Polybenzoxazines: Thermal Responsiveness of Hydrogen Bonds and Application as Latent Curing Agents for Thermosetting Resins

Shuai Zhang, Po Yang, Yun Bai, Tao Zhou, Rongqi Zhu, and Yi Gu

1 State Key Laboratory of Polymer Materials Engineering, College of Polymer Science and Engineering and 2 State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute, Sichuan University, Chengdu 610065, China

ABSTRACT: This work aims at exploring the application of polybenzoxazines as thermal latent curing agents for epoxy resins. Thorough studies have shown that hydrogen bonds of polybenzoxazines block the reactivity of phenolic hydroxyl at ambient temperatures and break at elevated temperatures to release the free phenolic hydroxyl. On the basis of these findings, polybenzoxazines are used as thermal latent curing agents. Mixtures of polybenzoxazines and epoxy resins exhibit a long shelf life at room temperature, and the corresponding copolymers possess enhanced properties. This novel insight into using polybenzoxazines as thermal latent curing agents for epoxy resins is anticipated to help researchers explore novel latent curing agents and apply polybenzoxazines more widely.

1. INTRODUCTION

As widely used thermosetting resins, epoxy resins have been applied in many areas, such as coatings and adhesives and in aerospace and microelectronics. Generally, as epoxy resins cannot cure in the absence of curing agents, various types of chemical compounds, for example, anhydrides, 4-6 imidazoles, 7-8 thiol, 6-8 primary amines, 9-12 and phenols 13 have been used to cure epoxy resins. Because curing agents greatly determine the properties of the resins, such as processability, electrical properties, and mechanical performance, many works focus on studying the curing agents.

Some curing agents, like imidazoles and thiols, can convert liquid epoxy into an insoluble solid even at room temperature (RT) due to their high reactivity. This leads to poor storage stability, and these curing agents cannot be used as one-component mixtures with epoxy resins. Other curing agents, for example, anhydrides and phenols, can be used as one-component mixtures with epoxy, but the curing temperature is so high that it leads to disadvantages in application. Therefore, the search for superior curing agents is still underscored by the academic and industrial community. Preparation of latent curing agents is regarded as an effective approach because latent curing agents not only possess good storage stability when used as a one-component mixture with epoxy but could also polymerize effectively under certain stimuli, such as heat, light, or pressure. An interesting technique to prepare latent curing agents is to take advantage of the thermal responsiveness of hydrogen bonds. Hydrogen bonds can block the reactivity of compounds at RT and break at an elevated temperature to unblock their reactivity toward epoxy resins. As small molecules, however, most thermal latent curing agents with hydrogen bonds may generate residues and hinder the properties of the corresponding resins. Hence, polymers that can react with epoxy resins and act as latent curing agents will be favored.

Polybenzoxazines, polymers with a \(-\text{CH}_2—\text{NR}—\text{CH}_2—\) structure obtained via the polymerization of corresponding benzoxazines, possess many excellent properties (for instance, molecular design flexibility, good mechanical strength, excellent dielectric properties, low water absorption and near-zero volumetric shrinkage), which is attributed to their hydrogen bonds. For classical polybenzoxazines, hydrogen bonds are formed between the generated phenolic hydroxyl (—OH) and hydrogen-bonding acceptors (i.e., —OH, —N—Ar, and \(\pi\)). Hydrogen bonds can block the reactivity of —OH at a low temperature and release active free phenolic hydroxyl with increasing temperature. In the case of polybenzoxazine, the hydrogen bonds may endow polybenzoxazines with thermal latency, which will be explored in this work. More importantly, benzoxazines can react with epoxy resins to produce copolymers, which exhibit several excellent properties and have been applied in many areas, such as electronic packaging, printed circuit boards, and mechanical technology. On the basis of these properties, polybenzoxazines are expected to act as thermal latent curing agents and enhance the properties of epoxy resins. Nonetheless, to the best of our knowledge, no such studies have been reported. Some key issues, such as whether polybenzoxazines can act as thermal latent curing agents and the reasons for thermal latency and the curing reaction still remain.

