

PREPARATION AND PROPERTIES OF FUMED SILICA/CYANATE ESTER NANOCOMPOSITES*

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Abstract Fumed silica/bisphenol A dicyanate ester (BADCy) nanocomposites were prepared by introducing different contents of nano-sized fumed SiO₂ into the BADCy matrix. Two different average primary particle diameters of 12 and 40 nm were chosen. Dibutyltin dilaurate (DBTDL) catalyst was chosen to catalyze the cyanate ester group into triazine group via cyclotrimerization reaction. The SEM micrographs indicated that the fumed SiO₂ particles were homogeneously dispersed in the poly(bisphenol A dicyanate) matrix by means of ultrasonic treatment and the addition of a coupling agent. The FTIR spectroscopy shows that, not only DBTDL catalyzes the polymerization reaction but also —OH groups of the SiO₂ particles surface help the catalyst for the complete polymerization of BADCy monomer. The thermal stability of the cured BADCy can be improved by adequate addition of fumed SiO₂. A slight increase in the dielectric constant and dielectric loss values were identified by testing the dielectric properties of the prepared nanocomposite samples. By increasing the SiO₂ content, there was a slight increasing in the thermal conductivity values of the tested samples. The obtained results proved that the fumed silica/BADCy nanocomposites had good thermal and dielectrical properties and can be used in many applications such as in the thermal insulation field.

Keywords: Cyanate ester; Fumed silica; Nanocomposites; Thermal conductivity; Dielectric properties.

INTRODUCTION

Cyanate ester resins (CE) are receiving a considerable attention owing to their highly desirable chemical, electrical, thermal and mechanical properties for several applications^[1–3]. Recent developments in electronic circuitry, wireless communications and also aerospace structural composites^[4–6] have pushed the demands for new materials that are light weight and yet possess a combination of excellent mechanical properties, good thermal stability and retention of these mechanical properties at high temperatures. Cyanate ester resins possess good mechanical properties at elevated temperatures up to 250°C compared to epoxy resins which retain their mechanical properties only up to 150°C which is unsuitable for aerospace applications. In addition, CE resins possess low dielectric constant ($\epsilon = 2.8\text{--}3.2$), low dielectric loss and relatively low moisture absorption and toxicity as compared with bismaleimide (BMI) resins. CE resins have emerged as a promising candidate that combines the advantages of both epoxy and BMI resins to meet the technological needs. With the rapid development of advanced industry, CE materials with unique functions are usually required. In recent years, many researches have focused on improving their performance by introducing different types of nano-sized

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fillers, such as nanoclays^[7–9], carbon nanotubes^[10, 11], carbon fibers^[12, 13] and polyhedral oligomeric silsesquioxanes (POSSs)^[14, 15].

Recently fumed silica has considered as one of the most important filler for inorganic/organic nanocomposite materials. Fumed silica, also known as pyrogenic silica because it is produced in a flame, consists of microscopic droplets of amorphous silica fused into branched, chainlike, three-dimensional secondary particles which then agglomerate into tertiary particles. Its three-dimensional structure results in viscosity-increasing, thixotropic behavior when used as a thickener or reinforcing filler. Fumed silica has an extremely large surface area and smooth nano-porous surface which could promote strong physical contact between the filler and the polymer matrix. The incorporation of fumed silica served to enhance the mechanical and rheological properties of the polymer and reduce thermal expansion without sacrificing glass transition or drastically altering curing kinetics. Fumed silica has been used extensively with thermosetting polymers such as epoxies^[16], polyurethanes^[17] and cyanate esters^[18, 19]. Goertzen *et al.*^[18] reported that fumed silica nanoparticles showed a slight catalytic effect on the curing behavior of bisphenol E cyanate ester (BECy).

In our work, a series of nano fumed SiO₂/bisphenol A dicyanate ester (BADCy) nanocomposites with different particle diameters and different contents of fumed silica were prepared. Dibutyltindilaurate (DBTDL) catalyst was chosen for catalyzing the cyanate ester group into triazine group *via* cyclotrimerization reaction. The preparation of CE nanocomposites with homogenous dispersed fumed silica was investigated. The effect of addition of nano-sized fumed silica on the thermal and dielectrical properties of fumed silica/BADCy nanocomposites was discussed in combination with the surface morphology observation. The thermal, dielectrical and morphological properties were investigated by using different tests such as FTIR, TGA, thermal conductivity, dielectric properties, SEM and TEM.

