

Curing Behavior and Mechanical Properties of Hollow Glass Microsphere/Bisphenol A Dicyanate Ester Composites

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ABSTRACT: Hollow glass microsphere (HGS)/bisphenol A dicyanate ester (BADCy) composites have been prepared by mechanical mixing, followed by a stepped curing process. The effect of HGS on the curing behavior of BADCy was studied using differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR). The mechanical properties of the composites were examined by mechanical tests, and the improvements of the mechanical properties were investigated by scanning electron microscopy (SEM) and dynamic mechanical analysis (DMA). The results show that HGS is catalytic for the polyclomeriza-

tion of the BADCy, which is advantageous to reduce the maximal processing temperature. The impact strength, flexural strength, flexural modulus and storage modulus of BADCy are improved. The improvements of the mechanical properties without sacrificing thermal properties, the ability of lowering processing temperature and the low cost make HGS good filler for cyanate ester resin. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1252–1256, 2010

Key words: cyanate ester resin; hollow glass microsphere; fillers; mechanical properties

INTRODUCTION

Cyanate esters constitute a high temperature resin family traditionally associated with aerospace applications and electronic devices, including structural adhesives, dielectric films and high-performance composite materials, because of their good thermal stability, low dielectric constant and extremely low moisture uptake compared to other resins of their class.¹ However, the cured polymers are very brittle, and need to be toughened to make them useful engineering polymers. It is therefore a primary aim of many researchers to provide cyanate ester with higher toughness, but without significantly sacrificing other important characteristics such as thermal mechanical property and elastic modulus, which are desired and required in many applications. Unfortunately, traditional toughening agents, such as liquid rubbers, epoxy resins, usually can not satisfy these requirements.²

Hollow glass microspheres (HGS) are widely used in industry, due to such advantages as strong filling ability, smooth spherical surface, small and well-distributed internal stress in products.^{3,4} In addition, power consumption and abrasion of the equipment

in processing can be reduced because of the good flow properties of the filled cyanate ester resin, which is beneficial to reduce the production cost. Many researchers have investigated HGS filled polymer composites. For example, Ho Sung Kim and Pakorn Plubrai investigated the failure mechanisms of syntactic foams under compression.⁵ Soo-Jin Park et al. studied the surface free energies, thermal stabilities, electrical properties, and fracture behaviors of particulate composites using HGS lowly filled diglycidyl ether of bisphenol A (DGEBA) as a model system.⁶ However, most of them focus on the syntactic foams using microsphere with the averaged diameter of 40 μm or more.

In this work, the HGS with a diameter of 2.5 μm has been introduced to bisphenol A dicyanate ester (BADCy) resin. The effects of HGS on the curing behavior as well as the mechanical properties of the resulting HGS/BADCy composite were studied.

EXPERIMENTAL

Materials

BADCy (2,2-bis (4-cyanatophenyl) propane) with a melting point of 79°C was supplied by Shanghai Huifen Kemao, HGS (average diameter: 2.5 μm , ranging from 1 to 5 μm , average true particle density: 2.30 g/cm^3) was provided by Shanghai Huijing sub-nano materials. Dibutyltin laurate (light yellow

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liquid) used as catalyst was purchased from Xi'an Chemical Reagent Company.

Sample preparation

BADCy was oligomerised at 140°C for 30 min in the presence of dibutyltin laurate (200 ppm). The required amount of HGS (dried at 100°C for 3 h before using) was added and thoroughly mixed to get a uniform dispersion of it. The resultant mixture was poured into a preheated mould (150°C) with release agent on the inner walls, and then, the mould was degassed under vacuum for 20 min at 140°C. The curing was done according to the following curing procedure: 160°C/2 h + 180°C/1 h + 200°C/1 h + 220°C/2 h (The neat BADCy needed postcuring at 240°C for 2 hours). After the curing procedure, the mould was cooled to room temperature naturally before the composite plaque was removed. Then the plaque was cut into specimens of certain dimensions.

