Effect of Nano-ZrO_2 on Properties of Room Temperature Vulcanization Phenyl Silicone Rubber

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Abstract. In this study, nano-ZrO_2, which was treated by silane couple agent, incorporated in phenyl silicone rubber at low concentration (≤3.0%) and cured by Room Temperature Vulcanized (RTV) method. The effects of different additive amount of nano-ZrO_2 on the mechanical properties, thermal conductivity and electrical conductivity of phenyl silicone rubber were investigated. The thermal conductivity, tensile strength and volume resistivity of nanocomposites increased firstly and then decreased. The dielectric constant of nanocomposites decreased firstly and then increased with the content of nanoparticles. We were interested to find that phenyl silicone rubber had a maximum thermal conductivity (0.399W/(m K)), a maximum volume resistivity ($1.08\times10^{12}\Omega\cdot$cm)and a minimum dielectric constant (2.775), with a definite total mass fraction of the particle (0.06%). Compared with the thermal comductivity of pure silicone rubber (0.130W/(m K)), it increased more than three times in the addition amount of 0.06wt%. Moreover, the silicone rubber keeps a high tensile strength.

Introduction

Light emitting diode (LED) has received a great deal of attention for lighting in industries and research because of their energy efficiency and durability. Thus, LED is expected to be the most powerful candidate for lighting sources in the near future[1-4]. As a packaging material of LED, phenyl silicone rubber is an important material among silicon material, which is formed by introducing phenyl into the main chain of dimethyl silicone rubber. With excellent oxidation resistance, radiation resistance and low temperature flexibility make this class of materials very attractive candidate for use in the outdoor applications[5].

However, with the power of LED (light emitting diode) increased, it produced more heat and ultraviolet radiation, which usually leads to the epoxy resin cracking and yellowing, so HB-LED (high brightness light emitting diode) usually use high temperature resistance and resistance to ultraviolet radiation organic silicon resin as a packaging material[6,7]. But the thermal conductivity and mechanical properties of organic silicon materials are relatively low, so the inorganic substances usually need to be added in organic matrix to improve its thermal conductivity and refraction[8-10]. The method to improve the thermal conductivity and the mechanical properties of organic silicon are effective, but there are also defects. However, the raw nanoparticles aggregate much severely because of their large cohesive strength and poor compatibility with polymers when the naked nanoparticles are dispersed into the polymers. In this case, the particles/polymer composites often display poor mechanical and dielectric properties. For example, the electrical breakdown strength of the composites always decreased remarkably so that the particles/polymer composites would be used only at low electrical field[11]. Therefore, it is often necessary to seek suitable nanoparticles in order that they can be well dispersed in the polymer. A better interfacial interaction between the nanoparticles and polymer matrix could be obtained, which is beneficial to the improvement of the mechanical properties and thermal conductivity of the composites.

So far, nano-ZrO_2 composites have been developed and mostly used in film materials as a wide range of applications in recent years, because of its excellent resistance to heat, optical properties, electrical properties, mechanical properties and chemical stability. The nanocomposites can be used for thermal barrier, insulation, wear resistance and anti-corrosion coating and optical devices, etc. The nano-ZrO_2 composites can be widely used in aerospace, ferrous metallurgy, machinery manufacturing, optical, electrical and other fields, which prospects are very broad. Yang D[12] studied the effect of ablative properties on zirconium carbide or zirconia silicone rubber. Few researchers studied silicone rubber treated with nano-ZrO_2, and focused on the effects of ZrO_2 nanoparticles on the physics and chemistry properties of phenyl silicone rubber at low concentration (≤1.0%)[13-15].

In this paper, ZrO_2 treated with silane couple agents were used to prepare nanoparticles/phenyl silicone rubber composites. The effects of the nanoparticles on mechanical properties, thermal conductivity and dielectric behavior of phenyl silicone rubber were investigated.

Experiment

Materials

Polydimethyldiphenylsiloxane (PDMDPS) were purchased from Shanghai resin factory, China. The ZrO_2 employed in this study was supplied by Beijing DK nano technology, China. The average particle size of ZrO_2 was 20nm. Ethyl silicate, dibutyltin dilaurate, absolute alcohol and 3-triethoxysilyl-1-propanamine (KH-550) were purchased from Sinopharm Chemical Reagent, China.