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Hence, this work focuses on exploring the application of polybenzoxazines as thermal latent curing agents. As thermosets, polybenzoxazines are polymerized from benzoxazines consisting of multiple oxazine ring groups. During polymerization, covalent crosslinking occurs and results in cross-linked networks that could resist heat softening and solvent attack, making polybenzoxazines impossible to blend with epoxy resins. For application as latent curing agents, soluble polybenzoxazines are required. Hence, in this work, two kinds of single oxazine ring-containing benzoxazine monomers were synthesized. One was synthesized from p-cresol and aniline (denoted p-C-a) and the other was synthesized from p-cresol and benzylamine (denoted p-C-b). Their polymers (PpC-a and PpC-b) were employed to explore their application as thermal latent curing agents. The results showed that polybenzoxazines exhibited good latency at RT and can become enhanced performance copolymers after blending with epoxy resins. For application as latent curing agents, soluble polybenzoxazines are required. Hence, in this work, two kinds of single oxazine ring-containing benzoxazine monomers were synthesized. One was synthesized from p-cresol and aniline (denoted p-C-a) and the other was synthesized from p-cresol and benzylamine (denoted p-C-b). Their polymers (PpC-a and PpC-b) were employed to explore their application as thermal latent curing agents. The results showed that polybenzoxazines exhibited good latency at RT and can become enhanced performance copolymers after blending with epoxy resins. This suggested that polybenzoxazines can act as good candidates for thermal latent curing agents. Detailed analyses and discussions are provided below.

2. RESULTS AND DISCUSSION

2.1. In Situ Fourier Transform Infrared (FTIR) Tests of Polybenzoxazines. Phenolic hydroxyl (—OH), generated from benzoxazines, could act as a hydrogen-bonding donor to form hydrogen bonds in polybenzoxazines and react with epoxy resins. Hence, this work probed the variation of phenolic hydroxyl of polybenzoxazines using in situ FTIR. We performed the experiment from RT to 200 °C, and the spectra of PpC-a and PpC-b in the region of 3800−2000 cm\(^{-1}\), corresponding to the absorption of —OH, are shown in Figures 1 and S2, respectively.

![Figure 1. In situ FTIR spectra of PpC-a from RT to 200 °C.](Image)

At RT, as can be seen from Figure 1, absorption by bonded —OH was observed from 3230 to 3450 cm\(^{-1}\) and almost no obvious absorption by free —OH was observed at ∼3566 cm\(^{-1}\), suggesting that most —OH of PpC-a formed hydrogen bonds. Because hydrogen bonds can block the reactivity of —OH, the reactivity of PpC-a toward epoxy would be blocked by hydrogen bonds at RT. As the temperature increased, the intensity of the bands between 3230 and 3450 cm\(^{-1}\) decreased, whereas absorption at ∼3566 cm\(^{-1}\) increased continually. This variation suggested that bonded —OH of PpC-a transformed into free —OH as the temperature increased, that is, the reactivity of —OH was unblocked with an increase in temperature. A similar trend was also observed for PpC-b (Figure S2). As the temperature increased, absorption by bonded —OH between 3200 and 3400 cm\(^{-1}\) became weaker, whereas the absorption by free —OH at ∼3600 cm\(^{-1}\) increased. However, this variation was not so obvious, probably because of the formation of hydrogen bonds (the absolute dominant hydrogen bond of PpC-b is the —OH···N hydrogen bond) resulting from the amine moiety.\(^{27,35}\) As for PpC-a-acylated (Figure S3), no changes were observed in the spectra owing to the absensice of —OH. These features indicated that the —OH of polybenzoxazines might possess a thermal latent effect.

