Effect of the addition of nano-SiO₂ particles with different contents on the dielectric properties of polyacrylate composites

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Abstract: *Dielectric elastomer (DE) is a class of electro-driven flexible smart polymer materials, often using polyacrylate as an elastomer material. Unmodified acrylates typically have a low dielectric constant, resulting in high drive voltages, low breakdown field strengths, and low electrical induced strain. In this study, SiO₂ nanoparticles were added to polyacrylate (CN 9021NS) to study the effect of nanoparticles on the dielectric properties of composites, and the frequency dependence of dielectric constant and dielectric loss was analyzedIt is concluded that the addition of SiO₂ nanoparticles to polyacrylate can effectively increase the dielectric constant of the composites, but it will also lead to an increase in dielectric loss. When the nano-SiO₂ particle content is 10 wt%, although it will lead to an increase in dielectric loss, it has the highest dielectric constant of 8.35, which is 1.165 times that of the elastomer prepared by the original CN 9021NS.*

Keywords: *Dielectric Elastomers; Polyacrylates; Nanoparticles; Dielectric Properties*

1. Introduction

Dielectric elastomers, as one of the flexible drives, play an indispensable role in promoting the development of the soft robot industry. Dielectric elastomers will be pulled by Maxwell's stress under the action of electric field, and the plane expansion of dielectric elastomers needs to be converted into effective motion that can drive the soft robot, so as to convert electrical energy into force and mechanical energy, thereby driving the displacement of the soft robot. Implement the drive of soft robots.

The dielectric constant of dielectric elastomer materials is a key factor influencing the drive strain. The larger the dielectric constant, the stronger the polarization of the elastomer material under the electric field, the more charge it stores, the greater the mechanical energy converted into it, and the greater the strain. In this way, the required high electric field is reduced, and the purpose of low voltage and large deformation is realized. We should also point out that there are often trade-offs between different material modification strategies. Elastomers with low mechanical stiffness tend to have composite elastomers with higher dielectric constants, typically with higher dielectric losses and lower dielectric strength, while low viscous elastomers with added plasticizers can have stability issues. Different methods have different advantages and disadvantages[1].

Due to the low force and large driving voltage of the dielectric elastomer driver currently studied, the development of dielectric elastomer driver still faces many problems. Therefore, there is a need to develop high-performance dielectric elastomer materials that can be used in a wider range of spaces to provide better services to human beings. Therefore, it is necessary and urgent to study the performance indicators and characterization analysis of electroactive elastomers[2].
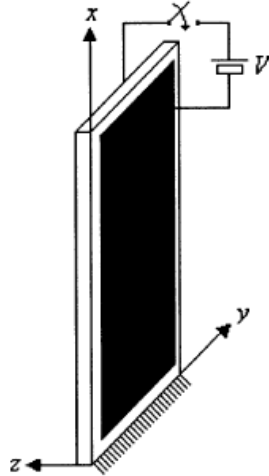
Figure 1: Schematic diagram of a dielectric elastomer plane actuator constrained at the lower end. The black area indicates the electrode.

As shown in Figure 1, when a dielectric elastomer is energized, it undergoes electro-induced deformation, and any observed strain shows a quadratic dependence on the square of the applied electric field[3], In principle, it can be attributed to the Maxwell stress effect caused by the coulombic electrostatic interaction between the free charges on the electrode and the electrostrictive effect caused by the change in the dielectric constant of the material due to strain[4]. Referring to the parallel-plate capacitors in the planar configuration above, we can consider a series of Cartesian coordinate systems: x, y, z. Its axis z is oriented in the direction of thickness，An electric field E_z is applied along it. The contribution of Maxwell stress and electrostriction to the total longitudinal stress τ_{zz} and the transverse stress τ_{xx}, τ_{yy} can be expressed as[5]:

$$\tau_{zz} = -\frac{1}{2}\varepsilon_0 E_z{}^2[\varepsilon - (a_1 + a_2)] \tag{1}$$

$$\tau_{xx} = \tau_{yy} = \frac{1}{2}\varepsilon_0 E_z{}^2(\varepsilon + a_2) \tag{2}$$

