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Study on Open Loop Curing Temperature Reduction and Heat Resistance of Benzoxazine

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In order to improve the open loop curing temperature reduction process, this paper studies the open loop curing temperature reduction and heat resistance of benzoxazine. Based on DSC and bisphenol-A, the curing reaction of benzoxazine intermediates under different catalytic conditions is analyzed. It is found that the curing temperature of benzoxazine is significantly reduced with the addition of acidic catalyst, and the activation energy is also further reduced. It can be seen that under the acidic catalysis, the secondary reaction of benzoxazine open loop will be changed to some extent.

1. Introduction

At present, Europe and America have increased their investment in aerospace, high-tech and other industries. With the development of high-tech industries, new requirements for chemical materials have put forward. For example, high-performance resin materials have been widely used in the field of national defense. However, the crosslinking density increase of materials by curing conventional thermosetting matrix will affect the materials effect. Based on this, this paper studies the open loop curing temperature reduction and heat resistance of benzoxazine. The curing reaction of benzoxazine intermediates under different catalytic conditions is analyzed based on DSC and bisphenol-A.

2. Literature review

The scientific name of the benzoxazine compound is 3,4-dihydro-3-substituted-1,3-benzoxazine. Polybenzooxazine inherits the advantages of traditional phenolic resin and overcomes many disadvantages of traditional phenolic resin. Due to the special six-element heterocyclic structure consisting of O and N and its unique open ring curing mechanism, polybenzooxazine shows excellent comprehensive properties of heat resistance and flame retardant, which is expected to replace traditional phenolic resin, polyester, epoxy resin, cyanate ester and polyimide in many fields. Since the preparation of benzoxazine resin is a ring opening polymerization reaction, there is no release of small molecules during the curing process, such as the preparation of phenolic resin, so the volume contraction during the curing process is approximately zero and has good dimensional stability, which is of great significance for the preparation of high-performance composite materials. Benzoxazine resin has a broad application prospect, at present, benzoxazine has been gradually used in Resin Transfer Molding (RTM). Flexible molecular designability is another important feature of benzoxazine. The introduction of reactive, heat-resistant and flame-retardant groups in the molecular structure can give different performance characteristics of benzoxazine to meet the requirements of different application fields.
Domestic and foreign scholars have done a lot of research on benzoxazine. Escobar et al. studied the reactions of phenolic compounds, amine compounds and formaldehyde in depth. They found that the molar ratios of three reactants directly affected the structure of the reaction products and synthesized a series of compounds containing benzodiazepines (Escobar et al., 2015). Feng et al. conducted in-depth and systematic research on benzooxazine, synthesized a series of benzooxazine compounds, and studied the effect of different ratio of reactants on product structure (Feng et al., 2015). Hariharan et al. have published a paper on the synthesis of benzoxazine and pointed out the application prospect of benzoxazine (Hariharan et al., 2018).

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Kimura et al. have done a lot of research on benzodiazepine. Taking bisphenol A as the phenol source, they have synthesized a series of bifunctional benzoxazine compounds, and conducted detailed research on the mechanical property, thermal property, volume effect and thermal decomposition performance of the monomeric curing mechanism agent polybenzoxazine (Kimura et al., 2015). Li et al. first synthesized granular benzoxazine monomers by suspension method. This method uses water as the medium for synthesis reaction to avoid environmental pollution caused by solvent (Li et al., 2017). Poorteman et al. studied the effect of the polarity of the solvent on the ring formation rate of the oxazine ring in the synthesis reaction. The results showed that the polarity of the solvent had a significant effect on the ring formation rate of the benzoxazine ring (Poorteman et al., 2016). Rajeshkumar et al. studied benzodioxazine resin containing alkynyl, and found that the curing substance of such resin had high thermal stability, which was the result of the synergistic effect of the polymerization of alkynyl and the ring opening polymerization of oxazine ring. Another kind of alkynyl group that had attracted much attention was propargyl ether. The reason why this group received a lot of attention was that the monomer containing such alkynyl group had low cost and high yield; while the synthesis cost of alkynyl monomers was relatively high and the yield was relatively low (Rajeshkumar et al., 2015). Russell et al. introduced the epoxy ring into benzoxazine monomers, which effectively increased the thermal stability of polybenzooxazine and increased its glass transition temperature, providing a new method for modification of benzoxazine resin (Russell et al., 2015). Xu et al. found that because DOPO-Gly was bulky and had large steric hindrance, it would reduce the crosslink density and can't effectively limit the movement of molecular chains. Therefore, the energy storage modulus, crosslink density and glass transition temperature of the copolymer would decrease with the increase of DOPO-Gly content, which deteriorated the thermal stability. The combustion test showed that the combustion resistance of phenolic resin modified benzoxazine resin could only reach level V-1, while that of benzoxazine resin containing phosphorus could reach level V-0 (Xu et al., 2015). Zhang et al. found that the nitrile group in the monomer would be cross-linked during the process of curing and formation of the carbon layer structure, which increased the carbon residue rate of the solidified material. These high crosslink density polymers had a glass transition temperature between 275 ℃ and 300 ℃, higher than their curing temperature (Zhang et al., 2018).

