

Characterization of pre-curing behavior of urea-formaldehyde resin affected by different temperatures

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Abstract. Differential scanning calorimetry (DSC) was applied to investigate the thermal behavior of pre-curing urea-formaldehyde (UF) resin as affected by different temperatures; the activation energies (E_a) in different stages during the pre-curing course were analyzed by Kissinger method. The results indicated that the curing time was decreased with temperature increasing. Under isothermal temperature, the DSC curves of pre-curing UF resin shifted to shorter time, the conversion increased with increasing temperature. In dynamic scanning, with the pre-curing degree increasing, the DSC curves shifted to lower temperature, while both the onset and peak temperature decreased due to the cross-linking degree increased. The E_a and Z value decreased obviously firstly due to the concentration and reactivity of the reactants increased with water evaporation in the first stage, and then the increasing cross-linking degree and the formation of the network structure lead to both the E_a and Z value increasing in the second stage, indicating that the pre-curing behavior appeared.

1. Introduction

Urea-formaldehyde (UF) resin is a dominant thermosetting wood adhesive for the production of wood composite boards, such as medium density fiberboard (MDF), particleboard (PB) and hardwood plywood for its good performance.

Initially, mechanical blending was the main method to apply UF resin to dried fibers in MDF manufacture, but it was soon replaced by blowline blending method due to the resin distribution was much more uniformly and resin spots would not remained on the board surface. In the drying blow-line, the environment of curing agents, high temperature, and humidity would induce the occurrence of cross-linking reactions and pre-curing behavior, resulting in low efficiency of the resin and high cost.

Thermosetting resins changed from liquid state to viscous stage then gelation and vitrification till cured for the tight network formation [1]. Agglomeration of resin appeared to occur during heating treatments and storing course [2], the formation of methylenes and dimethylene ethers were the main reaction, the active functional groups and molecular mobility of aged resin were decreased resulted in lowering of cure rate [3]. Siimer *et al* [4] evaluated the cure process of UF resins and the thermal stability of cured resin with TG-DTA method; it was found that the exothermic curing temperature shifted to higher temperature with decreasing of the content of hydroxymethyl groups during storage. With Dynamic Mechanical Analysis (DMA), Young No *et al* [5] found that the gel times shortened



and cure slope of the vitrification stage decreased with elapsed time increasing, due to the deleterious effects of polycondensation.

However, few researches have focused on the pre-curing behavior of the UF resin, and the correlativity between the temperature, elapsed time and the pre-curing behavior was unknown. In this study, the thermal behavior of the pre-curing UF resin affected by different temperature was discussed, and the pre-curing kinetics during the whole pre-curing course were also analyzed.

2. Materials and methods

2.1. Materials

The commercial Urea-formaldehyde resin powder adhesive (PreferTM 4405) was purchased from DYNEA ASA Chemical Co. Ltd (Shanghai, China). Based on the total resin weight, a 1% ammonium chloride (NH₄Cl) (25 % aqueous solution) was added as a curing agent. The UF resin with the solid content of 40 %, 50 %, 60% was prepared by dissolving the powder with the distilled water.

2.2. Samples Preparation

About 1g of UF and ammonium chloride mixture was placed in aluminum tube with the dimension of 96.6 mm × 160 mm × 0.7 mm (length × diameter × wall thickness). When the temperature of the glycerin reached 80, 100, 120 and 150 °C, the tubes were put into oil bath with 2 cm below the oil level. Once reaching the setting time, the tube was taken out and then immersed into the liquid nitrogen.

2.3. Curing time measurement

According to China Industry Standard (GB/T 14074-2006), about 10g UF resin by adding 1 wt% NH₄Cl (25 wt% solution) placed into a test tube with the dimension of 150 mm × 25 mm (length × diameter), and then the tubes were put into the oil bath with stirring manually with three replication for each sample. Once the gelation was occurred, the measurements were finished.

2.4. Thermal behavior measurement

2.4.1. Isothermal DSC analysis

About 5 mg of samples were placed between an aluminum cup and lid, then sealed tightly. The pans were placed into sealed cell of DSC (PE diamond) instrument and pressurized to 2.0 MPa with nitrogen. The setting isothermal temperature was 80 °C, 100 °C, 120 °C and 150 °C, the heating rate was 200 °C/min.