2.2. Synchronous PCMW2D Correlation of Polybenzoxazines. To further explore the thermal responsiveness of hydrogen bonds of PpC-a and PpC-b, perturbation-correlation moving-window two-dimensional (PCMW2D) correlation spectroscopy, a powerful and nimble tool to study molecular structure and molecular interaction, was applied. PCMW2D correlation spectroscopy combines generalized two-dimensional correlation\(^{36}\) and moving-window two-dimensional correlation\(^{37}\) spectroscopy. PCMW2D correlation spectroscopy produce contour maps of a spectral variable (abscissa) and perturbation variable (ordinate); here, the spectral variable and perturbation variable are, respectively, wavenumber and temperature. In this work, synchronous PCMW2D correlation, a direct correlation between spectral variation and perturbation variation (a linear change function), is employed.\(^{38,39}\)

In the classical synchronous PCMW2D correlation spectra, warm-color and cool-color contour areas represent positive and negative correlations with temperature change, respectively. In other words, warm color always indicates an increase in the absorption intensity of the corresponding groups, that is, a concentration increase. Cool-color contour areas, by contrast, signify a corresponding decrease in concentration. In the case of the synchronous PCMW2D correlation spectrum for PpC-a (Figure 2), three intense minimum correlation valleys corresponding to bonded —OH, in the range of 3230−3450 cm\(^{-1}\), emerged at ∼30, ∼60, and ∼180 °C, and three intense maximum correlation peaks assigned to free —OH (∼3566 cm\(^{-1}\)).
cm⁻¹) appeared at ∼48, ∼105, and ∼190 °C. These indicated that the bond in bonded —OH broke and generated free —OH. Similar observations were made in the in the synchronous PCMW2D correlation spectrum of PpC-b, as shown in Figure S4, that is, cool- and warm-color contour areas appeared at around 140 and 110 °C, respectively. Although, these areas appeared to a lesser extent compared to that in PpC-a, the results still imply that the massive dissociation of bonded —OH occurred at ∼110 °C and the generation of free —OH occurred at ∼140 °C. This suggests that the bonded —OH of polybenzoxazines can convert into free —OH as the temperature increases and further supports the fact that the reactivity of —OH would be unblocked at elevated temperatures.

2.3. Curing Reaction Behaviors. As mentioned previously, this work attempted to use polybenzoxazines as thermal latent curing agents. To evaluate the reactivity of polybenzoxazines toward epoxy resins, the curing reaction behaviors of the mixtures of E51 and PpC-a or PpC-b were studied by differential scanning calorimetry (DSC), as shown in Figure 3. As can be seen from Figure 3, obvious exothermic peaks were observed in the curves, showing that PpC-a and PpC-b were effective curing agents for E51. Multiple peaks, located at ∼150, ∼196, and ∼250 °C, were detected in the curve of E51/PpC-a, whereas a single peak around 245 °C was observed in the curve of E51/PpC-b. Interestingly, this is in accordance with the features of the synchronous PCMW2D correlation spectrum, further suggesting that the reactivity of the bonded —OH of polybenzoxazines can be unblocked at elevated temperature. To better understand the curing behavior, in this work, the conversion of epoxy resins was calculated from the exothermic peaks to assess the consumption rates (Figure S5). This showed that E51/PpC-a cured rapidly and reached a very high conversion at ∼250 °C; however, the curing of E51/PpC-b started at ∼180 °C. This is probably attributed to the difference in temperature of unblocking the reactivity of —OH between PpC-a and PpC-b, resulting from differences in the formation of hydrogen bonds. The interesting results also indicated that latent curing agents with different curing temperatures can be attained through designing and synthesizing polybenzoxazines.

To better understand the reaction between polybenzoxazines and epoxy resins, phenols (p-cresol), N,N-DEBA, and the ploybenzoxazines without phenol groups (PpC-a-acylated) were used to explore the reaction, as shown in Figure 3. Phenols can be used as curing agents for epoxy; yet, their poor reactivity leads to the requirement for a high curing temperature, and so, no obvious exotherm was observed in the DSC curve of E51/p-cresol. Tertiary amines can be used as cure accelerators but not as curing agents; therefore, no distinct exotherm was detected in the mixtures of E51 and N,N-DEBA, either. However, when the curing agents and accelerator coexisted, an exothermic peak appeared in the curve of E51/p-cresol/N,N-DEBA, with the starting exothermic temperature, ∼50 °C, being much lower than that for E51/PpC-a and E51/PpC-b, which further demonstrated that the formation of hydrogen bonds effectively blocked the reactivity of phenolic hydroxyl at a low temperature. As for PpC-a-acylated, in the absence of phenol groups, tertiary amine groups alone cannot cure E51, just like that for N,N-DEBA. These results suggest that the high reactivity between polybenzoxazines and epoxy resins was not due to —OH or —CH₂—NR—CH₂— solely but synergistically. All of these characteristics show that the interesting chemical structures and hydrogen bonds of polybenzoxazines not only made for good thermal latency but also produced high reactivity toward epoxy resins at elevated temperatures.

