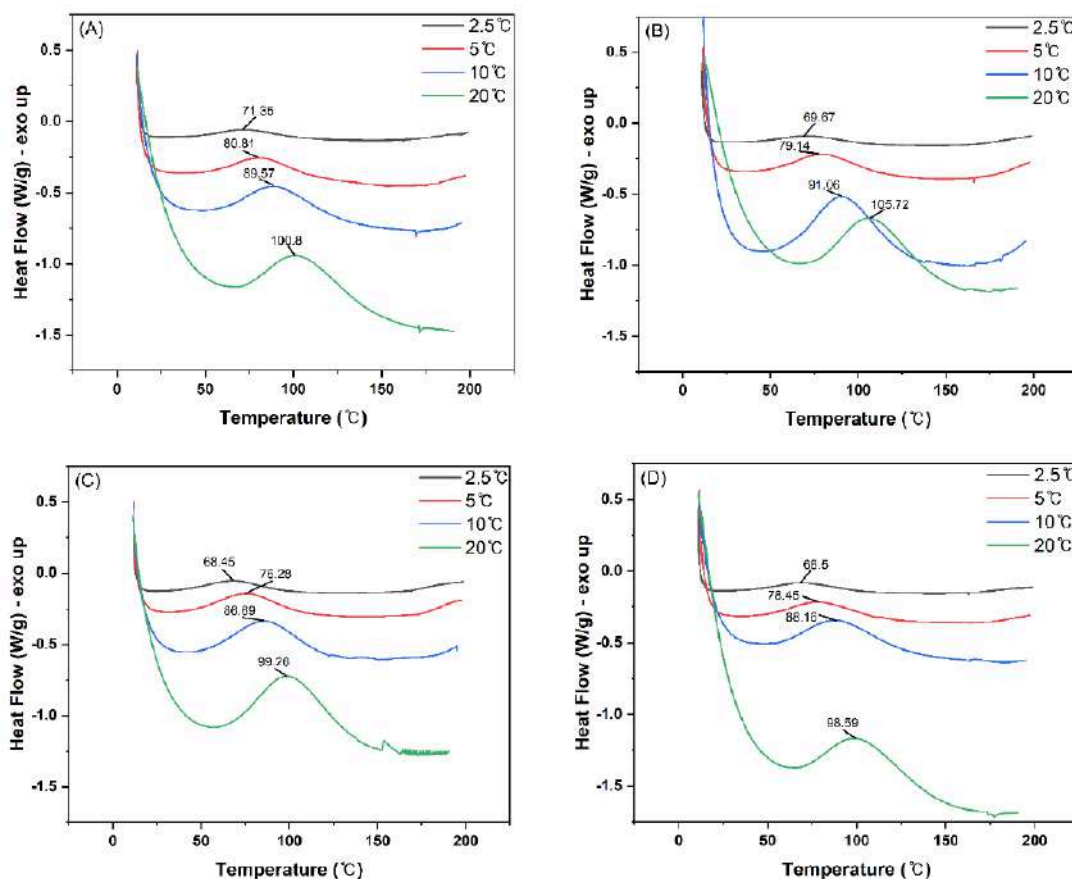


Figure 2: Heat flow thermograms acquired via DSC including (A) Resin #1, (B) Resin #2, (C) CTRL, and (D) Resin #7.