To sum up, the above researches mainly study the mechanical property, thermal property, volume effect, thermal decomposition performance, ring formation rate and combustion resistance level of benzooxazine compounds, but few studies are conducted on the technology of benzoxazine ring-opening curing temperature reduction and heat resistance. Therefore, based on the above research status, the ring-opening curing temperature reduction technology and heat resistance of benzoxazine are mainly studied. Based on DSC and bisphenol A, the curing reactions of benzoxazine intermediates under different catalytic conditions are analyzed.

3. Principle and Methods

Benzoxazine (Boz) monomers are six-membered heterocyclic compounds containing oxygen and nitrogen atoms. Boz monomers can be obtained by condensation reaction of aromatic phenols, primary or aromatic amines, and paraformaldehyde without catalyst. This process is environmentally friendly and free from pollution. Its chemical structure is shown in Figure 1. Polybenzoxazine (PBoz) can be obtained by the open loop polymerization of Boz monomers under thermal action. PBoz is a new type of phenolic resin material with low dielectric constant (k), excellent thermal, chemical, mechanical and flame retardant properties, low moisture absorption, and good heat resistance. It is also a thermosetting polymer designed in the flexible molecular structure. In addition, PBoz includes a new class of non-silicon or non-fluorinated polymer materials with low surface free-energy properties. They are widely used as demoulding materials in the nanoimprint technology and photoetching composition. Boz monomers can be used as super hydrophobic surface materials due to the strong hydrogen bond in molecules after the thermosetting polymer. In certain cases, PBoz is superior to some traditional thermosetting materials (including epoxy resin and bismaleimide). However, PBoz also has some disadvantages. For example, it needs to complete ring-opening polymerization at high temperatures. Compared with other thermosetting cross-linking materials, the application of resin matrix as high-performance composite is limited. The incorporation of organic functional groups (vinyl, allyl, methacrylic, nitrile, pbo and epoxy group), inorganic silicate (clay), carbon nanotubes, and polyhedral oligomeric silsesquioxane (POSS) can form a crosslinking network to restrict the movement of molecular segments, improving the thermal and mechanical properties of PBoz resin. Boz with excellent properties can be widely used in aerospace ablative materials, copper clad laminate in the electronics industry and resin matrix as the high-performance composite material.