2.4.2. Dynamic DSC analysis

A dynamic DSC scanning (TA Q2000) equipped with TA universal 2000 analysis software was used to evaluate the non-isothermal behavior. About 2 mg of the UF resins was weighted in high-pressure crucible prior to testing with the testing temperature range from 40 to 150 °C and the heating rate of 10, 15, 20 and 25 °C/min. The non-isothermal testing temperature was 80 °C, 100 °C, 120 °C and 150 °C.

2.5. Activation energy analysis

A single dynamic scan method was used to calculate the activation energy (E_a) based on the n th-order kinetics expressed by the following Kissinger equation (as shown in equation (1)):

$$-\ln\left(\frac{\beta}{T_p^2}\right) = \frac{E_a}{RT_p} - \ln\left(\frac{ZR}{E}\right) \quad (1)$$

On the basis of equation (1), the E_a (activation energy, kJ/mol) can be obtained from the the slope of the straight line between $-\ln(\beta/T_p^2)$ and $1/T_p$, while the Z (pre-exponential factor, 1/s) can be calculated from the y-intercept refers to $-\ln(Z \times R/E_a)$.

3. Results and discussion

3.1. Effect of the temperature on the curing time

As can be seen in figure 1, curing temperature showed significant effect on the curing time. The curing time of resin with the solid content of 40%, 50% and 60% decreased with increasing the temperature. When the solid content was 50%, the curing time was 193 s for 80 °C, 96 s for 120 °C and 47 s for 180 °C. It is generally believed that under the effect of temperature in drying pipe, the solid content of resin was increased due to the evaporation of free water. On the basis of hydrogen bonds, the changing amount and compatibility of the water, which was regarded as active component to form physical network, would lead to different sedimentation conditions during formation of network of different densities [6].

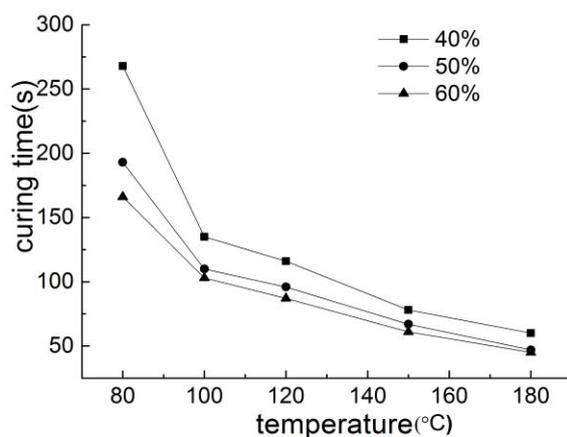


Figure 1. The curing time of UF resins with different temperature.

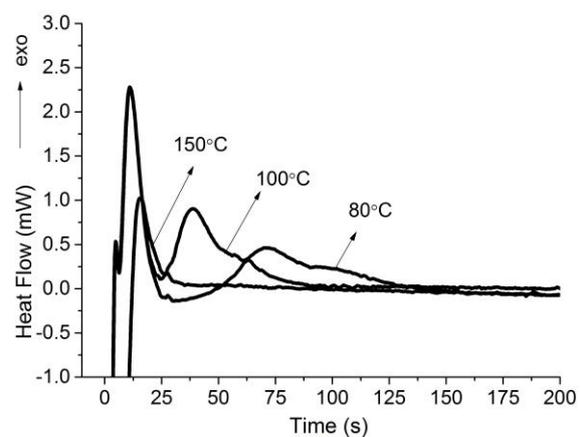


Figure 2. Isothermal DSC curves of UF resin under different temperature.

3.2. Thermal behavior of the pre-curing UF resin

3.2.1. Thermal behavior with isothermal condition

The results of thermal behavior of UF resins under the isothermal condition at different temperature were shown in figure 2 and table 1. As shown, the whole curing curves were shifted to shorter time with increasing temperature, and both the values of heat and areas of curing peak were similar between 80 °C and 100 °C. When temperature increased to 150 °C, the values of heat and peak area were lower than that of 80 °C and 100 °C, this deviation was mainly ascribed to fast curing under 150 °C, the section of initial curing curve was overlapped with the part of adjustment of instrument (the adjustment time of isothermal DSC was about 20 s), and the true onset and peak time were hid. As shown in figure 3, at the same time, the conversion values of UF resin were higher with increasing temperature.