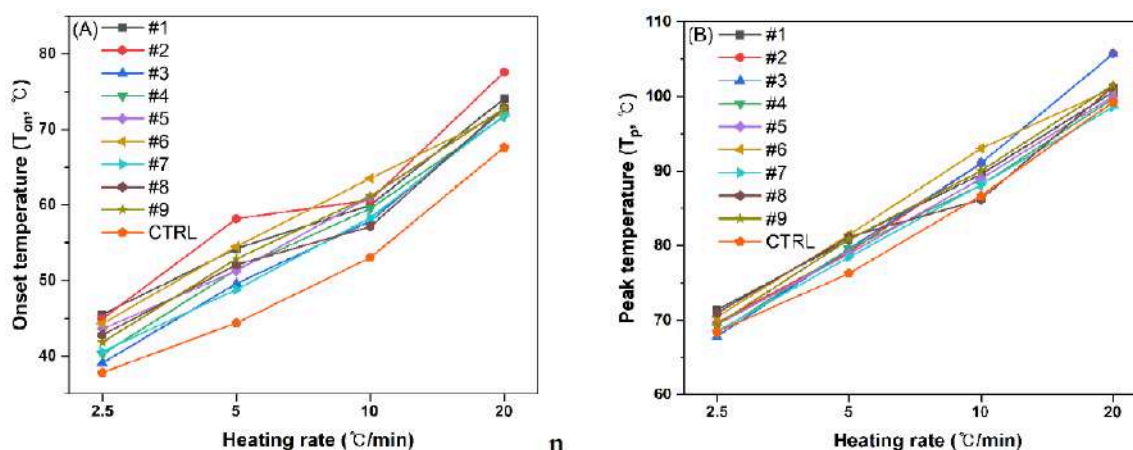


Figure 3: (A) shows typical low onset temperatures; (B) shows the peak temperature trends (T_p) observed.

of CS-MUF resins increases with an increase in the curing temperature.

4.3. Cure Kinetics of Modified CS-MUF Resins with Liquid Thickener

4.3.1. Model-Fitting Methods (MFT)

The Kissinger method was used to obtain information about the kinetics and reaction of order of

simplified degradation reactions. Therefore, kaolinite was used within the composition of the formulation of the samples used [10, 22-24]. Figures 5 and 6(a) show the parameters acquired from said MFT method. Acquirable parameters from the Kissinger method (E_a and A) were successfully calculated but as one sample followed a reaction model, parameter n was not included. Kissinger method being reliable as it is, the confirmation of the E_a , $\ln A$ value rely on the

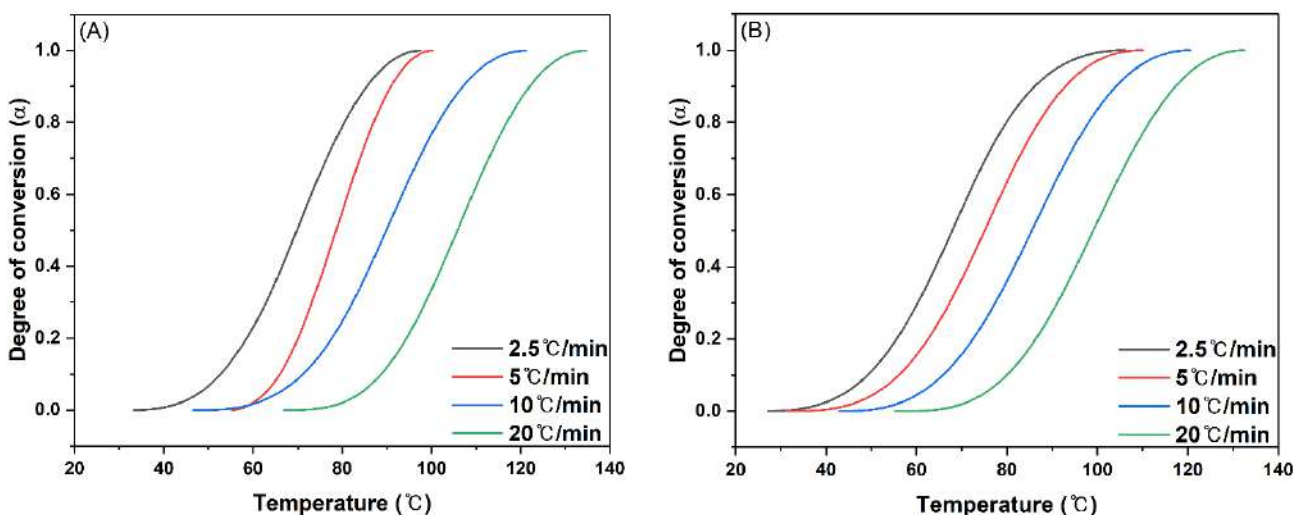


Figure 4: Degree of conversion (α) of (A) Resin #2 and (B) CTRL.