EXPERIMENTAL

Materials

BADCy (bisphenol A dicyanate ester, white particulate crystal with purity > 99.5% and mp = 79°C) was purchased from Shanghai Hui Feng Trade Co., Ltd. Hydrophilic fumed silica (two different types) were supplied by Degussa (Frankfurt, Germany) under the trade names of AEROSIL-200 (average primary particle diameter of 12 nm) and AEROSIL-(TT-600) (average primary particle diameter of 40 nm). γ -Aminopropyl triethoxysilane (APTES) coupling agent was purchased from Nanjing Shuguang Chemical Group Co., Ltd. China. Dibutyltindilaurate (DBTDL) used as a catalyst for BADCy and was purchased from Alfa Aesar Company, China.

Preparation of Fumed Silica/ BADCy Nanocomposites

Fumed silica was dried under vacuum at 110°C for 4 h to get rid of water. BADCy monomer was preheated at 90°C in an oil bath till a complete melting occurred. Fumed silica was added during stirring of the monomer with a 25 mm diameter high-shear blade at 600 r/min, and after keeping mixing for about 15 min the mixture was ultra-sonicated for 5 min by using a Fisher Model 100 Sonic Dismembrator with 3.2 mm diameter probe tip at a frequency of 23 kHz to achieve good dispersion. Add 5 wt% APTES and keep mixing for about 15 min then sonicate again. A predetermined amount of catalyst (DBTDL) was added during stirring of the mixture. The temperature of the mixture was maintained at 90°C throughout the entire process. Finally, the mixture was poured into a preheated stainless steel mold at 90°C in a convection oven for the final curing process. The mold was degassed for 1.5 h under vacuum, after that the mixture was cured at a programmed heating regime 160°C/2h + 180°C/2h + 200°C/2h then post cured to 250°C for 4 h in an air circulated oven and cooled to ambient temperature. Pure BADCy resin was cured in the same thermal process. All samples were dried at 120°C under vacuum for 6 h and kept in a dry environment prior to testing. For 12 nm and 40 nm particles, series of nanocomposites with the SiO₂ content of 0 wt%, 1 wt%, 2.5 wt%, 5 wt% and 10 wt%, were prepared by the similar procedure respectively.

Characterization

Transmission electron microscopy (TEM) tests of fumed silica with different grain sizes (12 nm and 40 nm) were done by using a JEM-2100F electron microscope purchased from JEOL Company. Scanning electron micrographs (SEM) were performed on a HITACHI S-4800 instrument. The fracture surface of the composites was sputtered with a thin layer (about 10 nm) of gold by vapor deposition on a stainless steel stub using a Polaron SC502 vacuum sputter coater. Fourier transform infrared spectroscopy (FTIR) tests were taken by using a WQF-300 FTIR spectrometer that was purchased from Beijing Optical Instrument Factory in China. The specimen was prepared by grinding the fumed silica/BADCy composite samples with potassium bromide (KBr). Thermal gravimetric analysis (TGA) tests were done by using a NETZSCH STA-449F3 instrument in the temperature range from room temperature till 650°C at a heating rate of 10 K/min under nitrogen atmosphere. Dielectric properties were measured by using a Precision Impedance Analyzer (Agilent 4294 A) of high frequency manufactured by Shanghai Aishi Electrical Instrument Corporation, China. Thermal conductivity tests were done by using a NETZSCH LFA-427 apparatus.

RESULTS AND DISCUSSION

Preparation and Characterization of Fumed Silica/BADCy Nanocomposites

Nano-sized fumed silica/bisphenol A dicyanate (BADCy) composites were prepared by incorporation of nano-sized fumed silica with different contents into the BADCy matrix. Two different average primary particle diameters of 12 and 40 nm were chosen. Figures 1(a) and 1(b) show TEM micrographs of the 12 nm and 40 nm fumed silica particles, respectively.

