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Curing kinetics of benzoxazine resin by torsional braid analysis

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Abstract

Benzoxazine precursor is synthesized and is tested by torsional braid analysis. The phenomena of gelation and glass transitions which occur in the formation of thermosets are found and studied. In particular, two special secondary glass transitions appear at the curing temperature and the time–temperature-transformation spectrum is obtained. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Benzoxazine; Torsional braid analysis; Time–temperature-transformation spectrum

1. Introduction

Recently, a newly developed class of novel thermosetting resin that is based on the benzoxazine resin, has received strong attention because of their high properties. Benzoxazine is synthesized by a ring-opening polymerization of aromatic oxazines. It neither produces byproducts nor requires strong catalysts. Some benzoxazine resins have been found to have near-zero shrinkage or volumetric expansion upon curing [1–5].

The curing mechanism of benzoxazine resins is poorly understood. The curing process is established only by differential scanning calorimeter or by the curing process parameters of traditional thermosetting resins [6]. The research of the phase change on curing of benzoxazine has not been reported before to our best knowledge. A torsional braid analysis (TBA) is an analysis of kinetics mechanism enzoxazine developed by Gillham [7]. The rheologic behavior of viscous state can be studied by TBA which also permits monitoring the changes occurred throughout the curing. The TBA is effective in studying the mechanical behavior and the relax phenomenon in the curing of thermosetting resins.

The purpose of this work is to study the mechanical relax behavior of benzoxazine during curing in order to establish the cure process parameters and offer reasons of achieving successful process.

2. Experiment

2.1. Preparing of benzoxazine monomer

A benzoxazine precursor based on bisphenol A, formaldehyde, and aniline, is synthesized. All chemicals are used as received. The bisphenol A and aniline are supplied by the Hebei Chemical Center. The formaldehyde (37 wt% in water) is available from Shijiazhuang Organic Chemical Factory. The synthesis of the precursor is synthesized by using a procedure explained by Ning and Ishida [8].

The monomeric fraction is separated from the precursor mixture. Reaction product is redissolved in ethyl ether, the solids are filtered out, and the solution is washed three times with a 3N NaOH aqueous solution in a separate funnel, then wash it three times with a 2N HCl aqueous solution; water is used for the final wash. The ether phase is dried over sodium sulfate and the solvent is evaporated in a rotary evaporator. A very fine white powder is obtained.

2.2. Preparing for TBA

2.2.1. Preparing of the gel solution

Benzoxazine monomer is resolved in toluene solution to prepare gel solution with the concentration of 60% (weight rate).

2.2.2. Preparing for the glass fiber braid

The glass fiber braid must be heated for 4 h at 400 °C in order to get rid of wax at the surface. The braids are cut to 15 cm and are fixed by clips. The distance of two sites of the clips is about 12 cm.

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2.2.3. *Preparing of the testing sample*

The treated braids are impregnated in the gel solution for some time. Then, they are heated in the oven to volatilize the toluene.

2.2.4. *Testing sample*

The samples are tested in the GDP-3TBA (made in the University of Jilin). The heating temperature is controlled at the rate of 3 °C/min and the selected temperature is 162, 170, 186, 200, 210, 229, and 242 °C in the time-mechanical spectrum.

2.2.5. *Testing glass transition temperature*

The glass fiber braids impregnated in the benzoxazine monomer are cured through a certain curing process. Then, the sample is tested by the GDP-3TBA to obtain the glass transition temperature with the rate of heating at 2 °C/min.

3. Results and discussion

3.1. *The analysis of the temperature-mechanical spectrum of the curing of benzoxazine by the TBA*

Fig. 1 is the temperature-mechanical spectrum of the curing of benzoxazine from 100 to 327 °C. The spectrum can be divided into three areas according to the behavior of the damping curve and the rigidity curve: melt transition area (100–148.7 °C), gelation transition area (148.7–237.2 °C), and glass transition area (237.2–327 °C).

Melt transition area (100–148.7 °C). It can be shown from Fig. 1 that the damping curve is dropped with the increase of the temperature, while the change of the rigidity is not sensitive. It has been proposed that benzoxazine monomer impregnated in the support-glass fiber braids is first melted into true solution, which causes that the loss modulus G'' reduce more rapidly than the storage modulus G'. Therefore, the loss modulus drops to the lowest point during this range of temperature ($\Delta = G''/G'$). Since the rigidity obtained from the TBA is the rigidity of the glass fiber braid itself, the change is little.

