Thermal Degradation Kinetics of Urea–Formaldehyde Resins Modified by Almond Shells

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ABSTRACT: Almond shell-modified urea–formaldehyde resins (AUF) were prepared in this study. The optimal addition amount of almond shells was selected by formaldehyde emission and wet shear strength. The activation energy (Ea) values at different conversion rates and the reaction kinetics were estimated based on the Flynn−Wall−Ozawa method. The results indicated that almond shells can significantly reduce the formaldehyde emission and increase wet shear strength and thermal stability of the urea–formaldehyde resin adhesive. The optimal addition of almond shells is 3 wt %.

1. INTRODUCTION

Urea–formaldehyde (UF) resins, a class of the most common adhesives, are applied widely in the wood industry owing to their many advantages, such as fast curing, high bonding strength, water solubility, and low costs. Nevertheless, the main disadvantage is the poor resistance to water, which causes a problem of formaldehyde release, due to unreacted formaldehyde and hydrolysis of the ether bond of resins. Reducing the molar ratio can reduce the formaldehyde emission of UF, but it will lead to the decrease of bonding strength at the same time. Many modifiers, such as melamine, phenol, and polyvinyl alcohol, were used in the modification of UF resins. However, all the above modifiers are chemical products, which are not friendly to the environment and costly to use in large quantities. Therefore, the modified UF resin based on biomass resources has a good development prospect.

Almond, a biomass nut shell, is widely distributed in temperate regions of the world. The global almond yield in 2016 was about 321 tons, and almond shells account for 35–75% of the total fruit weight; it means that 112–240 tons of almond shells is produced annually, and since they have no important industrial utilization, they are usually burned or discarded. Some components in almond shells, such as lignin, contain large amounts of hydroxyl groups and other chemical groups, which can react with formaldehyde to improve the thermal stability and water resistance of the resin. Therefore, lignin is thought to be an alternative to improve adhesive and mechanical properties and possibly reduce formaldehyde emissions. The lignin content in almond shells is about 30%, which is higher than that in most biomass nut shells.

Nowadays, research on almond shells is mainly focused on the production of bio-oil, the preparation of particleboards, activated carbon, etc. However, there are few studies on the performance of UF resins modified by almond shells.

In this article, different amounts of almond shells were added to the UF resin, and the formaldehyde emission and wet shear strength of the plywood were studied. Thermogravimetric (TG) analysis, which monitors the relationship between mass loss and temperature changes, is a common method to evaluate the thermal degradation behavior of thermosetting polymers. In this work, the thermal degradation kinetics of the resin was analyzed by the Kissinger and Flynn–Wall–Ozawa (FWO) methods. The thermal degradation activation energy (Ea) values at different conversions and the reaction kinetics were estimated based on the FWO method.

2. RESULTS AND DISCUSSION

2.1. Effect of Almond Shell Addition Amount on Properties of Plywood. The formaldehyde emission and wet shear strength of the plywood prepared by different resins are shown in Figure 1. After adding almond shells, the form-
aldehyde emission of plywood was lower than that of unmodified plywood and shows a trend of first decreasing and then increasing with the increase of the almond shell addition amount. The results showed that the addition of almond shells can effectively reduce the formaldehyde release of the plywood. This is mainly because lignin, the main component of almond shells, contains a large amount of high-reactivity phenolic hydroxyl groups, which can be combined with methylolurea and react with free formaldehyde. However, excessive almond shells will compete for the active sites of formaldehyde with urea, which will affect the addition of urea and formaldehyde, and eventually lead to higher formaldehyde release and lower bonding strength. The wet shear strength of plywood showed a trend of first increasing and then decreasing with the increase of the almond shell addition amount. When the addition amount of almond shells is 3 wt %, the formaldehyde emission and wet shear strength of plywood are 0.86 mg/L and 1.42 MPa, respectively, which are 28.93% lower and 42% higher than those of UF, respectively. The results showed that almond shells can effectively eliminate the release of formaldehyde due to the grafting reaction of lignin with formaldehyde, which makes the cross-linking network structure of the resin more complicated. Consequently, the optimal addition amount of almond shells is 3 wt %, and the almond shell-modified UF (AUF) resin mentioned later is the resin.