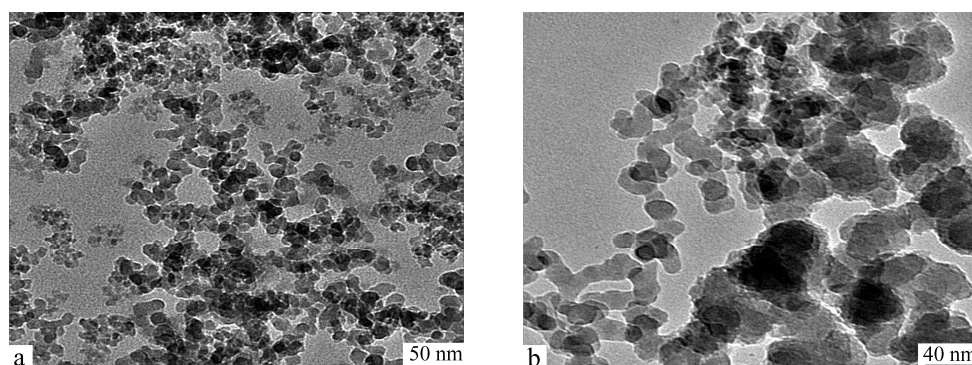


Fig. 1 TEM micrographs of fumed silica nanoparticles (a) 12 nm and (b) 40 nm

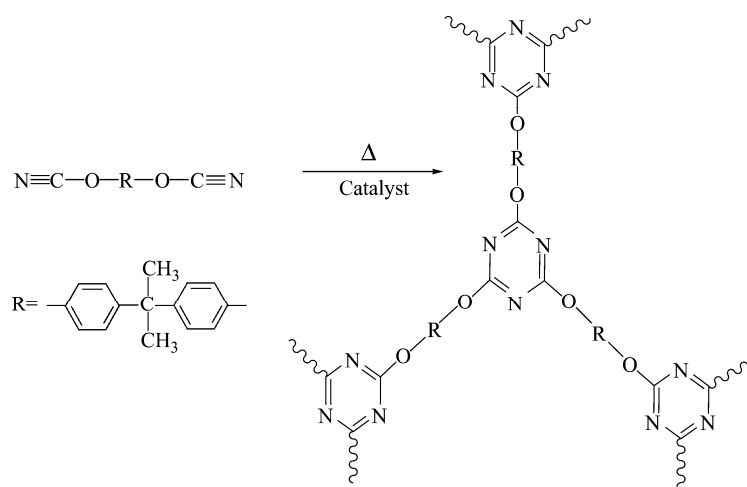


Fig. 2 Polymerization route of BADCy through the formation of triazine rings

A mixture of nano sized fumed silica /BADCy was prepared by adding fumed silica particles to the molten BADCy, and then the mixture was sonicated well to achieve good dispersion. BADCy monomer can not be fully polymerized so that dibutyltin dilaurate (DBTDL) catalyst was chosen for catalyzing the cyanate ester group into triazine group *via* a cyclotrimerization reaction as shown in Fig. 2. Curing and post-curing processes were done for the obtained mixture. A series of fumed silica/BADCy nanocomposites with different particle diameters and different contents of fumed silica were prepared.

The chemical structure of the post-cured samples was characterized by FTIR. Figure 3 shows the FTIR spectra of the BADCy monomer, cured BADCy and fumed silica/BADCy nanocomposites. From the figure, the intensity of the absorbed peak of cyanate ester group at 2230 cm^{-1} decreased gradually by increasing the content of fumed silica filler. Simultaneously, the intensity of the two peaks of triazine ring at 1360 and 1570 cm^{-1} had a gradual increase. From the cured BADCy spectrum, we can see a small peak of cyanate ester group still exists after post curing. That is because DBTDL catalyst is not enough for complete polymerization of the BADCy monomer. So that $-\text{OH}$ groups of fumed silica particles surface helped DBTDL catalyst for the complete polymerization of BADCy monomer. This indicates that the curing reaction took place and the filler content affected the conversion of cyanate group to triazine ring^[18]. Also it is clear from the spectrum of the cured BADCy nanocomposite with 10 wt% fumed silica, that the cyanate ester group absorption peak has completely disappeared which means that fumed silica has a catalytic effect on the polymerization of BADCy monomer.

