

Synthesis and properties of two kinds of alkyl containing benzoxazine

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Abstract. A novel benzoxazine with cyano group (CP-apa) was synthesized to study the impacts of cyano group on the properties of benzoxazine. The properties of CP-apa were compared with P-apa. DSC and FT-IR were used to track the curing reaction of CP-apa and P-apa. CP-apa shows excellent curing behaviors. Afterwards, the mechanical properties and heat resistance of the thermosets were investigated. The introduction of –CN would decrease the mechanical properties of cured CP-apa, but the good heat resistance of benzoxazine still remains.

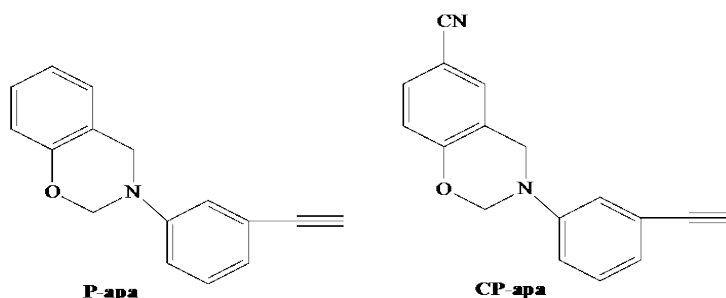
1. Introduction

Benzoxazine is a class of intermediates containing heterocyclic structures, which are generally synthesized by the condensation reaction of phenolic compounds, amine compounds and formaldehyde. As a new type of hexahydroxyN/O-containing heterocyclic compounds, ring-opening reaction would occur in benzoxazine, when it is catalyzed or heated. After the ring-opening reaction, a N-containing cross-linked network is formed, which is similar to phenolic resin. That is, benzoxazine can be used as a novel engineering thermosets[1-3]. There is no small molecule release in the curing polymerization of bezoxazine, and the volume shrinkage rate of the thermoset is almost zero, moreover, chemical resistance, thermal stability, low moisture absorption rate and excellent mechanical properties[4-6].

The C-N bond on the Mannich bridge (–CH₂–NR–CH₂) is a weak point in the cured structure in the polybezoxazine, and it is easy to break at high temperature, which leads to the initial weight loss of the polybezoxazine. If the reactive group is introduced into the benzene ring in R and participates in the copolymerization, the "hang" R will be immobilized, thus improving the thermal stability of the bezoxazine[7-8]. In order to improve the heat resistance of polybezoxazine, the designable ability of bezoxazine moleculars can be used to introduce aromatic heterocyclic rings, polymeric groups and inorganic elements into the molecule. For instance, the glass transition temperature (T_g) and the thermal stability of the resin can be improved by introducing other polymeric groups into the bezoxazine monomer. T. Agag[9-10] used allyl-containing amines to synthesize allyl-containing bezoxazine intermediates respectively. The obtained polybezoxazine has excellent heat resistance, mechanical properties, flame-retardant properties and outstanding process ability.

In this paper, the effect of –CN on bezoxazine was investigated. Cyano group was introduced into P-apa (scheme 1) and a novel CP-apa (scheme 1) was synthesized. DSC and FT-IR were used to monitor the different curing process of the two kinds of bezoxazine. Afterwards, mechanical properties and the heat resistance of two kinds of polybezoxazine were compared.





Scheme 1. Structure of P-apa and CP-apa

2. Experimental

2.1. Materials

3-Aminophenylacetylene(AR), Phenol(AR), 4-cyanophenol(AR), Toluene(AR), Paraformaldehyde(AR), Sodium hydroxide(AR), Sodium sulfate(AR), were bought from General Reagent Co., Ltd and used without further purification. Tetrahydrofuran (THF) was refluxed with sodium and benzophenone until the blue color of the ketyl of benzophenone was well established and then was distilled.