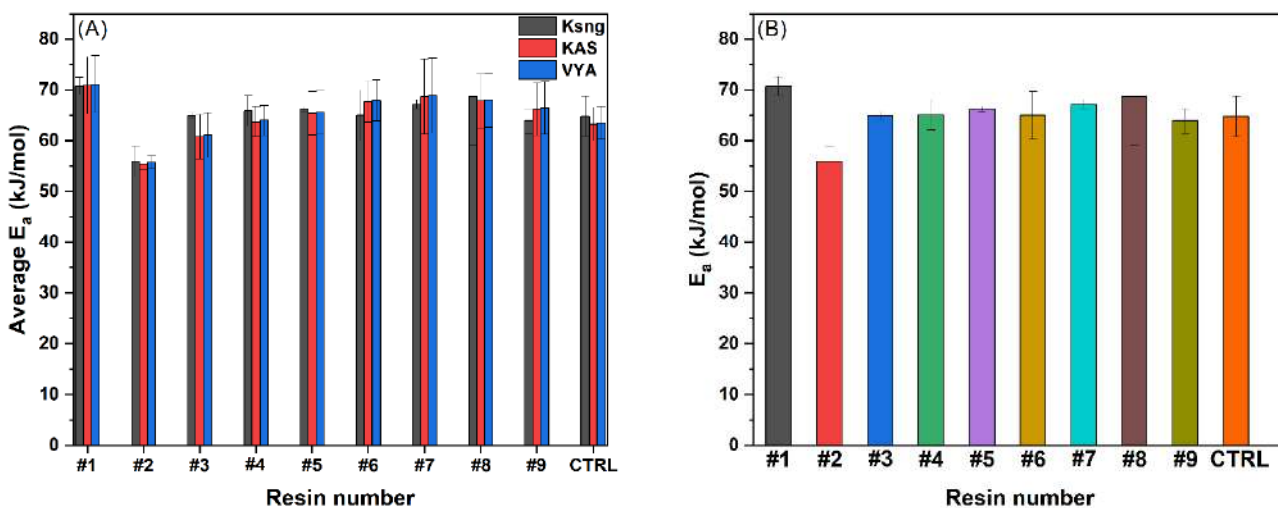


Figure 5: (A) Average E_a of all resins, (B) All E_a obtained via. KSNMG method.

correspondence of other methods to accurately prove its outcome. However, with differing proportions of sample compositions shown in Table 1, the connections between will be further discussed with the support of other models.

4.3.2. Model-Free Methods (MFK) and Nonlinear Isoconversional Method

Counterparts of the MFK methods, MFTs only produce single activation energy values for entire reaction processes which in turn generate a reliance on others. Therefore, MFK methods such as Kissinger-Akahira-Sunose (KAS) and Vyazovkin (VYA) were employed to produce values for each step of conversion during polymerization. Values generated with both methods can confirm MFT method's values and further support themselves due to the cooperation

of each other. Thus, the activation energy was employed as a function of the degree of conversion which generally vary closely between results that were acquired through the various methods mentioned. [10, 22–24] The analysis of two methods of MFT shows a straightforward increase of E_a throughout the reaction. By contrast, it was observed that CS-MUF resins with 20% or 30% melamine content increases E_a at the ends of reaction as the molecular weight and subsequent steric effect at polymer networks reduces molecular mobility [2]. Figure 5 summarizes the results of the average kinetic values obtained from two MFK methods.

As mentioned before, there is no major difference in parameters through all activation energies regardless of analysis method; this outcome provides a conclusion

that this composition of resin, liquid thickeners, and fillers had an E_a , R^2 that corresponds with the α . Therefore, it can be assumed that all methods of curing kinetics predictions were accurate. However, it is pivotal to acquire the complete and exact reaction model if parameters of two special functions, $y(a)$ and $x(a)$, will be shown to be fitting of a method in the autocatalytic reaction model displayed in Scheme 1. The Malek method was utilized to calculate the two special functions respectively, which can be expressed as Eqs. (14) and (15).

$$y(a) = \frac{da}{dt} e^x \quad \#(14)$$

$$z(a) = \pi(x) \frac{da T}{dt \beta} \quad \#(15)$$

Mentioned equations (14) and (15) can be approximated using the fourth degree of rational expression composed by Senum and Yang [19], and presented as Eq. (16)

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad \#(16)$$

Acquired from the Malek method, E_a should be calculated through various techniques that can obtain multiple scans and several measurements of several heating rates. Therefore, Kissinger and an isoconversional method, KAS, was utilized.

Both $y(a)$ and $z(a)$ functions need to be characterized within the autocatalytic reaction model to be able to find the best model to determine the curing process in a more detailed manner. Thus, maximum

values of both special functions can be characterized by α_M and α_p^∞ through plotting $y(a)$ at several a values that are the normalized in a (0,1) interval, therefore the result of $f(a)$ function can be obtained. However, $z(a)$ is the second part of the relationship of these two special functions that can indicate how proportional it is with $f(a)$ and $g(a)$. Furthermore, Figure 6 provides the plots of $y(a)$ and $z(a)$ as a function of a , covering several heating rates. As mentioned, appropriate functions will fit to their specific connected value(s) with typical shapes, indicating whether values fit the reaction model or not.