Characterization and testing

The cure behaviors of neat BADCy and composites were measured using a differential scanning calorimeter (Perkin-Elmer, DSC 6) under a nitrogen flow of 30 mL/min. FTIR (WQF-300IR, Beijing Optical Instruments Factory) was employed to investigate the conversion of -OCN during the curing process. Flexural and impact tests were performed on a universal testing machine according to GB2570-81 standard (rectangular specimen: 80 × 15 × 4 mm, span/depth = 16) and GB2571-81 standard (rectangular specimen: 15 × 10 × 4 mm, unnotched) of China, respectively. The fracture surfaces of the specimen for the mechanical tests were gold coated and then observed under Quanta 200-FEI Scanning Electron Microscope (SEM). Dynamic mechanical analysis (DMA 2980, TA Instruments) was carried out to study dynamic mechanical properties of the composites. Single cantilever clamping geometry 35 × 10 × 4 mm samples were tested at a heating rate of 2°C/min and a load frequency of 3 Hz.

RESULTS AND DISCUSSION

Study of the reactivity of HGS modified BADCy system

Polymerization of the pure BADCy resin normally happens at the elevated temperature, which brings difficulty to produce BADCy-based composites. So catalysts are usually needed to accelerate the reaction and reduce the processing temperature. The DSC curves of catalyzed BADCy (curve a) and 30 wt % HGS/BADCy composite (curve b) are shown in Fig-

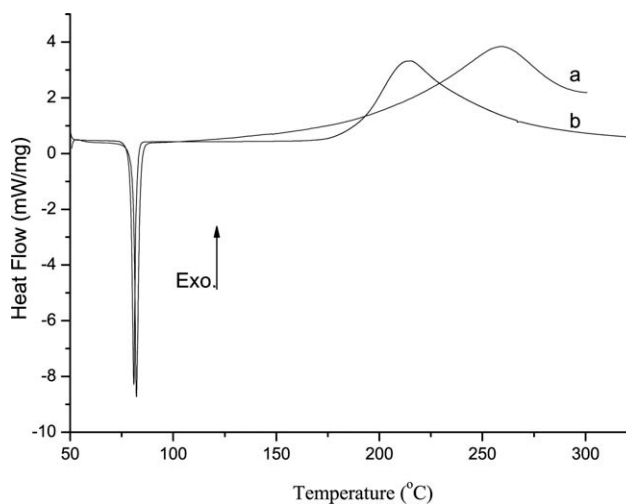


Figure 1 DSC curves: (a) Catalyzed BADCy, (b) Catalyzed BADCy containing 30 wt % HGS.

ure 1. Both curves have two peaks, a sharp melting endothermic peak (around 80°C) followed by an exothermic peak. When HGS is introduced, the temperature of the exothermic peak of BADCy decreases from 259°C to 215°C and the polymerization is almost finalized when the temperature reaches 300°C. These results mean that the addition of HGS can dramatically lower the processing temperature.

The curing traces of neat BADCy and 30 wt % HGS filled BADCy using FTIR spectra are plotted in Figure 2. The peaks at 2940 cm^{-1} (h_{2940}) and 2270 cm^{-1} (h_{2270}) are absorbance of methyl group and -OCN group, respectively. Absorbency of the FTIR band is illustrated by the height of the peak with methyl as the internal standard. The conversion rate of -OCN groups, $\alpha(t)$, at a certain curing point can be determined by the ratio of h_{2270}/h_{2940} in eq. (1).^{7,8}

$$\alpha(t) = 1 - \frac{h(t)_{2270}/h(t)_{2940}}{h(0)_{2270}/h(0)_{2940}} \quad (1)$$

where t is the curing time and 0 stands for zero curing time.

The calculated curves of conversion of -OCN vs. time are plotted in Figure 3. In general, the HGS/BADCy composites have a higher conversion rate than the neat BADCy throughout the curing procedure. As for the neat BADCy, the conversion rate increases linearly with the time at first hour of the first curing step, i.e., 160°C for 2 h. Then the polymerization process levels up at the second hour at 160°C. As the temperature increases, the conversion rate increases linearly with time. However, the conversion rate of -OCN is only about 80% after the curing procedure. So the neat BADCy needed the postcuring step. Until the conversion rate reaches about 90%, the HGS/BADCy composite has a similar curing pattern with the neat BADCy. After the