2.2. Thermal Degradation Analysis. In order to compare the thermal stability of UF and AUF resins and reveal the relationship between the mass loss of resin samples and temperature, the derivative thermogravimetric (DTG) curves were obtained from the measured TG curves numerically.
The $\alpha$ and DTG of UF and AUF are shown in Figure 2. As could be seen in the DTG curve, the pyrolysis process of resins can be divided into three stages. At the first stage, at temperatures below 493.15 K, the weight loss was mainly ascribed to the evaporation of surface and inherent moisture of the resin34 and the slow release of formaldehyde.35 The evaporation of water could be induced by the condensation reaction of unreacted hydroxymethyl and amino groups.36,37 Also, the moisture loss is usually less than 16% in this stage. In the second stage, at temperatures between 493.15 and 603.15 K, as a result of the decomposition of methylene and methylene ether bonds,38,39 approximately 72% of the mass loss was discovered. The final stage is the further carbonization process, during a wide temperature range, from 603.15 to 850 K. The mass loss is about 12% mainly due to the removal of the N, H, and O elements at a lower rate in this stage.40

The TG and DTG of UF and AUF are shown in Figure 2. As could be seen in the DTG curve, the pyrolysis process of resins can be divided into three stages. At the first stage, at temperatures below 493.15 K, the weight loss was mainly ascribed to the evaporation of surface and inherent moisture of the resin34 and the slow release of formaldehyde.35 The evaporation of water could be induced by the condensation reaction of unreacted hydroxymethyl and amino groups.36,37 Also, the moisture loss is usually less than 16% in this stage. In the second stage, at temperatures between 493.15 and 603.15 K, as a result of the decomposition of methylene and methylene ether bonds,38,39 approximately 72% of the mass loss was discovered. The final stage is the further carbonization process, during a wide temperature range, from 603.15 to 850 K. The mass loss is about 12% mainly due to the removal of the N, H, and O elements at a lower rate in this stage.40

The TG and DTG diagrams of UF and AUF at a heating rate of 5 K min$^{-1}$ are shown in Figure 3. It could be observed that UF and AUF resins each have a small shoulder at 508.15−522.23 K. The appearance of the shoulder is due to hemicellulose and lignin degradation and the gradual decomposition of free formaldehyde and other volatile organic compounds in the resin.41,42 The TG and DTG diagrams of UF and AUF at a heating rate of 5 K min$^{-1}$ are shown in Figure 3. It could be observed that UF and AUF resins each have a small shoulder at 508.15−522.23 K. The appearance of the shoulder is due to hemicellulose and lignin degradation and the gradual decomposition of free formaldehyde and other volatile organic compounds in the resin.41,42

### Table 1. TG/DTG Data on Peak Temperature and Mass Loss from UF and AUF

| Resins | Heating rate/K min$^{-1}$ | Peak temperature/K | Corresponding mass loss/% | Temperature/K | Corresponding temperature/K | Mass loss/% |
|--------|---------------------------|---------------------|---------------------------|--------------|-----------------------------|-------------|
| UF     | 5                         | 543.57              | 15.52                     | 493.15       | 11.82                       | 489.28      |
|        | 10                        | 554.30              | 15.36                     | 493.15       | 12.37                       | 488.31      |
|        | 15                        | 558.90              | 14.19                     | 493.15       | 12.50                       | 501.61      |
|        | 20                        | 560.82              | 14.64                     | 603.15−850   | 546.72                       | 547.74      |
| AUF    | 5                         | 546.32              | 14.99                     | 493.15       | 12.61                       | 493.17      |
|        | 10                        | 556.98              | 17.89                     | 493.15       | 12.53                       | 457.47      |
|        | 15                        | 561.15              | 10.23                     | 493.15       | 13.76                       | 513.17      |
|        | 20                        | 563.82              | 14.77                     | 603.15−850   | 535.34                       | 546.43      |

### Figure 3. DTG and $\alpha$ curves of UF (a) and AUF (b) resins at 5 K min$^{-1}$.

### Figure 4. Kissinger (a) and FWO (b) plots of UF and AUF resins.
The maximum thermal degradation peak temperature of AUF is mainly due to the lower free formaldehyde of the AUF resin. The DTG of AUF at the shoulder is less than that of UF, which may be related to the more stable cross-linking structure of the AUF resin, and the almond shell has a higher maximum thermal degradation peak temperature, which may be caused by the reaction of almond organic compounds in AUF. However, the DTG of AUF at the shoulder is less than that of UF, which is mainly due to the lower free formaldehyde of the AUF resin.

The maximum thermal degradation peak temperature of AUF is higher than that of UF; this may be related to the more stable cross-linking structure. The increase in the rate of warming rises the temperature, which may be caused by the reaction of almond shells with free formaldehyde and the formation of a more stable cross-linking structure.

