

Study on the Properties of Nano-Al₂O₃/Phenyl Silicone Rubber Composites

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Keywords: Nano-Al₂O₃, Phenyl Silicone Rubber, Composites, Low Loading.

Abstract. Nanoparticles filled silicone rubber is widely used in electric encapsulation for its excellent insulating properties, thermal and optical stability. This paper focuses on the effect of nano-Al₂O₃ on the properties of phenyl silicone rubber at low loading ($\leq 1\%$). Nano-Al₂O₃ was modified by silane coupling agent (KH550) and added to phenyl silicone rubber by solution mixing method. The mixture was cured at room temperature to obtain nano-Al₂O₃/phenyl silicone rubber composites. The structure of modified nano-Al₂O₃ and the resultant composites were characterized by FT-IR spectra, TGA, UV-vis spectroscopy, thermal conductivity meter and tensile testing. The results indicate that the composites showed high thermal conductivity of $0.216 \text{ W m}^{-1} \text{ K}^{-1}$, high tensile strength of 0.25MPa with the addition of 0.06wt% nano-Al₂O₃. The transmittance of phenyl silicone rubber is gradually decline with the increase of filler loading. In the ultraviolet-visible region, the transmittance of composites is lower than that of pure phenyl silicone rubber. Nano-Al₂O₃ shows a high UV shielding ability comparing to pure silicone rubber. The thermal and mechanical properties of modified silicone rubber do not improve obviously at the low filler loading.

Introduction

Silicone rubber is stable in a wide range of temperatures and has lots of distinctive characteristics, such as excellent elasticity, oxidation resistance, aging resistance, low toxicity and electrical-insulating properties[1-4]. Phenyl silicone rubber is one of the specific silicone rubber, which is formed by introducing a certain proportion of methyl phenyl siloxane or diphenyl siloxane segments into the main chain of dimethyl silicone rubber. It is commonly used as electronic packaging materials. However, the pure phenyl silicone rubber shows poorer heat-conducting and dielectric properties, which limits its application as flexible dielectric materials. In order to broaden the application of phenyl silicone rubber, we require to modify silicone rubber with higher thermal conductivity and electrical insulation, which can be achieved by the use of suitable heat conductive and electric insulated fillers such as nano AlN, SiC, Al₂O₃[5], etc.

Alumina (Al₂O₃) exists in a great variety of metastable transition phase commonly, including γ -, δ -, θ -, η -, χ -, and κ -Al₂O₃, as well as stable α -Al₂O₃ phase. Nano-Al₂O₃ as modified filler, not only has advantageous structure of uniform composition, fine particle size, narrow particle size distribution, no agglomeration, large surface area, but also has high conductive resistivity, high hardness, high melting point, excellent chemical stability[6-10].

The effects of content and particle size of nano-Al₂O₃ filler on the electrical conductivity, thermal conductivity and mechanical property of silicone rubber are already investigated[11-14]. However, reports with phenyl silicone rubber as the polymer matrix are relatively few. In this paper, γ -Al₂O₃ was chosen as filler and modified by silane coupling agent. The effect of low filler loading on the

thermal conductivity, transmittance and mechanical properties of the composites were investigated by thermal conductivity meter, UV-vis spectroscopy and tensile testing.

Experimental

Materials

Nano- Al_2O_3 (~20nm), γ -crysta, was provided by Beijing daoking nano technology, China.

Phenyl silicone rubber used in this study, is α,ω -dihydroxy poly dimethyl diphenyl siloxane (108-1), was purchased from Shanghai resin factory, China. The phenyl content was 9.3wt%.

Dibutyltin dilaurate (DBTDL) and tetraethyl orthosilicate (TEOS) used as catalyst and curing agent, were purchased from Sinopharm Chemical Reagent Co., Ltd, China.

Silane coupling agent(KH550), ethanol (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd, China.

Preparation of KH550 Modified Nano- Al_2O_3

The nano- Al_2O_3 was drying in the vacuum at 80°C for 3h to exclude the impact of air and moisture. Amounts of nano- Al_2O_3 were sonicated in anhydrous ethanol for 20min to form homogeneous dispersion. Moderate KH550 was added in the dispersion. The mixture was stirred and refluxed at 80°C for 3h. After cooling to room temperature, the resultant was centrifuged and washed repeatedly with anhydrous ethanol to remove the residual KH550. The solid product was dried in vacuum oven at 60°C overnight. After grinding, KH550 modified nano- Al_2O_3 (KH550/nano- Al_2O_3) was obtained.

