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ORIGINAL PAPER

Mechanical and thermal properties of bisphenol A-based cyanate ester and diallyl phthalate blends

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Abstract Cyanate ester resins are a high performance class of compounds. They have excellent mechanical properties, dielectric properties and thermal properties; however, their major drawback is their brittleness. An attempt was made to improve the impact strength of the cyanate ester resin. In the present study a commonly used cyanate resin, bisphenol A dicyanate (BADCy), was modified by the addition of diallyl phthalate (DAP) and was cured with benzoyl peroxide. The properties of the blends such as thermal and mechanical properties were investigated in detail by scanning electron microscope, dynamic mechanical analysis, thermogravimetric analysis, and mechanical measurement. The results indicate that the addition of the appropriate amount of DAP can effectively improve the impact toughness and the flexural strength while sacrificing the thermal properties of the blends. The maximum impact strength and flexural strength were observed on addition of 15 phr DAP content. However, the thermal stability of the blends was found to be lower than that of the unmodified BADCy resin.

Keywords Bisphenol A dicyanate · Diallyl phthalate · Mechanical properties · Thermal properties

Introduction

Cyanate ester resins have low shrinkage on cure, high thermal properties, and excellent mechanical and dielectrical properties along with excellent chemical resistance. They have been widely used as adhesives and matrixes for composites [1, 2]. Unfortunately, like most thermosetting resins, cyanate ester resins have the

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drawback of brittleness. To improve the toughness, many methods, such as polymer blending, filler filling, and fiber reinforcing, have been introduced to modification cyanate ester resins. Engineering thermoplastics, such as polysulfone, poly(ether imide), polyarylate, and poly(ether ketone ketone), are employed [3–6]. Blending with thermosets such as epoxies and bismaleimide resins were also examined to improve the toughness of cyanate ester resins [7–10].

Diallyl phthalate (DAP) is the most commonly used of the allylic esters and among the most versatile of the thermosetting resins. It is widely used in many fields because of its advantages, such as outstanding dimensional stability, ease of handling, low water absorption, and excellent electrical properties [11, 12]. The DAP is typically applied for electronic devices requiring high reliability under long-term adverse environmental conditions, which covers electrical connectors and insulators in communication, switches, automotive distributor caps, computer systems, and aerospace industry [13].

In this paper, the modification of bisphenol A dicyanate (BADCy) by DAP was reported. The effect of amount of DAP on the impact property of the resulting blends was examined. The thermal properties and mechanical properties of the blends were studied by DMA and thermogravimetric analysis (TGA) in detail.

Experimental

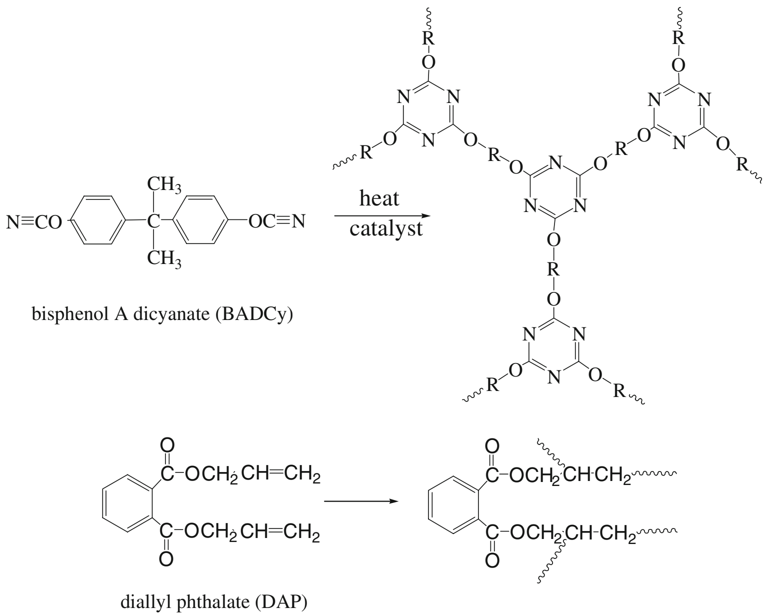
Materials

A BADCy ester (purity >99.5% and a cyanate equivalent of 139 g/eq), white granular crystal was purchased from Shangyu Shengda Biochemical Co. Ltd (Shangyu, China). Diallyl phthalate purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Benzoyl Peroxide (BPO), used as the free radical initiator of DAP was purchased from Chemical Plant of Hubei University (Hubei, China). Chemical structures and polymerization of the BADCy and DAP used in this work as shown in Scheme 1.

