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# Effect of functional nitrile groups on curing behaviors and thermal properties of epoxy resins as advanced matrix materials

**Abstract:** This paper reports the preparation of the amine/epoxy blends with various amines such as 4,4'-diaminodiphenylsulfone (DDS), one nitrile side chain-containing diamine (BDB), and phthalonitrile-containing amine (APN). Differential scanning calorimetry (DSC), rheological analysis, and thermal gravimetric analysis (TGA) were used to evaluate the curing behaviors and thermal properties of amine/epoxy blends with the effect of functional nitrile groups of amines. Interestingly, an amine/epoxy blend exhibited double curing reactions. The cured epoxy copolymers exhibited high glass transition temperatures ( $>220^{\circ}\text{C}$ ) and excellent thermal stabilities having 5% weight loss temperature in the range of  $375^{\circ}\text{C}$  to  $383^{\circ}\text{C}$ .

**Keywords:** double curing reactions; nitrile groups; phthalonitrile; thermal stability.

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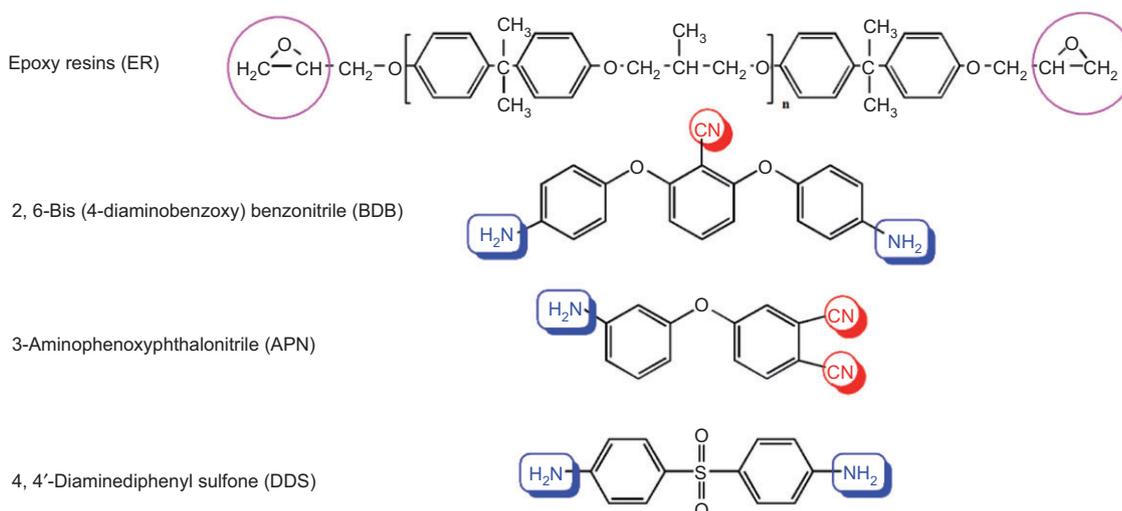
## 1 Introduction

For decades, epoxy resin (ER) has been widely used commercially in the applications such as coatings, adhesives, electrical insulating materials, and aerospace composites due to its excellent mechanical properties, good chemical resistances, and great electrical properties [1–3]. However, almost all epoxy resins are converted into three-dimensional thermoset networks by curing with some curing agents, and some of them are restricted to use due to their poor thermal stabilities. Therefore, selecting the proper curing agent is the subject of extensive investigations.

The amine 4,4'-diaminodiphenylsulfone (DDS) has a great advantage in providing the highest heat resistance of the cured amine/epoxy systems over other aromatic amines [4, 5]. But it is still not satisfactory for some restricted applications because of relatively lower thermal properties. The subject of this work is to evaluate the effect of nitrile groups of amines as a functional flame retardant in epoxy resin. Phthalonitrile-containing amine (APN) and one nitrile side chain-containing diamine (BDB) were used in the polymerization process of epoxy resin as comonomer and coreactive curing agents. Importantly, the functional groups, reactive nitrile groups, incorporated into the BDB [6] or APN [7], have a great tendency to improve the thermal stability of epoxy resin. Meanwhile, APN exhibits self-promoted curing behavior in the absence of curing agents and the APN/ER system has the double curing reactions.