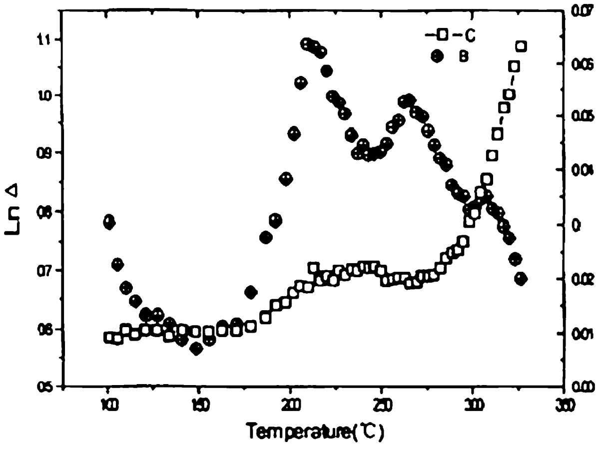


Fig. 1. Temperature-mechanical spectrum of TBA.

Gelation transition area (148.7–237.2 °C). According to Fig. 1, the damping curve increases dramatically with the rise of the temperature at first and reaches a maxim at about 200 °C. Then, the temperature continually increases while the damping curve decreases, in the meanwhile, the rigidity curve increases slowly. It means that the gelation transition occurs in the benzoxazine monomers. With the increase of the temperature, some parts of oxazine ring of benzoxazine monomers are opened to form the dimer, trimer and copolymer. When the reaction reaches to a certain degree, the gelation occurs according to the gelation theory of Flory. It is associated with the rapid increase of the viscosity which is caused by the network molecule formed from the linear molecule chains [9]. All of these are caused by the changes of the motion units in the curing system during the gelation transition. The motion units move relatively to the whole chain before the gelation transition, while once the gelation transition happens, the motion units are the segments of the network. It can be shown from the mechanical state that the gelation transition is the critical change from the viscous state to the rubber state, and it is a mechanical relax phenomena. Therefore, a loss peak in the damping curve takes place and a slope change occurs in the relative rigidity curve correspondingly [10].

Glass transition state (237.2–327 °C). It is shown that the damping curve goes up and down first then increases slightly and decreases again at about 308 °C with the temperature continually goes up. It means that two loss peaks will occur. The rigidity curve increases rapidly with the rise of the temperature, which indicates that the glass transition occurs during the curing reaction. The unopened oxazine rings continue to cure because of the motion of the segments in the network. With the increase of the crosslinks and the molecular weight, the cure reaction comes to the state controlled by diffusion [11]. However, when the cure reaction reaches to some degree, the motion units are immobile, as a result, the glass transition occurs, which leads to the second descend of the damping and the rapid rise of the relative rigidity. The reaction decreases sharply because the curing system is in a glass state which changes from rubber state. With the rise of the temperature, another loss peak appears near 308 °C, which indicates that the unopened oxazine rings are mobile again to form the crosslinks and the reaction goes to a higher degree at a higher temperature.

From the above, we know that the curing reaction of the benzoxazine occurs between 148.7 and 237.2 °C. With the rise of the temperature, the benzoxazine monomer is melted into viscous state firstly, then the oxazine rings open and the linear copolymer is formed. When the reaction goes to some degree, the gelation transition occurs. It indicates that the linear structure is changed into networks, therefore the viscosity raises rapidly and the system changes from the viscous state to the rubber state. With the rise of the degree of the reaction, the increase of the crosslink-points and the inter-molecular interaction leads to the immotion of the segments. The glass transition occurs and the curing system changes from the rubber state to the glass state. When the curing temperature rises continuously, the oxazine ring of benzoxazine immersed in the network is mobile again and the post-curing reaction happens.

3.2. The analysis of time-mechanical spectrum of the curing of benzoxazine by TBA

Generally speaking, the prepolymer is cured for some time under some temperature, then the temperature rises and it is cured continuously again. The state of dynamic mechanism can be determined by the time-mechanical spectrum of the curing of benzoxazine at some curing temperature and for some time by TBA. Since the dynamic mechanical state of the curing system affects the overall mechanical properties directly, the time-mechanical spectrum can be used to examine the reasonability of the curing process and offer the basis of the establishment of the new curing process [12,13].

The time-mechanical spectrum is made of damping and rigidity curve at some range of temperatures. According to the time-mechanical spectrum of the curing of benzoxazine by TBA, the purpose of this research is to study the results of it with the temperature range of 160–240 °C, for example, 162, 170, 186, 200, 210, 229, 242 °C. Fig. 2 is the time-mechanical spectrum by TBA.