Preparation of BADCy/DAP blends

The BADCy/DAP blend was prepared by the following steps: Firstly, the BADCy was heated at 100 °C to clear solution, and then polymerized at 140 °C for 120 min, the BADCy prepolymer can be obtained. Secondly, after cooling the BADCy prepolymer, the DAP was added. BPO, 2 wt %, of the weight of the DAP, was used as initiator. The resultant clear mixture was poured into a mold with release agent on the inner walls, which was preheated at 120 °C. After out-degassed for 10 min, the mixture was cured by the following procedure: 140 °C/3 h + 160 °C/3 h + 200 °C/2 h, and post-cured at 220 °C for 2 h.

In this work, the blends were designated by the weight ratio of their components in this method: for example, a binary blend containing 100 phr (phr is defined as per hundred resins) BADCy, 10 phr DAP was abbreviated as DAP10.



Scheme 1 Structures of components of the blend and mechanism of network formation

Instruments and testing

Mechanical properties testing

Mechanical properties of the cured blends were tested using an Instron universal testing apparatus. The impact strength of samples can be performed according to GB2571-1995 and the flexural strength of samples can be measured according to GB2570-1995 for determining impact, flexural strength properties, respectively. At least five specimens for each system were tested.

Scanning electron microscope (SEM)

The impact surface morphology of the cured blends was observed using a scanning electronic microscope of QUANTA200 (SEM, FEI). Samples were coated with a thin layer of Au (around 40 nm)

Dynamic mechanical analysis (DMA)

The DMA of cured blends was measured at a heating rate of 3 °C/min from room temperature to 300 °C using a Q800 dynamic mechanical analyzer (TA Instrument Company, USA) in nitrogen atmosphere. A single cantilever clamping geometry 35 × 10 × 4 mm samples were tested at a fixed frequency of 3 Hz.

Thermogravimetric analysis

A SDT Q600 (TA Instrument Company, USA) was used to investigate the TGA of the blends. The cured samples ca. 7 mg milled beforehand were placed in a Pt cell and heated at a rate of 15 °C/min from 50 to 700 °C in nitrogen atmosphere at a rate of 60 ml/min.

Discussion and results

Mechanical properties of BADCy/DAP blends

The mechanical properties of the cured blends were evaluated as function of the blends. Figure 1 show the influence of DAP on the impact strength of BADCy/DAP modified systems. It can be seen that the impact strength of BADCy/DAP blends first increased rapidly with the addition of DAP, then decreased slightly with further addition of DAP to the BADCy/DAP blends. The impact strength of the blends reached its maximum value of 15.5 kJ/m^2 when the amount of the DAP was 15 phr, which was 1.37 times as strong as the original BADCy. While further increments of amount of DAP (>15 phr) led to decrease of the impact strength, which also reached the value of 13.4 kJ/m^2 when 40 phr of DAP was introduced. It indicated that introduction of DAP to BADCy can improve its toughness effectively. The trend of the influence of increments of DAP on the flexural strength of the blends is similar to that of the impact strength as shown in Fig. 1. The flexural strength given an increasing trend till a loading of 15 phr DAP content for the blend and got its maximum value (138 MPa) at this point. This maximum value was greater than the unmodified BADCy by a factor of 1.13. There is a probability of cross linking of BADCy and polymerization of DAP taking place simultaneously. A DAP modified EP system has been reported by Shenoy et al. [14], they supposed the reason which caused the increase in the mechanical properties of EP/DAP blends is probability