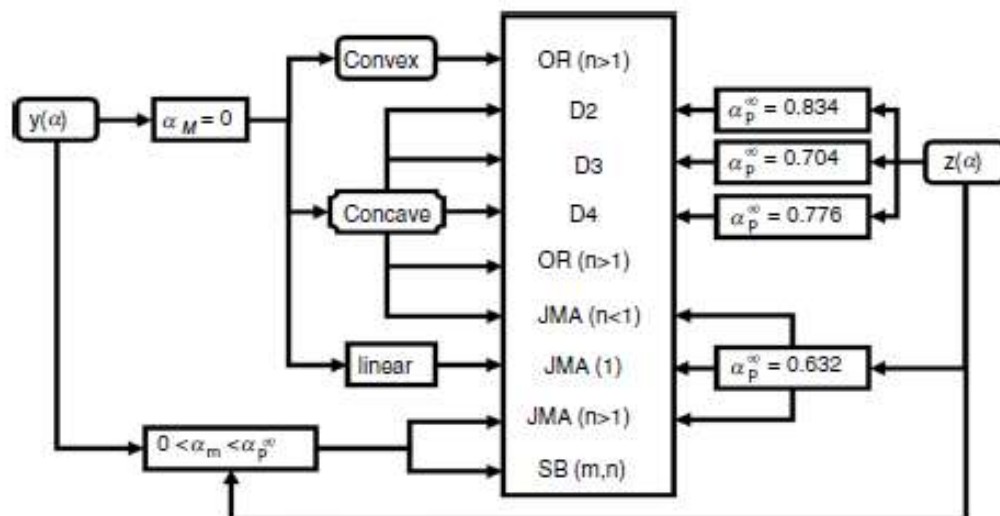
Observed results indicated all but one sample, Resin #2, didn't fully fit a model; The cure kinetic model of Resin #2 is fitted to autocatalytic Šestak-Berggren (SB) model based on the parameters obtained. The mentioned samples can be seen in Table 2, Figure 6, and compared with Scheme 1 to acquire a better understanding. Autocatalytic Šestak-Berggren (SB) reaction model was followed Eq. (17) as shown:

$$f(a) = a^m(1-a)^n \quad \#(17)$$

Logarithmic form of Eq. (17) and used with Eq. (5) could result in Eq. (18):

$$\ln\left(\frac{da}{dt}\right) + \frac{E_a}{RT} = \ln(A) + m \ln(a) + n \ln(1-a) \quad \#(18)$$

Since the E_a values were calculated separately using the KAS method it can be seen as a constant whilst moving E_a / RT to the left side of Eq. (18). Reaction order (m and n) and $\ln A$ can be calculated. However, it is crucial to mention the R^2 values to provide another confirmation; as shown in Table 3 and



Scheme 1: Autocatalytic reaction model determination diagram [20].

