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Effect of adding different contents of nano-ZnO particles on the dielectric properties of polyacrylate composites

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Abstract: *Dielectric elastomer (DE) is a kind of electrically driven flexible intelligent polymer material, the middle is an elastomer, the two sides are coated with flexible electrodes, after the driving voltage is applied on both sides, under the action of Maxwell stress, the elastomer will become thinner, the volume will be extruded and deformed, and the electrical energy will be converted into the mechanical energy of the dielectric elastomer doing external work and the elastic potential energy of the elastomer deformation. The elastomer material is typically polyacrylate, and unmodified acrylates typically have a low dielectric constant, requiring a higher drive voltage. In this study, polyacrylate (CN 9021NS) was used as the research object, and ZnO nanoparticles were added to polyacrylate (CN 9021NS) to study the effect of nano-ZnO particles on the dielectric properties of composites, and the frequency dependence of dielectric constant and dielectric loss was analyzed. The results show that the addition of ZnO 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-ZnO particle content is 10 wt%, although it will lead to an increase in dielectric loss, the dielectric constant is the highest, which is 13.9, which is 1.94 times that of the elastomer prepared by the original CN 9021NS. The dielectric loss reaches 0.103, which is 1.69 times that of the original CN 9021NS elastomer. Due to the small base of dielectric losses, the dielectric losses of both nanoparticles are relatively low.*

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

1. Introduction

Biological mechanisms and motion systems have inspired many robotic engineers and scientists to study multifunctional systems. The innovative results of these studies have created a new field of robotics, namely soft robotics. The movement of soft robots is mainly driven by their actuators. To achieve purposeful transformation of soft robots, the key is to consider the driving methods and materials of the drivers. The driving methods of soft robots are diverse, including cable drives composed of multi-degree-of-freedom articulated bodies driven by a single tendon, pneumatic drives that move by controlling the volume of gas, electrically active polymer (EAP) drives that move by electrification[1, 2], shape memory alloy (SMA) drives that convert thermal energy into mechanical energy[3, 4], chemical drives that convert the chemical energy stored in fuel into mechanical energy to drive robots, and ion polymer-metal composite (IPMC) drives, etc[5, 6].

Among all the driving methods of soft robots, dielectric elastomers (DE), as a kind of electrically active polymer, are a kind of flexible intelligent polymer material driven by electricity, which has high electromechanical conversion efficiency, light weight, low cost, flexible movement, easy molding, and not easy to fatigue and damage. Dielectric elastomers are a kind of capacitor that can convert electrical energy into mechanical energy after being coated with flexible electrodes on the surface[7]. When subjected to an external electric field, charges will gather on both sides of the dielectric elastomer, and the opposite charges between the electrodes attract each other to produce Maxwell stress, thereby compressing the film, causing compression in the thickness direction and stretching strain in the plane direction. When the external electric field is withdrawn, it can recover to its original shape, which is a kind of intelligent elastic material that converts electrical energy into mechanical energy. Dielectric elastomers are composed of a polymer film substrate in the middle and flexible electrodes on the upper and lower sides, which is a very typical sandwich structure. Its driving principle is shown in Figure 1.

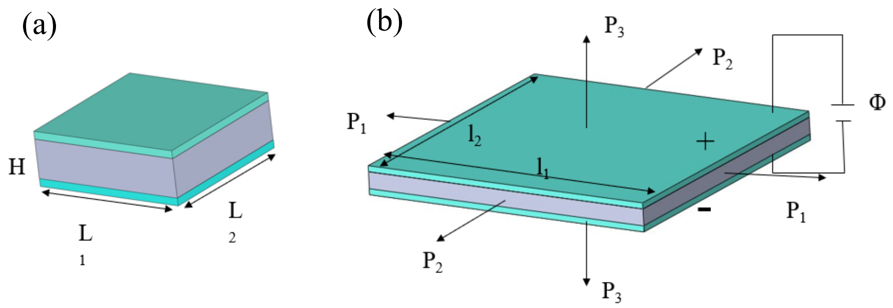

Figure 1: Deformation of the dielectric elastomer driven by an electric field, (a) natural size without applied voltage; (b) deformation under the action of Maxwell stress in the electrostatic field when voltage is applied

The Maxwell stress P generated on the insulating elastomer membrane is:

$$P = qE = \varepsilon_0 \varepsilon_\gamma \left(\frac{U}{h}\right)^2 \tag{1}$$

For low strain (strain is less than 20%), the Young's modulus, also known as the modulus of elasticity, can be approximated as a constant. That is, the stress-strain curve of the material can be considered linear. The thickness strain of the dielectric elastomer can be approximated as:

$$S_Z = -\frac{P}{Y} = -\frac{\varepsilon_0 \varepsilon_\gamma}{Y} E^2 = -\frac{\varepsilon_0 \varepsilon_\gamma U^2}{Y h^2} \tag{2}$$

