Effects of cellulose nanofibrils on the cure kinetics of the phenol formaldehyde resin

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Abstract
Phenol formaldehyde (PF) resin were treated with cellulose nanofibrils (CNF), and its effects on the cure kinetics of PF resin were evaluated. The curing of PF resin was a polycondensation exothermic reaction forming insoluble polymer. The Differential scanning calorimetry (DSC) analysis showed 3% CNF addition had prolonged the curing process of PF resin, and the Kissinger equation and Crane equation were introduced to show that the curing activate energy and reaction order of 3%-CNF-added-PF resin sample were obviously lower than control ones. The scanning probe microscopy (SPM) results exhibited that CNF particles were well-dispersed in the PF matrix. The non-isothermal kinetic study indicated that CNF had played a major role during late stage of non-isothermal polymerization, increasing the crosslinking points in the PF resin and reducing the energy needed for PF resin curing. Thus, the addition of CNF had a positive effect on the curing of PF and made the curing more perfect.

Introduction
Cellulose is an inexhaustible natural polymer widely found in plants, animals and bacteria, which is also an important raw material for paper, food and chemical production. The particle size of nanocellulose prepared by natural cellulose is generally between 1 and 100 nm, forming stable colloids in water. It promises good applications in composite reinforcement, tissue engineering support and filtration medium \cite{1, 2}. In recent years, many researches have focused on the preparation of rod-like, grain-like, or silk-mesh nanocellulose materials, such as cellulose nanocrystal, cellulose nanowhiskers, cellulose nanofibrils (CNF) etc. Thereinto, a high aspect ratio and mesh tangle structure made CNF higher strength, lower thermal expansion coefficient and density, promising a better application in high-performance products \cite{3–5}. Due to high surface areas, CNF particles were proved to improve the physical and mechanical properties of matrix effectively \cite{6}.

DSC has been widely used in plastics, rubber, fiber, coatings, adhesives, medicine, food, biological organisms, metal materials and composite materials field. The melting and crystallization process, crystallinity, glass transition, phase transition, reaction temperature and enthalpy of the material can be investigated by DSC. Furthermore, reaction kinetics can be analyzed from curing process of thermoset resin by DSC. Hayati \textit{et al.} \cite{7} examined the curing behavior of epoxy glass-reinforced prepreg/DICY system, and obtained the apparent activation energy and overall reaction order according to both isothermal and dynamic DSC methods. The approach of this work is to explore the influence of CNF on curing behavior of PF resin by DSC. In this paper, CNF/PF nanocomposite was prepared by dispersing CNF suspension into PF adhesive, and the cure kinetics of CNF/PF nanocomposite and control PF resin was analyzed by introducing the Kissinger equation and Crane equation.
Materials and methods

Materials

(1) A commercial PF resin with a thermoset property was provided by the Zhejiang Wood-based Panel Factory, reddish brown viscous liquid. The viscosity of the resin was measured between 0.8 and 1.53 Pa·s using a rotary viscosimeter at 20 °C, and the solid content was 46 wt%.

(2) CNF was bought from Intelligent Chemicals Ltd (Wuxi, Jiangsu, China), with 10% solid content. Its average length was 400–600 μm, and diameter was 10–50 nm. The morphology was shown in figure 1.

(3) DSC 200 was bought from Netzsch Co. (Bavaria, Germany).

Methods

Sample preparation

3% CNF was added to PF resin according to the solid content weight, and then distributed evenly in PF resin by electric stirring rod. Some cured samples were treated at room temperature.

DSC analysis

Both control PF resin samples and 3% CNF-added PF resin samples (1 ~ 3 mg each) were placed in an aluminum pot, respectively. The gas flow rate was 60 ml min⁻¹. Each sample was heat-treated at a heating rate of 5 k min⁻¹, 10 k min⁻¹, 15 k min⁻¹, 20 k min⁻¹ separately, and then the curing process was recorded by DSC.

Results and discussion

DSC curves

In the low temperature stage, PF resin absorbed heat and lost water. With 3% CNF addition, the polycondensation peak temperature \( T_p \) decreased and the range of endothermic peak widened. At 80 °C, PF resin decomposed at a very low rate, and the thermal crosslinking grew with temperature. In contrast to control PF resin, CNF addition accelerated PF resin’s thermal crosslinking process. Both figures 2(a) and (b) proved that the exothermic temperature of PF resin curing was intimately related to the DSC heating rate, the faster DSC heating rate grew, the more obvious the heating effect exhibited. And the thermal inertia and temperature difference subsequently increased, leading to the beginning and peak temperature increase of PF resin curing, as well as the temperature range widening [8]. From room temperature to 120 °C, the main reaction in PF resin was the molecular chain growth. Specifically, the hydroxymethyl group on the phenolic core reacted with the adjacent or opposite radical hydrogen on the other phenolic cores, lost unimolecular water, and formed the hypomethyl bond, which was noted as obvious endothermic peak at the heating rate of 15 and 20 k min⁻¹ in figure 2.
Curing in the range of 170 °C and 250 °C, the above-mentioned compounds can react either with unsaturated bonds, known as Diels-Alder reaction, or with hydroxymethyl phenol as oxidation—reduction reaction to produce aldehyde products as following.