2.2. Synthesis Routes

The synthesis of P-apa was carried out by using a typical synthesis procedure[11]. A three-necked 500 mL flask with a magnetic stirrer and nitrogen inlet fitted with a condenser was charged with 0.4 mol phenol, 0.4mol 3-Aminophenylacetylene and 0.8mol paraformaldehyde under a nitrogen atmosphere. The mixture was maintained at 90°C with stirring for 2 hours. The resultant solution was cooled to room temperature. Dissolved the crude product in a certain amount of toluene and washed three times with sodium hydroxide solution. Then, the solution was washed with deionized water to neutral. Finally, the solvent was evaporated under reduced pressure to obtain pale yellow viscous target product P-apa. FTIR: 3278 cm^{-1} ($\text{HC}\equiv\text{C}$); 2129 cm^{-1} ($\text{C}\equiv\text{C}$); 1029 cm^{-1} ($\text{C}-\text{O}-\text{C}$); 1237 cm^{-1} ($\text{C}-\text{O}-\text{C}$); 947 cm^{-1} ($\text{C}_8\text{NO}-\text{C}_6\text{H}_5$).

The synthesis route of CP-apa is similar to P-apa. FTIR: 2220 cm^{-1} ($-\text{C}\equiv\text{N}$); 3278 cm^{-1} ($\text{HC}\equiv\text{C}$); 2129 cm^{-1} ($\text{C}\equiv\text{C}$); 1029 cm^{-1} ($\text{C}-\text{O}-\text{C}$); 1237 cm^{-1} ($\text{C}-\text{O}-\text{C}$); 947 cm^{-1} ($\text{C}_8\text{NO}-\text{C}_6\text{H}_5$).

2.3. Preparation of Thermosets

P-apa and CP-apa were molten at 90°C and casted into the preheated mould, respectively. The mould was put into the oven and degassed at 130°C for 30 min under vacuum. The casted benzoxazine was cured under 170°C/2 h, 210°C/2 h and 250°C/4 h.

2.4. Measurements

The samples were mixed with potassium bromide powder and pressed into round pellets. The Fourier Transform Infrared (FTIR) spectra of the samples were recorded from 4000~400 cm^{-1} at a resolution of 4 cm^{-1} on an infrared spectrometer (Nicolet 6700). The molten samples were coated on KBr round pellets. The pellets were placed in a hot cell (Thermo HT-32) with a programmable temperature control to obtain in situ monitoring spectra. The spectra were collected from ambient temperature to 355°C at a heating rate of 5°C min^{-1} in the cell. The data were gathered in 25°C increments during the programmable heating. Each spectrum was the result of 16 scans with a resolution of 4 cm^{-1} . Differential Scanning Calorimetry (DSC) was performed on a TA Instrument (Q2000) with a scan from 35 to 400°C at a heating rate of 10°C min^{-1} and an empty aluminum pan as a reference. The 1~2 mg sample was sealed in the aluminum pan for testing. A nitrogen purge was used at a flow rate of 50 mL min^{-1} .

The flexural properties of the samples were measured on an electronic universal testing machine (CCSS-44100, Changchun Research Institute for Mechanical Science Co., Ltd.) at room temperature. The flexural properties of the resin casts were obtained using a rectangular shape with dimensions of 80 mm×15 mm×4 mm by measuring the three-point bend fixture according to Chinese Standard, GB/T 2567-2008. The cross-head speed was 2 mm min^{-1} . The impact strength of samples with dimensions of

80 mm×10 mm×4 mm was measured by the cantilever mode test on a CEAST9050 universal pendulum hammer impact instrument per GB/T 1843-2008.

Thermo gravimetric Analysis (TGA) was conducted using a Mettler-Toledo Instruments thermo gravimetric analyzer (TGA-DSC1). The 6~7 mg sample was weighed in a ceramic crucible for testing. Nitrogen was used as the purge gas with a flow rate of 50 mL min⁻¹, and a heating rate of 10°C min⁻¹ was used in the range of 40~1000°C for all tests. Dynamic mechanical analysis (DMA) was performed on a Mettler-Toledo Instruments (DMA1) using the three-point bending test to determine the glass-transition temperature, T_g , and storage modulus, E' . The specimens with a size of 30 mm×8 mm×2 mm were tested at a heating rate of 5°C min⁻¹ and a frequency of 1 Hz.