## 2 Experimental

Epoxy resin (E-44) was supplied by Blue Star New Chemical Material Co. Ltd (Guangzhou, China). DDS was purchased from SC Dongcai Chemicals (Mianyang, China). BDB was prepared according to the reference [6]. APN was synthesized from 4-nitrophthalonitrile and 3-aminophenol according to the published literature with minor modifications [7]. The structures of the amines and epoxy resin are shown in Figure 1. All the reagents were used without further purification.



**Figure 1** The structures of the amines and epoxy resin.

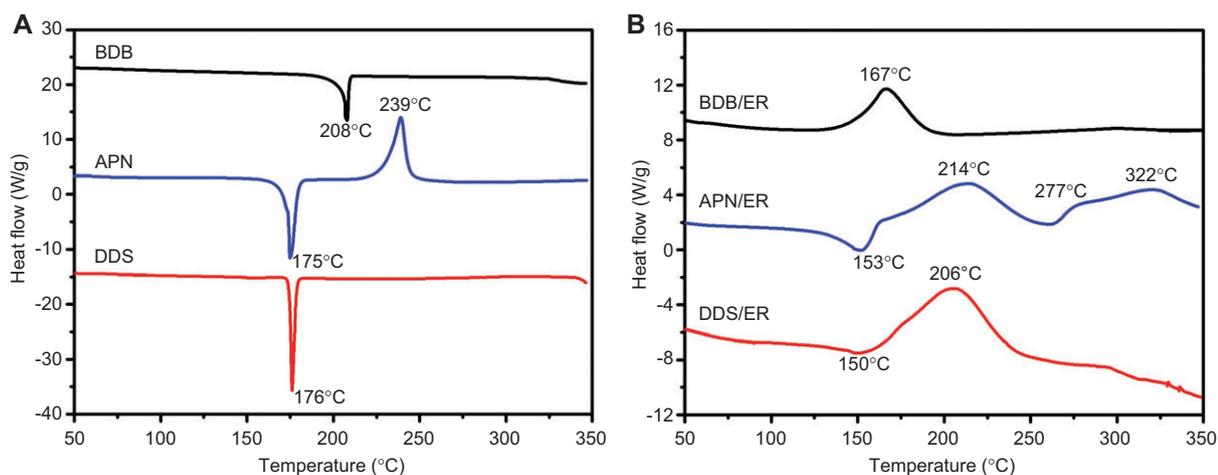
Three blends were prepared by mixing epoxy resin with the above-mentioned amines at room temperature. These blends were stirred vigorously for 30 min with the temperature in the range of 160–170°C, and the mixtures were cooled rapidly to room temperature. Then, the BDB/ER, APN/ER, and DDS/ER prepolymers were obtained. Meanwhile, the same melt was poured into a mold and thermally cured at 150°C for 1 h, 180°C for 1 h, 200°C for 1 h, and 220°C for 1 h. The BDB/ER, APN/ER, and DDS/ER copolymers were obtained.

DSC analysis was investigated by TA Instruments Modulated DSC-Q100 with a heating rate of 10°C/min and a nitrogen flow rate of 50 ml/min. Rheological analysis was performed by TA Instruments Rheometer AR-G2 at low strain values (0.5%) using 25-mm-diameter parallel plates and a frequency of 1 Hz. TGA analysis was done by TA Instruments Q50 thermogravimetric analyzer with a

heating rate of 20°C/min under nitrogen with a purge of 60 ml/min.

### 3 Results and discussion

The DSC curves of the amines are shown in Figure 2A. The peak melting temperatures for the BDB, APN, and DDS were 208°C, 175°C, and 176°C, respectively. APN showed an additional exothermic peak at 239°C, attributed to its self-promoted curing behaviors. The enthalpy of cure was 179.3 J/g, which was a result of the polymerization reaction of 3-APN between the amino group and the nitrile groups. Figure 2B showed the curing behaviors of the three blends, and DSC results are summarized in Table 1. For the APN/ER and DDS/ER blends, the peaks of the



**Figure 2** DSC curves of amines (A) and amine/epoxy blends (B).

Samples	$T_{\text{melt}}$ (°C)	$T_{\text{top1}}$ (°C)	$T_{\text{top2}}$ (°C)	$T_{\text{top3}}$ (°C)	$\Delta H_1$ (J/g)	$\Delta H_2$ (J/g)	$\Delta H_3$ (J/g)
BDB/ER	–	167	–	–	182.9	–	–
APN/ER	153	214	277	322	146.1	9.9	25.84
DDS/ER	150	206	–	–	182.2	–	–