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In this condition, the curing of PF resin was a polycondensation exothermic reaction, noted as an upward exothermic peak in figure 2. Compared with control PF resin sample, the polycondensation starting temperature of 3% CNF-added PF resin sample maintained constant, while the heat liberation rate reduced, and the temperature range of polycondensation reaction widened. It follows that the CNF addition prolonged the curing process of PF resin. Specifically, the reaction points in PF resin molecule increased, the crosslinking capacity of molecular chain further enhanced, and the polycondensation terminal temperature Tt increased. Meanwhile, the reaction time span extended, and the PF exothermic peak range increased by 100% especially from 160 °C to 170 °C. As the polycondensation process mainly depended on the reactive point, under the same mass fraction PF resin with CNF has more particle numbers, with its crosslinking capacity being improved. The

![Figure 2. DSC curves of PF resin samples at different heating rates ((a) Control PF resin, (b) 3% CNF-added PF resin; 1. heating rate 5 K min$^{-1}$, 2. heating rate 10 K min$^{-1}$, 3. heating rate 15 K min$^{-1}$, 4. heating rate 20 K min$^{-1}$).](image-url)
CNF particles were effectively dispersed in PF resin, of which the reaction point was increased and the polycondensation was prolonged, conducing it to cure into insoluble polymer. In conclusion, the exothermic peak was slowed down, the curing heat was decreased, and the curing terminal temperature was postponed, proving that at the same heating rate 3% CNF addition made the curing polycondensation slow and the reaction more adequate.

Non-isothermal and dynamic cure kinetics of PF resin

The kinetics of control PF resin and 3% CNF-added PF resin samples were analyzed by Kissinger method in this paper. According to the DSC curves of control PF resin and 3% CNF-added PF resin at different heating rate in figure 2, T\textsubscript{p} were listed in table 1, which represented the temperature corresponding to the maximum exothermic peak at the heating rate of 5 k min\textsuperscript{-1}, 10 k min\textsuperscript{-1}, 15 k min\textsuperscript{-1}, 20 k min\textsuperscript{-1}, respectively. Shown in table 1, the curing peak temperature T\textsubscript{p} of PF resin increased with heating rate. By measuring T\textsubscript{p} of PF resin at different heating rate, the curing kinetic parameters of PF resin could be obtained using the Kissinger equation and the Crane equation in which the activation energy and pre-exponential factor are considered to be constant [7, 9]. These methods assumed that more reliable data were obtained merely for the peak maxima in DSC (T\textsubscript{p}) for each heating rate. By plotting a straight line by pairs at different heating rates, the values of activation energy E\textsubscript{a} and pre-exponential factor A can be calculated from the slope and intercept of the straight line, respectively.

Table 1. Activity energy of different PF resin samples.

| PF resin Sample | 5 K min\textsuperscript{-1} | 10 K min\textsuperscript{-1} | 15 K min\textsuperscript{-1} | 20 K min\textsuperscript{-1} | Ea KJ mol\textsuperscript{-1} | n |
|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|---|
| Control        | 143.8           | 150.2           | 159.0           | 161.3           | 11.629          | 0.000 821 |
| 3% CNF-added   | 148.0           | 155.0           | 163.1           | 170.9           | 9.885           | 0.000 789 |

The hypothesis kinetics equation by Kissinger method [10], as follows,

\[
\frac{d\alpha}{dt} = A \cdot \exp \left( \frac{-E_a}{RT} \right) \cdot (1 - \alpha)^n \tag{1}
\]

In the equation, A is the pre-exponential factor, E\textsubscript{a} is the reaction activation energy, \( \alpha \) is the product concentration, R is the gas constant and T is the absolute temperature.

The Kissinger equation on the basis of mathematic deduction, as follows,

\[
- \ln \left( \frac{\beta}{T_p^2} \right) = - \ln \frac{AR}{E_a} + \frac{1}{R} \frac{E_a}{T_p} \tag{2}
\]

In the equation, \( \beta \) is the heating rate, T\textsubscript{p} is the peak temperature at different heating rate, and R is the gas constant 8.314 J/(mol K\textsuperscript{-1}).

Shown in figure 3, a straight line is plotted with \( \ln(\beta / T_p^2) \) for 1/T\textsubscript{p}. The slope of the line K\textsubscript{1} = E\textsubscript{a} / R, that is, activation energy E\textsubscript{a} = RK\textsubscript{1}. The activation energy E\textsubscript{a} and the pre-exponential factor A are solved by combining K\textsubscript{1} with the intercept obtained from the line [10, 11].

