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개량된 요소 수지의 열적 특성 분석

Wei Hong, Mianwu Meng†, Dingding Gao, Qingye Liu, Caiyan Kang, Siyu Huang, Zhenming Zhou, and Chunqiang Chen

Key Laboratory of Ecology of Rare and Endangered Species and Environmental Protection
Guangxi Key Laboratory of Environmental Pollution Control Theory and Technology
College of Environment and Resources, Guangxi Normal University
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Thermal Analysis Study of Modified Urea-Formaldehyde Resin

Wei Hong, Mianwu Meng†, Dingding Gao, Qingye Liu, Caiyan Kang, Siyu Huang, Zhenming Zhou, and Chunqiang Chen

Key Laboratory of Ecology of Rare and Endangered Species and Environmental Protection
Guangxi Key Laboratory of Environmental Pollution Control Theory and Technology
College of Environment and Resources, Guangxi Normal University, Guilin 541004, China
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Abstract: In this study, the structures and thermal stability of pure urea-formaldehyde resin (PR) and modified urea-formaldehyde (UF) resin are investigated by differential thermal gravity (TG/DTG), and differential scanning calorimetry (DSC) supported by data from Fourier transform infrared spectroscopy. FTIR analysis indicate that the modifiers such as polydimethylsiloxane, dicyclohexylcarbodiimide and phenol have actively participated in the curing reactions. TG/DTG and DSC curve of UF resin show that its pyrolysis process is conducted in three steps: desiccation and dehydration, flash pyrolysis and slow decomposition. Compared with pure urea-formaldehyde resin (PR), modified UF resin exhibited good thermal stability. The activation energy (E) of modified UF resin acquired by Kissinger and Ozawa method was higher than that of PR. $\Delta H > 0$, $\Delta S > 0$ and $\Delta G > 0$ in the thermal decomposition process of UF resin means that the decomposition reaction of UF resin before and after modification is a process of unnatural decalescence and entropy increase.

Keywords: modified UF resin, thermal properties, TG/DTG, thermodynamics, thermal decomposition kinetics.

Introduction

Urea-formaldehyde resin (UF) is one of the most common adhesive used for wood processing, building materials as well as man-made plank due to its simple technology and low cost. However, since the UF synthesized from urea and formaldehyde is often used as construction material, it has become a major source of high formaldehyde emissions in our indoor environment because of unreacted formaldehyde and hydrolysis of UF linkages.[1] These emissions not only increase environmental pollution, but also have an adverse effect on health and living comfort. Therefore, it is quite significant to find an effective material to depress formaldehyde emission. Recently, modification of urea-formaldehyde resin has become a hot research topic in chemistry and environmental protection area.[2-5]

As a powerful technique for studying the pyrolysis mechanism of physicochemical processes, thermal analysis mainly includes differential scanning analysis (DTA), thermomechanical analysis (TMA), differential thermal gravity (TG/DTG) and differential scanning calorimetry (DSC).[6-9] The last two kinds are the most widely used approach for studying pyrolytic reaction of thermosetting resin.[10-13] In most thermal decomposition kinetic research methods, Kissinger's[14] maximum weight-loss rate method and Ozawa's[15] equivalent weight-loss percentage method are applied for dynamic computation via relation between peak temperature and heating rate of DTG and DSC curves, involving no selection of mechanism func-

†To whom correspondence should be addressed.
E-mail: 897405894@qq.com
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tion and applying to any reaction order with more reliable result. Therefore, Kissinger and Ozawa method are two kinds of simple but effective thermomechanical analysis method.

In this research, polydimethylsiloxane, dicyclohexylcarbodiimide and phenol are used as modifier and bentonite as filler to produce urea-formaldehyde resin adhesive. Structures and thermal property of pure urea–formaldehyde resin (PR) and modified UF resin are characterized by the application of Fourier transform infrared (FTIR) spectroscopy, differential thermal gravity (TG/DTG) and differential scanning calorimetry (DSC). Application of Kissinger's maximum weight-loss rate method and Ozawa's equivalent weight-loss percentage method for studying thermal degradation kinetics of UF resin before and after modification and its pyrolysis thermodynamics will provide theoretical reference for using and researching modified UF resin.