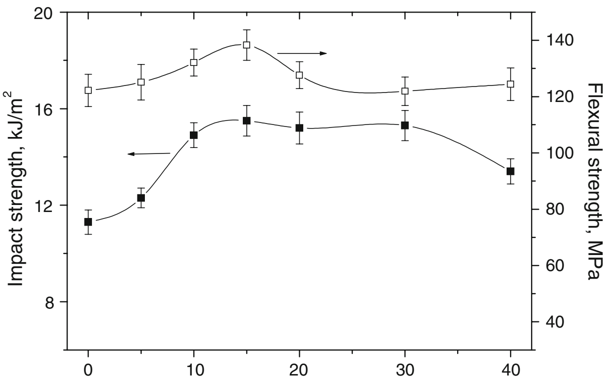


Fig. 1 Mechanical properties of BADCy/DAP blends

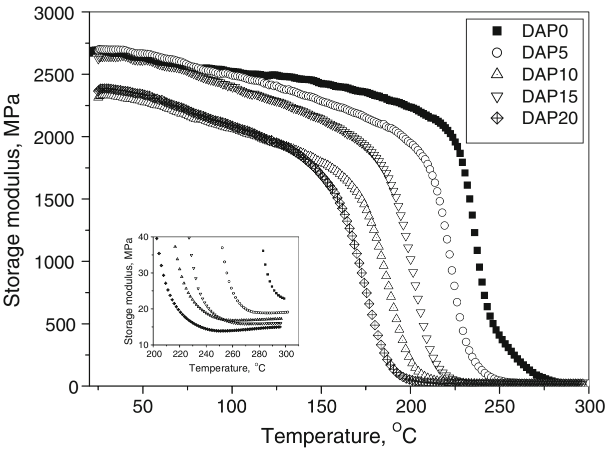


Fig. 2 Storage moduli (E') as a function of temperature for BADCy/DAP blends

giving rise an interpenetrating polymer network. Hence the net effect is an increase in the matrix rigidity and a consequential increase in mechanical properties. Low loading of DAP would make up the possible defects of BADCy resin. Further increments of DAP content led to a slightly decrease. The poly(diallyl phthalate) (PDAP) resin has poor mechanical properties than polycyanurate. So the flexural and impact strength of the blends will decreased while introduced further amount of DAP to BADCy.

Figure 2 is storage moduli (E') as a function of temperature for various BADCy/DAP blends and neat BADCy. The BADCy/DAP blends show lower values of E' over the entire temperature range of the study, except DAP5. For DAP5 blend, the E' exhibits a higher value under the temperature of 80 °C. From Fig. 2 it is also show that the rubbery modulus decreases as the DAP content was increased. For example, the rubbery modulus of the DAP0, DAP5, DAP10, DAP15 and DAP20 are 24, 19, 17, 16 and 13 MPa, respectively. From rubber elasticity theory, the rubbery modulus is proportional to the crosslink density [15]. Thus increasing the DAP content is concluded to lower the crosslink density of BADCy.

Scanning electron microscope observations of the fracture surface were indicative of the compatibility and the fracture mode of the materials. The fracture surface of the cured castings was analyzed by SEM. Typical micrographs of the fracture surface of pure BADCy and BADCy/DAP blends are shown in Fig. 3. The BADCy homopolymer is relatively tough ($K_{IC} = 0.65$ MN/m$^{3/2}$, $G_{IC} = 115$ J/m^2). The SEM picture of the cured pure BADCy showed a rough fracture surface (Fig. 3a). The DAP5 blend (Fig. 3b) showed a smooth fracture surface reveal the brittle failure. While more rough surfaces (Fig. 3c–f) were observed in the fracture surfaces of the modified systems, suggesting the addition of DAP to BADCy can obvious improve the toughness of the resulting blends, just agree with the results of mechanical properties tested in Fig. 2. The toughest of the modified blends tested here was blend DAP15 ($K_{IC} = 0.81$ MN/m$^{3/2}$, $G_{IC} = 152$ J/m^2). The rough surfaces which consisting of more and shorter crevices are indications of increased resin