The ε_0 denotes the vacuum permittivity($\varepsilon_0 = 8.85 \times 10^{-12} F/m$), ε is the relative permittivity of an unstrained material assumed to be isotropic. a_1, a_2 is the change in the dielectric constant of the material when it is deformed.$E_z{}^2$ can be expressed as:

$$E_z{}^2 = \frac{-2\tau_{zz}}{\varepsilon_0[\varepsilon-(a_1+a_2)]} = \frac{2\tau_{xx}}{\varepsilon_0(\varepsilon+a_2)} = \frac{2\tau_{yy}}{\varepsilon_0(\varepsilon+a_2)} \tag{3}$$

So from the formula, it can be concluded that the applied electric field E_z can be reduced by increasing the dielectric constant of the material

The dielectric constant is a measure of the polarizability of a dielectric, and when the polarizability of the material increases, the dielectric constant increases. In order to increase the dielectric constant of DE, the main method is to develop elastomeric composites. Ceramic particles with high dielectric constant, conductive nanoparticles, or elastomer blends are often added to the polymer matrix. The nanoparticles are assembled into a chain-like structure in a dielectric elastomer film matrix by using the dielectrophoretic effect of an alternative electric field, and then the chains are oriented to produce anisotropic properties in the desired direction. The orientation of the filler in the chain structure further increases the dielectric constant[6].

In this paper, the preparation of composites with high dielectric properties by adding cheap and readily available nano-SiO_2 particles to polyacrylate (CN 90212NS) was studied, and the effect of different contents of nano-SiO_2 particles on the dielectric properties of composites was expounded, and the mechanism of the effect of nanoparticles on the dielectric constant of composites was explained in detail. This method can effectively improve the dielectric constant of composite materials, and compared with other methods, it can save costs and improve the production efficiency of elastomers, which is of great significance to the development and promotion of dielectric elastomers.

2. Experiment

2.1 Experimental materials

The main experimental materials are: Acrylate resin oligomer (CN 9021NS), Isodecyl acrylate (IDA), 1,6-hexanediol diacrylate (HDDA), Isobornyl acrylate (IBOA), Trimethylolpropane triacrylate (TMPTA), Ethyl (2,4,6-trimethylbenzoyl) phenylphosphinate (TPO-L), SiO_2 nanoparticles (<100nm).

2.2 Preparation of composite materials

1) Mix CN 9021NS, IDA, HDDA, IBOA, TMPTA, TPO-L in a ratio of 90: 17: 5: 5: 1: 2.

2) Nano SiO_2 particles are taken according to the mass fractions of 0, 2.5 wt%, 5 wt%, 7.5 wt%, and 10 wt% respectively, and added to the CN 9201NS prepolymer solution, which is then sealed in a high-density polyethylene seal can.

3) The planetary solder paste mixer is used again to stir for 90 minutes, allowing the nanoparticles to fully mix with the mixed solution.

3. Material characterization

3.1 Microscopic morphology

In order to characterize the morphology of SiO_2 particles in the composite material and the distribution state of nanoparticles in the material, the prepared SiO_2 and CN 9021NS composite material was analyzed by the Supra 55 scanning electron microscope produced by the Japanese Zeiss company.

3.2 Dielectric property test

The dielectric property test mainly measures the dielectric constant and dielectric loss of the dielectric elastomer, using the Agilent 4294A impedance analyzer produced by the American Agilent company. Using injection molding, a circular thin piece with a diameter of 20 mm and a thickness of 1.5 mm is cast, and electrodes with a diameter of 12 mm are coated on both sides at corresponding positions. Then it is clamped in the middle position of the circular electrode piece, and finally tested, with a frequency range of 40 Hz-10 MHz. Three dielectric test samples are made for each material, and three dielectric tests are conducted to ensure the accuracy of the results.