Experimental

Materials. Urea (CON_2H_4, Aldrich Chemical Co., USA) and 35% formaldehyde (CH_2O, Tokyo Chemical Industry, Japan) and were used to synthesize urea-formaldehyde resin. Polydimethylsiloxane ($(C_2H_6OSi)_n$, Tokyo Chemical Industry, Japan), dicyclohexylcarbodiimide ($C_{13}H_{22}N_2$, Junsei Chemical Co., Japan), phenol (C_6H_5OH, Aldrich Chemical Co., USA) and bentonite (Aldrich Chemical Co., USA) were used to synthesize modified urea-formaldehyde resin. All other reagents were of laboratory-grade, and were used without any further purification.

Preparation of Resin Samples. Pure urea-formaldehyde resin (PR) with formaldehyde to urea (F/U) ratio 0.7 was synthesized in the laboratory. Synthesis procedure of modified UF resins was shown as follows: put 1.0 mol urea in a reactor with magnetic stirrer and add 500 cm^3 distilled water; then 0.05 mol dicyclohexylcarbodiimide, 0.05 mol phenol, 5 g bentonite, 5 mL polydimethylsiloxane and 1.0 mol 35% formaldehyde are added into the reaction mixture according to following order. Reaction mixture was blended for 5 h. The physical properties of urea resin before and after modification are shown in Table 1.

Table 1. Performance of UF Resin before and after Modification

Sample	Free formaldehyde (%)	Viscosity (Pa·s)	Solid content (%)	pH
Unmodified	0.644	17	79.63	3.26
Modified	0.338	120	83.48	2.75

Measurements of Resin Samples. The FTIR spectroscopy (Nicolet 380) is used for studying surface functional groups of resin sample. Grind 1-2 mg sample and then intensively mix it with 100~200 mg dry KBr powder, after which crush it into transparent slices by hydraulic machine and put them in the scanning area of FIIR for infrared scanning. The indoor temperature and humidity for test is 18~25 °C and < 80%. The spectra are obtained within the spectral area 4000-500 cm^{-1} with a resolution of 2 cm^{-1}. The thermal stability of samples are tested by differential thermal gravity (TG/DTG, Labsys evo series). The initial sample weight is 5±0.1 mg and the heating rate is controlled respectively at 5, 10, 15 and 20 °C/min with the working gas flow of 30 mL/min nitrogen. The thermal properties of the samples are also tested by differential scanning calorimetry (DSC, Dupont 910) in nitrogen gas. About 5±0.1 mg samples are encapsulated in aluminum pans with the protection of nitrogen for the experiment. The heating rate is respectively controlled at 5, 10, 15 and 20 °C/min and the test temperature ranges to 800 °C.

Pyrolysis Kinetics of Resin Samples. Kissinger's maximum weight-loss rate method[14] and Ozawa's equivalent weight-loss percentage method[15] are used to calculate pyrolysis kinetics parameter of UF resin and study pyrolysis kinetics according to non-isothermal kinetic theory in order to research pyrolysis mechanism of urea formaldehyde resin adhesive.

Equation of Kissinger's multiple-differential curve method is as following:[14]

$$\ln\left(\frac{\beta}{T_P^2}\right) = \ln\frac{AR}{E} - \frac{E}{RT_P} \quad (1)$$

Equation of Ozawa's equivalent conversion rate method is as following:[15]

$$\log\beta = \log\left[\frac{AE}{-R\ln(1-\alpha)}\right] - 2.315 - 0.4567\frac{E}{RT} \quad (2)$$

Where β(°C/min) is the heating rate, T_p(°C) is the peak temperature, T(°C) is the experimental temperature, E(J/mol) is the activation energy, A(s^{-1}) is the pre-exponential factor, R is the gas constant, and α(%) is the thermal weight loss percentage.