3. Results and Discussion

3.1 Curing Reaction of P-apa and CP-apa

The curing reaction of P-apa and CP-apa were characterized by DSC, and the DSC curves were shown in figure 1. The initial temperature (T_i), peak temperature (T_p), final temperature (T_f) and heat enthalpy (ΔH) of curing reactions were listed in table 1. The curing peak of CP-apa and P-apa is only a single peak, which indicates that the ring-opening reaction of benzoxazine and the cross-linking reaction proceed almost at the same time. The T_p of CP-apa is lower than that of P-apa, indicating that the electron-withdrawing effect of -CN makes the ring-opening exothermic peak temperature of benzoxazine shift to low temperature. CP-apa has an endothermic peak at low temperature, this is the melting endotherm of benzoxazine, which shows that the introduction of -CN makes the benzoxazine transition from liquid to solid state.

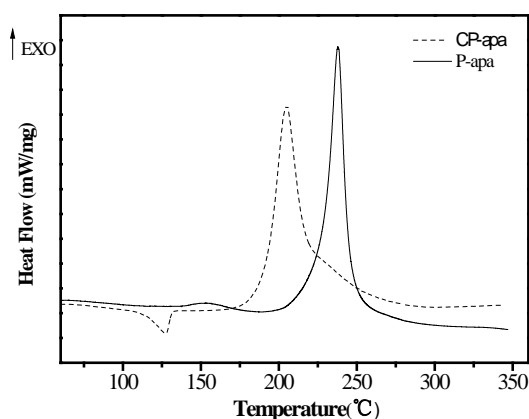


Figure 1. DSC curves of P-apa and CP-apa

Table 1. DSC analysis results of P-apa and CP-apa

Samples	$T_i/^\circ\text{C}$	$T_p/^\circ\text{C}$	$T_f/^\circ\text{C}$	$-\Delta H/\text{J/g}$
P-apa	227.4	237.7	249.7	930.0
CP-apa	191.1	204.7	222.7	952.5

High temperature micro-ATR IR spectroscopy is very attractive for monitoring the curing reactions of thermosetting resins at elevated temperatures [12]. In-situ IR spectroscopy was used to monitor the changes of the functional groups in P-apa and CP-apa. The FTIR spectra of P-apa and CP-apa at different temperatures were shown in figure 2 and figure 3, respectively.

For P-apa (shown in figure 2), at room temperature, the -C-H (942 cm⁻¹) out-of-plane bending vibration of the benzene ring and the -C-H of -C≡C-H (3291 cm⁻¹) vibrational peak of the benzoxazine were clearly observed. During the curing process from room temperature to 245°C, the characteristic absorption peak of terminal alkyne hydrogen (≡C-H) at 3291 cm⁻¹ disappeared, indicating that the alkyne group in P-apa has completely cross-linked at this temperature. During the curing process, the

C-O-C stretching vibration peak at 1251 cm^{-1} and the -C-H vibration peak intensity at 942 cm^{-1} greatly decreased, indicating that most benzoxazines have participated in the ring opening reaction. After 210°C , the characteristic peaks of short-chain conjugated polyenes at 1675 cm^{-1} were significantly enhanced, mainly due to the polymerization cross-linking reaction of acetylene groups.

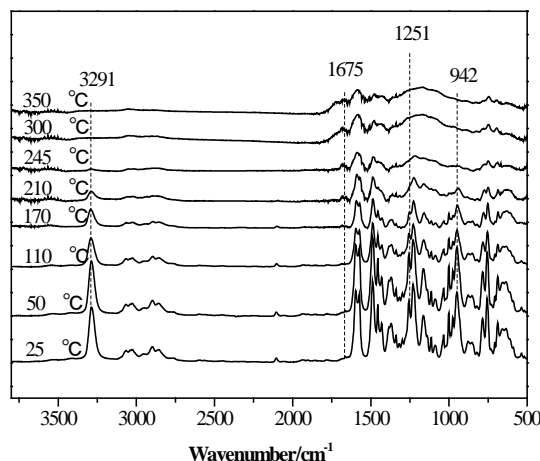


Figure 2. IR spectral changes for the thermal cure of P-apa at different curing stage