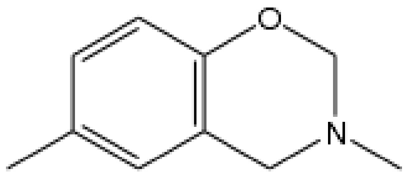

Figure 1: The structure of the benzoxazine

The polymer simply formed by curing Boz monomers cannot meet the rapid development of existing materials. Composite materials with high modulus, high strength and high performance are the main trend of future development. Therefore, researchers are working to develop better-performed Boz neither through monomers modification nor blend and copolymer. With the development of science and technology, the application of adhesive in civil and national defense fields is increasing. In special cases, adhesives should meet not only the mechanical performance requirements, but also some specific performance requirements, for example, the performance of ultralow temperature resistance, electrical conductivity, magnetic permeability, flame retardant, high temperature resistance, etc. The so-called high temperature resistant adhesive can be used at a certain high temperature for a long time without any obvious changes in the cohesive property. After the development for more than half a century, Boz is developed into a polyoxazine structure from the monoxazine ring, and into a macromolecule with various functional groups from the single-model molecular structure. Synthetic materials are also greatly developed. Green materials can be found in the natural. The development of Boz research has also benefited from the efforts of many researchers around the world to systematically study Boz, including the synthesis process, the curing process and the product purification.
BPAALF is a six-membered heterocyclic compound synthesized from Bisphenol-A, aniline and formaldehyde. There have been many reports on the synthesis, structure and properties of BPAALF, but few studies on their curing reaction have been reported.
The experimental materials and equipment in this paper are as follows:
BPAALF: self-made, ring forming rate 94%, melting temperature 79 to 82 ℃.
Organic acid and Lewis acid: pure analysis, Chengdu Chemical Reagent Plant product.
DSC: Perkin Elmer Company product, area integral software, nitrogen.
The process is as follows: BPAALF is weighed lOg added with a quantitative catalyst in the mortar, which is ground and mixed. Several samples are sealed in the sample pool. The curing reaction is conducted under 10 ℃ / min, 20 ℃ / min, and 40 ℃ / min.

4. Results and Analysis

Using DSC to track the change of curing enthalpy in the process of temperature rising can explain the curing of thermosetting resin. Figure 2 shows DSC curves of BPAALF in different reaction condition. The relevant data is shown in Table 1. According to Table 1, the initial temperature of BPAALF thermal open-loop polymerization is about 200 ℃. When organic acids, Lewis acids and other catalysts are added, the initial temperature is lower than 150 ℃. At the same time, the curing enthalpy is increased by more than 60 J/g. For the same reaction, adding the catalyst speeds up the reaction and makes it more complete. In addition, as can be seen from Figure 2, the maximum rate of such open-loop polymerization curing reaction occurs between 15% and 25% instead of the initial stage. This open-loop polymerization reaction is self-catalysis.
When DSC is used to study the kinetic parameters of curing reaction, it is basically assumed that :(1) the total area of exothermic peak is proportional to the total amount of heat released in the curing reaction; (2) the curing reaction is a simple n-level reaction; (3) the relation between reaction speed and temperature is subject to the Arrhenius equation. In this paper, the curing kinetic parameters of BPAALF under different conditions are calculated by the Freeman-Carroll and Kay-Westwood. These two methods are compared and their reliability is analyzed
From DSC curves, several dA/dt, (1-a) and 1/T values are chose, and then the difference between two groups is taken. For example, Y=KX+b regression analysis is performed. Activation energy and reaction order are obtained. The above results are used to analyze DSC curves, and the results are shown in Table 2.

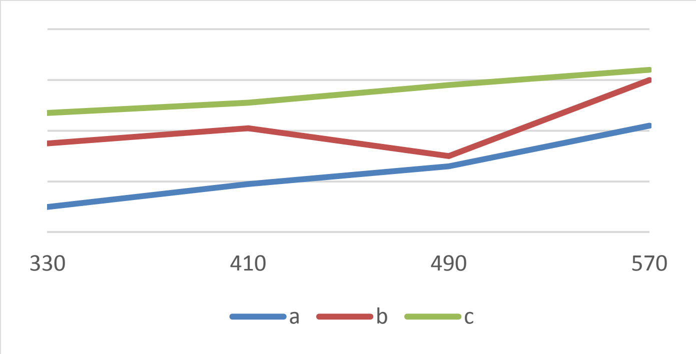

Figure 2: DSC curves of BPAALF in different reaction condition (Nz, 20 0C/min) catalyzed by organic acid , c: self}ured: catalyzed by Lewis acid.

*Table 1: Curing temperature and curing enthalpy of benzoxazine precursor**

Catalyst species	Curing temperature (K)*			ΔH (J/g)
	Tst	Texo	Tt	
	470	512	559	287
Organic acid	425	494	557	346
Lewis acid	421	480	560	387

*Based on DSC data ; **Tst: temp. of start polymerization ; Texo: temp. of exothermic peak ; Tt: temp. of termination polymerization.

