Preparation and characterization of fast-curing powder epoxy adhesive at middle temperature

Jie Xu¹,², Jiayao Yang¹,², Xiaohuan Liu¹,², Hengxu Wang¹,², Jingjie Zhang¹,² and Shenyuan Fu¹,²

¹Zhejiang Provincial Collaborative Innovation Center for Bamboo Resources and High-efficiency Utilization, 666 Wusu Street, Hangzhou 311300, People’s Republic of China
²School of Engineering, and Key Laboratory of Wood Science and Technology of Zhejiang Province, Zhejiang A&F University, 666 Wusu Street, Hangzhou 311300, People’s Republic of China

At present, the disadvantage of powder epoxy adhesive is the limited application area. In order to widen the application range of powder epoxy adhesive from heat-resistant substrates (such as metals) to heat-sensitive substrates (such as plastic products, cardboard and wood), it is necessary to decrease the curing temperature. In this article, a series of fast-curing powder epoxy adhesives were prepared by the melt blending method with bisphenol A epoxy resin (E-20), hexamethylenetetramine (HMTA) as a curing agent and 2-methylimidazole (2-MI) as an accelerant. The structure and properties of the E-20/HMTA/2-MI systems were characterized by Fourier transform infrared, thermogravimetric analysis, dynamic mechanical analyser and differential scanning calorimetry (DSC). 2-MI added into the E-20/HMTA systems can simultaneously enhance toughness, tensile strength, glass transition temperature ($T_g$) and thermal stability in comparison with the E-20/HMTA systems. The best mechanical properties were obtained at 100/8/0.6 weight ratio of the E-20/HMTA/2-MI systems. DSC experiments revealed that the exothermic peak of the E-20/HMTA/2-MI system was about 55°C lower than that of the E-20/HMTA system. The activation energy of the cure reaction was determined by both Kissinger’s and Ozawa’s methods at any heating rates. The activation energy and pre-exponential factor were about 100.3 kJ mol$^{-1}$ and $3.57 \times 10^{11}$ s$^{-1}$, respectively. According to the KAS method, the curing time of the E-20/HMTA/2-MI systems was predicted by evaluating the relationship between temperature and curing time.
1. Introduction

Bisphenol A epoxy resins (DGEBA) are a unique class of thermoset polymers, which have been gaining ground since their commercial debut in the 1940s [1]. Epoxy resins have found a myriad of applications as in coatings, adhesives, construction and electrical engineering for decades [2], owing to their superior mechanical and chemical properties, such as high tensile, good chemical and solvent resistance, and high heat distortion temperatures [3–5].

Powder epoxy resins, a novel kind of epoxy resins without any solvent, have recently received considerable attention because of the imposition of increased legislative restrictions on the emission of organic solvents to the atmosphere [6]. Additionally, powder epoxy resins have many advantages, such as non-toxicity, ease of use and high recycling rate. In practice, epoxy adhesives that cure fast at mild temperatures are needed because excessive heat cannot be applied to the peripheral components and adherend [7]. On the other hand, the demand for increased manufacturing throughput is driving cycle times down from hours to several minutes [8]. In consideration of energy saving and consumption reduction, a fast-curing powder epoxy system deserves to be explored.

Generally, resin curing time can be lowered by introducing and/or improving the catalytic behaviour of epoxy cross-linking with the curing agent or accelerator [9]. Many different kinds of curing agents or accelerators are applied to epoxy resins, and they are mainly divided into phenol formaldehyde resins, acid anhydrides, amines and imidazoles [3,10]. Among them, imidazoles have recently been paid attention because they can initiate the homopolymerization of the epoxy compounds [3,11,12]. Both nucleophilic and base-catalysed processes can be considered, and these properties can be altered by substituted groups on the imidazole ring [13]. When imidazoles are added into the epoxy resin for 1 h to a few days, the epoxy resin will transform into solid at low temperature, suggesting comparatively high reactivity of imidazoles [14].

Imidazole-based curing agents have been attracting increasing research interests. Pin et al. [15] earlier reported MHHPA cured epoxidized linseed oil catalysed by 2-methylimidazole (2-MI) with high thermal stability. The addition of 2-MI remarkably reduced the curing temperature of the reaction, and increased the mechanical, thermal properties of the blends because these were more active initiators for fast cross-linking [16]. Besides, 2-MI was more effective than 1-methylimidazole, 2-ethylimidazole, 2-phenylimidazole, 2-ethyl-(4)-methylimidazole or 1-(2-cyanoethyl)-2-ethyl-(4)-methylimidazole in initiating the polymerization of epoxy resin [3,17]. To the best of our knowledge, the incorporation of 2-MI into powder epoxy resin for developing fast-curing powder epoxy adhesive is rare.

The key aim of this paper is thus to deepen our understanding of the fast-curing powder epoxy adhesive [18]. Bisphenol A epoxy resin (E-20), hexamethylenetetramine (HMTA) and 2-MI are chosen to prepare fast-curing powder epoxy adhesive, and study its mechanical properties, structural characteristics, thermal stability and curing kinetics. The results of this study can be used to make recommendations for the optimal curing parameter of the E-20/HMTA/2-MI system.