Where P is the Maxwell stress on the material; The q is the charge density on the flexible electrodes on both sides; The ε_γ is the relative dielectric constant; The ε_0 is the dielectric coefficient of free space; E is the applied electric field, $E = U/h$; Y is the Young's modulus; Using $\beta = \varepsilon_\gamma / Y$ as a parameter to measure the dielectric properties of DE materials; Ratio ε_γ / Y quantifies the material performance improvement of DE. For strains greater than 20%, the equation is not satisfactory, because Y usually depends on the strain itself. It is obvious that the ideal material for DE will have high relative dielectric constant, high breakdown voltage, and low Young's modulus.

Commonly used dielectric elastomer materials mainly include acrylates (such as 3M's VHB-4910), silicone rubber, and polyurethanes. In recent years, carboxylated nitrile rubber (XNBR), styrene-butadiene-styrene block copolymers (SBS), hydrogenated nitrile rubber (HNBR) and other elastomers have also received some attention[8-11]. Acrylate, as a type of dielectric elastomer, has advantages such as high electric strain, good temperature adaptability, high rebound rate, and excellent biocompatibility that other dielectric elastomer materials cannot match. However, unmodified acrylates usually have a low dielectric constant, leading to high driving voltage, low breakdown field strength, and small electric strain. Therefore, its comprehensive performance is limited, which is not conducive to its widespread application.

The dielectric properties of dielectric elastomer materials are a key factor influencing the driving strain. The greater the dielectric constant, the stronger the polarization of the elastomer material under the electric field, the more charge it stores, i.e., the greater the mechanical energy converted, the greater the strain, thus reducing the high electric field it requires. Achieve the purpose of low voltage and large deformation.Existing research shows that adding highly polarized nanoparticle fillers to dielectric elastomers can improve the mechanical and dielectric properties of composite materials. The enhanced comprehensive performance of composite materials stems from the nanoscale size of the filler and the strong interaction between the filler and the polymer. It also increases the dielectric constant of the elastomer, thereby reducing the electric field strength required during the actuation process[12].

In order to prepare a dielectric elastomer with low power consumption, high strain, high dielectric constant and fast response, a solution of CN 9021NS prepolymer mixture based on polyacrylate (CN 9021NS) was prepared in this study. Different amounts of ZnO nanoparticles were added to the mixed solution to study the effect of ZnO nanoparticles on the dielectric properties of elastomers. The results showed that the addition of ZnO nanoparticles to polyacrylate could effectively improve the dielectric properties of elastomers.

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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), ZnO 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 ZnO 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. Dielectric property testing

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 The impact on dielectric constant

The dielectric constant is the main parameter of the dielectric or polarization properties of the material medium under the action of an electrostatic field, and is usually expressed in terms of ε. The dielectric constant refers to the ability of a substance to retain an electric charge, the larger the dielectric constant, the stronger the ability to bind the charge, if a high dielectric constant material is placed in an electric field, then the electric field strength inside the material will decrease[13]. The permittivity is a measure of a material's ability to be polarized or store energy. Yamada et al. showed that the expression of the dielectric constant of composites after the addition of nanoparticles to elastomers[14], that is:

$$K = K_p\left[1 + \frac{nq(K_c - K_p)}{nK_p + (K_c - K_p)(1+q)}\right] \tag{3}$$

Where K is the dielectric constant of composite materials; K_p and K_c are the dielectric constants of the composite matrix and the nanoparticles respectively; The q is the volume fraction of the nanoparticle, n is a parameter related to the geometry of the nanoparticles.

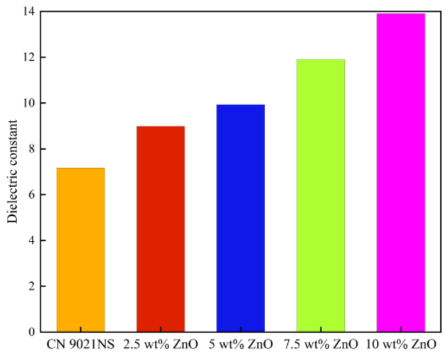

Figure 2: Dielectric constant of elastomers with different amounts of nano-ZnO particles at 40 Hz

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As shown in Figure 2, it represents the dielectric constant of the elastomer with different amounts of nano-ZnO particles added at a frequency of 40 Hz. It can be seen from the figure that adding nano-ZnO particles to CN 9021NS will improve the dielectric constant of the elastomer. As the content of nano-ZnO particles increases, the dielectric constant of the elastomer shows a gradually increasing trend. When no nano-ZnO particles are added, the dielectric constant of the elastomer is 7.17. When the content of nano-ZnO particles reaches 10 wt%, the dielectric constant of the elastomer reaches a maximum of 13.9, which is 93.9% higher than the dielectric constant of the elastomer prepared from the original CN 9021NS.