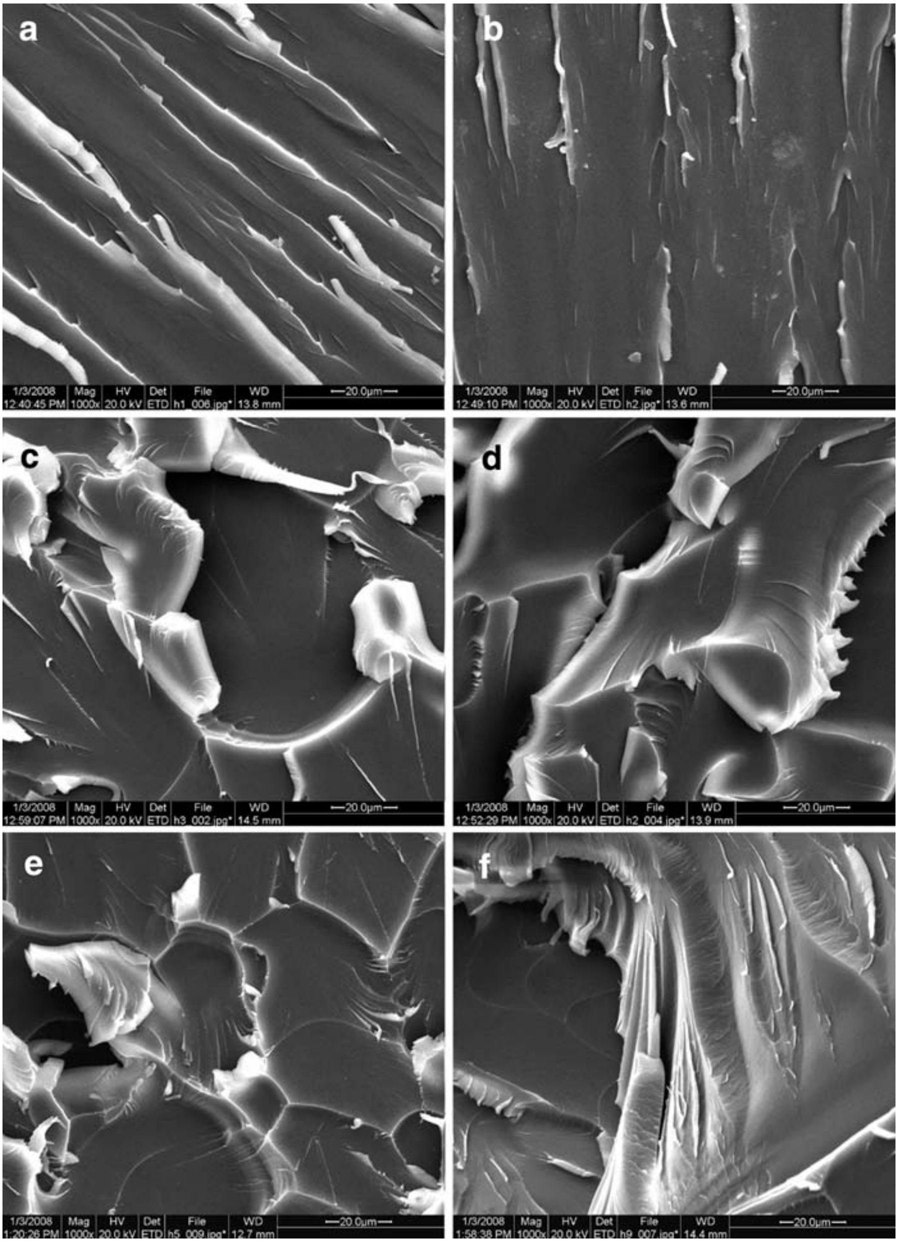


Fig. 3 SEM images of the fracture surface of BADCy/DAP blends: **a** DAP0; **b** DAP5; **c** DAP10; **d** DAP15; **e** DAP20; **f** DAP40

toughness as they are known to initiate microcracks and dissipate energy and change direction of crack propagation. The fracture patterns were nearly the same for all the blends. The significant increase of fracture strain suggests a change of fracture mode. It indicted that the DAP resin can be used as a modifier to toughen cyanate ester.

Thermal properties of BADCy/DAP blends

Thermal stability is an important thermal property of a material, which can be characterized by glass transition temperature and by TGA. In this study, the T_g of BADCy/DAP blends was detected by the DMA method, which can be taken as the maximum of the curve tan δ versus temperature, as shown in Fig. 4. It can be seen that the incorporation of DAP in BADCy resin tends to decrease the T_g of the blend, the more the DAP used, the lower the T_g value. The T_g of BADCy/DAP (DAP5, DAP10, DAP15 and DAP20) blends is 245.4, 204.4, 218.1 and 192.3 °C, respectively, while that of the neat BADCy is 266.8 °C. Since the glass transition process is related to the molecular motion, the shift of the tan δ peak to a lower temperature may be ascribed to the oligomers of DAP in the blend. The further addition of DAP to the blends will decrease the cross-link density of BADCy, consequently reducing the thermal stability of the blends [9, 16]. The main reason of the reduction of the T_g value of the blends may be the poor thermal stability of PDAP than that of BADCy lowered the T_g value of the blends.

Thermal stability can also be manifested by initial degradation temperature (IDT) and the degradation rate of a polymer: the higher the IDT value and maximum degradation rate temperature, the higher the thermal stability [17, 18]. The TGA and DTG curve of all BADCy/DAP blends as well as that of pure BADCy are shown in Fig. 5. The corresponding IDTs, maximum degradation rate, and char yield at 740 °C are summarized in Table 1. IDT is defined as the temperature at which the weight loss is 5%. Table 1 shows that IDT is decreased with the addition of DAP to the blends as compared to the pure polymer, the blends reveal almost similar maximum degradation rate temperature, but the former has a lower maximum