2. Material and methods

2.1. Materials

Hexamethylenetetramine ( assay greater than 99.5%, molecular formula: C₆H₁₂N₄, molecular weight (g): 140.18) and 2-methyl imidazole (molecular formula: C₄H₆N₂, molecular weight (g): 82.10) were supplied by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Epoxy resin (E-20) was supplied by Huangshan Jinfeng Industrial Co., Ltd.

2.2. Preparation of samples

Powder epoxy resin (E-20), curing agent (HMTA) in a 100:8 equivalent ratio, together with 2-MI (0.6 wt% on the basis of the total weight of E-20 and HMTA) was stirred together until the homogeneous mixture was well blended (figure 1). Next, the mixed powder was poured into the preheated metal mould. Then, the metal mould was pressed by the press vulcanizer at 130°C for at least 10 min. Finally, the cured E-20/HMTA/2-MI systems were prepared and the average value was reported. All of the mechanical test samples were cured under the same conditions (figure 2).
2.3. Preparation of composites

Firstly, the reconstituted bamboo had to be dried under a preheated press vulcanizer at 100°C for 20 min. Secondly, appropriate amount of powder epoxy adhesive was uniformly coated on the reconstituted bamboo (BS) surface, fibreglass membrane (GF) surface and PET foam (PF) surface. Three kinds of materials were sequentially stacked based on the order of BS–GF–PF–GF–BS, and then pressed by press vulcanizer at 130°C for at least 10 min. Finally, the composites were obtained.

2.4. Characterization

2.4.1. Fourier transform infrared analysis

FTIR spectra were recorded using a Perkin Elmer Model 1100 at room temperature. The wavelength range was from 4000 to 500 cm\(^{-1}\). Each powder sample was sandwiched between two KBr pellets. The spectra were obtained using 32 scans at a resolution of 4 cm\(^{-1}\).

2.4.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) experiment was carried out on an STA 409PC with high purity as purge gas at a scanning rate of 20°C min\(^{-1}\) from room temperature to 800°C. Each sample of 5–10 mg in the initial weight was kept in an open Pt pan.

2.4.3. Tensile test

The tensile properties of samples were characterized by an electronic universal testing machine with a 2 KN load cell at a cross-head speed of 2 mm min\(^{-1}\), according to the standard (GB/T1040.2-2006). The tensile strength, elongation at break and modulus of elasticity of both E-20/HMTA systems and E-20/HMTA/2-MI systems were obtained at room temperature. For each composition, the measurement was repeated with 10 samples.
2.4.4. Impact test

Unnoticed impact strength tests were conducted on a pendulum impact testing machine according to the standard (GB/T1043-93). Each sample measuring $80 \times 10 \times 4$ mm was used for this evaluation. For each composition, at least 10 samples were measured.

2.4.5. Internal bond strength test

The internal bond strength of composites was characterized by an electronic universal testing machine, according to the standard (GB/T17657-2013). Each sample measuring $50 \times 50$ mm was used for this evaluation. For each composition, the measurement was repeated with 10 samples.

2.4.6. Flexible strength test

The flexible strength of composites was performed by the electronic universal testing machine, according to the standard (GB/T1936.1-2009). Each sample measuring $300 \times 25 \times 25$ mm was used for this evaluation. For each composition, the measurement was repeated with 10 samples.

2.4.7. Dynamic mechanical analyser analysis

The dynamic mechanical properties at 1 Hz were measured using a TA Q800 dynamic mechanical analyser (DMA) in the single cantilever mode. Each sample measuring $35 \times 10 \times 3$ mm was used for this evaluation. DMA measurements were performed at the heating rates of $3 \degree C \text{min}^{-1}$ in a heat scan ranging from 60 to 210$\degree$C.

2.4.8. Theory of curing kinetics

The differential scanning calorimetry (DSC) analysis was performed on a Netzsch STA 409PC Maia instrument under a nitrogen gas atmosphere. Dynamic DSC measurements were performed at the heating rates of 5, 10, 20 and $30 \text{Kmin}^{-1}$ in a heat scan ranging from 40 to 300$\degree$C to acquire curing heat-flow curves of the powder samples (in nitrogen flow of 50 ml min$^{-1}$). The fresh samples of $5\text{–}10$ mg in weight were kept in an aluminium pan under N$_2$ atmosphere.

3. Results and discussions

3.1. Fourier transform infrared analysis

FTIR spectra were often used to identify the changes in the chemical structure. Referring to the spectra of the E-20, E-20/HMTA and E-20/HMTA/2-MI systems shown in figure 3, differences in the spectra of the cured samples were mainly observed in the fingerprint region of the spectrum.