4. Results and discussion
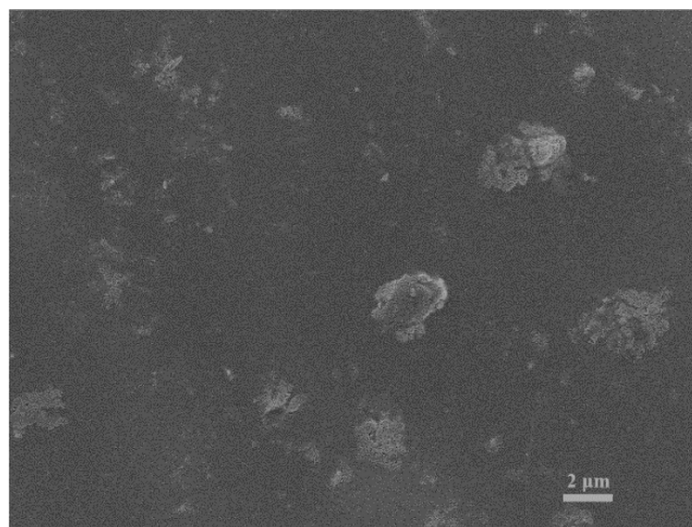
4.1 Distribution of nanoparticles

Figure 2: SEM image of the original CN 9021NS composite

As shown in Figure 2, it is the SEM scanning electron microscope image of the original CN 9021NS composite material without adding any nanoparticles. The SEM scanning electron microscope image of the original CN 9021NS composite material shows that it contains a small amount of bubbles and impurities inside.
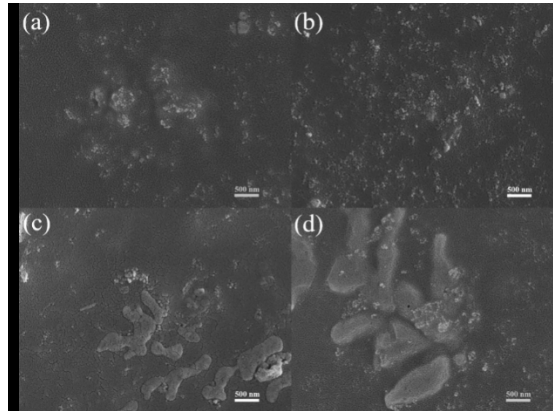

Figure 3: SEM images of composites with different nano-SiO$_2$ particle contents, (a) 2.5 wt% SiO$_2$; (b) 5 wt% SiO$_2$; (c) 7.5 wt% SiO$_2$; (d) 10 wt% SiO$_2$

As shown in Figure 3, with the increase of nano-SiO$_2$ particle content, the distribution of nanoparticles in the material becomes more and more dense. When the content of nano-SiO$_2$ particles is 2.5 wt%, some nanoparticles are distributed in the matrix without obvious defects; when the content of nano-SiO$_2$ particles is 5 wt%, more nanoparticles are dispersed in the composite material, the particle distribution is relatively dense, but the dispersion is good, the distribution is uniform; when the content of nano-SiO$_2$ particles is 7.5 wt%, due to the excessive nanoparticles that cannot be evenly dispersed, many nanoparticles are concentrated in the distribution, and agglomeration occurs in the matrix; when the content of nano-SiO$_2$ particles is 10 wt%, the nanoparticles in the matrix far exceed the limit they can bear, the nanoparticles exceed the threshold, are concentrated in the distribution, agglomeration occurs, they cannot be dispersed in the collective, forming closely connected particle agglomerates.

4.2 The impact on dielectric properties

Dielectric properties refer to the response characteristics of bound charges in material molecules to an external electric field, which manifests as the storage and loss of electrostatic energy, usually represented by dielectric constant and dielectric loss.

By integrating two or more materials with complementary properties, composite materials have the potential to far exceed the performance of their constituent materials[7]. Therefore, in this experiment, adding nanoparticles with a high dielectric constant to CN 9021NS can improve the dielectric properties of the elastomer.
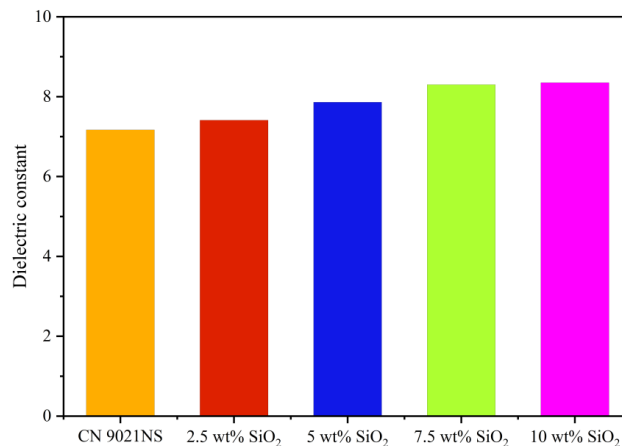
4.2.1 The impact on dielectric constant