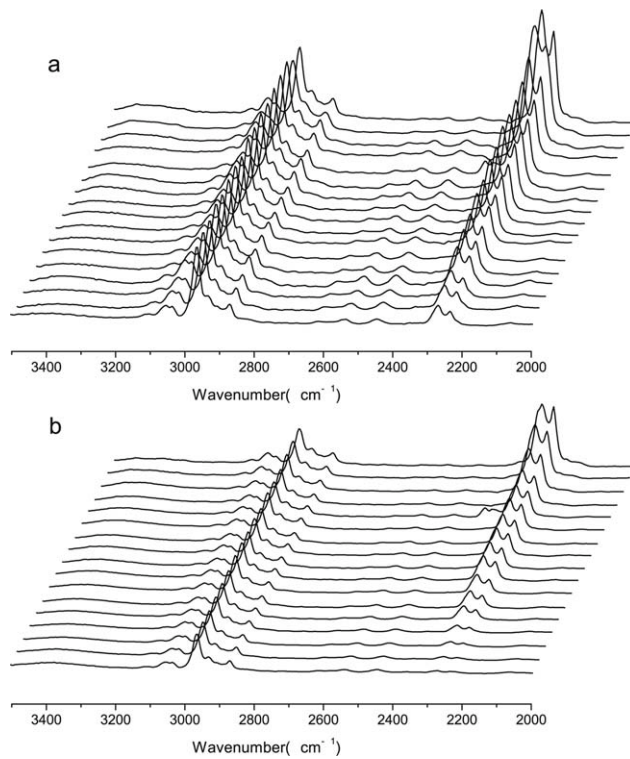


Figure 2 The curing trace using FTIR spectra: (a) Catalyzed BADCy, (b) Catalyzed BADCy containing 30 wt % HGS.

third curing step (200°C for 2 hours) where the conversion rate is about 90%, there are little BADCy monomers left. As a result, the conversion rate slows down and gradually approach 100%.

Both the DSC and the FTIR spectra indicate that HGS is catalytic for the polycyclomerization of the cyanate ester. The catalytic mechanism is still not clearly known. It has been reported that transition metallic ions such as Al^{+3} show strongly catalytic effects to the polycyclomerization of cyanate ester due to their low

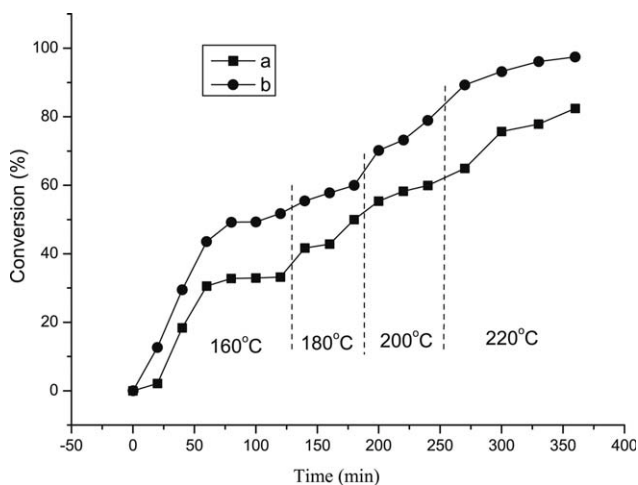


Figure 3 The conversion of $-OCN$ group vs. curing time (a) Catalyzed BADCy, (b) Catalyzed BADCy containing 30 wt % HGS.

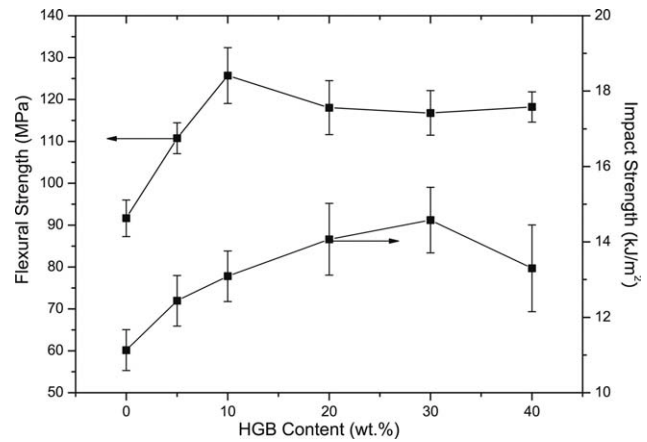


Figure 4 Flexural strength and impact strength of the cured composites.

coordination number and high ligand mobility during the cure process.⁹ In addition, some metal oxides, such as ZnO ,¹⁰ TiO_2 ,¹¹ CuO , Cu_2O ,¹² silicate^{13,14} also have catalytic effects to the polycyclomerization of cyanate ester. The main components of the HGS are SiO_2 and Al_2O_3 . It is assumed that though Al_2O_3 is insoluble in cyanate ester resin to form Al^{+3} , the reactivity of cyanate ester resin being in contact with the surface of Al_2O_3 may be enhanced.^{10,15} On the other hand, there may be little components of $Al(OH)_3$ and $Si(OH)_4$ in the HGS which make the surface of HGS have few $-OH$ groups, and it has been reported that $-OH$ can catalyze the polycyclomerization of cyanate ester.^{16,17}