Figure 3. FTIR spectra of E-20, E-20/HMTA and E-20/HMTA/2-MI system.
The peaks at 672 and 812 cm$^{-1}$ were attributed to the bending vibration of C–N. The peak at 918 cm$^{-1}$ was ascribed to the stretching vibration of epoxy structure [19]. The peaks at 1036 and 1181 cm$^{-1}$ were associated with the ether bond stretching vibration. The peak at 2926 cm$^{-1}$ was assigned to the methylene C–H stretching vibration. The peaks at 2872 and 2960 cm$^{-1}$ were associated with the methyl C–H stretching vibration [20]. The peak at 3400 cm$^{-1}$ was assigned to the –OH structure, which was attributed to the great hydroxyl bonding interaction of the phenol group [21].

After modification, the peak of epoxy structure at 918 cm$^{-1}$ gradually weakened and disappeared. The absorption peaks of –OH band at 3400 cm$^{-1}$ weakened. These results indicated the successful ring-opening reaction of the epoxy group to form cross-linked polymers (figure 4).

The reaction equation of the E-20/HMTA systems was described as follows:

HMTA cured epoxy resin by anionic polymerization reaction. The anionic polymerization curing agent first acted on epoxy group, made it open ring, generated oxygen anion, and oxygen anion attacked epoxy group, which led to ring-opening addition. Finally, epoxy resins were cured by chain reaction [22].

The reaction equation of the E-20/2-MI systems was described as follows:
The curing reaction of the E-20/HMTA/2-MI systems took place in two steps. 2-MI as an anionic polymerization. Reaction mechanism: first, the active hydrogen of the secondary amine on imidazole was added to the epoxy group, and intramolecular complexes of positive and negative ions could be formed by the resulting adduct and another epoxy group. The negative ion at the centre of complex, which could catalyse the epoxies ring-opening reaction, finally reacted with curing agents and other epoxy groups [23].

3.2. Thermogravimetric analysis

TGA was a simple method to evaluate the degradation behaviours and thermal stability of polymers [24]. The degradation behaviours and thermal stability of cured E-20/HMTA/2-MI systems were compared with E-20/HMTA systems from thermogravimetric (TG) and derivative thermogravimetric analysis (DTG) in N₂ atmosphere. The shapes of the derivative TGA curves (figure 5) for E-20/HMTA/2-MI systems were similar to those of E-20/HMTA, indicating that the structures in E-20/HMTA/2-MI systems were not significantly different from those of the E-20/HMTA systems in thermal stability [25]. There were two decomposition steps according to the two DTG peaks (figure 5a,b). Both the initial decomposition temperature ($T_\text{d}$) and the maximum decomposition temperature ($T_{\text{max}}$) of E-20/HMTA/2-MI increased. The E-20/HMTA system $T_\text{d}$ was 173.32°C, lower than that of E-20/HMTA/2-MI system (185.17°C). The E-20/HMTA system $T_{\text{max}}$ was 191.74°C and 444.82°C, respectively, lower than that of E-20/HMTA/2-MI system (205.32°C and 454.57°C). However, the E-20/HMTA system was about 7.66% char residues at 798.07°C, higher than that of E-20/HMTA/2-MI system (4.55%). The thermal stability of E-20/HMTA/2-MI system has been increased. The reason for the increase in the thermal stability of the E-20/HMTA/2-MI system was due to the incorporated 2-MI in the E-20/HMTA system. 2-MI could limit the intense motion of the polymer chain by different physico-chemical interactions.

3.3. Mechanical properties of the E-20/HMTA/2-MI systems

To investigate the toughening and reinforcing effects of the incorporated 2-MI in the E-20/HMTA systems, E-20/HMTA/2-MI systems with different 2-MI loadings were prepared and the mechanical properties were experimented, according to the m (E-20) : m (HMTA) : m (2-MI) = 100 : 8 : X ratio for the preparation of E-20/HMTA/2-MI systems (X = 0, 0.2, 0.4, 0.6, 0.8, 1).

As shown in figure 6a, it can be observed that the impact strength was obviously improved after adding 2-MI. The impact strength of E-20/HMTA/2-MI system up to 13.6 kJ m⁻² at 0.8 wt% 2-MI loadings showed the best toughening effect, which was higher than that of E-20/HMTA system (6.1 kJ m⁻²). These data showed that the incorporation of 2-MI could effectively toughen the E-20/HMTA system.

The impact strength of the resulting E-20/HMTA/2-MI systems increased and then decreased as the ratios of E-20/HMTA/2-MI increased from 100/8/0 to 100/8/1. The further increase in 2-MI loadings over 0.8 wt% led to a decrease in the impact strength, this result was probably due to the cross-linking density reduction effect.