Pyrolysis Thermodynamics of Resin Samples. Pyrolysis thermodynamics of UF resin is investigated based on pyrolysis thermodynamic parameter of it and TG-DTG curves to clarify its pyrolysis mechanism. Thermodynamic parameters of UF sample in thermal decomposition course mainly include variation of activation enthalpy (ΔH), activation entropy (ΔS)

and Gibbs free energy (ΔG),[16] and each of them can acquired via eq. (3)~(5):

$$\Delta H = E - RT \tag{3}$$

$$A\exp\left(-\frac{E}{RT}\right) = \frac{k_b T}{h}\exp\left(-\frac{\Delta G}{RT}\right) \tag{4}$$

$$\Delta G = \Delta H - T\Delta S \tag{5}$$

Where E(J/mol) is the activation energy, A is the pre-exponential factor, ΔH(J/mol) is the activation enthalpy, ΔG(J/mol) is the free energy, ΔS(J/(mol·K)) is the entropy change, T(°C) is the peak temperature, k_b is the Boltzmann constant, and h is the Palnck constant.

Results and Discussion

The formation of urea-formaldehyde resin before and after modification was confirmed based on its FTIR spectrum. The FTIR spectra of the unmodified and modified UF resin samples are shown in Figure 1. Compared with unmodified urea-formaldehyde resin sample, the modified sample shows decrease in vibration absorption peak at the position 3430-3437 cm^{-1}, 1630-1636 cm^{-1} and 620 cm^{-1} of the FTIR curve, which means that modifiers such as polydimethylsiloxane and dicyclohexylcarbodiimide have participated in UF curing reaction and changed the chemical bond ratio in product structure. The stretching vibration absorption peak of -OH, $-NH_2$ and -NH takes place at the strongest peak of 3430-3437 cm^{-1}, the carbonyl stretching vibration absorption peak of secondary amide takes place at 1630-1636 cm^{-1} and bending vibration absorption peak of -H takes place at 620 cm^{-1} probably due to mono-substituted benzene ring generated by phenol.[17] Modified UF resin has four small new vibration absorption peaks at the 803-1384 cm^{-1} with 803 cm^{-1} as the stretching vibration absorption peak of -O-CH_2-O-, near 1075 cm^{-1} as -OH deformation vibration absorption peak of -CH_2OH and 1262 cm^{-1} as the vibration absorption peak of asymmetry -CH for -NHCH_2NH-, indicating that dicyclohexylcarbodiimide has participated in UF reaction. C-O stretching and O-H surface deformation vibration characteristic absorption peak takes place at 1384 cm^{-1} and a faint benzene ring frame stretching vibration absorption peak at 1580 cm^{-1}, which means that phenol has participated in UF reaction.[18]

The TG-DTG curves of UF before modification are shown in Figure 2, which indicates that pyrolysis process of UF resin is comprised of three parts: desiccation and dehydration, flash pyrolysis and slow decomposition. It is also observed from Figure 2 that weight loss ratio of unmodified UF samples reaches 15.6% at the temperature near 102 °C, mainly derived from water evaporation in resin samples. The weight loss ratio

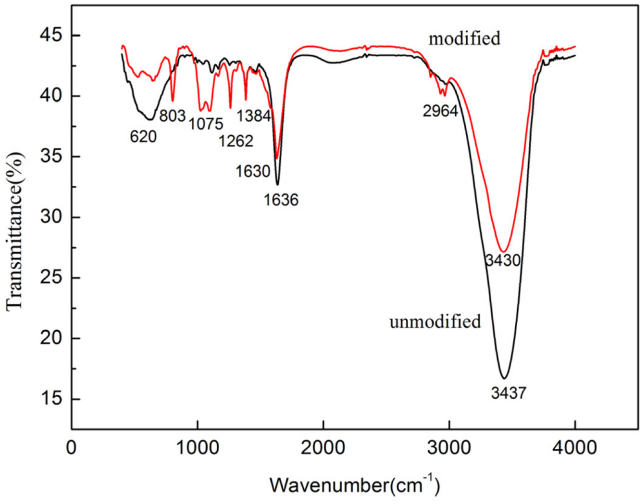

Figure 1. FTIR curves of UF before and after modification.

