Enhanced dielectric properties of epoxy resin with high content of nano-Al$_2$O$_3$ composites

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Abstract Epoxy resin was modified by adding different contents (30%, 60% wt.) of nano-Al$_2$O$_3$ particles, which were modified by silicon coupling agent KH560 (γ-amino propyl triethoxy silane), in the form of nano-Al$_2$O$_3$ particles/epoxy composites, via casting method to improve the dielectric properties. The chemical structures of modified and unmodified nano-Al$_2$O$_3$ particles and the morphologies of composites fractures were characterized by Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) respectively. And the thermal property and dielectric properties were also investigated. The results showed the modified nano-Al$_2$O$_3$ particles well dispersed in the epoxy matrix and the thermal stability of composites was improved. And the dielectric constant of the composites was up to 14 when the content of nano-Al$_2$O$_3$ was 60%, which was 2 times larger than that of pure epoxy. Moreover, the composites also exhibited good dielectric property under high frequencies ranged from 1x10$^7$ to 4x10$^7$ Hz.

Keywords. Epoxy matrix; nano-Al$_2$O$_3$; dielectric constant; dielectric loss.

1. Introduction
Epoxy resin composites with high filler content of Nano-Al$_2$O$_3$ are a kind of composite materials widely used in the aerospace or automotive industries due to its outstanding strength and inherent low density. Other advantages include an improved fatigue life, excellent corrosion resistance and reduced assembly costs. These properties make them a very attractive material for structural applications, especially in the aerospace industry due to the greater weight savings that results in improved performance, greater payloads, longer range and fuel savings [1-5]. Nano-structured nano-Al$_2$O$_3$, such as nanorods, Nan belts, and nanowires, has sparked great interest because they have many novel physical and chemical properties that are different from their bulk counterparts [6,7]. Although the electrochemical and optical properties of nano-Al$_2$O$_3$ nanomaterials had been extensively explored, until now, to our best knowledge, there is very little research on the dielectric properties of the polymeric composites enhanced by nano-Al$_2$O$_3$ nanostructures. To overcome these shortcomings, conductors were added into ceramic/polymer composites with a fixed loading of ceramics. Yu et al. [8] added different contents of carbon nanotubes (CNTs) into BaTiO$_3$/polypropylene (PP) composite with 40 wt% BaTiO$_3$. As the loading of CNTs increased, both dielectric constant and loss gradually increased, they remarkably jumped to 1000 and 300, respectively, when the content of CNTs was 3 wt%. Similar results were also reported by other groups[9, 10]. These results show that simply adding...
conductors into ceramic/polymer composites not only increases the dielectric constant, but also increases the dielectric loss; in addition, the ceramic phase still remains high loading. In this work, epoxy/nano-Al₂O₃ composites with high dielectric constant and low dielectric loss were prepared. Epoxy resin was selected as the host polymer matrix because of its perfect capacitor storage [11]. The relationship between the dielectric properties of composites and of nano-Al₂O₃ was analyzed. The variation of the dielectric properties of composites to frequency was also studied. A preliminary discussion was conducted to highlight the novelty of the dielectric properties of our proposed polymeric composite [12-14].

2. Experimental

2.1. Material
The nano-Al₂O₃ powder used in this research is a commercial product with a model number of XZ-L690 (Hefei Xiang Zheng Chemistry Technology Co., Ltd.), and the average diameter of which was 20 nm. γ-amino propyl triethoxy silage (KH-560) used as coupling agent was supplied by Jingzhou Chemical Group Co., Ltd., (Hubei, China). Ethyl alcohol (analytically pure), bought from Sichuan Chengdu Chemical Co., Ltd., China, was used as diluting agent. Liquid epoxy resin Biphenyl-A resin and liquid a curing agents were kindly supplied by the Chinese Academy of Engineering and Physics.

3. Characterizations.
FTIR spectra were performed by using smart part technique in the wavenumber range 4000-4 cm⁻¹ using Nicolet-5700 FTIR (Thermo Electron Scientific Instruments Corp) spectrophotometer. KBr disc method was used. The TGA and DTG curve was recorded with a TA instrument apparatus model TGA-Q500 (TA Instruments USA) using a heating rate of 10°C/min-1 in nitrogen atmosphere. The average masses of the samples were 3.5 mg. The morphological properties of the composites were analyzed by scanning electron microscope (SEM) on a Zeiss model EVO 18(Zeiss) microscope. Dielectric properties measurements were performed using an impedance analyzer (Agilent 4294A, USA) with 16451B Dielectric Test Fixture in the frequency range of 1x10⁷ Hz to 4x10⁷ Hz.

3.1. Surface Modification of Nano-Al₂O₃

![Image of hydrolytic progress of KH560 and modification on Nano-Al₂O₃](image)

Fig. 1. Hydrolytic progress of KH560 and modification on Nano-Al₂O₃

The modification of nano-Al₂O₃ with KH560 was carried out according to the scheme as shown in Figure 1. Nano-Al₂O₃ were introduced in porcelain crucibles and heated at 100°C for 1 h to remove the water. Firstly, the silicon coupling agent was 5-10 times diluted with anhydrous ethanol via the
sonication method. Secondly making the nano-Al\textsubscript{2}O\textsubscript{3} and the silicon coupling agent solution mixtures were heated to 80\textdegree{}C and subsequently stirred at 8000 rpm for another 30 min to allow nano-Al\textsubscript{2}O\textsubscript{3} and KH-560 to enough react. Lastly, the product was dried at 70-80\textdegree{}C for 48 h.