2.4. Evaluation of Storage Stability. Storage stability, depending on the reactivity of curing agents, plays an important role in processability; hence, this work probed storage stability by detecting the viscosity variation at RT (Figure 4). After mixing E51 with p-cresol or PpC-a-acylated, due to the poor reactivity, nearly no viscosity change of E51/p-cresol and E51/PpC-a-acylated was observed during the evaluation period. However, after mixing E51 with p-cresol and N,N-DEBA, owing to the high reactivity, the viscosity of E51/p-cresol/N,N-DEBA increased by 90 times in 4 days and the mixture solidified in 5 days. Although no obvious reactions occurred between N,N-DEBA and E51, judging from the DSC test results, the viscosity of E51/N,N-DEBA increased rapidly and the mixture solidified in 8 days. This might have resulted from the impurities, such as

![Figure 3. DSC curves of E51/PpC-a, E51/PpC-b, E51/p-cresol, E51/N,N-diethylbenzylamine (N,N-DEBA), E51/N,N-DEBA/p-cresol, and E51/PpC-a-acylated.](image)

![Figure 4. Summary of storage stability.](image)
the primary amine and secondary amine, in \( N,N\)-DEBA. In the case of E51/PpC-a and E51/PpC-b, as expected, a slight increase in viscosity was observed during the evaluation period (4 weeks). This indicated that E51/PpC-a and E51/PpC-b possessed excellent storage stability, owing to the blocking of hydrogen bonds at RT, and the shelf life of epoxy/polybenzoxazine mixtures surpassed that of the mixtures of epoxy and small molecular latent curing agents, which made polybenzoxazines great thermal latent curing agents for epoxy resins.

### 2.5. Dynamic Mechanical Analysis (DMA)

As mentioned previously, this study also attempted to enhance the properties of epoxy resin using polybenzoxazines as curing agents; hence, DMA was applied to evaluate the performance. The results are shown in Figures S6 and S7 and Table 1. As can be seen from Table 1, when the molar ratio of polybenzoxazines/epoxy is 1:4, the storage moduli of the copolymers were highly boosted in comparison to those of the polymers cured by p-cresol and \( N,N\)-DEBA. As the amount of the curing agent increased (molar ratio 1:2), the performance of the copolymers derived from E51/polybenzoxazines improved; for example, the \( T_g \) and the modulus of poly(E51/PpC-a) were 147.8 °C and 4013 MPa, respectively. Nevertheless, because of the excess of residues in poly(E51/\( N,N\)-DEBA/p-cresol), the desired samples were not obtained. So, as thermal latent curing agents, polybenzoxazines not only possess good storage stability but also can enhance the performance of the epoxy resin.

### 3. CONCLUSIONS

In summary, this work focuses on applying polybenzoxazines as thermal latent curing agents. The interesting chemical structures and hydrogen bonds make polybenzoxazines very suitable for use as thermal latent curing agents. At ambient temperature, hydrogen bonds of polybenzoxazines can block the reactivity of phenolic hydroxyl and give the polybenzoxazines/epoxy mixtures excellent storage stability; as the temperature increases, active phenolic hydroxyl is generated and the curing reaction occurs rapidly. More interestingly, the afforded copolymers of polybenzoxazines and epoxy resins exhibit enhanced properties. This finding is anticipated to motivate researchers to search for novel superior curing agents and apply polybenzoxazines more widely.

### 4. EXPERIMENTAL SECTION

#### 4.1. Materials

Aniline (≥99%), p-cresol (≥98%), benzylamine (≥99%), acetyl chloride (≥98%), toluene (≥99%), acetone (≥99%), triethylamine (≥99%), and ethanol (≥99%) were purchased from Chengdu Kelong Chemical Reagents Corp. (Chengdu, China) and were utilized without further purification. Paraformaldehyde (≥97%) was purchased from Fydya (Spain). \( N,N\)-dimethylbenzylamine (≥98%) was purchased from Aladdin Industrial Corporation and utilized without further purification.