Preparation of Nano- Al_2O_3 /phenyl Silicone Rubber Composites

The filler were dispersed in ethanol by ultrasonic for 20min. The dispersion was mixed with phenyl silicone rubber uniformly. The mixture was dried in vacuum oven at 80°C. Then 5wt% TEOS and 2wt% DBTDL were added to the mixture with stir. The mixture was then poured into round polypropylene mold and vacuumed at room temperature for 30min to remove bubbles generated during the process of mixing. At last, the mixture was cured at 80°C for 2 h to obtain nano- Al_2O_3 /phenyl silicone rubber.

Characterization

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 380 (USA) Fourier transform infrared spectrometer, with KBr pellets, scanning from 4000-400 cm^{-1} repeatedly for 8 times.

Weight loss of the nano- Al_2O_3 was characterized by thermogravimetric analysis (TGA) using a TGA-7 thermogravimetric analyzer (PerkinElmer, USA) under air atmosphere from 40 to 800°C at a heating rate of 10°C/min.

The transmittance of nanocomposites was measured by 754N ultraviolet visible (UV-Vis) spectrophotometer (Shanghai APL instrument, China), on the base of air, in the range of 200-1000nm at a resolution of 1nm.

Thermal conductivity was investigated under steady state condition, utilizing LFA447 laser thermal conductivity meter (NETZSCH instruments North America, LLC, Germany) according to ASTM E-1461. This thermal analyzer was chosen over the flash method under 25°C. The samples were cut into circular with the diameter of 12.7mm and thickness of 2mm.

The mechanical properties of the cured silicone rubber were tested by GALDABINI SUN500 tensile tester (Italy) at room temperature. The samples were cut into dumbbell shape. The extension rate was 50mm/min.

Results and Discussion

Characterization of Modified Nano- Al_2O_3

FT-IR spectra of modified nano- Al_2O_3 (Fig.1) were tested to confirm the effective functionalization of nano- Al_2O_3 with KH550. It is shown that the stretching and bending vibration absorption peaks at 3436 cm^{-1} and 1630 cm^{-1} represent -OH and H-OH, indicating the existence of hydroxyl on the nano- Al_2O_3 surface. After the modification with KH550, the absorption position and peak intensity of nano- Al_2O_3 particles changes obviously. The absorption peak at 1566 cm^{-1} represents N-H bending, the absorption peak at 2930 cm^{-1} represents the stretching vibration of $-\text{CH}_2$, 1440 cm^{-1} and 1340 cm^{-1} represent the deformation vibration of $-\text{CH}_2$ and $-\text{CH}_3$, and 1018 cm^{-1} represents the Si-O-Si bond, which indicate that KH550 has been grafted onto the surface of Al_2O_3 nanoparticles.

Thermal gravimetric analysis (TGA) was allowed to quantitative analyze the grafting density of the KH550 units on the surface of nano- Al_2O_3 accurately. The weight loss of nano- Al_2O_3 and KH550 modified nano- Al_2O_3 in the range of 40 to 800°C is shown in Fig.2. The thermal stability of $\gamma\text{-Al}_2\text{O}_3$ is relatively stable and no decomposition under 800°C . The weight loss in the temperature range of 40 to 800°C is only 12.32% , mainly the removal of surface adsorbed water. However, the thermal stability of modified nano- Al_2O_3 is worse than the unmodified nano- Al_2O_3 , mainly contributed to the thermal decomposition of KH550 on the surface of nano- Al_2O_3 . Thus the amount of grafted KH550 on nano- Al_2O_3 can be calculated from the TGA data by measuring the difference of weight loss, is about 26.14% .