As is shown from Fig. 2, the dynamic mechanical behavior of the curing system of benzoxazine varies when the curing temperature changes. The curing temperature can be divided into three groups on the basis of the different phenomena of dynamic mechanism behavior. The first group of curing temperatures are 162, 170, 186, and 200 °C, the second is 210 °C, and the third are 229, and 242 °C. The curing behavior in the first group of curing temperatures at 162, 170, 186, and 200 °C.

The gelation transition. From the time-mechanical spectrum at the curing temperature of 162, 170, 186, and 200 °C, respectively, a loss peak caused by the gelation transitions first appears. The relationship of the gelation time and the temperature is shown in Fig. 3. It is clear from Fig. 3 that the gelation time becomes short with the rise of the curing temperature. It is because the degree of the gelation transition is a constant [9,14]. The higher the temperature, the faster the rate of the reaction and the shorter the gelation time.

The second group of glass transition. The time-mechanical spectrum indicates that four gelation transitions occur at the temperature of 162, 170, 186, and 200 °C. Two small loss peaks (β and γ transition) appear in the damping curve during both the changes from the viscous state to the rubber state and the happening of the glass transition. It illustrates the changes of the motion units and these changes do not show in the time-mechanical spectrum of the common thermosetting resins such as the epoxy resins and the phenol resin by TBA [15].

The change of the motion units reflects the change of the inter-molecular interaction. The relationship between the change of the motion units and the inter-molecular interaction is shown in the following equation [16]:

$$\mathrm{lp} = l \exp(\Delta\varepsilon/\mathrm{kT}) \tag{1}$$

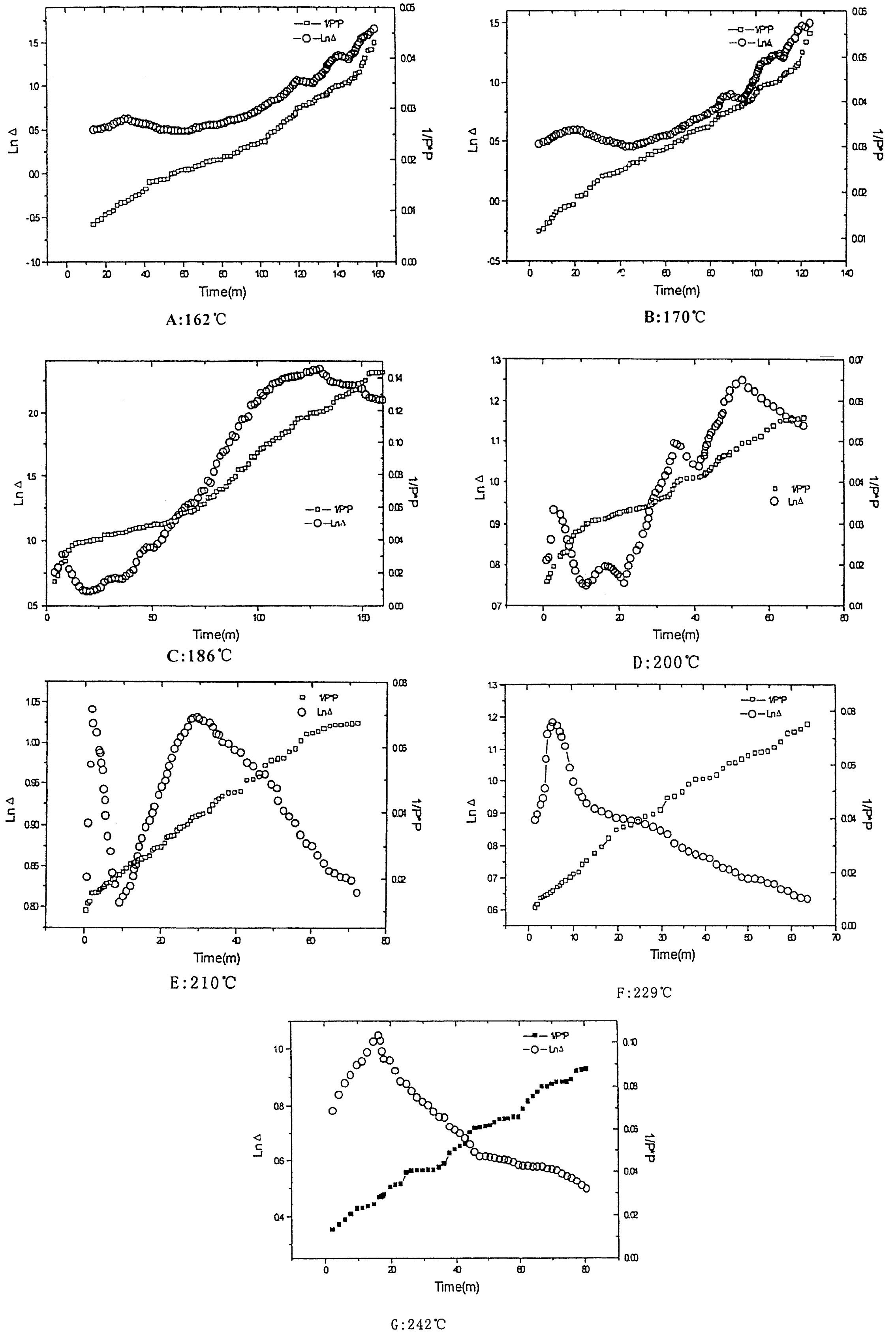
lp denotes the length of the segment, l the length of the single bond, $\Delta\varepsilon$ the activated energy needed to rotate the single bond and it is relative to the inner-molecular interaction. When the inner-molecular interaction rises, both lp and $\Delta\varepsilon$ increase, so the rigidity also increases. It is associated with the change of the special inner-molecular interaction in the curing system of benzoxazine. In fact, Ishida has found that there are a lot of the hydrogen bonds in the curing products during the ring-opening polymerization of benzoxazine [17]. Compared with the epoxy resins, much greater inter-molecular interaction is formed in the structure of the phenolic hydroxyl. With the degree of the curing reaction increases, the force of the hydrogen bonds get greater, which results into the rise of both the force of the network molecular and the activated energy of the segment motion. As it is known from the earlier equation, with the decline of the flexibility, the motion units become smaller and β and γ transition occur. γ transition normally describes the motion of the main-chain segment containing 2–4 carbon atoms and β transition typically describes a motion in the flexible side chains of the polymer [18]. In the case of polybenzoxazine resin, this transition refers to the motion of the heterocyclic ring structure. Because of the prevalence of the inter- and intra-molecular hydrogen bond in the polybenzoxazine resin, these hydrogen bonds are sufficiently strong to confine the mobility of segment and contribute to the rigidity in the glass state that would normally be expected only from a much tighter network structure [17].