It also can be seen that the conversion of AUF is lower than that of UF at the same temperature before 500 K, which means that decomposition of free formaldehyde and other volatile organic compounds in AUF is less than that of UF at the same temperature, which may be caused by the reaction of almond shells with free formaldehyde and the formation of a more stable cross-linking structure.

As shown in Table 1, with the increase of heating rate, the maximum thermal degradation peak of UF and AUF resin shifts to a higher temperature. It might be relevant to the heat transfer between the instrument and samples. Furthermore, the increase in the rate of warming rises the temperature required for the same mass loss, which may be due to the sample having a too short time at a specific temperature to decompose completely.

### 2.3. Kinetic Analysis

Deemed as an essential factor in studying the kinetic stability of materials, activation energy is used to reflect the amount of energy required for a chemical reaction. The thermal degradation activation energy at the peak of UF and AUF was calculated by the Kissinger and FWO methods, and the results are shown in Figure 4.

The fitting degree of experimental curves was high, and the fitting correlation coefficients $R^2$ of the two methods are both greater than 0.97. Therefore, the two ways are applied to analyze thermal degradation data. Among them, the activation energies of UF and AUF thermal degradation calculated by the Kissinger method are 185.77 and 188.84 kJ mol$^{-1}$, respectively. The activation energies of UF and AUF thermal degradation calculated by the FWO method are 185.38 and 193.88 kJ mol$^{-1}$, respectively. The activation energies calculated by the two methods are slightly different, but it can be seen that the activation energy of the AUF resin is fractionally higher than that of the UF resin, indicating that the cross-linking structure of AUF is more stable, and the degradation of this requires more energy.

The pre-exponential factor ($A$) is obtained by the intercept of fitted linear, and it can be used to evaluate the number of effective collisions of activated molecules. The larger the $A$ value, the more effective the collision. It can be seen from Table 2 that the pre-referential of AUF is higher than that of the UF resin, indicating that the addition of almond shells increases the production of active sites and the number of collisions during thermal degradation.

The linear regression curve of activation energy and conversion at the main conversion range from 0.2 to 0.75 is shown in Figure 5. However, when the conversion is less than 0.2 or greater than 0.75, there is little or no linear relationship between $\ln \beta$ and $1/T_p$, and the lack of correlation would introduce the evaluation value unreliable in this range.

According to Figure 6, it could be known that the thermal degradation activation energy is different at different conversions, mainly because the resin pyrolysis reaction breaks various chemical bonds at different decomposition stages. It can be seen that when the conversion is 0.2, the activation energy of UF thermal degradation is higher than that of AUF, probably because UF contains more small molecules, which is consistent with the higher conversion of UF in the early stage in Figure 3. When the conversion is higher than 0.2, the activation energy of the AUF thermal degradation is higher than that of UF due to the fact that the cross-linking structure of AUF is more stable, and the degradation of AUF requires more energy.

### Table 2. Relevant Data of UF and AUF Resins Were Obtained by the Kissinger and FWO Methods

| resin | method  | fitted equation | $E$ / kJ mol$^{-1}$ | $A$ / s$^{-1}$ | $R^2$ |
|-------|---------|-----------------|-------------------|---------------|-------|
| UF    | Kissinger | $y = -22.34x + 30.07$ | 185.77 | $2.58 \times 10^{14}$ | 0.9759 |
|       | FWO     | $y = -23.45x + 44.71$ | 185.38 | | 0.9780 |
| AUF   | Kissinger | $y = -22.71x + 30.54$ | 188.84 | $4.17 \times 10^{14}$ | 0.9824 |
|       | FWO     | $y = -24.52x + 46.45$ | 193.88 | | 0.9707 |

### Figure 5.

Relationship of $\log \beta$–$T^{-1}$ of UF (a) and AUF (b) resins based on the Ozawa equation.
more energy, which further shows that the thermal stability of AUF is higher than that of UF; it is consistent with the increased wet bond strength of AUF in Figure 1.

2.4. Estimation of Reaction Kinetics. The linear equation of \(\ln G(\alpha) - \ln \beta\) is formed by the least square method at 550 K, and the result is shown in Figure 7. The slope value of the straight line is close to \(-1\) as the standard to determine whether it conforms to the reaction kinetics in this region. After comprehensive analysis, the reaction kinetics equation corresponding to the UF resin is \(G(\alpha) = [-\ln(1 - \alpha)]^3\), and that corresponding to AUF is \(G(\alpha) = [-\ln(1 - \alpha)]^4\) (Table 3).