#### 4.2. Instruments

FTIR spectra were obtained with a Nicolet-S60 spectrometer in the range of 4000–400 cm⁻¹ at a resolution of 4 cm⁻¹. All samples were dissolved in CH₂Cl₂, and the solutions were coated on the KBr pellets; once CH₂Cl₂ evaporated, the samples were ready for testing. In situ FTIR spectra were recorded with an accessory heater. The samples were coated in the middle of two KBr pellets and inserted into the hot cell at the desired temperature. Three spectra were recorded per minute, with a heating rate of 5 °C/min. 1H NMR spectra were recorded on a Bruker TD-600 (NMR spectrometer operating at a proton frequency of 400 MHz. All specimens were dissolved in DMSO-d₆ with tetramethylsilane as the internal reference. DSC tests were conducted using DSC Q20 (TA Instruments), at a heating rate of 5 °C/min, using nitrogen as the purge gas. Calibration was performed using an indium standard. DMA measurements were performed on DMA Q800 (TA Instruments), at 1 Hz, with the heating rate of 5 °C/min. Viscosity tests were conducted using a Brookfield viscometer, DV-2+ Pro.

### 4.3. Synthesis and Characterization of PpC-a, PpC-b, PpC-a, and PpC-b

The specific synthesis and characterization of PpC-a and PpC-b have been described elsewhere (Scheme 1).[10]

#### Scheme 1. Synthesis Route of PpC-a, PpC-b, PpC-a, and PpC-b

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Table 1. DMA Data for Poly(E51/PpC-a), Poly(E51/PpC-b), and Poly(E51/\( N,N\)-DEBA/p-cresol)

| Polymer                  | \( T_g \) (°C) | \( T_g \) total (°C) | \( E' \) (MPa, 30 °C) |
|--------------------------|----------------|---------------------|---------------------|
| Poly(E51/PpC-a)          | 56.0⁰         | 127.0⁰              | 3164⁰, 4013²        |
| Poly(E51/PpC-b)          | 65.0³         | c,d                 | 3585¹, 3729¹        |
| Poly(E51/\( N,N\)-DEBA/p-cresol) | 53.2⁰       | c,d                 | 1434⁰              |

“Molar ratio: the mole of —OH groups versus that of epoxide groups. "Molar ratio 1:4. "Molar ratio 1:2. “Data cannot be obtained.
produced; then, the oil phase was washed several times with distilled water until the pH of the washing water was neutral. Then, the water was separated and the organic solvent was evaporated in a rotary evaporator to remove most of the solvent. Finally, the product was dried under vacuum at 70 °C for 3 h, yielding a pale yellow powder (Scheme 2).

**Scheme 2. Synthesis Route of PpC-a-acylated**

![Scheme 2](image)

4.5. Curing Procedure of E51/PpC-a, E51/PpC-b, and E51/N,N-DEBA/p-cresol. E51 and polybenzoxazine were mixed homogeneously by stirring at 120 °C; then, the mixtures were transferred to aluminum molds. The samples were degassed at 120 °C for 1 h, followed by heating at 120, 140, and 160 °C for 2 h, respectively, and 180 °C for 1 h. For E51/N,N-DEBA/p-cresol, due to the volatility of N,N-DEBA and p-cresol at high temperature and their high reactivity, curing was conducted at a relatively lower temperature (50, 60, 70, 80, 90, 100, 110, 120, and 130 °C for 2 h, respectively). Then, the corresponding cast samples were polished to DMA specimens.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00075.

Characterization spectra of PpC-a-acylated; FTIR spectroscopic measurement of PpC-b and PpC-a-acylated at various temperatures; synchronous PCMW2D correlation of PpC-b; consumption of epoxy resin (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**

*E-mail: yangpo@scu.edu.cn (P.Y.).
*E-mail: guyi@scu.edu.cn (Y.G.).

**ORCID**

Po Yang: 0000-0002-2657-2408
Tao Zhou: 0000-0003-3581-2925

**Notes**

The authors declare no competing financial interest.

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