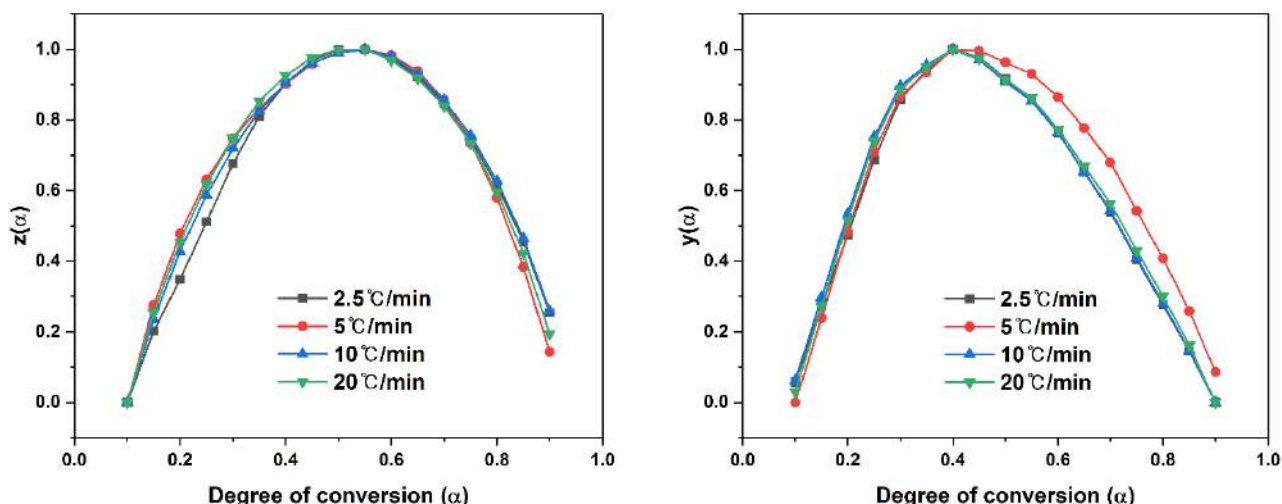


Figure 6: $y(\alpha)$ and $z(\alpha)$ function that fit the Šestak-Berggren (SB) reaction model for Resin #2.

Table 2: α_M and α_p^∞ at various β of CS-MUF resins

Resin No.	$\beta/^\circ\text{C min}^{-1}$	2.5		5		10		20	
		α_M	α_p^∞	α_M	α_p^∞	α_M	α_p^∞	α_M	α_p^∞
CTRL		1.00	0.53	1.00	0.54	1.00	0.53	1.00	0.52
#1		1.00	0.51	1.00	0.52	1.00	0.50	1.00	0.50
#2		0.41	0.53	0.44	0.54	0.40	0.53	0.40	0.53
#3		0.77	0.51	0.77	0.51	0.79	0.50	0.75	0.51
#4		0.67	0.52	0.60	0.53	0.79	0.50	0.75	0.51
#5		1.00	0.50	1.00	0.50	1.00	0.50	1.00	0.50
#6		1.00	0.49	1.00	0.48	1.00	0.49	1.00	0.49
#7		1.00	0.49	1.00	0.47	1.00	0.48	1.00	0.48
#8		1.00	0.48	1.00	0.49	1.00	0.49	1.00	0.48
#9		1.00	0.49	1.00	0.50	1.00	0.49	1.00	0.48

Table 3: Calculated kinetic parameters of Resin #2 resin using the autocatalytic reaction model SB (m, n)

Resin No.	B / $^\circ\text{C min}^{-1}$	ln A/s $^{-1}$	m	n	R2
#2	2.5	23.50 \pm 0.12	1.17 \pm 0.07	1.45 \pm 0.08	0.9719
	5	23.64 \pm 0.09	1.04 \pm 0.06	1.17 \pm 0.06	0.9717
	10	23.57 \pm 0.10	1.05 \pm 0.07	1.37 \pm 0.07	0.9767
	20	23.41 \pm 0.10	0.99 \pm 0.07	1.25 \pm 0.07	0.9710

Figure 7, all values, similarly to the other method's calculated parameters exhibit a similar trend of them.

5. CONCLUSIONS

As liquid thickeners are often used to control the viscosity of CS-MUF resins, this study investigated the impact of the liquid thickeners to the curing behavior and kinetics of the modified CS-MUF resins using DSC. Methods, such as MFT and MFK, were employed to

analyze the several parameters related to the cure kinetics and curing behavior of neat and modified CS-MUF resins. The results showed that the E_a wasn't enough to have a significant impact on the cure kinetics and curing behavior except Resin #2, indicating that the addition of liquid thickeners to CS-MUF resins didn't affect the cure kinetics and curing behavior of the modified CS-MUF resins. These results suggest that liquid thickener is used to control the viscosity of CS-

