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Mechanism and dynamic thermomechanical analysis of ZIF-61/bisphenol-A cyanate ester(BCE) composites

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ABSTRACT

ZIF-61 modified BCE composites were first prepared by solvent method. The catalytic mechanism of ZIF-61 in the curing process of BCE resin was analyzed by Fourier Transform Infrared Spectroscopy (FTIR) under different temperature. ZIF-61 with Lewis acidity could accelerate the curing reaction rate of ZIF-61/BCE composites. The detailed kinetic data of ZIF-61/BCE composites and pure BCE resins was calculated. Dynamic thermomechanical analysis (DTMA) showed that the glass-transition temperature of ZIF-61/BCE (0.5 wt%) composites was increased ca.60 °C than that of pure BCE.

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1. Introduction

The application of high performance cyanate ester (CE) resins is limited by high requirements for equipment because of high curing temperature and low elasticity caused by rigid triazine ring formed in curing process. In order to reduce the curing temperature and increase the elasticity, great efforts were dedicated to modify CE by adding fillers such as carbon nanotubes and graphene [1,2]. In general, active hydrogen catalyst, transition metal catalyst or UV activated catalyst are all applied to promote the CE curing in lower temperature. Among these, transition metal catalyst has confirmed to be the best [3].

Zeolitic imidazolate frameworks (ZIFs) are a series of metal organic frameworks composed by the coordination interaction of Zn with the N in imidazolate or its derivative. Due to the high polarity and large internal surface areas, ZIFs have been applied to capture carbon dioxide by using polymer as matrix [4]. However, as a kind of ZIFs which has relative lower inner surface areas, ZIF-61 has not attract enough attention since it was first synthesized [5,6]. But owing to the Zn atom in it, ZIF-61 can be viewed as a kind of transition metal catalyst. Recently, ZIF-61 showed good catalysis performance on accelerating the nucleation of tetrahydrofuran (THF) hydrate by its similar structure with THF [7]. Subsequently, as reported [8], our group had mainly introduced

the fast microwave ionothermal synthesis of ZIF-61, simply tried to mix ZIF-61 with BCE by melting method and confirmed that ZIF-61 could effectively reduce the peak curing temperature of BCE. However, there is no further research on the curing mechanism or mechanical properties of ZIF-61/BCE composite.

In this work, we analyzed the curing mechanism of ZIF-61/BCE by FTIR. As a Lewis acid, the unoccupied orbit of Zn atom in ZIF-61 was considered to be the main reason for the effective catalysis in the curing process of BCE. Kinetic data revealed that the curing reaction of ZIF-61/BCE composites was easier to happen than pure BCE resins. The loss factor tangent value ($\tan \delta$) and storage modulus (E') demonstrated that ZIF-61/BCE had higher Tg temperature and better elasticity than pure BCE.

2. Experimental

ZIF-61 was synthesized as reported before by our group [8]. Typically, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.00 g, 6.7 mmol), imidazole (2.75 g, 40.4 mmol) and 2-methylimidazole (1.11 g, 13.5 mmol) were mixed in $[\text{Bmim}]\text{BF}_4$ (60.85 g, 269.2 mmol) at room temperature and kept stirring for 8 h. Then, the homogenous mixture was poured into an open conical flask and heated in microwave oven at 140 °C for 40 min. After cooling down, the precipitate was filtrated and washed with deionized water and acetone. Last, the product was dried in 40 °C vacuum oven for 4 h.

ZIF-61/BCE composites were prepared by a solvent blending method. Firstly, ZIF-61 and BCE at different proportions (0/100, 5/

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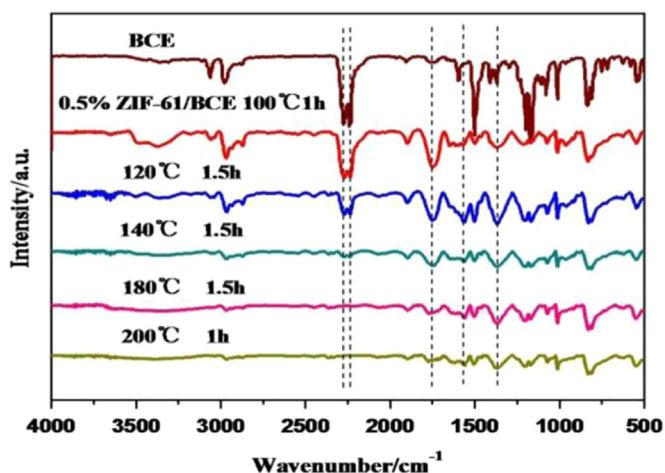


Fig. 1. FTIR curves of ZIF-61/BCE at 0.5 wt% under different curing temperatures.

995, 1/99,1.5/98.5, 2/98, wt%) were mixed and dissolved by chloroform. After 20 min ultrasonic bath, the uniform mixtures were standing in fume hood. When all the solvent was gone, the mixtures were dried in oven at 40 °C for 4 h. After that, the products were grinded into powder.