Tensile properties of tensile strength and elongation at break are shown in figure 6b. The average values of tensile and impact experiments-related parameters are shown in table 1. For most of the epoxy materials, improving toughness was achieved by sacrificing the stiffness [21]. However,
compared with E-20/HMTA systems, the tensile experiment data of E-20/HMTA/2-MI systems showed that tensile strength and elongation at break were distinctly increased with the incorporation of 2-MI. Tensile properties of the resulting E-20/HMTA/2-MI systems increased and then decreased as the ratios of E-20/HMTA/2-MI increased from 100/8/0 to 100/8/1. The tensile strength and elongation at break of E-20/HMTA/2-MI systems with 0.6 wt% 2-MI loadings were up to 51.48 MPa and 3.15%, respectively, which were 21.3% increase in tensile strength and 20.7% increase in elongation at break with respect to E-20/HMTA systems. Tensile strength was determined by the structure and cross-linking density [26]. The further increase in 2-MI loadings over 0.6 wt% led to a decrease in the tensile strength, this result was probably because the internal deformation ability of E-20/HMTA/2-MI system was enhanced, thus the cross-linking density was decreased.

Impact and tensile test indicated that incorporating 2-MI into the E-20/HMTA systems could improve toughness and stiffness. When the 2-MI loadings were under 0.6 wt%, elongation at break, impact strength and tensile strength all increase with 2-MI loadings. The increase in fractional free volume was beneficial to increase in impact strength and elongation at break, whereas the cross-linking density could be used to explain the increase in tensile strength [27]. Finally, the best mechanical properties were obtained at 100/8/0.6 ratio of E-20/HMTA/2-MI.

3.4. Dynamic mechanical analyser analysis

The storage moduli ($E'$) and loss tangent (tan δ) as a function of temperature for the cured E-20/HMTA and E-20/HMTA/2-MI systems are shown in figure 7. For clarity, we only show data of E-20/HMTA systems and E-20/HMTA/2-MI systems with 0.6 wt% 2-MI loadings, which have biggest structure differences for easy comparison. E-20/HMTA and E-20/HMTA/2-MI systems showed a clear glass transition with the rubbery plateau modulus ($E_r$). With the increasing temperature, the moduli reached the elastomeric region through the glass transition region, where more segments in the chains were moving in a cooperative manner [25]. According to the classical rubber elasticity, $E_r$ was proportional to the average cross-linking density [28].
The cross-linking density \( \rho \) of cured epoxy network can be calculated by the following equation:

\[
\rho = \frac{E_r}{3RT},
\]

where \( \rho \), \( E_r \), \( R \) and \( T \) are the cross-linking density per unit volume (mol cm\(^{-3}\)), rubbery plateau modulus, the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)) and the absolute temperature, respectively. As shown in figure 7a, at 0.6 wt% 2-MI loadings, the cross-linking density of E-20/HMTA/2-MI systems increases by 16.5% compared with E-20/HMTA system (equation (3.1)). The increase in cross-linking density was due to the involvement of 2-MI in epoxy network as a chemical cross-linking point.

As shown in figure 7b, the curves of E-20/HMTA/2-MI systems were similar to that of E-20/HMTA systems and showed only one distinct peak, indicating that no sign of phase separation was found in the E-20/HMTA and E-20/HMTA/2-MI systems [29]. The half peak width of E-20/HMTA/2-MI systems was narrower than that of the E-20/HMTA systems, suggesting that cured E-20/HMTA/2-MI systems appear to be more uniform in structure than those of the E-20/HMTA systems [30]. Tan \( \delta \) was defined as the ratio of loss modulus to the storage modulus, and the peak of the tan \( \delta \) versus temperature curve was taken as \( T_g \). The E-20/HMTA/2-MI systems containing 0.6 wt% 2-MI showed \( T_g \) of 164.5°C, which was 12.5°C higher than the E-20/HMTA systems (152°C). \( T_g \) was affected by both the cross-linking density and the chain flexibility. As was mentioned before, the cross-linking density increased after adding 2-MI, the increase in \( T_g \) was probably due to the structure of 2-MI, which enhanced the chain rigidity.

### 3.5. Cure kinetics of powder epoxy adhesive

Non-isothermal curing behaviours of E-20/HMTA systems with or without 2-MI were investigated by DSC. With the introduction of 2-MI into the E-20/HMTA system, the exothermic peak of E-20/HMTA system was about 55°C higher than that of E-20/HMTA/2-MI system as shown in figure 8a, which indicated that the incorporation of 2-MI could decrease the activation energy and increase the rate of curing reaction.

A curing reaction kinetics study of E-20/HMTA/2-MI systems played an important role in optimizing curing reaction cycles [31]. Figure 8b exhibits DSC curves of E-20/HMTA/2-MI systems at different heating rates (5, 10, 20 and 30 K min\(^{-1}\)). Each curve showed a single exothermic peak corresponding to the ring-opening reaction between epoxy and amine. The exothermic curing reaction of E-20/HMTA/2-MI systems occurred in the temperature range of 85–177°C. As shown in table 2, the peak curing temperature shifted with different heating rates. With an increase in heating rate, the initial and peak temperature were higher, the curing time could be reduced greatly and have a broader range of curing temperature, because the thermal effect per unit time was increased, it could have a greater thermal inertia, and the onset and peak temperature deviated to high temperature direction with an increase in heating rate [9].