Mechanical properties

Impact strength and flexural strength of the cured composites are shown in Figure 4. The impact strength increases slowly with the increase of HGS weight percentage and reaches its peak value of 14.6 kJ/m^2 when HGS weight percentage is 30 wt %, increasing by 26%. The flexural strength increases by

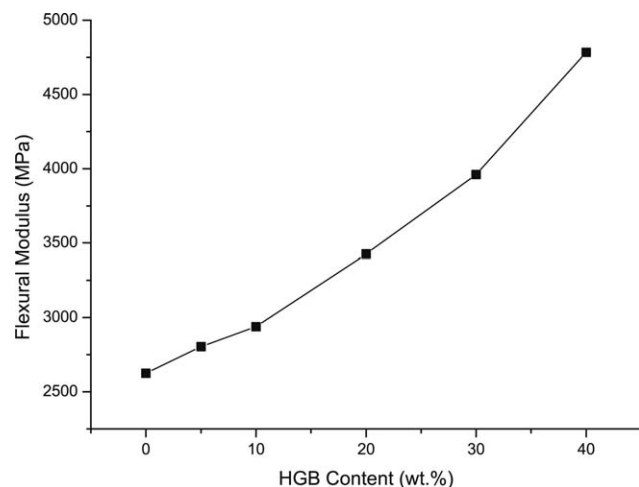


Figure 5 Flexural modulus of the composites.

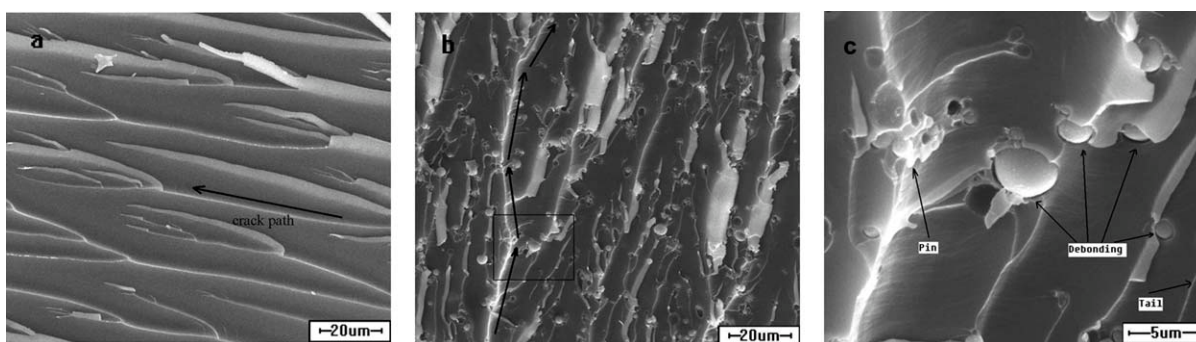


Figure 6 The morphology of the fracture surface: (a) Neat BADCy, (b) and (c) HGS/BADCy composite.

37% with the HGS weight percentage up to 10 wt % where the maximum is reached. When the concentration of HGS is higher than 10 wt %, the flexural strength decreases, and then, arrives at a plateau. Figure 5 is the flexural modulus of the composites. The value of the flexural modulus increases with the HGS weight percentage.

There exist several mechanisms that can explain the toughness increase introduced by microspheres. One of the most generalized explanations for this toughness increase is the crack-pinning-bowing mechanism.^{18–21} In unfilled systems, the crack is able to move forward in the matrix without restrictions [Fig. 6(a)], while in filled systems, the propagating crack is pinned to sphere positions. To move ahead the crack bows out between the dispersion of spheres while remains pinned at sphere position [Fig. 6(b)]. The propagating crack front has to round out and to surpass the impenetrable particle. Therefore, tails are formed at the rear of the inclusions due to the meeting of the two crack arms that are propagating through different fracture planes [magnified micrograph Fig. 6(c)]. Figure 6(c) also gives the evidence of debonding between HGS and matrix. Debonding is a kind of microcracks generates along the interface between fillers and matrix. When the sample is loaded, the bonding between HGS and BADCy matrix breaks first because it is weaker than the bonding between BADCy and BADCy in the bulk of matrix. Around debonded HGS, there are gaps which may have resulted from the plastic dilatation of the matrix when debonding happens.²² This debonding procedure absorbs lots of energy and increases the impact strength.