For CP-apa (shown in figure 3), at room temperature, the out-of-plane bending vibration of -CN (2221 cm^{-1}) and the -CH (988 cm^{-1}) on the phenyl ring, and the vibration peak of $\text{-C}\equiv\text{CH}$ (3285 cm^{-1}) were clearly observed at room temperature. After curing at 170°C , the vibrational intensity of -C-H on the benzene ring connected to the oxazine ring at 988 cm^{-1} was weakened, indicating that the ring opening reaction has been occurred. It is notable that, starting from 245°C , the characteristic peaks of -CN at 2221 cm^{-1} began to weaken, but the characteristic peaks of the triazine ring were not found near the 1367 cm^{-1} . It is indicated that the cyano group in CP-apa can participate the curing reaction at high temperature, but the structure of triazine ring is not formed during curing. During the curing process from room temperature to 300°C , the characteristic absorption peak of terminal alkyne hydrogen ($\text{C}\equiv\text{C-H}$) at 3285 cm^{-1} disappeared, indicating that the alkynyl group in CP-apa has been cross-linked completely.

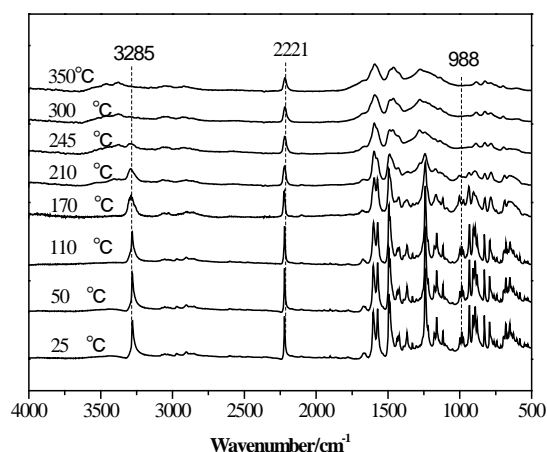


Figure 3. IR spectral changes for the thermal cure of Cp-apa at different curing stage

3.2 Mechanical Properties of P-apa and CP-apa

The flexural and impact strength of cured P-apa and Cp-apa are shown in figure4. The flexural strength of cured P-apa is 87.2 MPa , and the impact strength is 8.47 KJ/m^2 . It is 23.0% and 25.5%

higher than that of Cp-apa, respectively. It can be seen that both the flexural and impact strength of the cured Cp-apa are inferior to that of the P-apa, due to the introduction of cyano group. This is because cyano group can increase the crosslinking density during curing. Meanwhile, the influence of cyano group on the phenolic hydroxyl group would decrease the hydrogen-bond interaction, thus, the mechanical properties are decreased.

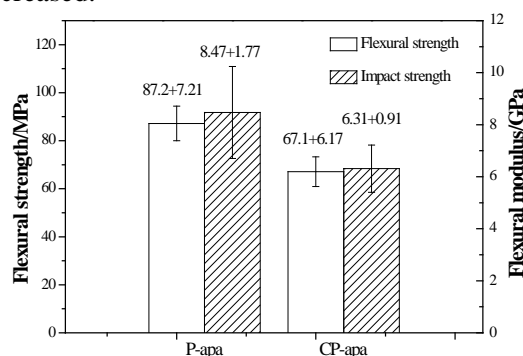


Figure 4. Flexural and impact strength of P-apa and Cp-apa

3.3 Thermal Properties of P-apa and CP-apa

The thermal stability of the cured P-apa and CP-apa were characterized using TGA. Figure 5 and Table 2 showed the results obtained from TGA test. The temperature of 5% mass loss (T_{d5}) and the residual yield at 800°C ($Y_{800^\circ\text{C}}$) of the cured resins can be seen from the table. The T_{d5} and $Y_{800^\circ\text{C}}$ of the cured P-apa reached to 388°C and 57%, respectively; the T_{d5} and $Y_{800^\circ\text{C}}$ of the cured CP-apa reached to 350°C and 59%, respectively. The TGA results indicate both the two kinds of bezoxazine have good heat resistance.