The curing of PF resin is a complex multi-stage chemical reaction process, which involves the crosslinking and polymerization of all branching chains and functional groups in PF resin. The reaction order of curing can be calculated by the Crane equation,

\[
\frac{d(\ln \beta)}{d(1/T_p)} = - \frac{E_a}{nR} \tag{3}
\]

In the equation, \( \beta \) is the heating rate, T\textsubscript{p} is the peak temperature at different heating rate, E\textsubscript{a} is the activation energy of the curing reaction, n is the reaction order of the curing, and R is the gas constant 8.314 J/(mol K\textsuperscript{-1}).

Shown in figure 4, a straight line is plotted with \( \ln(\beta / T_p) \) for 1/T\textsubscript{p}. The slope of the line is K\textsubscript{2} = -E\textsubscript{a} / nR, then the reaction order n of the curing reaction series could be solved by combining with the E\textsubscript{a} obtained by the Kissinger equation.

From figure 2, it could be concluded that the CNF addition had affected the curing performance of PF resin. Thus, studying the role CNF played in PF resin curing is significant to understand the curing process. Shown in table 1, the E\textsubscript{a} obtained from the slope of the Kissinger plot were 11.629 and 9.885 kJ mol\textsuperscript{-1}, and the reaction order n were 8.2118 × 10\textsuperscript{-4} and 7.8917 × 10\textsuperscript{-4}, respectively. The curing difficulty depends on reaction activation energy, and the premise of the curing reaction is that the molecules participating in the reaction obtain more energy than the activation energy. The PF resin curing is a dynamic equilibrium process, with molecule functional groups contacting, colliding and reaching the energy peaks necessary for the reaction. Compared with...
control PF resin, the activation energy of 3% CNF-added PF resin curing reduced by 1.74 kJ mol\(^{-1}\), about 15% decrease, indicating that 3% CNF added PF resin required less energy for curing. Pure PF resin had relatively high thermal stability and needed to overcome higher energy barrier during the curing process, and the activation energy was subsequently large. With 3% CNF addition, the activated functional groups in PF resin increased, and the molecule amount absorbing energy to overcome the curing reaction energy peak decreased. Correspondingly, the energy range of curing grew. Shown in figure 2, in the range of 170 °C–250 °C, the resin curing time was also prolonged with 3% CNF addition. Since 3% CNF-added PF resin had more small molecular groups, when phenol reacted with formaldehyde to form small molecular groups with active groups, it was easier for small molecular groups to move and contact large molecular groups in PF resin curing between 170 °C and 250 °C. Possibly attribute to the effective dispersion in PF resin during the curing process, CNF increased crosslinking points in PF resin and reduced the energy required for PF resin curing, with the reaction points of PF resin curing into insoluble polymers increasing. CNF particles in the composite became the growing points of the polyester macromolecule, and further formed the crosslinking structure, making the curing activation energy obviously lower than the control ones. The reaction order of the 3% CNF added PF resin samples is lower than that of control ones, also proving that the CNF addition increased the collision times of various curing reaction groups in PF resin. That is, the probability of molecular chain collision in PF resin was increased, and the time spent to reach the same curing degree for the resin in this condition also was shortened.

Evidence of PF resin curing modified by CNF
Shown in figure 5(a), the wood was glued with 3% CNF added PF resin, and the interface of CNF and the glue line in the sample was blurry. With the cure kinetics analysis of PF resin above, we can conclude that CNF
particles were well-dispersed in the PF matrix and the addition of CNF increased crosslinking points for PF resin curing, having a positive effect on the crosslinking structure of PF resin. As figure 5(b) shown, the PF resin filled up the pores of the wood microstructures, indicating that the individual fibrils entangled each other and formed an inter-connected network as PF resin occupied the pore structure of the CNF [12]. As PF resin was fully in contact with CNF particles in the hot-pressing process, the reaction of wood hydroxyl-OH and phenolic adhesive increased, which makes the wood unit and the adhesive component tightly bond.

Conclusion

With CNF addition, the starting temperature of PF resin polycondensation was basically the same as control ones, while the heating rate reduced and the polycondensation temperature range broadened. It can be concluded that the addition of CNF prolonged the curing process of PF resin. The Kissinger equation and Crane equation were introduced to analyze the PF resin curing, and compared with control PF resin, the activation energy of 3% CNF-added PF resin curing reduced by 1.74 kJ mol$^{-1}$, indicating that 3% CNF added PF resin required less energy for curing. The reaction order of 3% CNF added PF resin samples was lower than that of control ones, also proving that the CNF addition increased the collision times of various curing reaction groups in PF resin. The SPM picture showed that the CNF particles were effectively dispersed in the PF resin. In summary, the non-isothermal kinetic study indicated that CNF had played a major role during late stage of non-isothermal polymerization, increasing the crosslinking points in the PF resin and reducing the energy needed for PF resin curing, which effectively improved the curing effect of the PF resin.

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Figure 5. The interface images between wood and 3% CNF added PF resin ((a) optical microscope images, (b) SPM image (30 μm × 30 μm)).
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