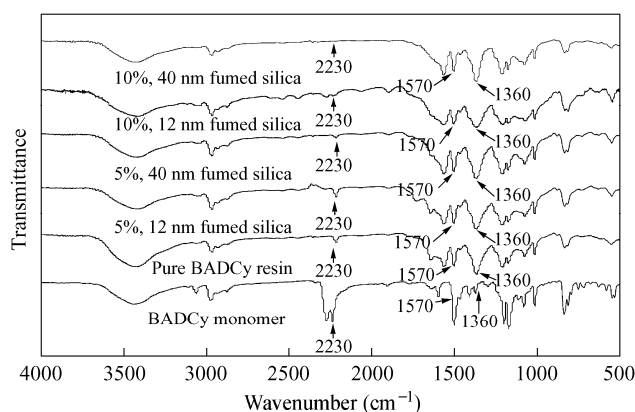


Fig. 3 FTIR of pure BADCy and cured fumed silica/BADCy nanocomposites

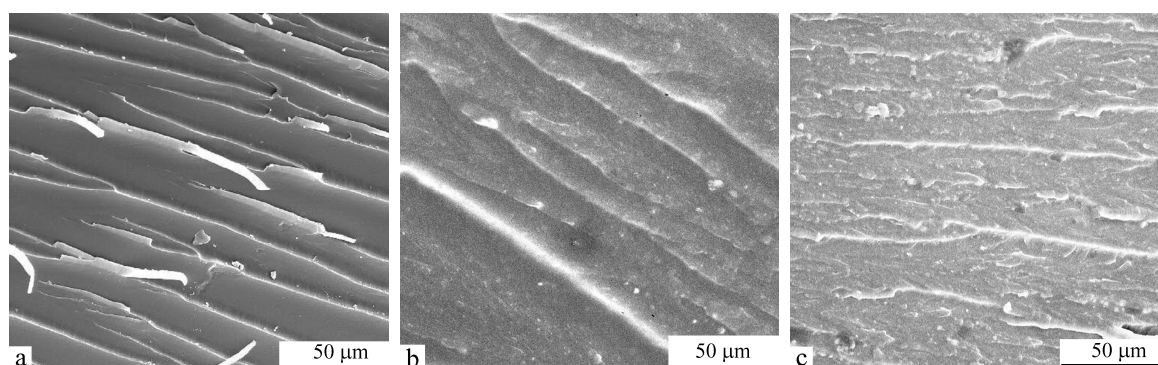


Fig. 4 SEM cross-section micrographs of (a) pure BADCy resin, (b) cured fumed silica (10 wt%, 12 nm)/BADCy nanocomposite and (c) cured fumed silica (10 wt%, 40 nm)/BADCy nanocomposites

Figure 4 shows SEM micrograph of the cross section morphology of fumed silica/BADCy nanocomposites. The SEM micrographs show that small white particles of fumed silica exist in the cured BADCy matrix and are

homogeneously dispersed by means of ultrasonic treatment and the addition of coupling agent. It is clear that the cured BADCy as most thermosetting resins has a smooth surface, but when it forms composites with fumed silica, it has rough surfaces. Also Fig. 4 shows that the composite contains 40 nm fumed silica has rougher surface than that of the 12 nm one.

Dielectric Properties of Cured Fumed Silica/BADCy Nanocomposites

The dielectric permittivity of cured fumed silica/BADCy nanocomposites was measured over a wide range of frequency using dielectric spectroscopy. In the present case, the results (Fig. 5) show that the dielectric constant has a slight increased with increase of fumed silica content. When the content of fumed silica was 10%, the dielectric constant (Table 1) was 3.38 and 3.48 for composites with silica particles of diameters 12 nm and 40 nm, respectively which were relatively higher than that of the pure BADCy resin ($\epsilon = 3.18$). The dielectric constant of polymeric systems results from permanent dipole motions within the system. The cyanate ester resins have a characteristically low dielectric constant due to a low polarity of the central triazine ring. The addition of fumed silica filler, with its surface hydroxide groups being polar, was thought to act to increase composite dielectric constant. Also the increasing of the dielectric constant may be attributed to that the increase of fumed silica particles content increases the proportion of the interface between padding and polymer, which leads to enhance the dipole of the interface which in turn leads to a slight increase of dielectric properties values^[20–22]. The results (Table 1) also show that the dielectric loss ($\tan\delta$) has a slight increase with increasing of fumed silica content. When the content of fumed silica was 10%, the dielectric loss ($\tan\delta$) of the composites was 0.0089 and 0.0099 for composites with filler sizes of 12 nm and 40 nm, respectively which were relatively higher than that of the pure BADCy resin ($\tan\delta \approx 0.0066$). The results indicate that the dielectric performance of fumed silica/BADCy nanocomposites was enhanced by relatively high dielectric constant and dielectric loss.