The activation energy of the cure reaction was determined by both Kissinger’s [32] and Ozawa’s [33] methods at any heating rates. The Kissinger equation was the most extensively used method to calculate...
Figure 8. (a) DSC curves of E-20/HMTA and E-20/HMTA/2-MI system; (b) DSC profiles of E-20/HMTA/2-MI system for heat flow against temperature with heating rates of 5, 10, 20 and 30 K min\(^{-1}\); (c) linear plot of \(-\ln(\beta/T_p^2)\) versus \(1/T_p\) based on Kissinger’s equation; (d) \(\ln\beta\) versus \(1/T_p\) based on Ozawa’s theory; (e) \(T – \beta\) diagram; (f) degree of cure at different heating rates for the E-20/HMTA/2-MI systems; (g) model-free prediction of isothermal cure from 110 to 130°C using the KAS method.
the activation energy. Kissinger’s equation can be expressed as follows:

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

(3.2)

and

$$A = \frac{\beta \cdot E_a \exp(E/T_p)}{RT_p^2}$$

(3.3)

where $R$, $E_a$, $\beta$ and $T_p$ are the gas constant (8.314 J mol$^{-1}$ K$^{-1}$), apparent activation energy, heating rate and exothermic peak temperature, respectively. Among them, $E_a$ can be obtained from the plot and the intercept of $-\ln(\beta/T_p^2)$ versus $1/T_p$.

Ozawa’s equation can be expressed as follows:

$$\frac{d(\ln \beta)}{d(1/T_p)} = -\frac{1.052E_a}{R}.$$ 

(3.4)

Crane’s equation can be expressed as follows:

$$\frac{d(\ln \beta)}{d(1/T_p)} = \frac{E_a}{nR} - 2T_p,$$ 

(3.5)

where $R$, $E_a$, $\beta$, $T_p$ and $n$ are the gas constant (8.314 J mol$^{-1}$ K$^{-1}$), apparent activation energy, heating rate, exothermic peak temperature and curing reaction order, respectively. Among them, $n$ can be obtained from the plot of $\ln \beta$ versus $1/T_p$.

The plot of $-\ln(\beta/T_p^2)$ versus $1/T_p$ based on Kissinger’s equation, as well as $\ln \beta$ versus $1/T_p$ based on Ozawa’s theory are shown in figure 8c,d. According to Kissinger’s method: the activation energy ($E_a$) and pre-exponential factor ($A$) could be obtained from the plot and the intercept of $-\ln(\beta/T_p^2)$ versus $1/T_p$, the activation energy and pre-exponential factor were about 100.3 kJ mol$^{-1}$ and $3.57 \times 10^{11}$ s$^{-1}$, respectively (equations (3.2) and (3.3)). Ozawa’s method: the activation energy could be calculated by the plot of $\ln \beta$ versus $1/T_p$, the activation energy was 107.25 kJ mol$^{-1}$ (equation (3.4)). It can be seen that the apparent activation energy acquired using Ozawa’s equation was higher than that of Kissinger’s equation [34–36]. E-20/HMTA/2-MI systems have a lower activation energy and higher catalytic activity, because epoxy groups were attached to oxygen atoms, the inductive effect could increase the polarization degree of epoxy groups, the ring-opening reaction of epoxy groups was promoted. According to the Crane method, the curing reaction order of the E-20/HMTA/2-MI system was 0.94 (equation (3.5)).

As shown in figure 8e, the epitaxial method was used to obtain $T_i$, $T_p$ and $T_f$ when $\beta = 0$ (onset temperature ($T_i$), peak temperature ($T_p$) and post-treatment temperature ($T_f$)). $T_i$, $T_p$ and $T_f$ temperatures could be used as the actual curing reference temperature, combined with the actual situation to determine the curing conditions [37]. According to the extrapolation curve of the E-20/HMTA/2-MI system, it could be concluded that $T_i = 0.515\beta + 85.06$, $T_p = 0.938\beta + 128.49$, $T_f = 1.17\beta + 177.32$. By extrapolating the $\beta$ to 0, the $T_i$, $T_p$ and $T_f$ were obtained at 85.06°C, 128.49°C and 177.32°C, respectively. Optimal curing parameter was suggested to be from 130°C.

For that, various curing degrees ($\alpha$) were evaluated by measuring the total area ($dH_2$) under the DSC curve and partial area ($dH$) at a definite temperature. The degree of curing ($\alpha$) is the ratio of $dH$ to $dH_2$ [38]. A transformation was performed to convert non-isothermal DSC scans into degree of cure versus isoconversional temperatures at different heating rates. A representative of this transformation is exhibited in figure 8f for the E-20/ HMTA/2-MI system. The curing rate was slow due to the induction period of reaction at a lower temperature. Then, the curing rate reaches maximum value.

### Table 2.
The exothermic peak temperature of the E-20/HMTA/2-MI system at different heating rates. ($T_i$, initial temperature; $T_p$, peak temperature; $T_f$, final temperature).

| $\beta$ (K min$^{-1}$) | $T_i$ (K) | $T_p$ (K) | $T_f$ (K) |
|------------------------|----------|----------|----------|
| 5                      | 360.05   | 403.15   | 453.25   |
| 10                     | 364.25   | 414.15   | 464.55   |
| 20                     | 368.55   | 422.15   | 476.85   |
| 30                     | 373.45   | 428.15   | 483.35   |
Finally, the curing rate decreases gradually. Curing degree and temperature showed 'S' curve during the whole curing process.