The increase in the dielectric constant of an elastomer can be understood in terms of the "boundary layer capacitance effect"[15]. When nanoparticles are dispersed into a composite, the individual nanoparticles or agglomerates are isolated by the thin dielectric insulation of the matrix, so microcapacitances can be formed between the nanoparticles or agglomerates, which can act as electrodes to absorb the charge when the elastomer is subjected to an externally applied electric field. As the content of added nanoparticles increases, the more microcapacitance is distributed in the elastomer, resulting in a gradual increase in the dielectric constant of the elastomer as the content of added nanoparticles increases.

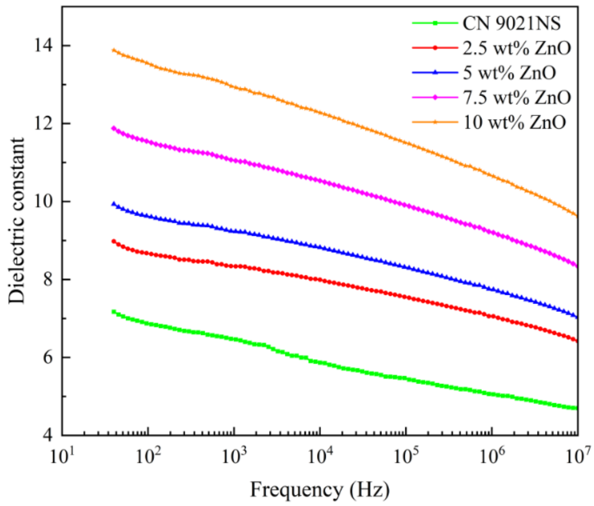

Figure 3: Changes in dielectric constant of elastomers with different amounts of nano-ZnO particles at different frequencies

Figure 3 shows the change of dielectric constant of elastomers with different nanoparticle content at different frequencies. As can be seen from the figure, with the increase of frequency, the dielectric constant of elastomers decreases gradually. Exhibits a certain frequency dependence. At low frequencies, elastomers have a higher dielectric constant, and at high frequencies, elastomers have a lower dielectric constant. This is mainly related to the polarization mechanism of dielectric elastomers. At low frequency, the speed of electric field change is slow, and the charge captured at the interface between the nanoparticles and the CN 9021NS matrix has enough time to accumulate, and the speed of interfacial polarization can keep up with the speed of frequency change, and the effect of interfacial polarization is obvious. At higher frequencies, the speed of charge accumulation at the interface between the nanoparticles and the substrate cannot keep up with the speed of electric field changes, and the number of charges accumulated is lower than that accumulated at low frequencies, resulting in a decrease in the dielectric constant of the elastomer.

4.2. The impact on dielectric loss

Dielectric elastomers can be seen as an ideal capacitor that can establish polarization instantaneously and be fully charged in a short time. Composites with the addition of nanoparticles are inhomogeneous, so there is a build-up of space charges in the regions of the interface, and in these areas of uneven charge distribution, an electric dipole moment is formed, which is called interfacial polarization or spatial charge polarization. The dipole polarization and interfacial polarization inside the capacitor will not keep up with the change of the applied electric field during the polarization process, resulting in the phase difference between the change of the applied electric field and the reaction current. The dipole polarization and interfacial polarization inside the capacitor will not keep up with the change of the applied electric field during the polarization process, resulting in the phase difference between the change

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of the applied electric field and the reaction current, so the complex dielectric constant ε^* can be used to represent the properties of the dielectric constant and the dielectric loss. The formula is:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \quad (4)$$