Table 1. The isothermal DSC parameters of UF resin.

Temperature (°C)	Onset time (s)	Peak time (s)	End time (s)	Heat (J/g)	Peak area (mJ)
80	51.12	70.02	122.22	20.027	29.039
100	28.26	39.18	54.72	17.832	28.695
150	12.42	15.6	22.98	4.098	7.376

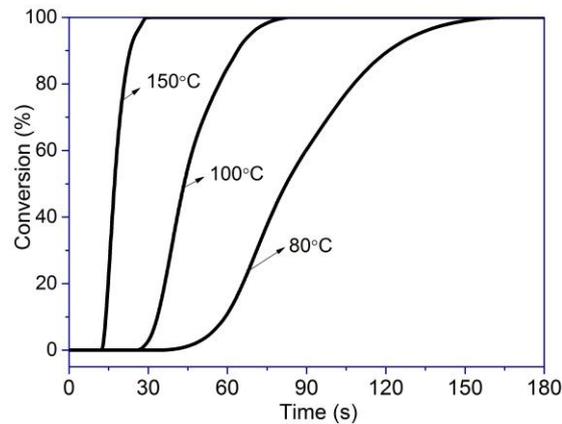


Figure 3. The conversion of UF resin under different temperature.

3.2.2. Thermal behavior with non-isothermal condition

Figure 4 shows typical DSC curves of UF resins with different pre-curing time under the temperature of 100°C and 150°C. It can be seen that most curves showed more than one exothermic peak (i.e., the control and 10 s in the figure 4(a)), this phenomenon could be attributed to the specific conditions of synthesis formulas of the high formaldehyde [7] content, the different NaOH content [8] and urea component [9,10]. It can be seen that the exothermic peaks shifted to lower temperature and became smaller with the pre-curing time prolonging.

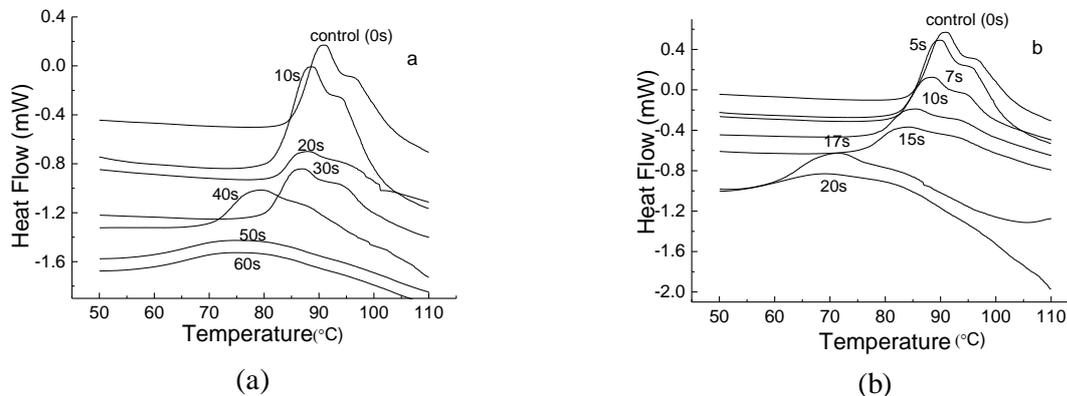


Figure 4. The DSC curves of UF resins with different pre-curing time ((a) 100 °C, (b) 150 °C).