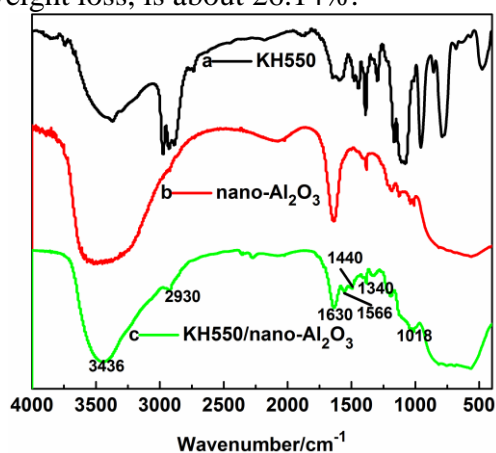


Fig.1 FT-IR of KH550, nano- Al_2O_3 and KH550/nano- Al_2O_3

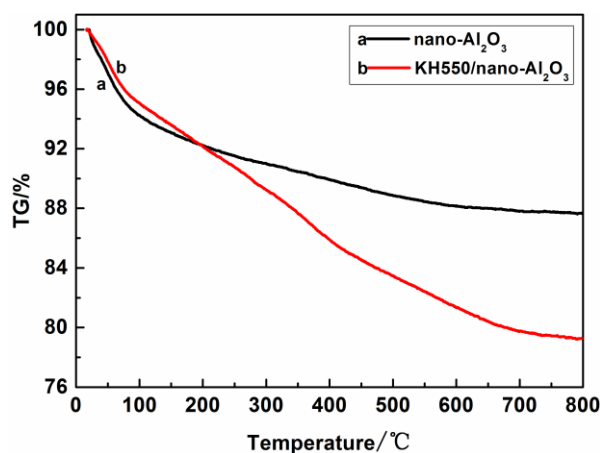


Fig.2 TGA curves of nano- Al_2O_3 and KH550/nano- Al_2O_3

Optical Property

Nano- Al_2O_3 , with remarkable dispersion, is easy mixing with dispersant, therefore it has excellent transparency. The transmittance of the phenyl silicone rubber composites is shown in Fig.3. It can be seen from Fig.3, the transmittance of phenyl silicone rubber composites drops with the increase of nano- Al_2O_3 . The transmittance of pure phenyl silicone rubber is about 90% in the visible wavelength region, which indicates the optical transparency of phenyl silicone rubber is very good. The composites, with the addition of nano- Al_2O_3 , displays obvious shielding effect in the ultraviolet region, especially in the UV ($320\text{-}400\text{nm}$) region reveals remarkable absorption effect. In addition, when the mass content of nano- Al_2O_3 is 0.3% , the transmittance of phenyl silicone rubber composites has a sharp drop. This maybe that the increase amount of nano- Al_2O_3 results in nano- Al_2O_3 agglomerating in the phenyl silicone rubber. The agglomeration of nano- Al_2O_3 can effectively shield and absorb ultraviolet light, but also result in the transmittance of visible light declining inevitably.

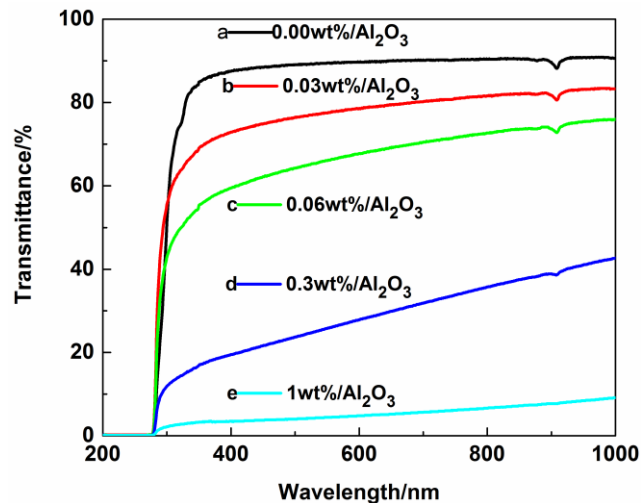


Fig.3 The transmittance of composites with various nano-Al₂O₃ contents

Thermal Property

γ -Al₂O₃ possesses favorable thermal stability. Fig.4 displays the influence of nano-Al₂O₃ on the thermal conductivity of composites. It is observed that the thermal conductivity of various nano-Al₂O₃ filled phenyl silicone rubber with the filler loading is from 0.13 W m⁻¹ K⁻¹ up to 0.216 W m⁻¹ K⁻¹. In the dispersion system with low mass content of nano-Al₂O₃, few particles in the composite system touch each other, and the polymer matrix is also continuous. The contribution of nanoparticles on the thermal stability of the composites seems to be less than the phenyl silicone rubber matrix. While the filler mass content is more than 0.06%, the thermal conductivity starts to decrease. It may be due to the agglomeration of some nano-Al₂O₃ particles in the phenyl silicone rubber. Amounts of nano-Al₂O₃ particles touch each other to hinder the formation of conductive chains, which greatly contribute to the decrease of thermal conductivity of composites.