Where ε' is the capacitance term (energy storage), ε'' is the dielectric loss factor. The loss tangent $tan\delta$ is used to indicate the dielectric loss. Its main form of loss is the conversion of electrical energy into thermal energy[16]:

$$tan\delta = \varepsilon''/\varepsilon' \quad (5)$$

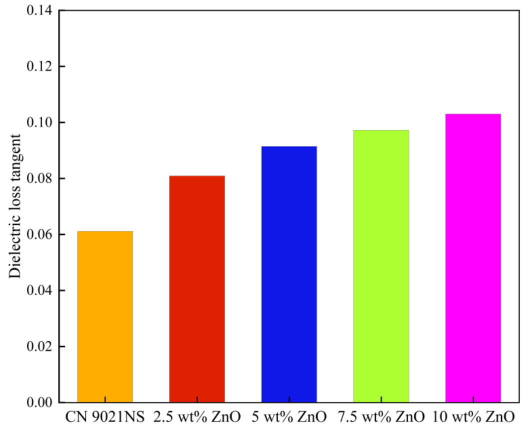

Figure 4: Dielectric loss of elastomers with different amounts of nano-ZnO particles at 40 Hz

As shown in Figure 4, it represents the dielectric loss of the elastomer when different amounts of nano-ZnO particles are added at a frequency of 40Hz. As can be seen from the figure, adding nano-ZnO particles to CN 9021NS will increase the dielectric loss of the elastomer. As the content of added nano-ZnO particles increases, the dielectric loss of the elastomer shows a gradually increasing trend. When no nano-ZnO particles are added, the dielectric loss of the elastomer is 0.0611. When the content of added nano-ZnO particles reaches 10wt%, the dielectric loss of the elastomer reaches a maximum of 0.103, which is 68.6% higher than the dielectric loss of the elastomer prepared by the original CN 9021NS.

The main causes of dielectric losses in materials are conductive losses, interfacial polarization losses, and dipole orientation[17]. For composites, the nanoparticles are inorganic and the matrix is organic. Since the inorganic-organic phases are not fully compatible, the addition of nanoparticles can bring defects to the elastomer. These defects cause the generation of space charges, which are polarized by an electric field[18], and this polarization generates losses. As the amount of nanoparticles added increases, more defects are generated, which also leads to an increase in dielectric losses. This means that under the action of the electric field, more electrical energy is dissipated in the form of heat, and less electrical energy is actually used to convert into mechanical energy, which is not good for the driving performance of the elastomer.

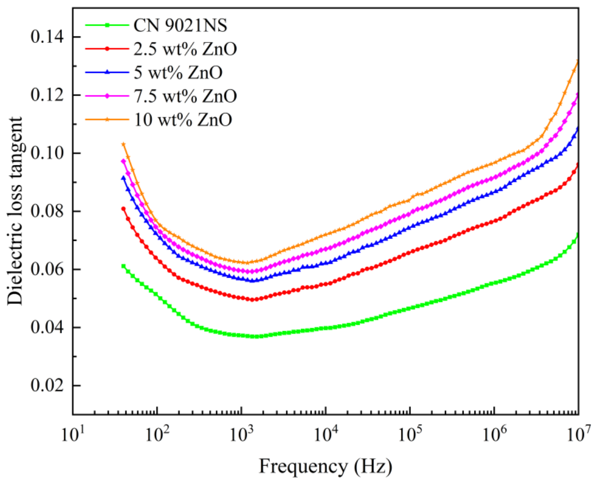

Figure 5: Variation of dielectric loss of elastomers with different contents of nano-ZnO particles at different frequencies

As shown in Figure 5, 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[19].

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[20]. 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 was reached when the content of ZnO nanoparticles was 7.5 wt% added to the material, and the ZnO nanoparticles were evenly dispersed in the material with less agglomerates. When the content of nanoparticles is too high, a large amount of agglomerates is generated.

(2) The addition of nanoparticles to CN 9021NS increases the dielectric constant and dielectric loss of the elastomer.

1) When the content of nanoparticles reached 10 wt%, the dielectric constant of the elastomer with nanoparticles reached a maximum of 13.9, which was 1.94 times that of the elastomer prepared by the original CN 9021NS. Therefore, the addition of nano-ZnO particles can effectively improve the dielectric constant of elastomer composites. This means that composites can have greater electro-induced strain.

2) When the content of nanoparticles reached 10 wt%, the dielectric loss of the elastomer with nano-ZnO particles reached a maximum of 0.103, which was 1.69 times that of the elastomer prepared by the original CN 9021NS.

Based on the dielectric property analysis, the addition of nano-ZnO particles to CN 9021NS can effectively improve the dielectric properties of dielectric elastomers due to the small dielectric loss value and the greater increase in dielectric constant.

The addition of nano-ZnO particles to polyacrylate is a good way to improve the dielectric properties of composites, which is of great significance for the fabrication of low-cost and high-efficiency elastomer composites. At the same time, elastomer composites with excellent performance are of great significance and value for the manufacture of dielectric elastomer drives and a wider range of applications.

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