The grinded ZIF-61/BCE composites were melted at 80 °C, transferred into metallic molds (40 × 8 × 2 mm) and heated in vacuum oven as follows: 100 °C/1 h, 120 °C/1.5 h, 140 °C/1.5 h, 180 °C/1.5 h, 200 °C/1 h. After cooling, the samples were removed from the molds and polished to 30 × 6.5 × 1.5 mm solid DTMA samples. Moreover, FTIR samples were also prepared in the same heating procedure but taken out one in the end of each temperature period.

The catalytic mechanism of ZIF-61 in the curing process of BCE was demonstrated by FTIR (Nicolet Nexus 470, 400–4000 cm⁻¹). DSC was tested by METTLER TGA/DSC 1 SF/1382 under N₂ flow from 30–400 °C at four kinds of heating rate (5 °C/min, 10 °C/min, 15 °C/min and 20 °C/min). The dynamic storage modulus (*E'*) and loss factor (*tan δ*) were performed on a Rheometrics Scientific™ DTMA V at 1 Hz. The samples were heated at a rate of 5 °C/

min over the range of 20–350 °C.

3. Results and discussion

FTIR curves of ZIF-61/BCE (0.5 wt%) composites in different curing temperatures are shown in Fig. 1. With the increase of temperature, the absorption peaks of isocyanate at 2262 cm⁻¹ and 2233 cm⁻¹ were grandly disappeared. Meanwhile, the characteristic peaks of carbimide appeared at 1564 cm⁻¹ and 1370 cm⁻¹. As well-known, carbimide is the characteristic group of triazine ring. This further illustrated that ring trimerization reaction happened in the curing process. In addition, the absorption peak of ester carbonyl formed at 1740 cm⁻¹. But, after that, it decreased gradually. This meant that ester carbonyl was presence as intermediate in the curing reaction.

Generally speaking, with the inference of other reports [9–11], we could preliminary infer the curing mechanism as follows: Firstly, due to the Lewis acidity of ZIF-61, the Zn atom in ZIF-61 which had unoccupied orbit could absorb extra electrons or had an effect on electron shift. This feature contributed to gather the free BCE monomers around Zn by complexation. Secondly, some co-catalysts which contained active hydrogen in the curing system, such as phenols (HO-R' in Fig. 2) and amines, could promote the addition reaction of BCE monomers. Carbimide gradually formed in this process. This addition reaction was kept running until a triazine ring generated. Note that, the ligands of ZIF-61 could also be considered as co-catalyst. Furthermore, the free H₂O loading in ZIF-61's opening holes also had the possibility to promote curing reaction. The detailed schematic is illustrated in Fig. 2.

For further analysis the catalytic function of ZIF-61, activation energies (*E_a*, J/mol) of ZIF-61/BCE composites and pure BCE resins were calculated by Kissinger equation [8]. Fig. 3A and B were the DSC curves of BCE resins and 0.5 wt% ZIF-61/BCE composites at different heating rate. From the detailed data in Table 1, we got the fit lines based on Kissinger equation, as shown in Fig. 3C and D. According to multiply the slope of fit lines by *R* (8.314 J mol⁻¹ K⁻¹), the *E_a* of 0.5 wt% ZIF-61/BCE composites which was 3693 J/mol was proved to be less than that of BCE resins (6468 J/mol). This indicated that the curing process of 0.5 wt%

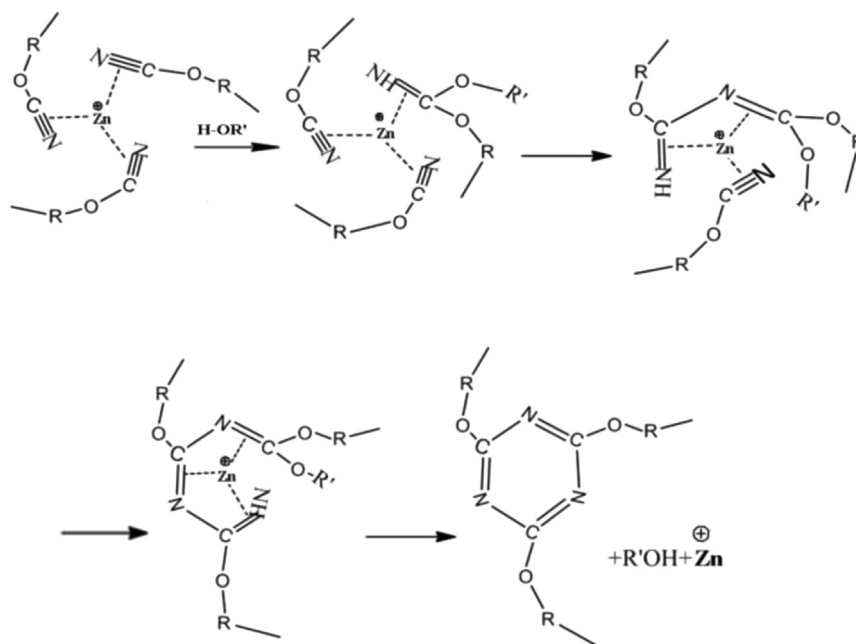


Fig. 2. Mechanism diagram of ZIF-61 as a catalysis in the curing process of BCE.

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