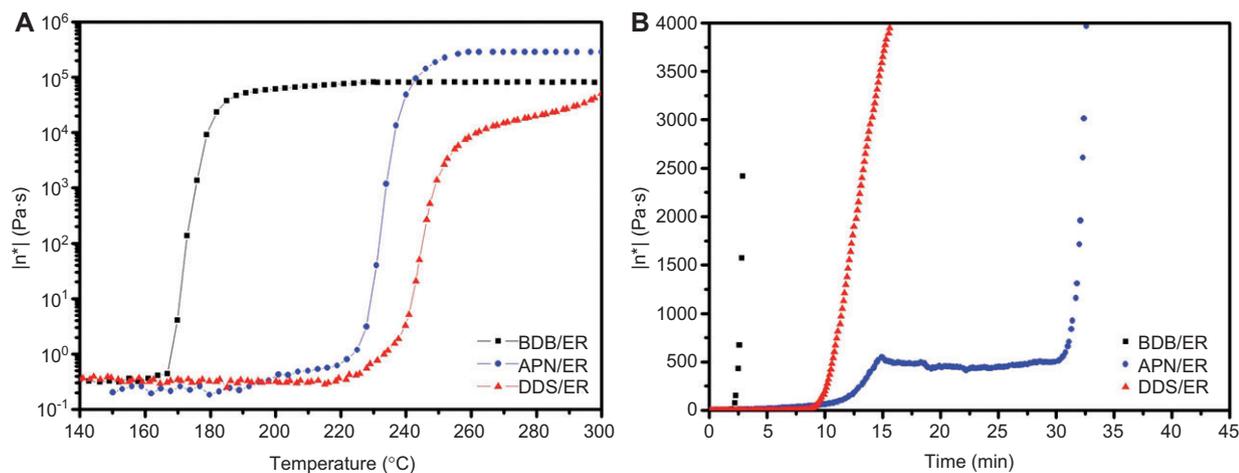
**Table 1** Thermal curing properties of the amine/ER blends.

exothermic transitions were observed at 153°C and 150°C, respectively. The melt peaks of the transitions and the melt enthalpies appeared to be related to the blend compositions. For the BDB/ER, APN/ER, and DDS/ER blends, the peaks of the exothermic transitions were centered at 167°C, 214°C, and 206°C, respectively. The exothermic transitions corresponded to the ring-opening polymerization of epoxy resin with amino groups. Interestingly, two exothermic additional transitions were observed at 277°C and 322°C for the APN/ER blends. The first exothermic transition was attributed to the polymerization of the nitrile groups of the APN. The second higher temperature exotherm was due to the decomposition reaction of unreacted epoxy resins.

The rheological behaviors were performed with changes in the viscosity accompanying the curing reaction of the three blends. In Figure 3A, the complex viscosity of the blends was determined as a function of temperature from 140°C to 300°C. In each case, the viscosity remained in the range of 0.1–1 Pa·s, while the temperature increased. The BDB/ER, APN/ER, and DDS/ER blends displayed a rapid increase in viscosity upon melting at 170°C, 225°C, and 240°C, respectively. The abrupt increase in the viscosity was attributed to the polymerization reaction of the amines and epoxy resin. To determine the curing behaviors,

complex viscosity changes of the amine/epoxy blends were noted as a function of time at 200°C. In Figure 3B, obviously, the complex viscosity of the BDB/ER, APN/ER, and DDS/ER blends rapidly increased to 500 Pa·s at about 3, 10, and 15 min, respectively. In addition, the viscosity of the APN/ER blend was maintained almost constant in 15–30 min. After 30 min, there was again an observed abrupt increase in the viscosity. The first abrupt increases were observed, which indicated that the ring-opening polymerization of the epoxy resin was progressing. Then, the second abrupt increases showed the polymerization reaction of the nitrile groups of the APN [8].