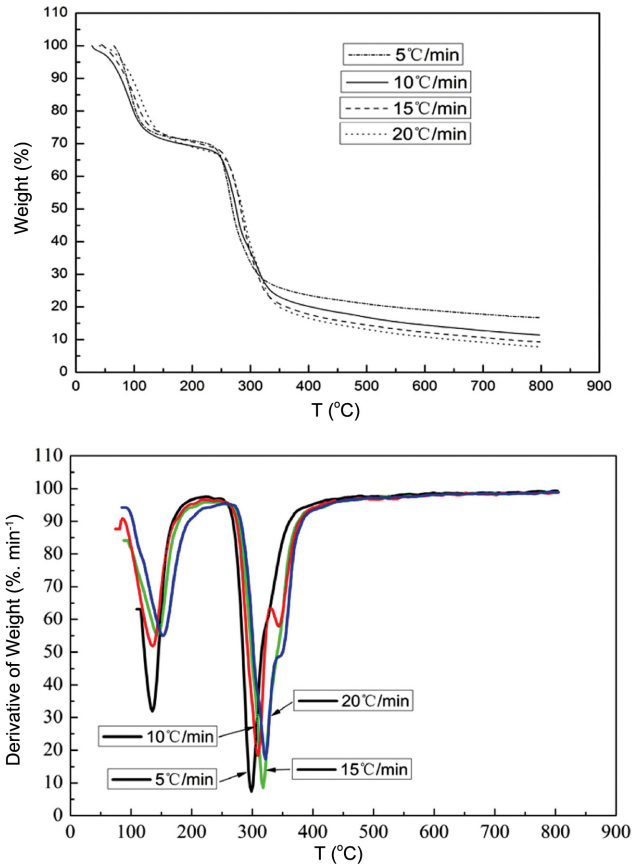

Figure 2. TG-DTG curves of unmodified UF resin.

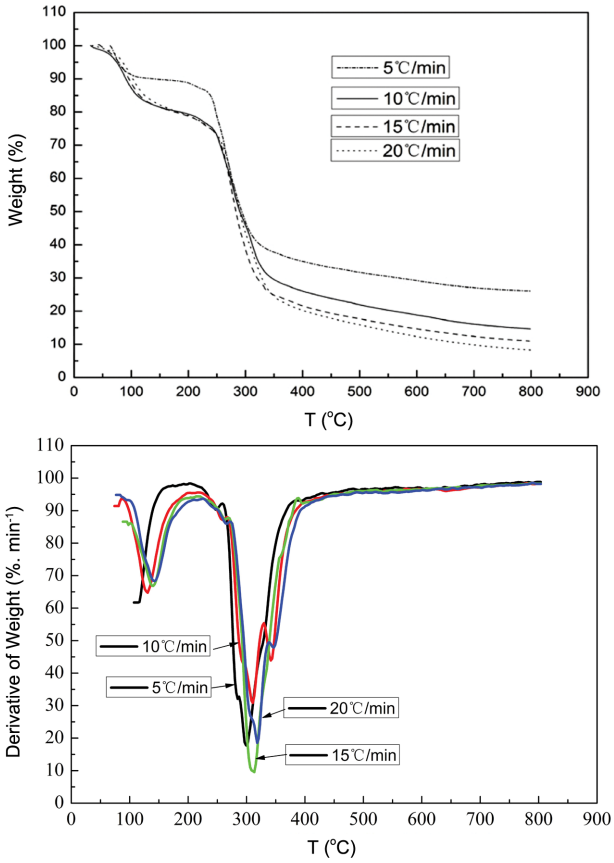

Figure 3. TG-DTG curves of modified UF resin.

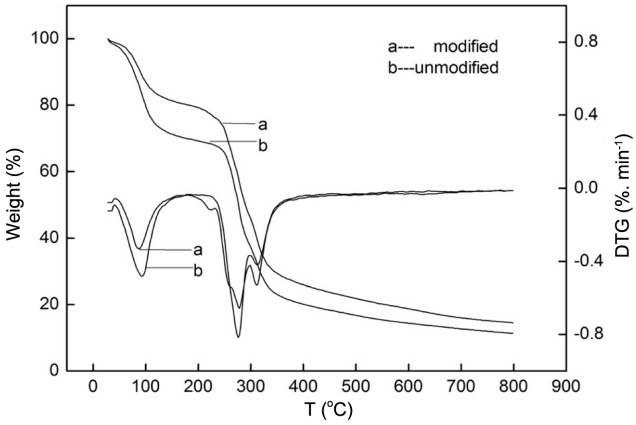

Figure 4. TG-DTG curves of UF resin before and after modification.

is 14.3% within the temperature range of 103~198 °C when incompletely cured UF resin gradually decomposes out volatile organic compound such as free formaldehyde. The weight loss ratio of urea formaldehyde adhesive arrives at 47.8% with the temperature 200~330 °C, probably due to pyrolysis of cured UF accompanies with the formation of diureidomethane, hydroxymethyl and ureogenesis as well as formaldehyde emission.[17]

The TG-DTG curves of modified UF are shown in Figure 3, It could be seen that weight loss ratio of modified UF sample is 10.9% at 102 °C, 9.5% within 103~198 °C and 46.1% within 200~330 °C. It means that moisture content of modified resin has decreased and pyrolysis weight loss reduces within the low temperature range.