3.2. Preparation of epoxy/nano-Al\textsubscript{2}O\textsubscript{3} composites
The epoxy resin matrix composite filled with modified nano-Al\textsubscript{2}O\textsubscript{3} was prepared by molding. Specifically, modified nano-Al\textsubscript{2}O\textsubscript{3}, and Bisphenol-A resin were putting into beaker then were mechanically stirred for 1 h after 5 min curing agents B was putted. The obtained composites with content of nano-Al\textsubscript{2}O\textsubscript{3} 30\% and 60\% were prepared. And samples with 0\%, 30\%, 60\% nano-Al\textsubscript{2}O\textsubscript{3} were prepared by cast molding using acetone as diluent. Then curing procedure of these samples was heated at 80\textdegree{}C for 12 h. Lastly, the samples with a thickness of 2 nm were obtained.

3.3. FT-IR spectroscopic analysis of epoxy/nano-Al\textsubscript{2}O\textsubscript{3} composites
The FT-IR spectroscopy of the modified nano-Al\textsubscript{2}O\textsubscript{3} was shown in Fig. 2 (a) which revealed that the characteristic absorption bands for nano-Al\textsubscript{2}O\textsubscript{3} with silicon coupling agent. The absorption band at 3434 and 1630 cm\textsuperscript{-1} is due to the stretching vibration of -OH on the surface of nano-Al\textsubscript{2}O\textsubscript{3} while the modification of nano-Al\textsubscript{2}O\textsubscript{3} weakened obviously. The reason of nano-Al\textsubscript{2}O\textsubscript{3} surface water absorption decreased. Peaks at 2924 and 2865 cm\textsuperscript{-1} are due to the stretching vibration of -CH\textsubscript{2} of the silicon coupling agent. And peak at 1396 cm\textsuperscript{-1} is due to the stretching vibration of O-C-O of the nano-Al\textsubscript{2}O\textsubscript{3}. The bands at 1105 cm\textsuperscript{-1} are caused by the stretching vibration of Si-O. All of these adsorption bands can also be observed in the spectra of the prepared the KH560-Nano-Al\textsubscript{2}O\textsubscript{3}. These bands are common features of all the ferrites as reported in the literature\cite{14, 15}. These bands are clearly increased in the KH560-Nano-Al\textsubscript{2}O\textsubscript{3} compared with pure Nano-Al\textsubscript{2}O\textsubscript{3}. The results are indicating that nano-Al\textsubscript{2}O\textsubscript{3} was chemical combined with silicon coupling agent.

![Fig.2. FTIR (a) KH560-Nano-Al2O3 and (b) Nano-Al2O3 Powders](image-url)
3.4. Scanning electron microscopy of epoxy/nano-Al₂O₃ composites

The morphological photographs of nano-Al₂O₃/epoxy nano-composites were examined by SEM micrographs as shown in Figs.3. [16, 17]. They consist of agglomerations of crystallites having similar shape. It is obvious that the nanoparticles are tightly embedded in the epoxy matrix with evidence of composite formation. This indicates good cohesion between the nanoparticles and matrix, which is very important to reach a strong interfacial adhesion. In addition, the micrograph shows a good distribution of nanoparticles within the polymer matrix. High compatibility between the nanoparticles and polymer matrix is observed.

Fig. 3. SEM micrographs for nano-Al₂O₃/epoxy composite of (A) 0%, (B) 30%, (C) 60%.
4. Results and discussion

4.1. Thermal stability of epoxy/nano-\(\text{Al}_2\text{O}_3\) composites

![TG curves of neat epoxy resin as well as its nano-Al\(_2\)O\(_3\) composites under nitrogen atmosphere](image1)

**Fig. 4.** TG curves of neat epoxy resin as well as its nano-Al\(_2\)O\(_3\) composites under nitrogen atmosphere

![DTG curves of neat epoxy resin as well as its nano-Al\(_2\)O\(_3\) composites under nitrogen atmosphere](image2)

**Fig. 5.** DTG curves of neat epoxy resin as well as its nano-Al\(_2\)O\(_3\) composites under nitrogen atmosphere
Table 1. TGA data nano-Al₂O₃ epoxy composite under nitrogen Atmosphere

| Sample            | T_{max} (°C) | R_{450} |
|-------------------|--------------|---------|
| Pure epoxy        | 340          | 12.2    |
| 30%-nano-Al₂O₃    | 385          | 28.3    |
| 60%-nano-Al₂O₃    | 391          | 31.3    |

