Preparation and Properties of Cyanate/Epoxy-based Composite with Thermal Conductive Silica Particles

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Abstract. Cyanate/epoxy (CE/EP) was added with surface-modified silica (\text{SiO}_2) particles to form a composite system. Microstructure of the composites was observed to find the dispersion effect of SiO\textsubscript{2} particles in the CE/EP matrix. Thermal conductivity, thermal stability and dielectric properties were also tested to investigate the effects of SiO\textsubscript{2} particles. CE/EP-based composite with 50 wt\% SiO\textsubscript{2} exhibited thermal conductivity of 0.492 W.m\textsuperscript{-1}.K\textsuperscript{-1}, thermal decomposition temperature of 420 °C and dielectric constant of 4.1 at 1 MHz.

1. Introduction
Signal transmission at high speed calls for the low dielectric properties of polymer matrix since large dielectric loss can result in signal attenuation to limit signal integrity of electronic products \cite{1, 2}. In addition, working reliability of electronic products could be challenged due to heat accumulation from high-power components \cite{3}. Thus, good heat dissipation and low dielectric loss of polymer are needed to meet the requirement of high-efficiency working for electronic products.
Cyanate resin exhibits good heat stability and dielectric performance \cite{4}. Cyanate/epoxy (CE/EP) blend from the coreaction of cyanate and epoxy monomers can also provide excellent performance due to the modification of network crosslinking density and the improvement of reaction extent form the individual functional groups. Thus, cyanate/epoxy is generally used as polymer matrix in composite system to further enhance its performance in the application of electronic products.
In this work, CE/EP was filled with modified silica (\text{SiO}_2) to enhance polymer performance. Thermal and dielectric properties were investigated to find out the effect of SiO\textsubscript{2} fraction on the composite system.

2. Experimental
SiO\textsubscript{2} particles were dispersed in \gamma-aminopropyltriethoxy silane (APS), ethanol and water solution with glacial acetic acid to regulate pH value of 3. The mixture was stirred to realize the adsorption of above silane agent for 1 h. After the centrifugation of above mixture at 2000 rpm for 15 min, the precipitate was then dried at 160 °C to completely remove the solvent. Thereby, surface-modified SiO\textsubscript{2} particles were obtained.
39 g CE and 8 g EP were blended to achieve a clear solution at 60 °C. Thereafter, modified SiO\textsubscript{2} particles with the fraction ranging from 10~50 wt\% were added into the clear polymer solution under
stirring for 2 h at 120 °C. Above mixture was then transferred into polytetrafluoroethylene mould when SiO\textsubscript{2} particles were well dispersed in the polymer solution. Above mixture was then curried for 6 h at 200 °C after air bubbles were avoided during the vacuumizing for 1 h. Thus, CE/EP-based composites with SiO\textsubscript{2} particles were finally obtained. CE/EP and CE/EP-based composites were shown in Fig.1.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{image1.png}
\caption{Optical images of CE/EP (a) and CE/EP-based composites (b)}
\end{figure}

Fourier-transform infrared (FT-IR) spectroscopy was used to determinate chemical composition of SiO\textsubscript{2} particles. Cross sections of SiO\textsubscript{2}/CE/EP composites were observed using a scanning electron microscope (SEM). A thermal conductive measurement was used to evaluate thermal conductivity of SiO\textsubscript{2}/CE/EP composites and CE/EP matrix. Thermo gravimetric analysis (TGA) of the composites was performed from room temperature to 650 °C at a heating rate of 10 °C/min under nitrogen atmosphere. Measurements of dielectric properties were performed at the frequency of 1 MHz on a broadband dielectric spectrometer.

3. Results and Discussion

3.1. Chemical Composition of SiO\textsubscript{2}

Silane coupling agents with silane functionalization at the surface of inorganic particles can improve wettability and dispersion of inorganic particles in the polymer matrix. SiO\textsubscript{2} particles were treated by APS to enhance their dispersion due to the decrease ofinterface energy. The chemical compositions of SiO\textsubscript{2} particles were characterized with FTIR spectra, as shown in Fig. 2. The peaks at 1085.8 cm\textsuperscript{-1} and 791.5 cm\textsuperscript{-1} was assigned to the characteristic absorption of SiO\textsubscript{2} particles. The absorption bands at 1090 cm\textsuperscript{-1} and 1220 cm\textsuperscript{-1} corresponded to stretching vibration of siloxane Si–O–Si and flexible vibration of Si–C in SiO\textsubscript{2} particles with surface treatment of APS(SiO\textsubscript{2}-APS). Thus, the interface of SiO\textsubscript{2} particles has adsorbed by the oligomeric silsesquioxane after the reaction of APS.
3. Microstructure of Composites.