Surface Modification of ZrO_2 Nanoparticles

The nanoparticles were kept at the temperature of 80 ℃ and vacuum condition for 3 h to remove air and moisture. Moderate absolute alcohol and the silane coupling agent KH-550 were added and ultrasonic dispersion for 20min. The mixture was stirred under reflux condition at 80 ℃ for 3h. The resultant was centrifuged and then washed with absolute alcohol to remove the residual KH-550. The nanoparticles were dried in vacuum oven at 120 ℃ for 24 h and the treated particle was formed.

Preparation of Nanoparticles /Phenyl Silicone Rubber Nanocomposites

The treated particle was dissolved in moderate absolute alcohol under ultrasonic dispersion for 20min. The PDMDPS was added and mixed uniformity. The mixtures were conditioned in a vacuum oven for 2h at the temperature of 80 ℃ to remove the air bubbles. Composition (100 parts by weight) mixed with ethyl silicate (crosslinking agent; 5 parts by weight) and dibutyltin dilaurate (catalyst; 2 parts by weight). The mixtures were conditioned in a vacuum oven for 30min to remove air bubbles generated during mixing and then cured at room temperature for 2 days.

Results and Discussion

The FT-IR Spectra of Nano-ZrO_2

Fig. 1 shows the FT-IR spectra of nano-ZrO_2 and nano-ZrO_2 treated with KH-550. Compared with the IR spectra of untreated nano-ZrO_2, the absorption peak intensity of Zr-OOC at 1632 cm^{-1} significantly weakened. And the absorption peak of hydroxyl ligand at 1348cm^{-1} disappeared. Meanwhile, there were three new absorption peaks appear at 2920 cm^{-1}, 2850 cm^{-1}, 1560cm^{-1}, which attribute to the spectra of KH550. The absorption peaks at 2920cm^{-1} and 2850cm^{-1}which corresponding to the characteristic of bending vibrations of methylene groups, absorption peak at 1560cm^{-1} was assigned to $-NH_2$. These characteristic absorption peaks of silane coupling agent reflected the successful modification of nano-ZrO_2.