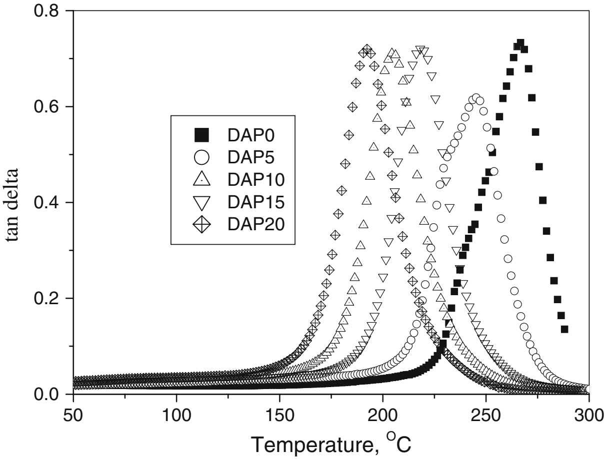


Fig. 4 Tan δ as a function of temperature for BADCy/DAP blends

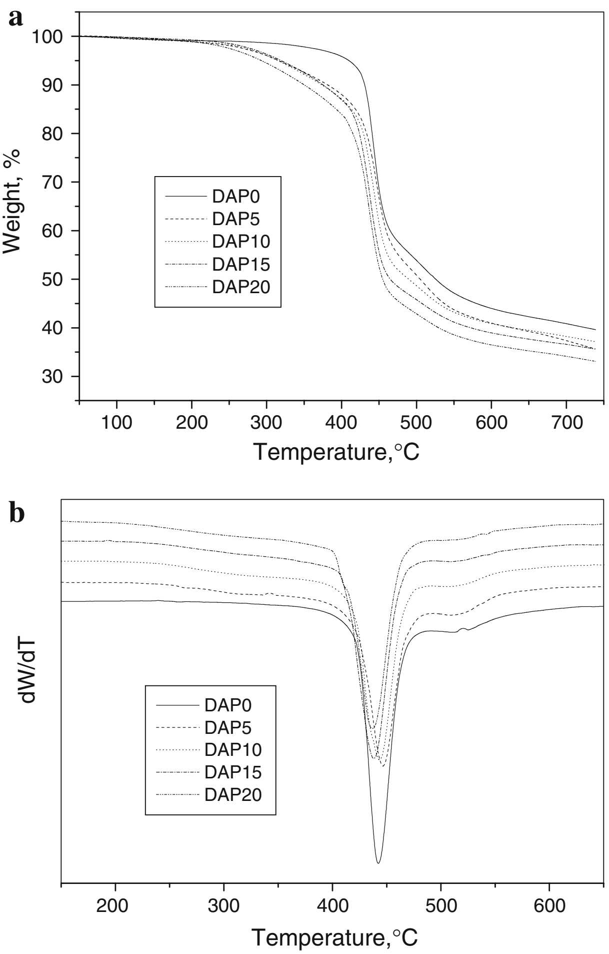


Fig. 5 **a** Weight loss as a function of temperature for BADCy/DAP blends; **b** Decomposition rate as a function of temperature for BADCy/DAP blends

Table 1 Characteristic date from TGA analysis

	DAP0	DAP5	DAP10	DAP15	DAP20
IDT (°C)	409.7	315.9	315.1	319.2	292.9
Maximum degradation rate (%, °C)	1.30	0.92	0.99	1.08	1.03
Maximum degradation temperature (°C)	442.3	446.6	443.5	438.1	436.3
Char yield (%)	39.6	35.64	37.13	35.61	33.08

degradation rate than does the latter. The IDTs of blends decrease with the increase amount of DAP. The reason may be the thermal stability of DAP is lower than that of the BADCy, and higher DAP loading will deteriorate the thermal stability of

BADCy/DAP blends. Another reason is the presence of DAP in the blends will decrease the cross-link density of BADCy, which also will lower the thermal stability of BADCy/DAP blends.

Figure 5 and Table 1 also show that the blends have lower char yields than pure polymer and it decreases with increasing DAP loadings. The reason is that DAP molecules have lower thermal stability than that of BADCy.

Conclusion

The BADCy/DAP blends were prepared, and the effect of DAP on BADCy were investigated. The mechanical properties results show that the incorporation of DAP into BADCy improve the impact strength and flexural strength, but decrease the storage modulus of the blends. The thermal properties such as glass transition temperature and thermal stability of resulting blends have been compared with neat BADCy, and decreased with the increase in DAP content. The reduction in the T_g of BADCy/DAP blends may be result from the presence of DAP in the blend reduced the cross-link density of BADCy.

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