3. CONCLUSIONS

In this research, different amounts of almond shells were used to modify the UF resin, and the formaldehyde emission and wet shear strength of the plywood were studied. The activation energy values at different conversions and the reaction kinetics were estimated based on the FWO method. When the addition amount of almond shells is 3 wt %, the formaldehyde emission of plywood was reduced by 28.93% to 0.86 mg/L and the wet shear strength was increased by 42% to 1.42 MPa, compared with that of UF. The \(E_a\) of UF and AUF calculated by the Kissinger method are 185.77 and 188.84 kJ mol\(^{-1}\), respectively. The activation energies of UF and AUF thermal degradation calculated by the FWO method are 185.38 and 193.88 kJ mol\(^{-1}\), respectively. When the conversion is 0.2, the activation energy of AUF thermal degradation is lower than that of UF, while when the conversion is greater than 0.2, the result is just the opposite, and the reaction kinetics is predicted. The reaction kinetics equations corresponding to UF and AUF are \(G(\alpha) = [-\ln(1 - \alpha)]^3\) and \(G(\alpha) = [-\ln(1 - \alpha)]^4\), respectively.

4. MATERIALS AND METHODS

4.1. Materials. Formaldehyde (37%), urea (>99%), sodium hydroxide (>96%), formic acid (>98%), and ammonium chloride (NH\(_4\)Cl, > 98%) were purchased from Chengdu Cologne Chemical Co., Ltd. All the above reagents are analytical reagents and were used without further purification. Almond shells, supplied by an agricultural market, were ground into a uniform material with a particle size of 48 μm.

4.2. Methods. 4.2.1. Resin Preparation. The UF resin was prepared with three stages of “alkali–acid–alkali”, and the molar ratio of formaldehyde to urea was 1.2, with the resin called UF; in the first alkaline stage, a certain amount of almond shell powder was added, and the addition amounts were 1, 3, 5, 7, and 9 wt %, which were based on the weight of the almond shell and urea. The resin added with superfine almond shell powder was named AUF-1, AUF-3, AUF-5, AUF-7, and AUF-9.

4.2.2. Production of Type II Plywood. Type II of three-layer eucalyptus plywood was made with a double spread of 300 g/m\(^2\). The hot pressing temperature and time were 393.15 K and 330 s, respectively.

4.2.3. Determination of Plywood Properties. The formaldehyde release from the plywood and wet shear strength of plywood were tested according to the GB/T 17657-2013 “Test Method for Physical and Chemical Properties of Wood-Based Panels and Veneered Panels”.

4.2.4. TG Analysis. All the samples were dried and milled to powder less than 200 mesh, and the mass was around 5.0 mg. In an atmosphere with a flow of nitrogen (50 mL min\(^{-1}\)), the

![Figure 6. Thermal degradation activation energy diagrams of UF and AUF resins at different pyrolysis conversions rates.](https://doi.org/10.1021/acsomega.1c03896)

![Figure 7. \(\ln(G(\alpha)) - \ln \beta\) fitted line graph of UF (a) and AUF (b) resins.](https://doi.org/10.1021/acsomega.1c03896)
test was carried out by heating samples from room temperature up to 850 K with constant linear heating rates of 5, 10, 15, and 20 K min⁻¹.

4.2.5. Kinetic Analysis. In this study, kinetic analysis was carried out by a non-isothermal method.²⁵,²⁸⁻⁵⁰ The Kissinger and FWO methods were used to obtain the activation energy by analyzing the thermal degradation kinetics of resins.

α is the conversion corresponding to a certain moment in the pyrolysis process, which can be calculated from the mass loss data obtained by TG, as shown in eq 1

\[ \alpha = \frac{m_i - m_t}{m_i - m_f} \]

(1)

where \(m_i\) is the initial mass of the sample, \(m_t\) is the residual mass at the end of the experiment, and \(m_f\) is the mass of the sample at a certain time during the thermal degradation process.

By deriving eq 1, the conversion rate \(\frac{da}{dt}\) can be expressed as eq 2. This equation is combined with the Arrhenius equation (eq 3), which can be shown as eq 4

\[ \frac{da}{dt} = kf(a) \]

(2)

\[ k = A \exp\left(\frac{-E}{RT}\right) \]

(3)

\[ \frac{da}{dt} = A \exp\left(-\frac{E}{RT}\right)f(a) \]

(4)

where \(A\) is the pre-exponential factor, \(R\) is the universal gas constant \((R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1})\), \(E\) is the activation energy \((\text{kJ mol}^{-1})\), and \(f(a)\) is the differential kinetic model function model determined by the reaction type.