The Vyazovkin method uses the following equations:

\[ g(\alpha) = t_a A_a \exp\left(\frac{-E_a}{RT_0}\right) \tag{3.6} \]

and

\[ g(\alpha) = \left(\frac{A_a}{\beta}\right) \int_{T_0}^{T_a} \exp\left(-\frac{E_a}{RT}\right) dT. \tag{3.7} \]

Equations (3.6) and (3.7) stand for the isothermal \((T_0 = \text{const})\) and non-isothermal \((\beta = \text{const})\) conditions, respectively. To obtain \(t_a\), equation (3.7) can be divided by equation (3.6).

\[ t_a = \frac{\int_{T_0}^{T_a} \exp\left(-\frac{E_a}{RT}\right) dT}{\beta \exp\left(-\frac{E_a}{RT_0}\right)}. \tag{3.8} \]

Equation (3.8) was a unified model-free method, which can enable the determination of time at which a given conversion will be reached at any temperature and will be computed [39]. Figure 8g shows the isothermal curing reaction of E-20/HMTA/2-MI systems cured from 110 to 130°C as predicted by using the conversion-dependent apparent activation energy curve \((E_a)\). When the conversion rates were greater than 50%, the curing time of KAS prediction was lower than the actual reaction time.

3.6. Applications of powder epoxy adhesives in bamboo wood-based panel

Effects of epoxy adhesive amount on the mechanical properties of bamboo wood-based panel were evaluated. Internal bond strength and flexible strength of bamboo wood-based panel composites with different powder epoxy adhesives loadings are shown in figure 9. It can be observed that the internal bond strength and flexible strength were obviously improved after adding powder epoxy adhesives. The bamboo wood-based panel composites with 20 g m\(^{-2}\) powder epoxy adhesive loadings show the best internal bond strength and flexible strength. At 5 g m\(^{-2}\) powder epoxy adhesive loadings, the composites will generate debonding and bursting. Internal bond strength and flexible strength were both decreased when the powder epoxy adhesive loadings were over 20 g m\(^{-2}\), indicating that the amount of powder epoxy adhesives was increased too much, which caused thickening of the adhesive layer and increasing of the stress [40]. Finally, in consideration of the cost, the best powder epoxy adhesive loadings were obtained at 15 g m\(^{-2}\).

4. Conclusion

In this work, we have successfully synthesized a series of fast-curing powder epoxy adhesives. The structure and properties of the E-20/HMTA/2-MI systems were characterized by FTIR, TGA, DMA and DSC. With
the development of curing reaction, the peak of epoxy structure at 918 cm\(^{-1}\) gradually weakened and disappeared and the absorption peaks of \(-\text{OH} \) band at 3400 cm\(^{-1}\) weakened. These results indicated the successful ring-opening reaction of the epoxy group to form cross-linked polymers. Impact and tensile test indicated that the incorporated 2-MI in the E-20/HMTA systems could improve toughness and stiffness. The main reason was that 2-MI as a Lewis base, led to a higher cross-linking density by anionic chain-growth reaction mechanism. The best mechanical properties were obtained at 100/8/0.6 weight ratio of E-20/HMTA/2-MI systems. The TGA results showed that E-20/HMTA/2-MI systems have a higher thermal stability in comparison with the E-20/HMTA systems. The main reason was that the incorporated 2-MI in the E-20/HMTA systems could limit the intense motion of the polymer chain by different physico-chemical interactions. DSC experiments revealed that with the introduction of 2-MI into the E-20/HMTA system, the exothermic peak of E-20/HMTA/2-MI system was about 55°C lower than that of E-20/HMTA system. The main reason was that the incorporated 2-MI in the E-20/HMTA systems could decrease the activation energy and increase the rate of curing reaction. Based on Kissinger and Crane kinetic analysis, the action energy and the order of curing reaction were obtained by kinetic calculation, 100.3 kJ mol\(^{-1}\) and 0.94, respectively. According to the KAS method, the curing time of the E-20/HMTA/2-MI systems was predicted by evaluating a relationship between temperature and curing calculation, 100.3 kJ mol\(^{-1}\) and 0.94, respectively. According to the KAS method, the curing time of the E-20/HMTA/2-MI systems was predicted by evaluating a relationship between temperature and curing time. Because of these attractive properties as well as advantages of non-toxicity, ease of use and high recycling rate, powder epoxy adhesive was valuable for industrial application.

Data accessibility. All the data are provided in the main text.

Authors’ contributions. S.F. conceived and designed the experiments; J.X. performed the experiments; J.X. and X.L. analysed the data; J.Z., J.Y. and H.W. assisted in part of the experiments and testing. J.X. wrote the paper. J.X. and X.L. contributed to the revision and proofreading of the manuscript.