The thermal stabilities of the cured amine/epoxy copolymers were determined by TGA analysis. TGA and DTG curves are presented in Figure 4A and B, and the test data are summarized in Table 2, respectively. The 5% weight loss temperature ( $T_{5\%}$ ) of amine/epoxy resin copolymers is in the range of 375–383°C, and the char yields were in the range of 19–47%. Compared with the DDS/ER and BDB/ER copolymers, the APN/ER copolymer has a relatively high thermal stability due to the high aromatic nature and cross-linking density, which is consistent with the formation of flame retardant networks such as isoindoline, triazine, and phthalocyanine [9–13]. However, for the BDB/ER, APN/ER, and DDS/ER



**Figure 3** Complex viscosity ( $\eta^*$ ) for the amine/epoxy blends: (A) as a function of temperature; (B) as a function of time at 200°C.

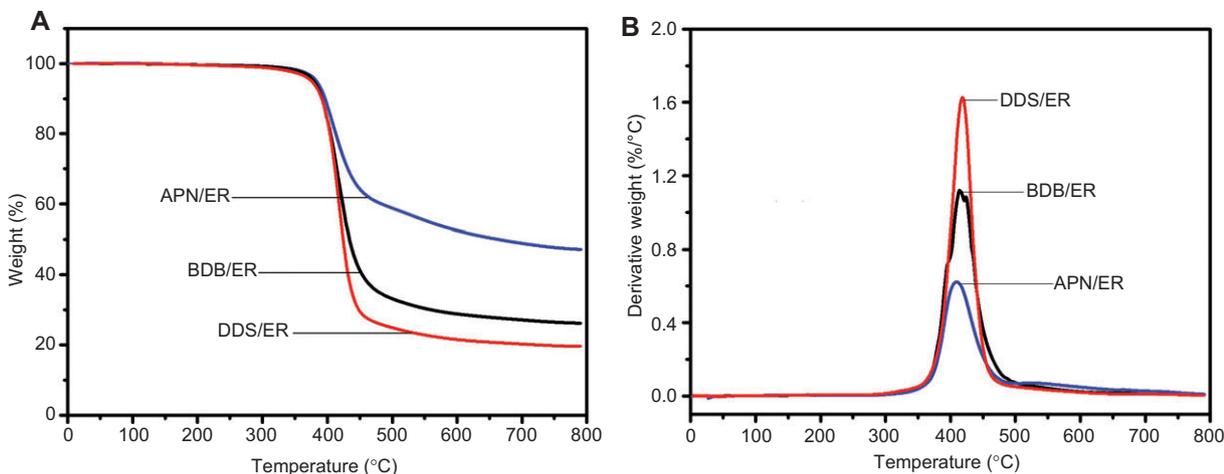


Figure 4 TGA (A) and DTG (B) curves of amine/epoxy copolymers in nitrogen.

Samples	$T_g$ (°C)	$T_p$ (°C)	$T_{5\%}$ (°C)	Char yield (%) at 800°C
BDB/ER	119	413	379	26
APN/ER	221	409	383	47
DDS/ER	105	418	375	19

Table 2 Thermal properties of the amine/ER copolymers in nitrogen.

copolymers, there is a main process of degradation ( $T_p$ ), which starts at about 413°C, 409°C, and 418°C, respectively. These results indicated that functional nitrile groups are important to enhance the thermal stability of epoxy resin. Furthermore, the thermal properties of the amine/epoxy polymers were evaluated by the glass transition temperatures ( $T_g$ ) in DSC analysis and the  $T_g$ s are listed in Table 2. All of them showed thermally induced phase transitions with  $T_g$  in the range of 105–221°C. Therefore, the amine/epoxy polymers have a high  $T_g$  and excellent thermal stability, which depend on the effect of functional nitrile groups.

## 4 Conclusion

The BDB/ER, APN/ER, and DDS/ER blends were successfully prepared. The effect of reactive nitrile groups on the curing behaviors, rheological behaviors, and thermal properties of three systems have been studied. The  $T_g$  and  $T_{5\%}$  of the cured copolymers increased with the increase of nitrile groups due to high aromatic nature and cross-linking density. The APN/ER blends exhibited double curing reaction and desirable processing feature. The APN/ER blend has the potential to be used as a matrix for advanced composites.

**Acknowledgements:** The authors are grateful to the Major Science and Technology Project in Sichuan Province (2010 FZ 0117), National Natural Science Foundation (No. 51173021) and “863” National Major Program of High Technology (2012AA03A212) for the financial support in this work.

Received April 12, 2012; accepted June 6, 2012; previously published online July 12, 2012.

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