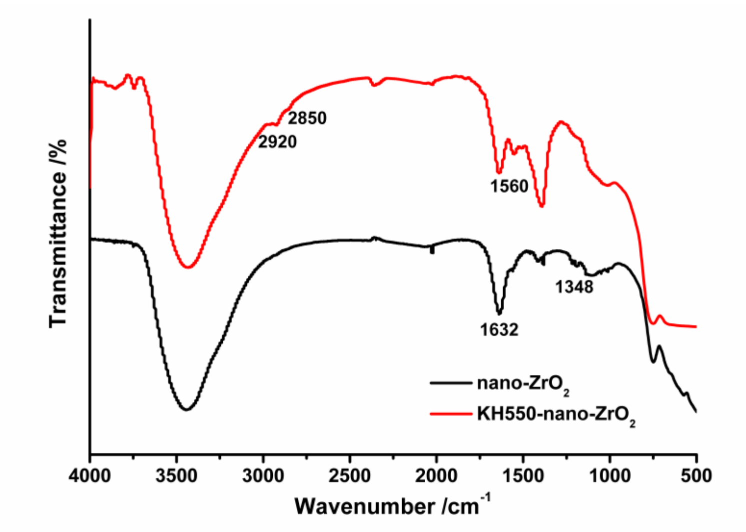

Fig.1 The FT-IR spectrum of nano-ZrO_2 and nano-ZrO_2 treated with KH-550

Effect of ZrO_2 Nanoparticles on Thermal Conductivity of Phenyl Silicone Rubber

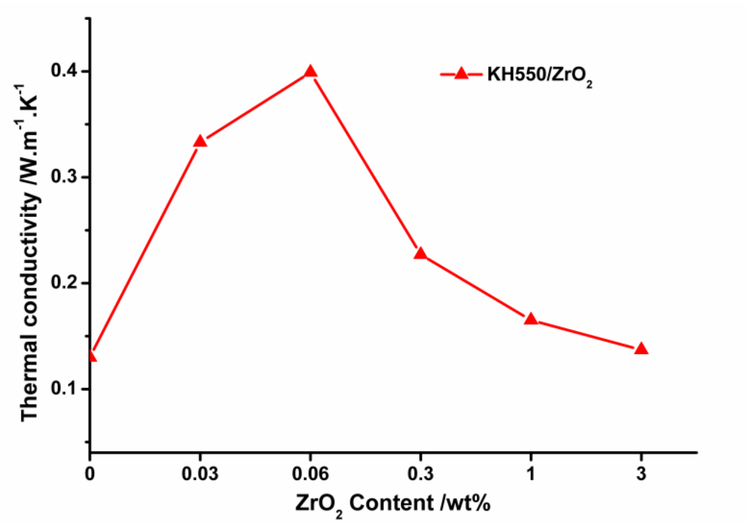

Fig.2 The effect of ZrO_2 content on thermal conductivity of silicone composite

The thermal conductivity as a function of nanoparticles concentration in the total mass, for a silicone rubber containing the particles is shown in Fig. 2. The thermal conductivity of phenyl silicone rubbers nanocomposites increases from 0.130 to 0.399 W/(m K) firstly, and then decrease with the increase of the loading amount of treated ZrO_2, which probably due to the large specific surface area of nanoparticles increase the phonon scattering area, improved thermal resistance. With the increasing of the content of nanoparticles, the nanoparticles distributed more closely, which formed a good thermal conductivity network, increased the heat transfer rate and thermal conductivity. The thermal conductivity of phenyl silicone rubbers reaches a maximum value at the nanoparticles concentration of 0.06 wt%. However, the decreasing of thermal conductivity is attributed to the low thermal conductivity of ZrO_2 with the ZrO_2 concentration exceeds 0.06 wt%.

Effect of ZrO_2 Nanoparticles on Dielectric Behavior of Phenyl Silicone Rubber

As shown in Fig.3, a sharp decrease of the dielectric constant from 3.78 to 2.77 is observed when the concentration of ZrO_2 particles increases from 0wt% to 0.06 wt%, which attribute to the nanoparticles having unique dielectric confinement effect, could produce induced polarization at heterogeneous medium which contact with organic matter. In other words, electron cloud can be able to radial localization which contact with the medium, restrict electron cloud polarization. The dielectric constant of the material can be significantly reduced. Between nano-particles and polymer have better compatibility and interaction, which can play the dielectric confinement effect of nanoparticles more effectively. Then, the material presents a lower dielectric constant.

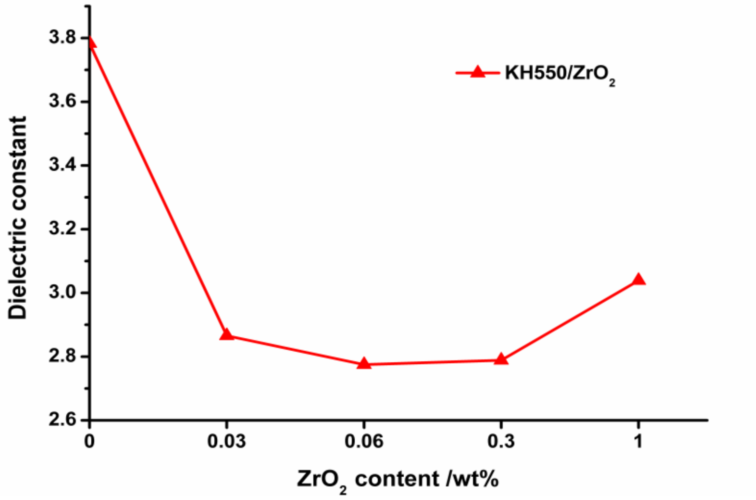

Fig.3 The effect of ZrO_2 content on dielectric constant of silicone composites under 800 KHz