The TG-DTG curves of UF before and after modification are shown in Figure 4. It could be seen that weight loss ratio (11.3%) of modified UF resin sample within 103~198 °C is lower than that (14.3%) of unmodified one and overall weight loss ratio of modified UF resin sample is 6.5% lower than unmodified UF resin, meaning that heat stability of UF resin grows significantly after modification.

The DSC curve of UF resin before and after modification at different heating rate is shown in Figure 5. It could be observed that unmodified UF resin has an obvious crystal transfer endothermic peak within 102.1~113.3 °C while that of modified UF resin shifts to a high temperature, which further

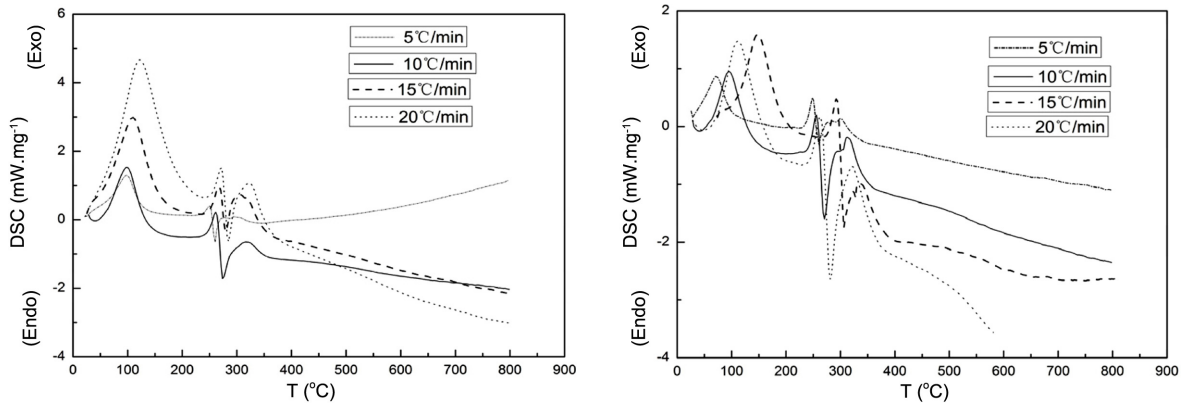

Figure 5. DSC curves of UF resin before and after modification at different heating rates.

verifies good thermal stability of modified resin sample. Additionally, there is a fusing endothermic peak at 273.6 ºC, which may be incomplete mainly because that partial melting process of UF resin is concealed by the immediately following rapid exothermic decomposition course. With heating rate increasing, fusing endothermic peak becomes more and more evident and peak temperature (T_p) rises, which means that the pyrolysis behavior of UF resin is a heterogeneous process of simultaneous reaction of solid and liquid.[19]

Relationship of logβ-1/T_p of UF resins based on Kissinger equation are shown in Figure 6. It is observed from Figure 6 that $\ln(\beta/T_p^2)$ of urea-formaldehyde resin adhesive before and after modification is linear to 1/T_p and with good fitting result ($R^2 > 0.9971$). Slope of the straight acquired by linear fitting of it is the activation energy (E) of urea-formaldehyde resin adhesive and other parameters such as pre-exponential factor (A) can be obtained by intercept with the result presented as Table 2.