The reason of the flexural strength increase is not very clear. We assume that there may be two reasons. One is attributed to the fact that the reaction between BADCy and $-OH$ groups on the surface of HGS.²³ This reaction terminated the crosslink reaction of BADCy and produces a kind of interface layer which has lower crosslink density. This interface layer is tougher than the BADCy matrix and felt the HGS and BADCy matrix together. The other

reason is the propagating crack is pinned at sphere positions, which delays the form of through check. The increase of the flexural modulus is easy understood because the modulus of HGS is higher than that of cyanate ester resin.

Dynamic mechanical analysis

Viscoelastic behavior is also a macroscopic reflex of the variation of the inner structure. The DMA test results of cured BADCy and 30 wt % HGS/BADCy composite are shown in Figures 7 and 8. Figure 7 show that the addition of HGS decreases the glass transition temperature (T_g , defined as the temperature where the loss modulus reaches a peak) and increases the loss modulus when temperature is lower than T_g . The slight decrease of T_g is attributed to the interface layer which has lower crosslink density. The reason of the increase of the loss modulus is that there are more interface in HGS filled BADCy composite, which will increase the internal friction. Figure 8 shows that the storage modulus of HGS filled BADCy composite is higher than that of BADCy. This increase is reasonable because the

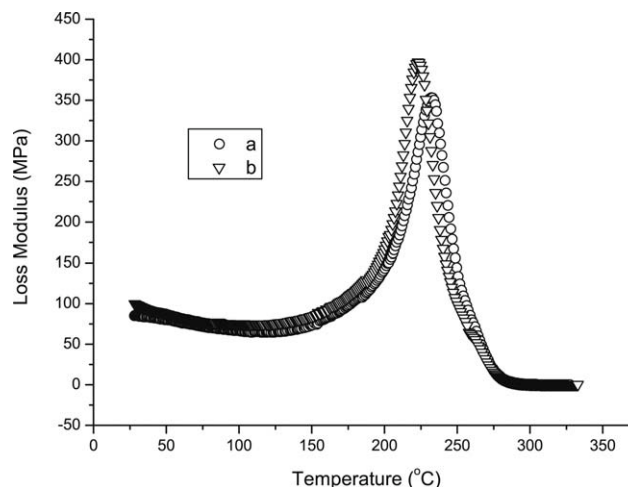


Figure 7 Loss modulus (a) Neat BADCy, (b) Composite of BADCy containing 30 wt % HGS.

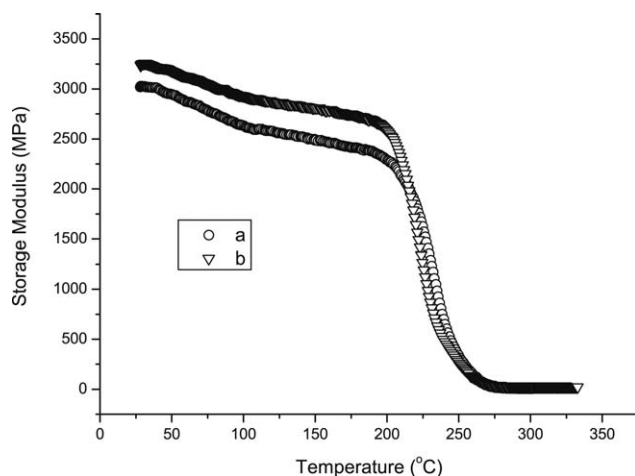


Figure 8 Storage modulus (a) Neat BADCy, (b) Composite of BADCy containing 30 wt % HGS.

storage modulus of HGS is much higher than BADCy and the higher storage modulus is reflected in the composite because of the interface layer which felt the HGS and BADCy matrix together.

CONCLUSIONS

HGS has catalytic effect to the polyclomerization of the BADCy, which is advantageous to reduce the maximal processing temperature. The impact strength and flexural strength are improved by 26 and 37%, respectively. The improvement of impact strength can be explained by crack–pinning–bowing mechanism and debonding mechanism. DMA results show that a tougher interlayer is formed between HGS and BADCy matrix, which maybe a reason resulting in the increase of flexural strength. The flexural modulus and storage modulus of BADCy

are also increased attributed to the higher modulus of HGS and good interface bonding between HGS and BADCy matrix.

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