Figure 4: Dielectric constant of elastomers with different amounts of nano-SiO$_2$ particles at 40 Hz

As shown in Figure 4, it represents the dielectric constant of the elastomer with different amounts of nano-SiO_2 particles added at a frequency of 40 Hz. As the content of nano-SiO_2 particles increases, the dielectric constant of the elastomer shows a gradually increasing trend. When no nano-SiO_2 particles are added, the dielectric constant of the elastomer is 7.17. When the content of nano-SiO_2 particles reaches 10 wt%, the dielectric constant of the elastomer reaches a maximum of 8.35, which is 16.5% higher than the dielectric constant of the elastomer prepared from the original CN 9021NS.

The increase in the dielectric constant of the elastomer can be understood according to the "boundary layer capacitance effect"[8]. When nano-particles are dispersed into the composite material, the individual nano-particles or agglomerates are isolated by the thin dielectric insulation layer of the matrix, then micro-capacitors can be formed between the nano-particles or agglomerates. When the elastomer is subjected to an externally applied electric field, these nano-particles or agglomerates can act as electrodes to absorb charges. The applied electric field will distort around the nano-particles or agglomerates, and the electric field strength in this area will be higher[9], causing the micro-capacitors to absorb more charges, thereby improving the dielectric constant of the elastomer. As the content of nano-particles increases, the more micro-capacitors are distributed in the elastomer, which leads to the gradual increase in the dielectric constant of the elastomer as the content of nano-particles increases. With the increase in the content of nano-particles, the Young's modulus of the composite material is gradually increasing, and the elastomer with a high Young's modulus has a more compact structure, the distance between the nano-particles is smaller, the local field strength is higher, and more charges can be captured[10], which also leads to the increase in the dielectric constant of the elastomer.
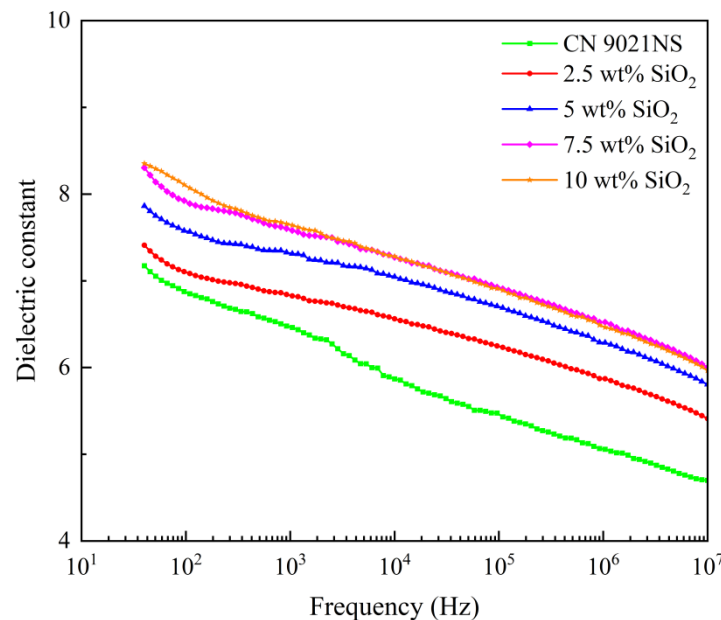

Figure 5: Changes in the dielectric constant of elastomers with different amounts of SiO₂ nanoparticles at different frequencies