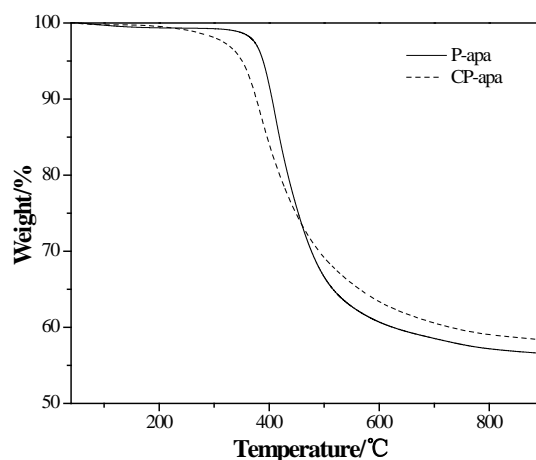


Figure 5. TGA curves of P-apa and CP-apa

Table 2. Thermal stability of the cured P-apa and CP-apa

Samples	$T_{d5}/^\circ\text{C}$	$T_{d10}/^\circ\text{C}$	$Y_{800^\circ\text{C}}/\%$
P-apa	388.8	405.3	57.2
CP-apa	350.7	376.7	59.2

The dynamic mechanical thermo grams of the cured P-apa and CP-apa were shown in figure 6. From the loss factor ($\tan \delta$) peak of the cured resins, we can know the glass transition temperature (T_g) of the cured P-apa and CP-apa. The T_g of P-apa and CP-apa is 329.4°C and 288.5°C, respectively. The glass transition temperature of P-apa is higher than CP-apa, this is because the introduction of -CN increases the free volume of the poly-benzoxazine network.

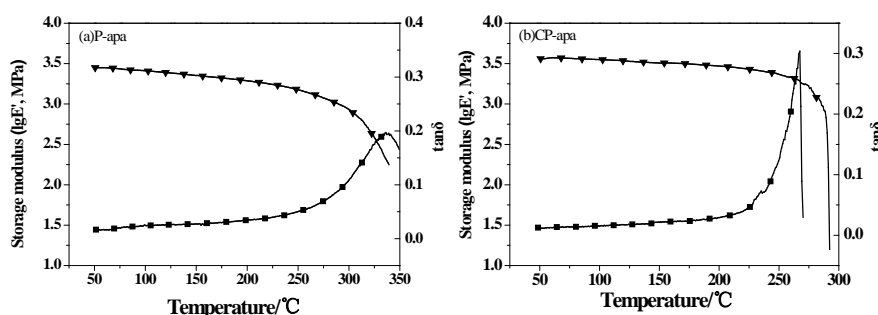


Figure 6. DMA curves of the cured P-apa and CP-apa

4. Conclusions

A novel benzoxazine with polar cyano group (CP-apa) was synthesized, and the properties of CP-apa was compared with P-apa. DSC and FT-IR show that the electron-withdrawing effect of $-CN$ catalyzes the ring-opening of benzoxazine at low temperature ($\sim 191^{\circ}\text{C}$), and the cyano group would participate the curing reaction at high temperature ($\sim 245^{\circ}\text{C}$). The cyano group in thermosets can increase the crosslinking density and decrease the hydrogen-bond interaction, resulting a reduction of mechanical properties. The cured CP-apa shows good heat resistance with T_{d5} at 350.7°C and T_g at 288.5°C , though slightly lower than the cured P-apa.

References

- [1] Kiskan B, Ghosh N N, Yagci Y, 2011 *Polym. Int.* vol 60 p 167.
- [2] Kim H J, Brunovska Z, 1999 *Polymer* vol 40 p 1815.
- [3] Kim H J, Brunovska Z, 1999 *Polymer* vol 40 p 6565.
- [4] Agag T, Geiger S, Alhassan M S, 2010 *Macromolecules* vol 43 p 7122.
- [5] Yu D S, Chen H, Shi Z X, 2002 *Polymer* vol 43 p 3163.
- [6] Hong Y L, Ishida H, 1999 *Polymer* vol 40 p 4365.
- [7] Brunovska Z, Lyon R, Ishida H, 2000 *Thermochim. Acta* vol 357 p 195.
- [8] Ishida H, Sanders D P, 2000 *Polym. Sci. Polym. Phys. Ed.* vol 38 p 3289.
- [9] Agag T, Takeichi T, 2001 *Macromolecules* vol 34 p 7257.
- [10] Agag T, Takeichi T, 2003 *Macromolecules* vol 36 p 6010.
- [11] Goffaux R, 1978 *IEEE Transactions on Electrical Insulation* vol 1 p 1.
- [12] Celina M C, Giron N H, Rojo M R, 2012 *Polymer* vol 53 p 4461.