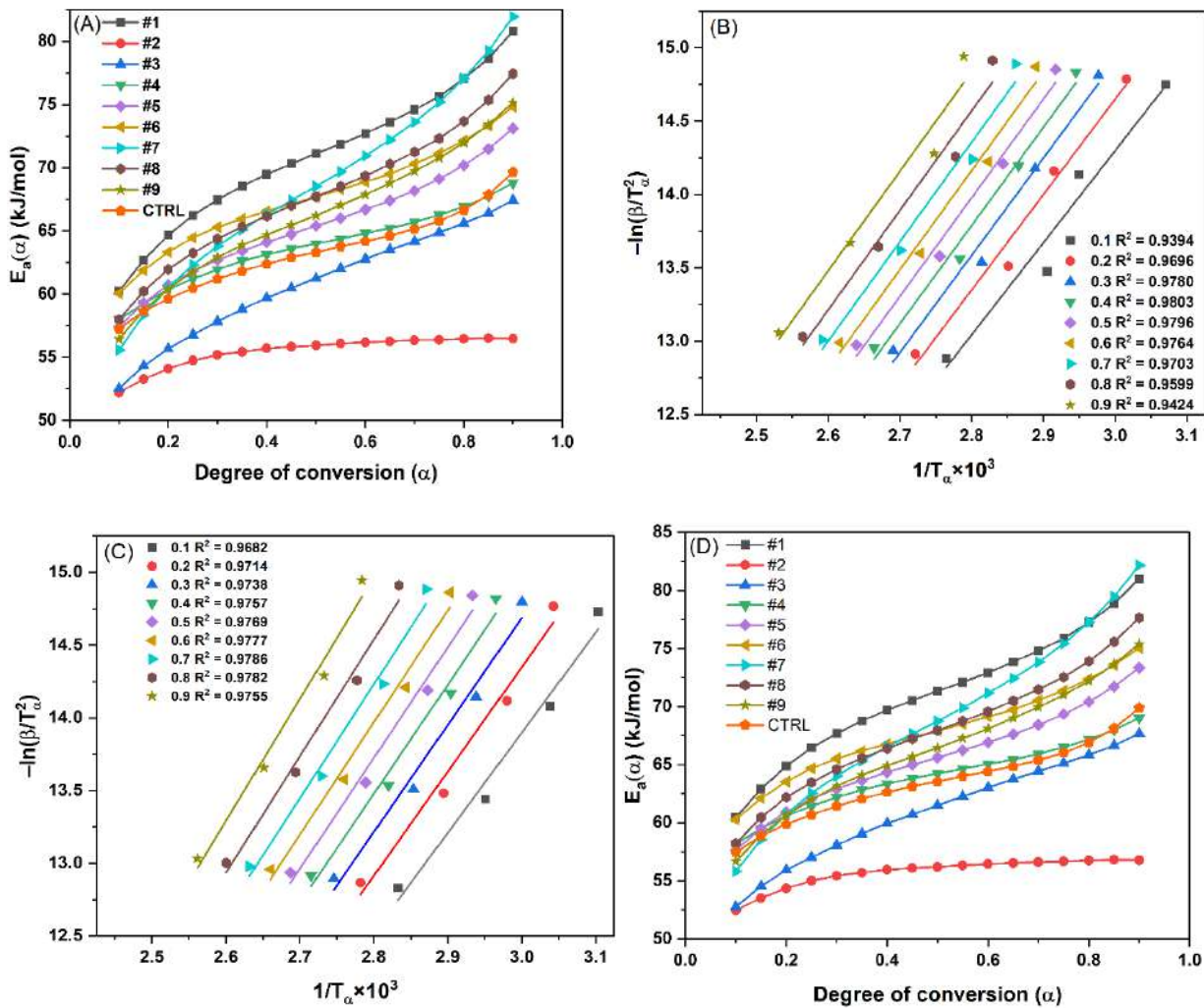


Figure 7: (A) Changes in E_a obtained with KAS method, (B) Data from only Resin #2 R^2 , (C) Data only containing CTRL R^2 values, and (D) Changes in E_a obtained with VYA method.

MUF resins without a significant impact on their curing kinetics and behavior.

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DECLARATIONS

Conflict of interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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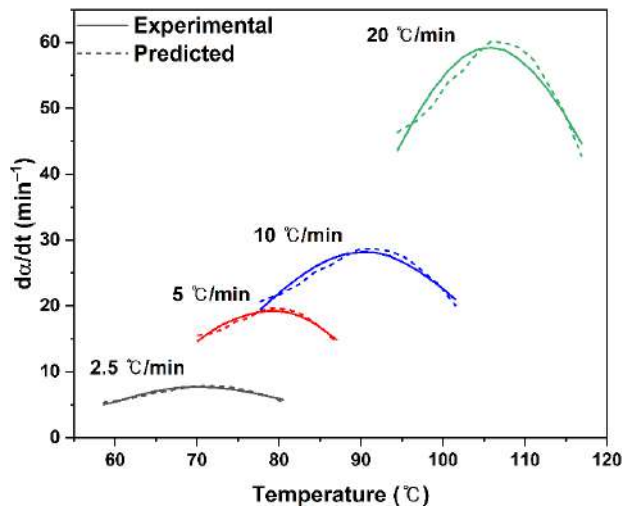


Figure 8: Comparison of the experimental and prediction values based on Málek method for Resin #2.

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