As shown in Figure 5, they represent the change in the dielectric constant of the elastomer with different nanoparticle contents at different frequencies. As can be seen from the figures, as the frequency increases, the dielectric constant of the elastomer shows a gradually decreasing trend, showing a certain frequency dependence. At low frequencies, the dielectric constant of the elastomer is higher, and at high frequencies, the dielectric constant of the elastomer is lower. This is mainly related to the polarization mechanism of the dielectric elastomer. The polarization mechanism of the dielectric elastomer mainly includes dipole polarization and interface polarization, among which the Maxwell-Wanger-Sillars (MWS) interface polarization effect is the main reason for the change in the dielectric constant with the electric field frequency[11]. At low frequencies, the speed of the electric field change is slow, and the charges captured on the interface between the nanoparticles and the CN 9021NS matrix have enough time to accumulate. The speed of interface polarization can keep up with the speed of frequency change, and the interface polarization effect is obvious, so the elastomer with added nanoparticles has a high dielectric constant at low frequencies. At higher frequencies, the speed at which charges accumulate at the interface between the nanoparticles and the matrix cannot keep up with the speed of the electric field change, and the number of accumulated charges is lower than the charges accumulated at low frequencies, resulting in a decrease in the dielectric constant of the elastomer.
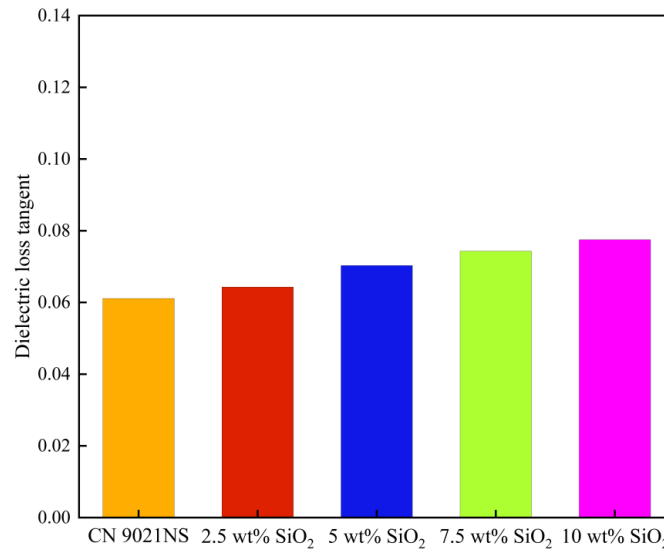
4.2.2 The impact on dielectric loss

Figure 6: Dielectric loss of elastomers with different contents of nano-SiO₂ particles at 40 Hz

As shown in Figure 6, it represents the dielectric loss of the elastomer when different amounts of nano-SiO_2 particles are added at a frequency of 40 Hz. As can be seen from the figure, adding nano-SiO_2 particles to CN 9021NS will increase the dielectric loss of the elastomer. As the content of added nano-SiO_2 particles increases, the dielectric loss of the elastomer shows a gradually increasing trend. When no nano-SiO_2 particles are added, the dielectric loss of the elastomer is 0.0611. When the content of added nano-SiO_2 particles reaches 10 wt%, the dielectric loss of the elastomer reaches a maximum of 0.0775, which is 26.8% higher than the dielectric loss of the elastomer prepared by the original CN 9021NS.