Glass transition. According to Fig. 2(A)–(D), the damping curve goes up and the glass transition does not appear at the lower temperature such as 162, 170 °C, which indicates that the glass transition time is longer than that at the same temperature. With the rise of the curing temperature, the rate of the reaction accelerates and the glass transition time becomes short. For example, when the curing temperatures are 186 and 200 °C, the glass transition time are 142 and 63 min, respectively.

3.2.1. The curing behavior at the curing temperature of 210 °C

As is shown from Fig. 2(E), when the curing temperature is 210 °C, the loss peak resulted from the gelation appears at 1.8 min and that resulted from the glass transition appears at 29.7 min in the damping curve in the curing system of benzoxazine. It indicates that the time of both the gelation and the glass transition are cut down because of the fast reaction.

It can also be seen from Fig. 2(E) that the secondary glass



A:162℃

B:170℃

C:186℃

D:200℃

E:210℃

F:229℃

G:242℃

Fig. 2. Isothermal TBA spectra at different temperature (A: 160, B: 170, C: 186, D: 200, E: 210, F: 229, and G: 242 °C) for different times. Relative rigidity (right) and logarithmic decrement (left) vs. time.

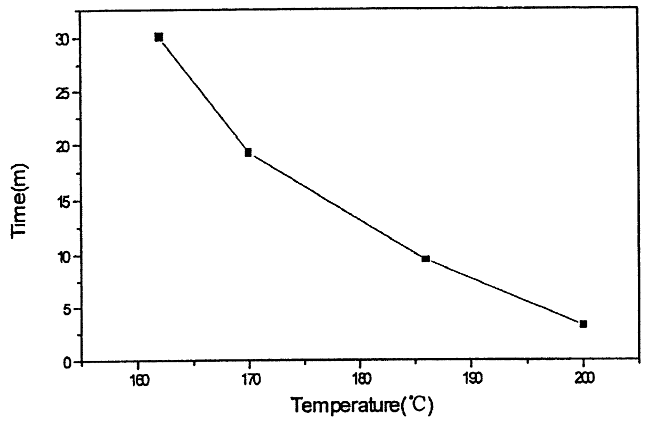


Fig. 3. The relationship between gelation time and cure temperature.

transition does not appear between the glass transition and the gelation transition. We think that it is due to the high curing temperature. On the one hand, the hydrogen bonds formed by phenolic hydroxyl are destroyed at the high temperature; on the other hand, Eq. (1) indicates that the increase of $\Delta\varepsilon$ has little effect because of the high temperature, as a result, the segments of motion units have little changes.