Competing interests. We declare we have no competing interests.

Funding. The financial support is from the Special Fund for the Program for Zhejiang Provincial Natural Science Foundation of China (LZ16C160001), the National Science and Technology Support Project (2015BADC14B0305), the National Key project (2017YFD0601105) and the Program for Key Science and Technology Team of Zhejiang Province (2013TD17).

Acknowledgements. The authors thank Zhejiang A & F University for the provision of research facilities.

References

1. Javadinezhad M, Berg DC, Duemichen E, Ziegmann G. 2016 An iterative approach for isothermal curing kinetics modelling of an epoxy resin system. Thermochim. Acta 623, 72 – 79. (doi:10.1016/j.thermasci.2015.11.014)
2. Auvergne R, Caillol S, David G, Boutevin B, Ham YR, Kim SH, Shin YJ, Lee, DH, Yang M, Min 2017 Differentiation of curable epoxy resins using 2-MI as thermal latent curing agent for thermosetting resins. ACS Macro. Lett. 4, 1085 – 1088. (doi:10.1021/acs.macrolett.5b00601)
3. Ham YR, Kim SH, Shin YJ, Lee, DH, Yang M, Min 2018 Fast-curing epoxy polymers with silica nanoparticles: properties and rheo-kinetic modelling. J. Mater. Sci. 53, 236 – 251. (doi:10.1007/s10853-015-9158-y)
4. Xu YJ, Wang J, Tan Y, Qi M, Chen L, Wang YZ. 2018 A novel and feasible approach for one-pack flame-retardant epoxy resin with long pot life and fast curing. Chem. Eng. J. 337, 30 – 39. (doi:10.1016/j.cej.2017.12.066)
5. Wai N, Zhao J, Gao B, Li C, Molla-Aldeaquia J, Zhan Y, Wang DY, 2016 Ultrastiff bio-based epoxy resin with high T\(_g\) and low permittivity: from synthesis to properties. ACS. Sustain. Chem/Eng. 4, 2869 – 2880. (doi:10.1021/acs.suschemeng.6b00479)
6. Shikda O, Kamani PK, Shulla MC. 2003 Studies on synthesis of water-borne epoxyester based on RBO fatty acids. Prog. Org. Coat. 47, 87 – 94. (doi:10.1016/S0300-9440(02)00159-5)
7. Kamiya K, Suzuki N. 2016 A low-temperature fast curing latent catalyst microencapsulated in a porous resin structure. J. Adhes. Adhes. 68, 333 – 340. (doi:10.1016/j.jadadh.2016.04.013)
8. Keller A, Masania K, Taylor AC, Dranfeld C, 2016 Fast-curing epoxy polymers with silica nanoparticles: properties and rheo-kinetic modelling. J. Mater. Sci. 53, 236 – 251. (doi:10.1007/s10853-015-9158-y)
9. Laktha DA, Yao D, Cho K, Ishaq M, Wang Y. 2017 Study of the curing kinetics toward development of fast-curing epoxy resins. Polym-Plast. Technol. 56, 161 – 170. (doi:10.1080/03602559.2016.1185623)
10. Arimitsu K, Fuse S, Kudo K, Furutani M. 2015 Imidazole derivatives as latent curing agents for epoxy thermosetting resins. Mater. Lett. 161, 408 – 410. (doi:10.1016/j.matlet.2015.08.141)
11. Yen WP, Chen KL, Yeh MY, Uramaru N, Lin HY, Wong ST. 2016 Investigation of soluble PEG-imidazoles as the thermal latency catalysts for epoxy-phenolic resins. J. Taiwan Inst. Chem. 59, 98 – 105. (doi:10.1016/j.jtice.2015.08.007)
12. Maka H, Spychaj T, Pilawka R. 2012 Epoxy resin/imidazole systems - the influence of imidazolium cation size and anion type on reactivity and thermomechanical properties. Ind. Eng. Chem. Res. 51, 5197 – 5206. (doi:10.1021/ie302321j)
13. Kudo K, Furutani M, Arimitsu K. 2015 Imidazole derivatives with an intramolecular hydrogen bond as thermal latent curing agents for thermosetting resins. ACS Macro. Lett. 4, 1085 – 1088. (doi:10.1021/acs.macrolett.5b00601)
14. Li C, Tan J, Gu J, Yue X, Quo L, Zhang Q. 2017 Facile synthesis of imidazole microcapsules via thiol-click chemistry and their application as thermally latent curing agent for epoxy resins. Comp. Sci. Technol. 142, 198 – 206. (doi:10.1016/j.compsctech.2017.02.014)
15. Pin JM, Sbirrazzuoli N, Mija A. 2015 From epoxidized linseed oil to bioresin: an overall approach of epoxy/anhydride cross-linking. ChemSusChem. 8, 1232 – 1243. (doi:10.1002/cssc.201402623)
16. Supanchayamat N, Shuttleworth PS, Hunt AJ, Clark HJ, Matharu AS. 2012 Thermosetting resin based on epoxidised linseed oil and bio-derived crosslinker. Green Chem. 14, 1759 – 1765. (doi:10.1039/C2GC35154D)
17. Patel SR, Patel RG. 1992 Effect of the anhydride structure on the curing kinetics and thermal stability of tetrafunctional epoxy resin. Thermochim. Acta 202, 97 – 104. (doi:10.1016/0040-6031(92)80515-8)
18. Geissberger R, Maldonado J, Bahamonde N, Keller A, Dranfeld C, Masania K. 2017 Rheological modelling of thermoset composite
processing. Compos. B: Eng. 124, 182–189. (doi:10.1016/j.compositesb.2017.05.040)