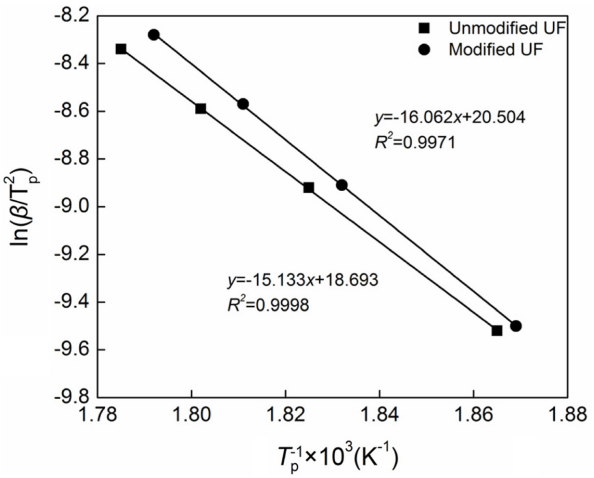

Figure 6. Relationship of $\ln(\beta/T_P^2)$–$1/T_p$ of UF resins by Kissinger equation.

Table 2. Pyrolysis Kinetic Parameters of UF by Kissinger's Analysis

Kissinger	β(ºC/min)	T_p(K)	R^2	E(kJ/mol)	ln$A$(s^{-1})
Unmodified UF	5	536	0.9998	125.822	23.22
	10	548			
	15	555			
	20	560			
Modified UF	5	535	0.9971	133.556	23.09
	10	546			
	15	552			
	20	558			

Thermal pyrolysis kinetic parameters of UF by Kissinger's analysis are shown in Table 2, which showed that different heating rate corresponds with different peak temperature and peak temperature of UF adhesive will increase with heating rate. It also indicates that pyrolytic activation energy (E) of modified UF adhesive is higher than unmodified one.

Relationship of logβ-1/T_p of UF resins based on Ozawa equation are shown in Figure 7. Activation energy (E) of urea-formaldehyde resin adhesive is calculated via slope acquired by linear fitting and pre-exponential (A) is obtained by intercept. The characteristic parameter of UF resin by Ozawa analysis are shown in Table 3.

Table 3 showed that activation energy (E) is different under different weight loss ratio mainly due to various chief fractured chemical bonds of UF resin pyrolytic reaction in different decomposition stages. It is also observed from Table 3 that average pyrolytic activation energy (E) of modified UF resin is higher than that of unmodified. After comparing Table 2 and Table 3, it is found that activation energy (E) of modified UF

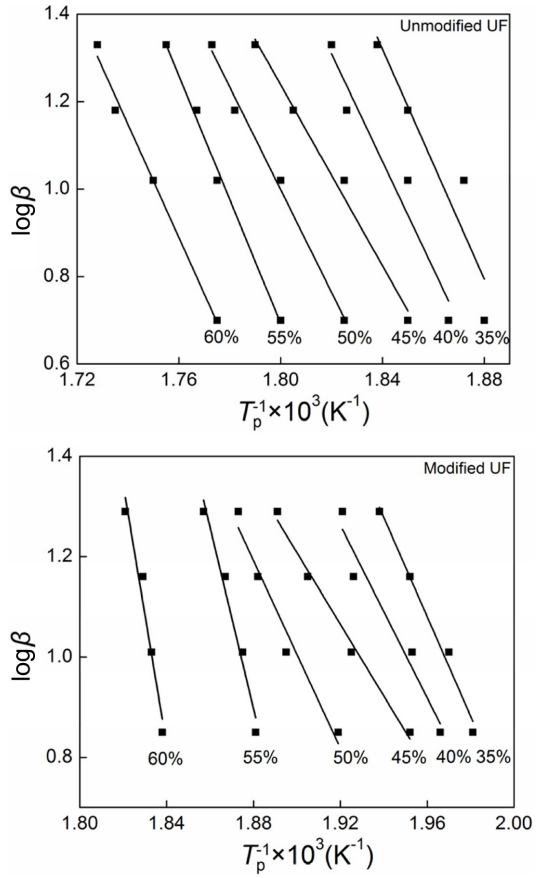

Figure 7. Relationship of logβ-1/T of UF resins based on Ozawa equation.