Silane coupling agents with both inorganic and organic groups can absorb at the interface of inorganic fillers to create a wetting bridge to well blend with organic polymer [2, 5]. Fig. 3 presented the microstructure of SiO$_2$/CE/EP composites. SiO$_2$ particles were well dispersedly in the CE/EP matrix when the fraction of SiO$_2$ particles reached 10 wt% since SiO$_2$ particles with the absorption of silane coupling agent could provide stable surface for SiO$_2$ particles to break their mutual aggregation. However, contact chance between SiO$_2$ particles increased when 50 wt% SiO$_2$ was added into the CE/EP matrix. This could be due to gradual saturation of SiO$_2$ in polymer matrix.
3.3. Thermal Conductivity of Composites

Fig. 3 displayed the thermal conductivity of the composites with different fractions of SiO$_2$ filler. CE/EP matrix exhibited very low thermal conductivity of 0.225 W.m$^{-1}$.K$^{-1}$. However, the addition of SiO$_2$ particles into CE/EP matrix led to an obvious increase of thermal conductivity for the composite system. The thermal conductivity of the composite reached to 0.312 W.m$^{-1}$.K$^{-1}$ when 10 wt% SiO$_2$ particles were added into the polymer matrix. In addition, the thermal conductivity had a jump in the condition of the composites with more than 30 wt% SiO$_2$ particles. Especially, the thermal conductivity of the composite with 50 wt% SiO$_2$ particles dramatically increased to 0.492 W.m$^{-1}$.K$^{-1}$, 0.267 W.m$^{-1}$.K$^{-1}$ higher than the CE/EP matrix without filler. The phenomenon on the change of thermal conductivity for the compositesd could be attributed to inorganic higher thermal conductivity of SiO$_2$ particles and the formation of conductive network from more mutual contact between SiO$_2$ particles in high fraction [6].
3.4. Thermal Stability of Composites
TGA of CE/EP-based composites with different filler contents was measured to investigate the effects of SiO$_2$ particles on thermal stability, as indicated in Fig. 5. The composites exhibited an increase of thermal decomposition temperature from 300 °C to 420 °C when the fraction of SiO$_2$ particles increased from 10 wt% to 50 wt%. In addition, the char residue of the composites increased after thermal decomposition. CE/EP-based composite with 50 wt% SiO$_2$ particles had 51% char residue, 32% bigger than the case for the composite with 10 wt% SiO$_2$ particles. Generally, high concentration of SiO$_2$ particles as the obstacle could influence the copolymerization of long network chain for polymer to weaken the thermal stability of the composite system. However, SiO$_2$ particles performed not only the effect of heat absorption but also heat transmission to act probably as a barrier for oxygen diffusion so that the composites with high fraction of SiO$_2$ particles exhibited good thermal stability [7, 8].

3.5. Dielectric Constant of Composites
CE/EP with low dielectric constant was usually employed to avoid signal distortion for electric devices with high-speed signal transmission [2, 9]. However, the defect of low thermal conductivity for polymeric CE/EP matrix resulted in the limitation on its application of high-power electric devices. Thus, SiO$_2$ particles with low dielectric constant and high thermal conductivity were added into CE/EP matrix in order to improve its performance. Fig. 5 presented dielectric constant of the composites with SiO$_2$ particles at 1 MHz. Higher concentrations of functionalized particles resulted in higher dielectric constant of composites. At 50 wt% fraction in the CE/EP-based composite, surface-modified SiO$_2$ particles provided the dielectric constant of 4.1 at 1 MHz, 0.9 higher than that of CE/EP matrix. The
addition of SiO$_2$ particles in the composite system resulted in a small increase of dielectric constant due to the small difference of dielectric constant between SiO$_2$ filler and CE/EP matrix [10]. In this way, SiO$_2$ particles were a potential filler to modify the thermal and electric properties of polymeric CE/EP matrix.

![Figure 6. Dielectric constant of composites with different fractions of SiO$_2$ particles at 1 MHz](image)

4. Conclusions
In this study, SiO$_2$ particles with surface modification of $\gamma$-aminopropyltriethoxy silane were used as the inorganic filler to enhance the performance of polymeric CE/EP. SiO$_2$ particles were well dispersedly in the CE/EP matrix after their surface modification. Thermal conductivity of CE/EP-based composite increased to 0.492 W.m$^{-1}$.K$^{-1}$ when the fraction of SiO$_2$ particles reached 50 wt%. Higher fraction of SiO$_2$ particles led to better thermal stability of the composite system. SiO$_2$ particles with low dielectric constant caused limited influence on the dielectric constant of the composite system.

5. Acknowledgements
The authors gratefully acknowledge the support of the projects of National Natural Science Foundation of China (No.61240055 and No.61604034), and we also express our sincere thanks to project of science and technology planning of Guangdong Province China (No.2016B090918095).

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