Table 2: Reaction order (n) and activation energy (E)

Catalyst species	n	E(kJ/mol)
Without catalyst	1.96	343
Organic acid	1.01	59
Lewis acid	1.09	73

Kay-Westwood: the formula is as follows:

$$\frac{dH/H_T}{dt} = A \exp(-E/RT)(1-H/H_T)^n \qquad (1)$$

, where HT is the total heat released in the curing reaction. The derivative of equation (5) with respect to time t is:

$$\frac{(1\text{-}H/H_T)d/dt(dH/dt)}{\beta(dH/dt)^2} = \frac{E}{R} \qquad (2)$$

, whereβ=dT/dt is the temperature rise speed. The regression analysis of Y=KX+b is performed with the left side of equation (2) as Y and the right side as X, and the results are shown in Table 3. As can be seen from Table 3, the kinetic parameters obtained are similar to those by the Freeman-Carroll. The activation energy is high in self-cured, and the reaction order is close to 2. The activation energy can be reduced and the reaction order is close to 1 with acidic compounds.

Table 3: Reaction order and activation energy

β (K/S)	Reaction order			Activation energy		
	a	b	c	a	b	c
1/6	1.08	1.90	1.02	77.53	324.96	54.04
1/3	1.10	1.97	1.07	71.67	365.80	70.40
2/3	1.14	1.90	1.00	70.60	330.28	54.53

a: Lewis acid ; b: self-cured ; c: organic acid.

According to the Arrhenius equation, the relation between reaction rate constant k and temperature T is:

$$k = A\exp\left(-\frac{E}{RT}\right) \quad (3)$$

The reaction order n obtained by the Freeman-Carroll is represented as lgk [namely lg da/dt-nlg(1-a)]] ~1/T curve, as shown in Figure 3. The kinetic parameters and linear correlation coefficients obtained are shown in Table 4. In addition to the deviation due to the diffusion effect determining the reaction rate at the later stage, the linear relation of lgk ~ (1/T) is very good during the reaction, which proves that the obtained kinetic parameters are reasonable.

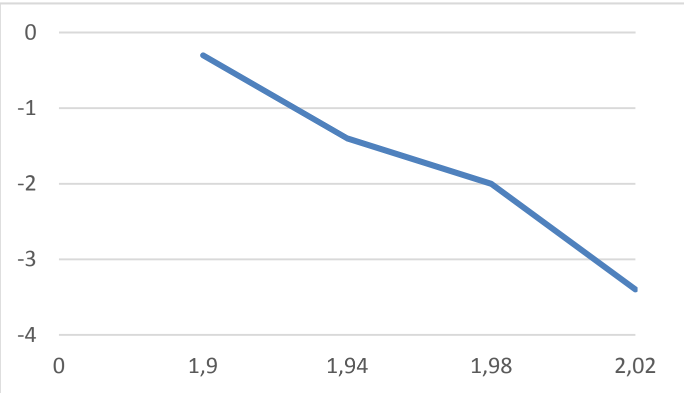

Figure 3: Relationship of lgk and 1/T

Table 4: Kinetic parameters obtained from equation (9)

Species	n	E(kJ/mol)	lgA	Appropriate coefficient
Self-crued	1.96	335	32.6	0.9996
Organic acid	1.01	67.2	5.2	0.9901
Lewis acid	1.09	74	5.8	0.9908

5. Conclusion

It is found that the open loop curing temperature of Boz is significantly reduced with the addition of acidic catalyst, and the activation energy is further reduced. According to the experimental results, under the acidic catalysis, the secondary reaction of Boz open loop will be changed to some extent.

The mechanical properties of resin materials have always been one of the important factors restricting their development. The preparation of resin materials with excellent high-temperature resistance and mechanical properties can accelerate the development of high-end technology and national defense. Future experiments need to try a variety of other polymers containing reactive groups to modify resins. It is expected to explore the modified process of modified resins with reactive groups and study their properties with the comparison of corresponding modified resins and with the combination of theoretical analysis.

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