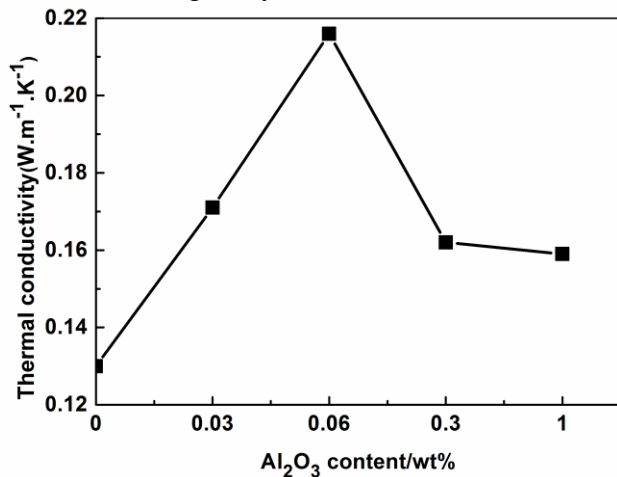


Fig.4 The effect of nano-Al₂O₃ on thermal conductivity of phenyl silicone rubber

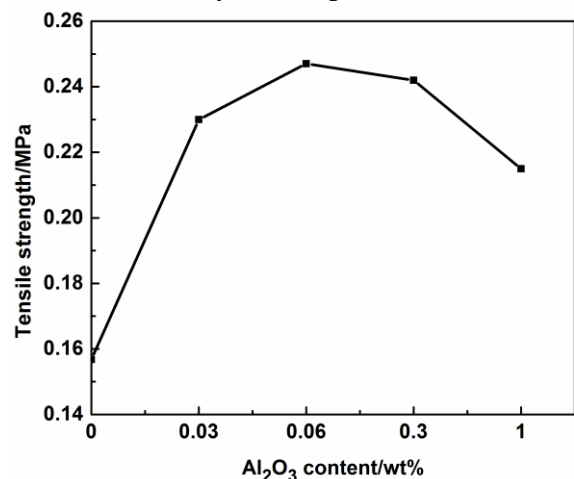


Fig.5 The tensile strength curve of composites with various nano-Al₂O₃ contents

Mechanical Property

As is well known, nanoparticles have predominant reinforcing effect to silicone rubber^[15]. Nano-Al₂O₃ has natural characteristics of high strength, high hardness. The tensile strength of the phenyl silicone rubber filled with different content of nano-Al₂O₃ is shown in Fig.5. While the content of nano-Al₂O₃ is less than 1wt%, the tensile strength of phenyl silicone rubber composites increases little as the raise of the filler content, with the highest value less than 0.25MPa at the mass

content of 0.06%. A small amount of nano- Al_2O_3 added into phenyl silicone rubber will increase the crosslinking density of the phenyl silicone rubber, meanwhile increase the tensile strength. While excess nano- Al_2O_3 will weaken the interaction between the polymer chain segments. And the interface interaction between the two increase with the increase of the filler loading, so the tensile strength decreased.

Conclusion

In this paper, the effects of nano- Al_2O_3 on the properties of phenyl silicone rubber were investigated. The results revealed that the low loading fillers had a little influence on thermal and mechanical properties. When the addition of nano- Al_2O_3 is 0.06wt%, the composites showed higher thermal conductivity of $0.216 \text{ W m}^{-1} \text{ K}^{-1}$ and higher tensile strength of 0.25MPa, comparing to the pure phenyl silicone rubber. However, a change of nano- Al_2O_3 concentration had great effect on the transmittance of the phenyl silicone rubber. The mass content of nano- Al_2O_3 is 0.3%, the transmittance of composites had dropped to 42.7% in the visible region, nearly half of the pure phenyl silicone rubber, which indicates that nano- Al_2O_3 has a high light absorption to phenyl silicone rubber.

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