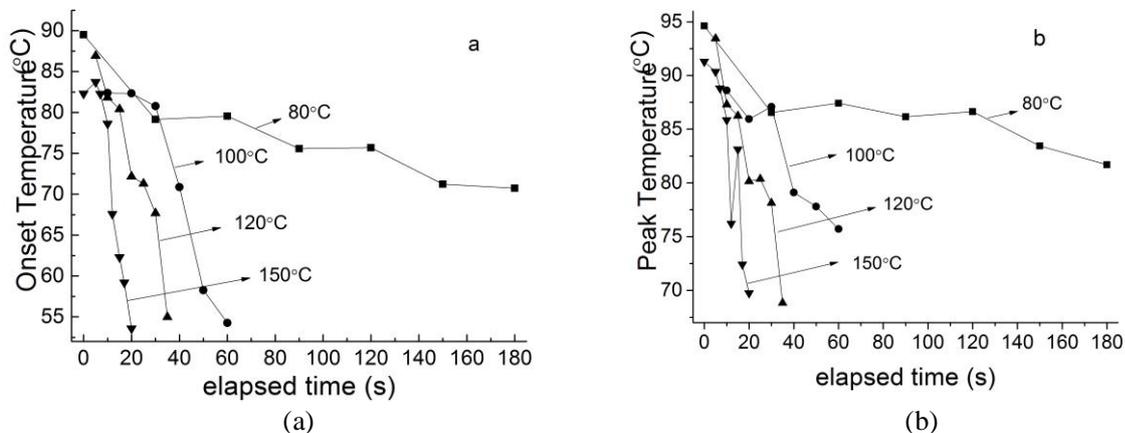


Figure 5. The onset and peak temperature of DSC with different temperature and elapsed time ((a) onset temperature, (b) peak temperature).

According to DSC curves, the onset and peak temperature was the time point when curing reaction began and the conversion rate reached a maximum during a dynamic scan, respectively [11]. As shown in figure 5, the temperatures of the onset and peak decreased remarkably with time elapsing. It can be concluded that the curing temperature were higher, the polycondensation rate of the active functional groups became faster leading to the cross-linking degree of the pre-curing UF increased.

3.3. Curing Kinetic of pre-curing UF resin under different temperature

The results of the E_a , Z and corresponding regression coefficient (R_a^2) calculated by the Kissinger method were shown in table 2 and figure 6.

Table 2. The activation energy of pre-curing UF resins.

Pre-curing time (s)	heating rate (°C /min) β	Peak Temperature (°C)	LN (β/T_p^2)	$1/T_p$	E_a (kJ/mol)	Z-pre exponential	R_a^2		
control 0	10	94.62	-9.512	0.0027	100.24	1.61×10^{11}	0.946		
	15	98.72	-9.129	0.0027					
	20	100.21	-8.849	0.0027					
	25	104.77	-8.650	0.0026					
80 °C	30	10	86.55	-9.468	53.97	3.31×10^4	0.917		
		15	97.45	-9.122				0.0027	
		20	100.37	-8.850				0.0027	
		25	102.63	-8.639				0.0027	
	90	10	86.17	-9.466	0.0028	49.89	9.67×10^5	0.840	
		15	89.53	-9.079					0.0028
		20	93.72	-8.814					0.0027
		25	103.30	-8.643					0.0027
	150	5	76.46	-10.104	0.0029	84.98	2.27×10^9	0.930	
		10	81.70	-9.441					0.0028
		15	90.14	-9.082					0.0028
		20	90.31	-8.796					0.0028
100 °C	10	10	89.21	-9.483	0.0028	96.13	6.53×10^{10}	0.967	
		15	92.66	-9.096					0.0027
		20	97.40	-8.834					0.0027
		25	98.36	-8.616					0.0027
	30	10	83.79	-9.453	0.0028	65.17	2.05×10^6	0.977	
		15	91.63	-9.091					0.0027
		20	95.01	-8.821					0.0027
		25	97.74	-8.613					0.0027
	50	10	77.81	-9.419	0.0028	167.65	1.75×10^{22}	0.855	
		15	78.14	-9.015					0.0028
		20	80.63	-8.742					0.0028
		25	82.46	-8.529					0.0028
120 °C	10	10	87.30	-9.472	0.0028	65.64	1.97×10^0	0.947	