The main reasons for the dielectric loss of materials are conductive loss, interface polarization loss, and dipole orientation[12]. For composite materials, nanoparticles are inorganic, and the matrix is organic. Since the inorganic-organic two phases cannot be completely compatible, the addition of nano-SiO_2 particles will introduce defects into the elastomer, such as bubbles, agglomerates, etc. These defects will cause the generation of space charges, these charges will polarize under the action of the electric field[13], and this polarization will generate loss. As the content of added nanoparticles increases, more defects will be generated, which will also lead to an increase in dielectric loss. This means that under the action of an electric field, more electrical energy is dissipated in the form of heat, and the electrical energy actually used to convert into mechanical energy is reduced, which is detrimental to the driving performance of the elastomer.
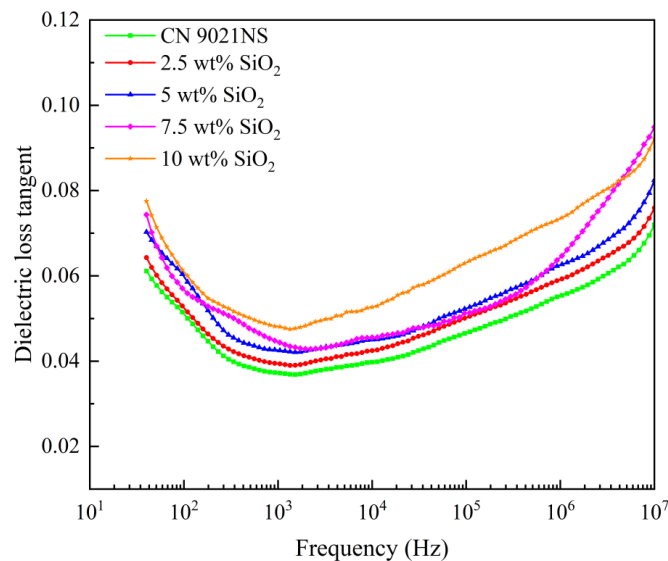

Figure 7: Variation of dielectric loss of elastomers with different contents of nano-SiO₂ particles at different frequencies

As shown in Figure 7, they represent the changes in dielectric loss of the elastomer with different amounts of nano-particles at different frequencies. The dielectric loss of the elastomer also has frequency dependence. As the frequency increases, the dielectric loss of the elastomer shows a trend of first decreasing and then increasing.

When the frequency is less than 100 Hz, the induced charge accumulation and dipole orientation on the interface of the nano-particles and the elastomer can keep up with the changes in the electric field, forming a larger conductive current and consuming more electrical energy, so the dielectric loss is larger.

As the frequency increases, when the frequency gradually increases from 100 Hz to 1 kHz, the dielectric loss is gradually increasing, which is attributed to the relaxation mechanism. As the frequency increases, the time allowed for charge migration to the interface is shorter, the accumulation speed of induced charges and the orientation of dipoles cannot keep up with the speed of electric field changes, the formed conductive current is smaller, the consumed electrical energy is reduced, so the dielectric loss of the elastomer appears to decrease.

When the frequency exceeds 1 kHz, the dielectric loss of the elastomer gradually increases. This is mainly related to the gradual improvement of the internal conductive path of the composite material. The formation of the conductive path directly leads to an increase in current, more electrical energy will be converted into heat and dissipated, increasing the dielectric loss. Therefore, the dielectric loss gradually decreases below the frequency of 1 kHz, and when the frequency exceeds 1 kHz, the dielectric loss gradually increases.

5. Conclusions

(1) Saturation is achieved when SiO_2 nanoparticles are added to the material with a content of 5 wt%, and the dispersion is more uniform and dispersed, with less agglomerates. When the content of nanoparticles is too high, a large amount of agglomerates will be produced due to the proximity of the nanoparticles.

(2) Adding nanoparticles to CN 9021NS will improve the dielectric constant and dielectric loss of the elastomer.

1) When the content of nano-SiO_2 particles is added to reach 10 wt%, the dielectric constant of the elastomer reaches a maximum of 8.35, which is 1.165 times that of the elastomer prepared by the original CN 9021NS. Therefore, the elastomer with nano-SiO_2 particles has a higher dielectric constant, stronger ability to bind charge, better electrical insulation, higher breakdown voltage, and can withstand higher applied electric field, which is equivalent to achieving greater electrolytic deformation.

2) When the content of nanoparticles reaches 10 wt%, the dielectric loss of the elastomer with nano-SiO_2 particles reaches a maximum of 0.0775, which is 1.268 times that of the elastomer prepared by the original CN 9021NS. Due to the small base of dielectric losses, both elastomers have relatively low dielectric losses.

According to the comprehensive analysis of dielectric properties, the addition of SiO2 nanoparticles to CN 9021NS can improve the dielectric properties of dielectric elastomers. When the content of nano-SiO_2 particles is 10 wt%, it has the highest dielectric constant (8.35), although it will lead to an increase in dielectric loss.

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