From Fig. 4 it can be seen that the thermal stability of epoxy/nano-Al₂O₃ composites increases with the content of nano-Al₂O₃. In the literature there are many interesting reports dealing with the role of inorganic additives in influencing the thermal stability of epoxy resin composites. Lakshmi et al. [18] reported an enhancement effect of montmorillonite (MMT) clay on improving the thermal stability of epoxies composites. Likewise, Guo et al. [19] reported an improvement of the thermal stability of the cocamidopropyl betaine epoxy resin via the formation of epoxy nano-composites with MMT-clay. This was attributed to the protection of epoxy polymer chains present between hard MMT-clay nanolayers that act as a barrier protecting from volatilizing the epoxy polymer matrix [18]. Thus it is plausible to suggest that the added nano-Al₂O₃ nanoparticles could prevent from degrading the epoxy matrix. The parameter R_{450} (Table 1) T_{max} (initial decomposition temperature) and R_{450} (the temperatures of the finally residual amount weight loss, respectively), refer to the residue remaining at 450 °C. It is seen that even after complete degradation; char residue is around 12.2% for neat epoxy resin whereas higher values 28.3-31.3%, are obtained for the different composites. The highest residue values were observed for the samples having 30% and 60% for the composites containing nano-Al₂O₃, whereas the lowest one was exhibited by the pure epoxy. Such residue is due to the presence of thermally stable char together with nano-Al₂O₃ phases. The increased rate of mass loss beyond 350 °C, Fig. 4, Illustrates the continued degradation of the for all the nano-Al₂O₃ containing samples. The temperature at which decomposition is maximum (T_{max}) can be calculated from the DTG curves presented in Fig. 5. In this context, char residue was obtained during the thermal decomposition of epoxy resins/nano-Al₂O₃ composites [20]. The char at 450 °C of the composites increased gradually with increasing nano-Al₂O₃ content [20]. Concurrently, Wu et al. [21] has reported the formation of a char with excellent thermal stability via the thermal decomposition of water resistance of epoxy/microencapsulated ammonium polyphosphate composite.
4.2. Dielectric properties of epoxy/nano-Al₂O₃ composites

![Graph showing dielectric constant vs frequency for different content of nano-Al₂O₃.](image)

**Fig. 6.** Dependence of the dielectric constant of the epoxy resin composites on content of nano-Al₂O₃ measured at room temperature.

![Graph showing dielectric loss vs frequency for different content of nano-Al₂O₃.](image)

**Fig. 7.** Dependence of the dielectric loss of the nano-Al₂O₃ composites on the content of nano-Al₂O₃ measured at room temperature.

The data of impedance and phase angle measured were converted into the relative dielectric constant and dielectric loss, considering the appropriate geometric coefficient. From Fig.6. Compared with the reported epoxy resin composite material with low content of Al₂O₃ composite, the dielectric...
constant of nano-Al2O3 composites is significantly higher at low filler content [22-26]. Furthermore, it can be obviously found that the nano-Al2O3 composites possess higher dielectric constant than other semiconductor/polymers nano-composites. Thus, it indicates that the incorporation of nano-Al2O3 into epoxy resin is an effective way to improve its dielectric constant. Dielectric loss is another important dielectric property for capacitors. It should be as low as possible in an ideal capacitor. It can be seen from Fig. 7 that the dielectric loss increases with the increase of nano-Al2O3. When the content of nano-Al2O3 below 30%, the dielectric loss of the composites is lower than 0.07, which is still acceptable for practical applications. Generally, for the composites, the increase of dielectric loss is mainly attributed to the enhancement of charge carriers in the system induced by the fillers. Percolation phenomenon widely exists in polymer composites with conducting or semiconducting fillers [26, 27]. When the concentration of fillers approaches to the percolation threshold, dielectric constant of polymers increases dramatically. The micro-capacitor model is proposed to be responsible for high dielectric constant at percolation threshold [27]. The micro-capacitor model assumes that the dispersion of fillers into polymer matrix is equal to the introduction of a large amount of micro-capacitor when the volume fraction of the fillers is close to the threshold. Furthermore, the increase of dielectric loss is also ascribed to the high leakage current at percolation threshold. Therefore, to achieve good dielectric properties, the content of nano-Al2O3 for the epoxy resin composites should not be over 60%. The dependences of the dielectric constant and dielectric loss of the composites on the frequency are shown in Fig. 8 and Fig.9 respectively. The dielectric constant of pure epoxy exhibits low value at the same high frequency. While dielectric constant become higher with the increasing of nano-Al2O3, and get the highest value of 14 when the content of nano-Al2O3 is 60%. The reason for such frequency dependence is that interfacial polarization and orientation polarization of dipoles can follow with external electric field gradually and therefore leads to the increases of dielectric constant [28].

5. Conclusion
A kind of polymeric composites consisting of epoxy resin and nano-Al2O3 were synthesized by a facile processing procedure. The dielectric constant of the composites shows remarkable increase with the increase content of nano-Al2O3. When the content of nano-Al2O3 is 60%, the dielectric constant of the composites can reach 14. The increase of frequency is found to impose a negative effect on the dielectric constant of the composites. The dielectric loss is not affected by the variation of frequency significantly. The produced high dielectric constant and low dielectric loss of epoxy/nano-Al2O3 composites make it a capacitors material.

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