19. Pitcuraru C, Lažu I, Lažu R. 2017 Kinetic studies of the dehydroxylation and crystallization of raw kaolinite and fluorodes-modified kaolinite. J. Therm. Anal. Calorim. 127, 239 – 246. (doi:10.1007/s10973-016-5763-5)

20. Beňová E, Zeleňák V, Halamová D, Almáši M, Petrušová V, Poštka M, Honebečq V. 2017 A drug delivery system based on switchable photo-controlled p-coumaric acid derivatives anchored on mesoporous silica. J. Mater. Chem. B 5, 817 – 825. (doi:10.1039/C6TB02040B)

21. Fei X, Wei W, Zhao F, Zhu Y, Luo J, Chen M, Liu X. 2016 Efficient toughening of epoxy–anhydride thermosets with a bio-based tannic acid derivative. ACS Sustain. Chem/Eng. 5, 596 – 603. (doi:10.1021/acssuschemeng.6b01967)

22. Milne NJ. 1998 Oxygen bleaching systems in domestic laundry. J. Surf. Deter. 1, 253 – 261. (doi:10.1007/s11743-998-0029-z)

23. Miao X, Meng Y, Li X. 2015 Epoxide-terminated hyperbranched polymer as a new modifier for anhydrides as alternatives to petrochemical curing agents. Macromol. Rapid. Commun. 36, 1304010. (doi:10.1002/marc.200300023)

24. Liu X, Xin W, Zhang J. 2009 Rosin-based acid anhydrides as alternatives to petrochemical curing agents. Green Chem. 11, 1018 – 1025. (doi:10.1039/b909395s)

25. Luo L, Meng Y, Qi T. 2013 An epoxy-ended hyperbranched polymer as a new modifier for toughening and reinforcing in epoxy resin. J. Appl. Polym. Sci. 130, 1064 – 1073. (doi:10.1002/app.39257)

26. Wang R, Zhou D, Weng Z, Wu L, Cheng X, Zhou Y, Xuan B. 2015 A novel nano silica/graphene oxide hybrid and its flame retardancy epoxy resin with simultaneously improved mechanical, thermal conductivity, and dielectric properties. J. Mater. Chem. A 3, 9826 – 9836. (doi:10.1039/C5TA00722D)

27. Xuan B, Meng Y, Li X. 2015 Tannic acid as a bio-based modifier of epoxy/anhydride thermosets. Polym. 3, 314.

28. Liu T, Nie Y, Zhang L. 2015 Dependence of epoxy toughness on the backbone structure of hyperbranched epoxy modifiers. RSC Adv. 5, 3408 – 3416. (doi:10.1039/C4RA10974K)

29. Liu T, Nie Y, Chen R. 2015 Hyperbranched polymer as an all-purpose epoxy modifier: controlled synthesis and toughening mechanisms. J. Mater. Chem. A 3, 1188 – 1198. (doi:10.1039/C4TA00023)

30. Mashouf Roudsari G, Mohanty AK, Misra M. 2013 Comparative DSC curing kinetics and thermogravimetric study of epoxy/anhydride thermosets. Bull. Chem. Soc. Jpn 86, 1881 – 1888. (doi:10.1246/bcsj.86.1881)

31. Ren R, Xiong X, Ma X, Liu S, Wang J, Chen P, Zeng Y. 2016 Isothermal curing kinetics and mechanism of DGEBA epoxy resin with phthalide-containing aromatic diamine. Thermochim. Acta 623, 15 – 21. (doi:10.1016/j.tca.2015.11.011)

32. Thanki JD, Parsania PH. 2017 Dynamic DSC curing kinetics and thermogravimetric study of epoxy resin of 9,9-bis (4-hydroxyphenyl) anthrone-10. J. Therm. Anal. Calorim. 130, 2145 – 2156. (doi:10.1007/s10973-017-6751-y)

33. Kuo PY, Sain M, Yan N. 2014 Synthesis and characterization of an extractive-based bio-epoxy resin from beetle infested Pinus contorta bark. Green Chem. 16, 3483 – 3493. (doi:10.1039/C4GC00459K)

34. Khodaei M, Valanezhad A, Watanabe I. 2017 Surface and mechanical properties of modified porous titanium scaffold. Surf. Coat. Tech. 315, 61 – 66. (doi:10.1016/j.surfcoat.2017.02.032)