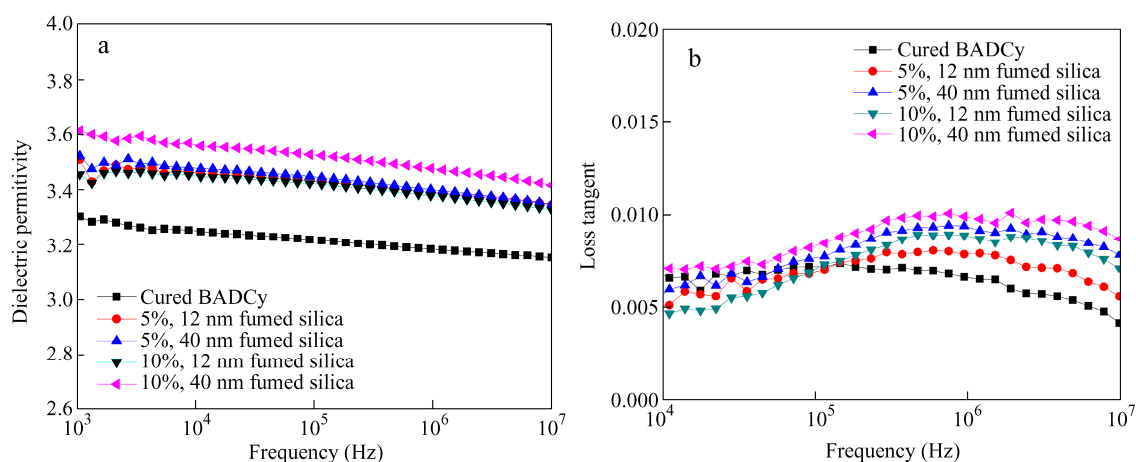


Fig. 5 Dielectric permittivity (a) and loss (b) of cured fumed silica/BADCy nanocomposites

Table 1. Dielectric properties of cured fumed silica/BADCy nanocomposites (at 10^6 Hz)

	Grain size	0%	5%	10%
Relative permittivity	12 nm	3.18	3.40	3.38
	40 nm		3.40	3.48
$\tan\delta$	12 nm	0.0066	0.0078	0.0089
	40 nm		0.0094	0.0099

Thermal Conductivity of Cured Fumed Silica/BADCy Nanocomposites

The influence of silica filler on the thermal conductivity of BADCy composites is depicted in Fig. 6. The results show that the coefficient of thermal conductivity has a slight increase with increasing of fumed silica content. When the content of fumed silica was 10%, the thermal conductivity coefficient values of the nanocomposites

are 0.3662 W/(m·K) for 12 nm silica and 0.2603 W/(m·K) for 40 nm silica, which are relatively higher in value compared to the pure BADCy resin ($\lambda = 0.1635$ W/(m·K)). The slight increase of the thermal conductivity of the nanocomposites is mainly from the moderate thermal conductivity of the silica (1.5 W/(m·K))^[20, 23]. Also as expected, addition of silica filler, itself a poor thermal conductor, does not result in a large increase in composite thermal conductivity. The maximum thermal conductivity coefficient values of fumed silica/BADCy nanocomposites are less than 0.37 W/(m·K) and the obtained nanocomposites can be applied in a thermal insulation field.