Table 3. Characteristic Parameters of UF by Ozawa's Analysis

Ozawa	α(%)	Linear equation	R^2	E(kJ/mol)	lg$A$(s^{-1})
Unmodified UF	60	y=-12.887x+25.040	0.9701	234.602	25.867
	55	y=-11.487x+22.160	0.9839	209.115	22.977
	50	y=-10.182x+19.532	0.9761	185.358	20.340
	45	y=-11.703x+22.054	0.9557	213.047	22.737
	40	y=-13.566x+25.101	0.9187	246.962	25.651
	35	y=-13.440x+24.412	0.8705	244.669	24.893
	Average			222.292	23.744
Modified UF	60	y=-15.606x+30.675	0.9926	284.100	31.537
	55	y=-16.202x+31.233	0.9912	294.950	32.019
	50	y=-13.078x+35.173	0.8198	243.503	36.221
	45	y=-11.871x+27.126	0.8705	221.612	28.019
	40	y=-13.814x+24.501	0.7998	247.528	25.893
	35	y=-14.331x+26.585	0.9887	277.719	27.893
	Average			261.569	30.264

resin adhesive acquired by Kissinger and Ozawa method is higher than that of unmodified, which further showed that the good heat stability of modified UF resin. It is also found that activation energy (E) acquired by Kissinger analysis is lower than Ozawa mainly due to that data used for activation energy (E) calculation by Kissinger adoptes the peak value corresponding to maximum decomposition rate of UF resin while what Ozawa adopts is the average value of UF resin in different weight loss ratio. Weight loss ratio between 35~60% has weaken the weightless influence of non-pyrolytic reaction at the initial and final stage and activation energy (E) acquired by Ozawa method is closer to the actual value in thermal decomposition process.

Since peak temperature is used in Kissinger method for calculating activation energy (E) to solve the decomposition course of urea-formaldehyde resin adhesive, the acquired activation energy (E) might be smaller than the average value of the whole process. Activation energy (E) acquired by linear fitting calculation in weight loss ratio via Ozawa method is the average value. To realize the reliability of thermodynamic parameter calculation and approach it to the real value of UF resin thermal decomposition process, activation energy (E) acquired by Ozawa method is used to calculate variation of activation enthalpy (ΔH), activation entropy (ΔS) and Gibbs free energy (ΔG) in thermal decomposition of UF sample. The calculation result of thermodynamic parameters for UF are shown in Table 4.

Table 4. Thermodynamic Parameters of UF

Ozawa	α(%)	ΔH(kJ/mol)	ΔS(J/(mol·K))	ΔG(kJ/mol)
Unmodified UF	60	230.03	236.87	99.81
	55	204.54	181.54	104.74
	50	180.79	131.08	108.73
	45	208.48	176.97	111.19
	40	242.39	232.74	114.44
	35	240.10	218.23	120.13
	Average	217.72	196.24	109.84
Modified UF	60	279.55	345.43	90.34
	55	290.40	354.67	96.03
	50	267.43	338.56	91.25
	45	278.48	357.13	90.16
	40	298.56	341.27	97.34
	35	295.34	363.35	94.18
	Average	284.97	350.07	93.22

According to the Table 4, it could be known that enthalpy change (ΔH), entropy change (ΔS) and Gibbs free energy (ΔG) are 217.72 kJ/mol, 196.24 J/(mol·K) and 109.84 kJ/mol in the thermal decomposition process of unmodified UF sample. ΔH, ΔS and ΔG are 284.97 kJ/mol, 350.07 J/(mol·K) and 93.22 kJ/mol in the thermal decomposition process of modified UF sample. $\Delta H > 0$, $\Delta S > 0$ and $\Delta G > 0$ in the thermal decomposition process of UF resin, which means that decomposition

reaction of UF resin before and after modification is a process of unnatural decalescence and entropy increase. It also indicates that proper change in temperature will realize $\Delta G < 0$ and that UF resin spontaneously decompose to release formaldehyde.

Conclusions

In this study, it is indicated that the modifiers such as polydimethylsiloxane, dicyclohexylcarbodiimide and phenol have actively participated in the curing reactions. The pyrolysis process of UF resin is conducted in three steps: desiccation and dehydration, flash pyrolysis and slow decomposition. The modified UF resin is featured with better thermal stability than pure urea-formaldehyde resin (PR). The activation energy (E) of modified UF resin acquired by Kissinger and Ozawa method is always higher than that of PR. $\Delta H > 0$, $\Delta S > 0$ and $\Delta G > 0$ in the thermal decomposition process of UF resin means that decomposition reaction of UF resin before and after modification is a process of unnatural decalescence and entropy increase.

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