3.2.2. The behavior at the curing temperature of 229, 242 °C

It can be shown from Fig. 2(F) and (G) that when the curing temperature rises, the gelation transition time is too short to test by the time-mechanical spectrum. Therefore, only glass transition exists at this curing temperature. With the rise of the temperature, the time of the glass transition increases from 5.3 to 16.3 min. It is associated with two competition factors in the glass transition. With the rise of the curing temperature, the glass transition requires high degree of crosslink, which needs long reaction time [19]. As is shown from the curing behavior, when the curing temperature is below 229 °C, the former is the decided factor, so the glass temperature time drops with the rise of the curing temperature; while when the curing temperature is above 229 °C, the last is the decided factor, so the glass transition time raises with the increase of the temperature.

From the above, mechanical relax behavior appears at different time in the curing system of benzoxazine. With the increase of the curing temperature, the gelation transition time becomes short. When the curing temperature is below 210 °C, special secondary glass transition (β and γ transition) is occurred and the secondary glass transition time between short with the increase of the temperature. The glass transition time drops with the increase of the temperature when gelation transition is below 229 °C, while it increases with the rise of the temperature when the curing temperature is above 229 °C.

3.3. The time–temperature-transition spectrum of benzoxazine curing system at 160–242 °C

Fig. 4 is the time–temperature-transition (TTT) spectrum of benzoxazine curing system at 160–242 °C. It can be inferred that the mechanical relax phenomena occurs during this curing temperature. We can divided it into five areas as indicated in Fig. 4 (I, sol glass area; II, gelation transition area; III, γ transition area; IV, β transition area and V, vitrification transition area). When the curing temperature is at the range 160–200 °C, gelation transition, secondary glass transition and glass transition occur. When the curing temperature is at the range 200–229 °C, gelation and glass transition occur and both time are very short because of the high curing temperature. When the curing temperature is at the range 229–242 °C, the gelation transition is too short to be tested by the TBA used in this paper; however, the glass transition time is prolonged because that glass transition requires high degree of crosslink at high temperature. In brief, with the progress of the curing reaction, the system of benzoxazine has appeared two mechanical relax phenomena: the transition from viscous state to

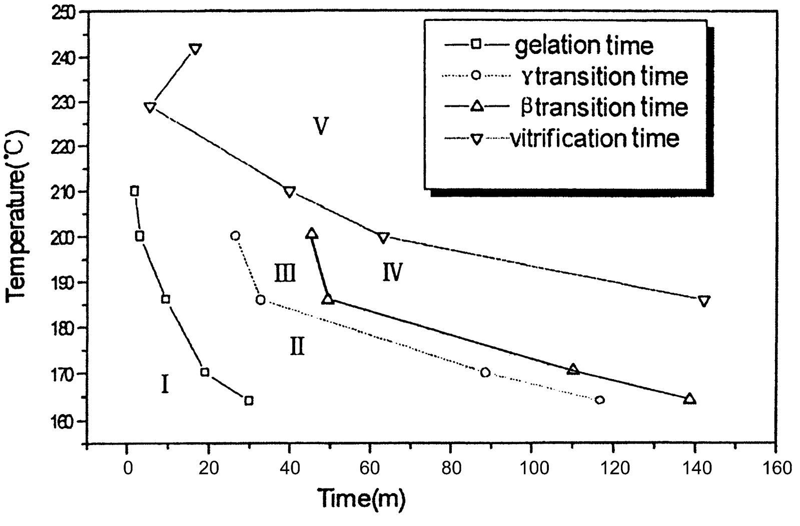


Fig. 4. TTT cure diagram between 160 and 240 °C.

rubber state and the transition from rubber state to glass state.

On the base of the spectrum of the TTT, the curing process of the system of the benzoxazine can be established and the mechanical behavior under the certain curing temperature can be studied. For example, the glass transition time is longer than 60 min when the curing temperature is below 200 °C, while the curing products of thermosetting resins with high property can be obtained only by gelation and glass transition during curing. So the glass transition time must be longer than 60 min when the curing temperature is below 200 °C [12,13]. On the base of above, TTT spectrum offers reliable ground to establish the curing process of the benzoxazine.

4. Conclusion

According to the TBA of the curing of benzoxazine, the curing reaction occurs during the temperature between 148 and 237 °C. With the increase of the temperature, the curing system comes into the melting area, the gelation transition area and the glass transition area. Also, the mechanical relax behavior of benzoxazine during curing is studied. Two special secondary glass transition is found at the curing temperature of 210 °C. All of these supply the reasons of the curing process of benzoxazine.

Acknowledgements

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