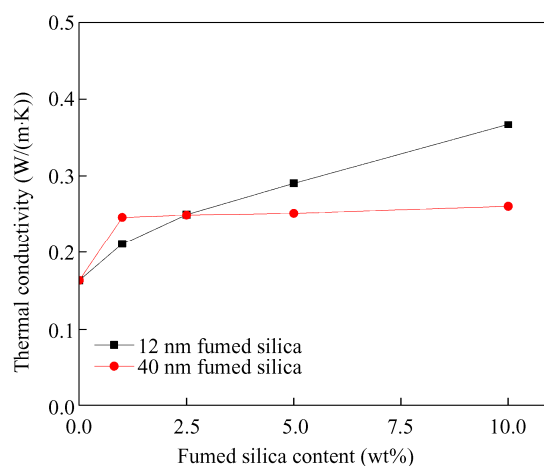


Fig. 6 Thermal conductivity of cured fumed silica/BADCy nanocomposites

Thermal Stability of Cured Fumed Silica/BADCy Nanocomposites

Thermal scans were carried out in the temperature range of 25°C to 650°C by the TGA method. Figure 7 shows the results of TGA analysis for fumed silica/BADCy nanocomposites with different content of fumed silica. All curves exhibit a stage of loss below 200°C due to the loss of the adsorbed water. Above 200°C, the curves are quite similar. Table 2 shows that the pure BADCy resin gives the decomposition temperature at 5% weight loss (T_5) of 425°C and the decomposition temperature at 10% weight loss (T_{10}) of 475°C. The temperature values (T_5) and (T_{10}) of different nanocomposites increase as the loading content of fumed silica increases. The fumed silica/BADCy nanocomposite shows its best thermal stability at 10 wt% loading content, at which decomposition temperature (T_5) are higher than that of the pure BADCy resin by 43 K and 50 K, and T_{10} values are enhancing

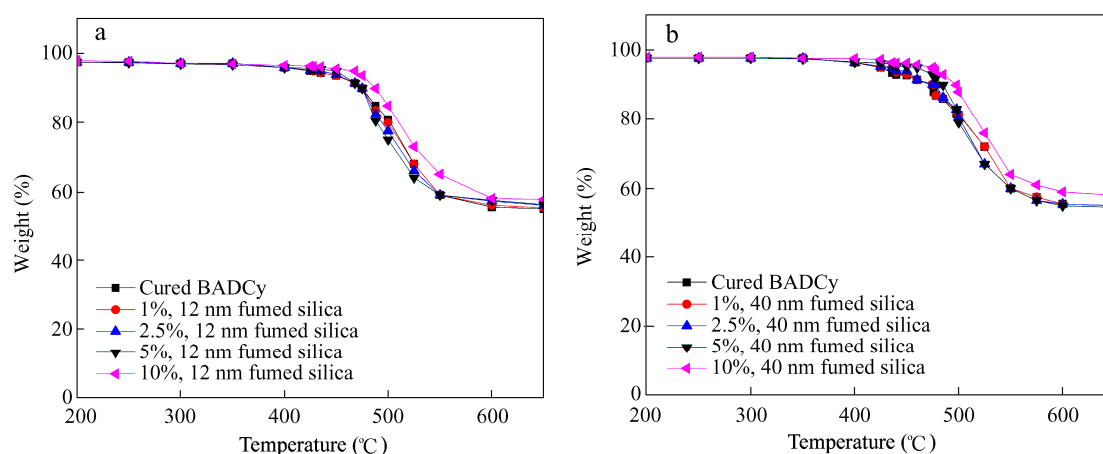


Fig. 7 TGA thermograms of cured fumed silica/BADCy nanocomposites with (a) 12 nm silica and (b) 40 nm silica

by 13 K and 23 K for filler size of 12 nm and 40 nm respectively. This reveals that an increase in the thermal stability has occurred which is due to good interaction/chemical bonding between the BADCy matrix and the fumed silica.

Table 2. Thermal properties of cured fumed silica/BADCy nanocomposites

Fumed silica content	T_5 (°C) ^a		T_{10} (°C) ^b	
	12 nm	40 nm	12 nm	40 nm
0%		425		475
1%	428	436	475	476
2.5%	435	440	475	478
5%	450	460	475	485
10%	468	475	488	498

^a T_5 : The decomposition temperature at 5% weight loss;

^b T_{10} : The decomposition temperature at 10% weight loss

CONCLUSIONS

A series of fumed silica/bisphenol A dicyanate ester (BADCy) nanocomposites with different particle diameters and different contents of fumed silica were prepared. The fumed silica particles were successfully dispersed in the BADCy matrix by means of the ultrasonic treatment and the addition of a coupling agent. The FTIR spectroscopy shows that, not only DBTDL catalyzes the polymerization reaction but also —OH groups of the SiO₂ particles surface help the catalyst for the complete polymerization of BADCy monomer. The thermal stability of the cured BADCy can be improved by adequate addition of fumed silica. A slight increase in the thermal conductivity and dielectric properties was identified by testing the prepared nanocomposite samples. The obtained results proved that fumed silica/BADCy nanocomposites had good thermal and dielectrical properties and can be applied in many applications such as in the thermal insulation field.

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