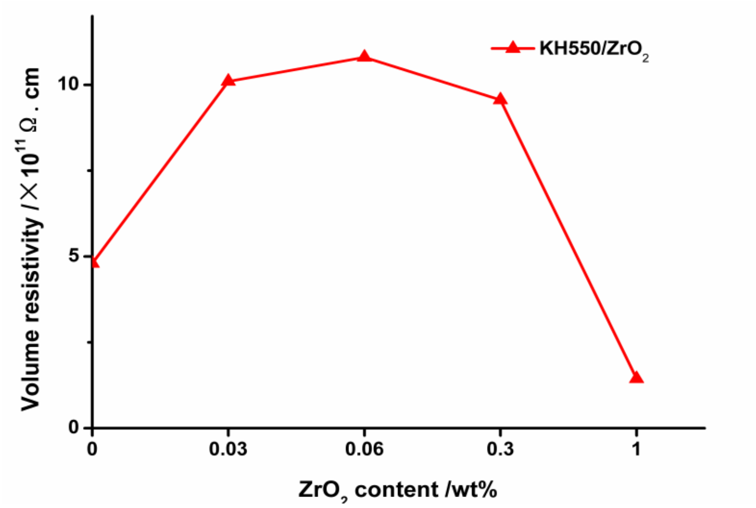

Fig.4 The effect of ZrO_2 content on volume resistivity of silicone composite

The volume resistivity (ρ_{υ}) of phenyl silicone rubber with different mass fraction of ZrO_2 is shown in .Fig. 4. The volume resistivity gradually increased with nanoparticles concentration before 0.06 wt%. This phenomenon might be ascribed to the electrode polarization and the interface polarization between nanoparticles and phenyl silicone rubber phases as numerous interfaces occur with nanoparticles content increasing. The main factor influencing the resistivity of a composite is the interfacial interaction which produces energy barrier and blocks the transport of electrons[16]. In the case of treated ZrO_2 nanoparticles, tightly combined with the rubber matrix, and that causes a high transport barrier for electrons in terms of tunneling mechanism. Moreover, due to the modification of ZrO_2 particles, the effect of electron tunneling would be greatly weakened by the coupling agent as effective barriers. The electrons would be distributed evenly under electric field owing to the strongly enhanced interfaces between treated nanoparticles and phenyl silicon rubber matrix [17]. However, the decreasing of volume resistivity is attributed to the excess ZrO_2 increase the imperfection of the polymer with the ZrO_2 concentration exceeds 0.06 wt%.

Mechanical Properties

The mechanical properties of phenyl silicone rubbers with ZrO_2 nanoparticles were tested, the results were shown in Fig.5.

As shown in Fig. 5, the tensile strength of phenyl silicone rubbers increases from 0.157 MPa to 0.334 MPa firstly, and then decrease with the increase of the loading amount of treated ZrO_2.

Apparently, comparing with the unfilled rubbers, the appropriate addition of nanoparticles can improve the tensile strength. This can be ascribed to the physical and/or chemical reactions between the nanoparticles and the polymer chains. The surface energy of the nanoparticles usually decreases when it was pretreated with coupling agent. In addition, coupling agent has groups that react with the silanols on the particles bond and another group that has better compatibility with phenyl silicone rubber matrix. So the nanoparticles will have good interfacial adhesion with phenyl silicone rubber matrix because of the presence of coupling agent. Thus a better load transfer can be realized between nanoparticles and phenyl silicone rubber matrix. However, particle agglomeration tends to reduce the strength of the material acting as strong stress concentrators and the decrease in tensile strength can be attributed to the agglomeration of particles[18].

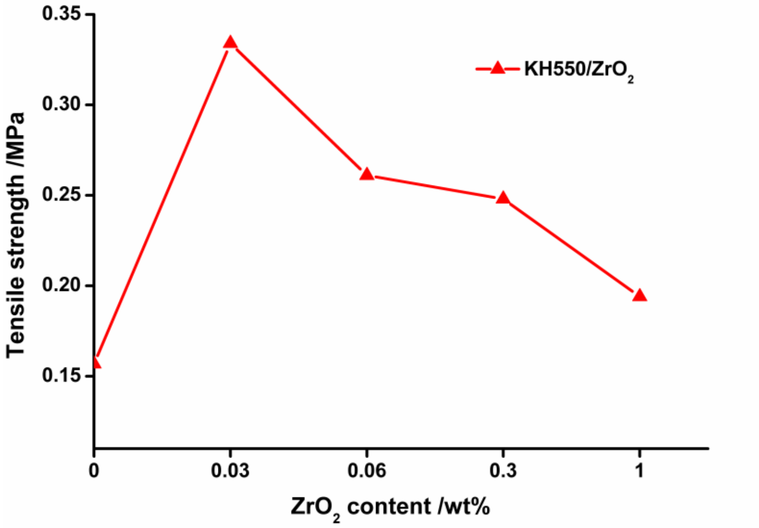

Fig.5 The effect of ZrO_2 content on tensile strength of silicone composite

Conclusion

This paper systematically studied the effects of different additive amount of nano-ZrO_2 on the mechanical properties, thermal conductivity and electrical conductivity of phenyl silicone rubber. Through the study we can found that:

The thermal conductivity and volume resistivity of composites increase firstly and then decrease, and reach a maximum value at the nanoparticles concentration of 0.06 wt%, which implies a good interfacial interaction between silicone rubber and ZrO_2. The thermal conductivity of treated nanocomposites is three times of that of pure silicone rubber at the nanoparticles concentration of 0.06 wt%. In summary, the nano-ZrO_2/phenyl silicone rubber composites at the nanoparticles concentration of 0.06 wt% can achieve a balance among high thermal conductivity, good electrical insulation properties and mechanical properties of silicone rubber.

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