The Kissinger method of obtaining the activation energy \(E_a\) consists in the calculation based on eq 5

\[ -\ln\left(\frac{\beta}{T_p^2}\right) = \frac{E}{RT_p} - \ln\left(\frac{AR}{E}\right) \]

(5)

where \(T_p\) is the temperature of the peak and \(\beta\) is the heating rate \((\text{K min}^{-1})\).

There is a linear relationship between \(\ln\left(\frac{\beta}{T_p^2}\right)\) and \(1/T_p\). Theoretically, the activation energy and pre-exponential factor can be calculated using eq 5.

In the FWO methods, eq 6 is used

\[ \ln \beta = \ln \left(\frac{G(a)E}{AR}\right) - 1.0516 \left(\frac{E}{RT_p}\right) \]

(6)

where the activation energy can be determined by the slope of the linear equation.²¹,²²

\(E_a\) can be calculated by the peak temperature and equal conversion of the FWO method.²³ The \(\alpha\) value on different TG curves at the same temperature is brought out into different reaction kinetics functions to obtain \(G(a)\), and then, the linear regression is carried out with \(\ln\left(\frac{G(a)E}{AR}\right)-\ln \beta\) by the least square method. Considering the linear relationship and the slope of the fitting line, it is the most probable reaction kinetics function when the slope value is closest to \(-1.0516\).

### Table 3. Parameters of \(\ln (G(a)) - \ln \beta\) Fitting Degree Obtained by Different Reaction Models

| resins | reaction model \(G(a)\) | slope | intercept | \(R^2\) |
|--------|-------------------------|-------|-----------|---------|
| UF     | \(G(a) = a\)           | −0.25 | −0.14     | 0.9897  |
|        | \(G(a) = \ln (1 - a)\)  | −0.36 | 0.44      | 0.9848  |
|        | \(G(a) = [1 - (1 - a)^{-1}] / -1\) | −0.50 | 1.14      | 0.9802  |
|        | \(G(a) = [1 - (1 - a)^{-1}] / -2\) | −0.67 | 1.94      | 0.9762  |
|        | \(G(a) = [1 - (1 - a)^{-1}] / -3\) | −0.86 | 2.83      | 0.9732  |
|        | \(G(a) = a^2\)         | −0.49 | −0.29     | 0.9897  |
|        | \(G(a) = (1 - a) \ln (1 - a) + a\) | −0.55 | −0.62     | 0.9882  |
|        | \(G(a) = [1 - (1 - a)^{1/3}]^2\) | −0.63 | −1.73     | 0.9865  |
|        | \(G(a) = 1 - (1 - a)^{1/3}\) | −0.30 | −0.56     | 0.9873  |
|        | \(G(a) = 1 - (1 - a)^{1/3}\) | −0.32 | −0.86     | 0.9865  |
|        | \(G(a) = [-\ln (1 - a)]^3\) | −0.71 | 0.88      | 0.9848  |
|        | \(G(a) = [-\ln (1 - a)]^5\) | −1.07 | 1.32      | 0.9848  |
|        | \(G(a) = [-\ln (1 - a)]^5\) | −1.42 | 1.76      | 0.9848  |

| AUF    | \(G(a) = a\)           | −0.19 | −0.23     | 0.9781  |
|        | \(G(a) = \ln (1 - a)\)  | −0.28 | 0.33      | 0.9752  |
|        | \(G(a) = [1 - (1 - a)^{-1}] / -1\) | −0.40 | 1.00      | 0.9724  |
|        | \(G(a) = [1 - (1 - a)^{-1}] / -3\) | −0.55 | 1.76      | 0.9700  |
|        | \(G(a) = [1 - (1 - a)^{-1}] / -3\) | −0.71 | 2.61      | 0.9683  |
|        | \(G(a) = a^2\)         | −0.38 | −0.45     | 0.9781  |
|        | \(G(a) = (1 - a) \ln (1 - a) + a\) | −0.44 | −0.81     | 0.9772  |
|        | \(G(a) = [1 - (1 - a)^{1/3}]^2\) | −0.50 | −1.93     | 0.9761  |
|        | \(G(a) = 1 - (1 - a)^{1/3}\) | −0.23 | −0.65     | 0.9766  |
|        | \(G(a) = 1 - (1 - a)^{1/3}\) | −0.25 | −0.96     | 0.9761  |
|        | \(G(a) = [-\ln (1 - a)]^3\) | −0.57 | 0.66      | 0.9752  |
|        | \(G(a) = [-\ln (1 - a)]^5\) | −0.85 | 1.00      | 0.9752  |
|        | \(G(a) = [-\ln (1 - a)]^5\) | −1.13 | 1.33      | 0.9752  |

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Notes

The authors declare no competing financial interest.

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