		15	93.73	-9.102	0.0027			
		20	99.77	-8.847	0.0027			
		25	100.08	-8.626	0.0027			
	20	10	80.15	-9.432	0.0028	65.47	3.41×10^6	0.947
		15	84.34	-9.050	0.0028			
		20	85.47	-8.769	0.0028			
		25	93.40	-8.589	0.0027			
	30	10	76.67	-9.412	0.0029	67.37	7.30×10^6	0.900
		15	85.68	-9.058	0.0028			
		20	86.87	-8.777	0.0028			
		25	88.68	-8.563	0.0028			
150 °C	5	10	90.36	-9.489	0.0028	96.04	5.34×10^{10}	0.884
		15	96.01	-9.114	0.0027			
		20	98.80	-8.842	0.0027			
		25	100.00	-8.625	0.0027			
	10	10	85.36	-9.461	0.0028	66.45	3.12×10^6	0.944
		15	89.63	-9.080	0.0028			
		20	96.78	-8.831	0.0027			
		25	97.67	-8.613	0.0027			
	15	10	83.38	-9.450	0.0028	120.02	4.26×10^{14}	0.990
		15	87.44	-9.067	0.0028			
		20	89.62	-8.792	0.0028			
		25	91.14	-8.577	0.0027			

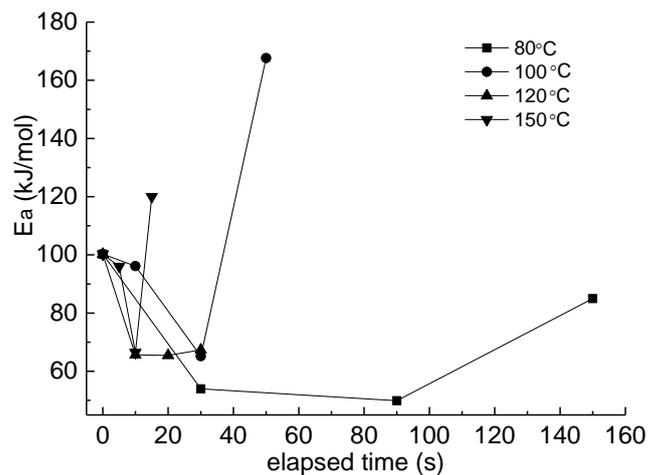


Figure 6. The E_a of UF resins in the different pre-curing stages.

As shown in figure 6, the changes in activate energy (E_a) were decreased initially, then ascended dramatically. On the basis of collision theory, the Z value is on behalf of the number of active sites and collision possibilities [12], the variation tendency of Z values was in accordance with that of the values of E_a .

The variations of the E_a and Z values were obviously decreased firstly and then increased, however,

the time nodes of each stage were unsynchronized with different temperature, in other words, the higher of the curing temperature, the shorter of the time course in which both the values of E_a and Z begin to decrease and then increase.

This result was quite reasonable, (1) the collision chances of molecules were reduced in the early stage of the curing process due to the abundant water in the fresh resin. When resin was heated under isothermal conditions, the constant effect of heat promoted evaporation of water, and the concentration of the reactants increased resulting in the decreasing of active sites and increasing of cross-linking degree. This was the cause of the decreasing of E_a and Z in the first stage. (2) In the second stage, the water was locked in the macro-molecular structure due to the formation of the super-cluster and the tight network [3,13], and then more energy was required to promote the water evaporation, which lead to the E_a and Z value increased and the reaction rate decreased along with pre-curing time increasing. And the increase of E_a and Z value make it possible to judge the occurrence and the degree of the pre-curing behavior. These results were in a good agreement of the conclusion in our previous researches [14].

In general, activation energy has a positive relationship with the pre-curing behavior of the UF resin; these results indicated that pre-curing behavior of the UF resin could be predicted by evaluating of the variation of the activation energy by DSC.

4. Conclusions

- The temperature had strong effect on the curing time. The resin curing action was subjected to double effects of drying temperature and solid content due to the evaporation of free water in the drying process.
- Under the isothermal temperature, with temperature increasing, the whole curing curves were shifted to shorter time, both heat and peak areas were similar at 80 °C and 100 °C, while these two values were higher than that of 150 °C due to overlapped of curing curves.
- With the dynamic scanning, the whole DSC curves of UF resin shifted to lower temperature and the onset temperature and peak temperature decreased remarkable with increasing of the pre-curing degree. Meanwhile, the value of E_a and Z decreased initially and then increased due to the evaporation of water and the formation of the in tight network of UF resin. These results indicated that pre-curing behavior of the UF resin could be predicted by evaluating of the variation of the activation energy by DSC. In short, lowering the drying temperature is a proper method to slow down the pre-curing reaction of UF resin.

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