Pressure-sensitive behaviors, mechanisms and model of field assisted quantum tunneling composites

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Abstract

Field assisted quantum tunneling composite (FAQTC) is a unique pressure-sensitive material with the advantages of large resistance change range under external force, easy preparation and excellent mechanical properties. In this paper, with attentions to the pressure-sensitivity of the FAQTCs, the effects of silicon rubber matrix, diameter and dosage of nickel particles as well as magnetic field treatment are systematically investigated. The reproducibility of the pressure-sensitivity of the FAQTCs under cyclic load is explored. Based on Cotton's equation and Burger's model, the descriptions of stress relaxation behavior and electrical resistance relaxation behavior of the composites under static compressive loading are given respectively. The results show that external magnetic field during curing process allows better adjustment of the pressure-sensitivity of the FAQTCs with fewer nickel particles. The increase of the dosage of nickel particles can improve the stability and reproducibility of the pressure-sensitivity of the composites. Electrical resistance relaxation behavior of the composites is partly controlled by the

stress relaxation behavior. Moreover, based on the theory of percolation conduction, the mechanism of the pressure-sensitivity of the FAQTCs under uniaxial load is discussed and further qualitatively explained by adopting effective conducting path model. Finally, on the basis of this model combined with quantum tunneling effect, a mathematical model describing the pressure-sensitivity of the composites is established, which can well describe the pressure-sensitivity of the composites.

Key Words: Conductive polymer composites; Pressure-sensitivity; Quantum tunneling effect; Field emission effect; Sensors

1 Introduction

Intelligent transportation system (ITS) is an effective way to solve the increasingly serious traffic problems, in which sensor technology is a critical link between multiple traffic parameters detection and efficient traffic control management. This has led to the development of various traffic sensors with various sensing principles such as optical sensors, acoustic sensors, magnetic sensors and pressure-sensitive sensors ^[1-3]. Over the last few decades there has been a huge interest in using pressure-sensitive composites for fabricating traffic sensors due to the advantages of simple structures, enhanced properties, versatile surveillance and robust multifunctional applications ^[2, 4-6]. The pressure-sensitive composite refers to a system composed of insulating or semi-conducting matrix (e.g. rubber, epoxy, ceramic or cement) and conductive fillers (e.g. carbons including carbon nanotubes, carbon fiber, graphite, pyrolytic carbons and carbon blacks or metals including metal powders, metal fiber or metal oxides), with the property of the electrical resistivity of which decreases under compression as the separation of the fillers decreases, while the electrical resistivity increases when the composites are stretched ^[7-15]. By choosing the proper

type and amount of matrix and fillers, desirable pressure-sensitivity for various applications can be achieved from finger sensing ^[16] to vehicle sensing ^[17]. Among these hybrid systems, field assisted quantum tunneling composites (FAQTCs) have generated a large interest in both the scientific community and industrial research due to their unique electrical properties and ultrahigh pressure-sensitivity ^[18-20].

FAQTCs (or often called QTCs) are fabricated by adding spiky spherical nickel particles into conventional rubber-, epoxy- or cement-based materials (usually silicon rubber). Peratech Ltd ^[21] firstly developed the FAQTCs by wetting spiky spherical nickel particles with silicone rubber intimately. Generally, the electrical properties of pressure-sensitive composites are described by percolation theory ^[22]. According to classical percolation theory, with increasing conductive filler content, considerably, a jump in conductivity can be observed when a critical filler content is reached in the matrix, i.e. termed the electrical percolation threshold. However, the FAQTCs show entirely different conductive behavior from traditional pressure-sensitive composites using carbon black, carbon nanotubes, graphite or other metal particles as conductive fillers, which act as an insulator even the nickel particles incorporated as high as 94 wt% ^[23, 24]. However, under modest compression the electrical resistance can fall drastically from 10^{12} - $10^{13} \Omega$ to less than 0.01Ω due to the field-assisted quantum tunnel effect. It means that the FAQTCs can switch from good insulators to excellent conductors when suitably deformed. This near-perfect insulation characteristic of the FAQTCs in unstressed state is explained as the intimate coating of rubber on nickel particle surfaces, preventing the nickel powders from direct physical contact, thus continuous conductive network fails to form throughout the composites. In addition, the sharp nano-tips on the surface of spiky spherical nickel particles are restrained due to the rubber coating. Once the QTC sensors are deformed by compression, the inter-particle separation distance

between the nickel particles is reduced, increasing the amount of conductive paths across the matrix material. The most dominant factor is that the sharp surface features of the nickel particle are released when deformed. A high local electrical field is generated around sharp surface of the nickel particle, i.e. the barrier height and breadth between the nickel particles decrease and the potential energy of charge carriers through tunneling barrier increases when the external constant voltage injected into the both ends of the FAQTCs. As a result, the electrical resistivity of the FAQTCs exponentially decreases by several orders of magnitude when the composites are deformed^[7, 19, 20]. Therefore, one of the major advantages of sensors based on these composites is energy saving as an open circuit is formed when the FAQTCs sensors are in non-operating state, which is particularly of great importance in long-term monitoring application.

The combination of high sensitivity and tunable electrical behavior from the insulating to conductive makes FAQTCs the ideal candidate for the design and development of multi-purpose sensors. Some reports of tactile sensing capabilities of the FAQTCs have shown the significant prospect in human robotic applications^[18, 25, 26]. Applications of the FAQTCs as chemical sensors responding to volatile organic compounds have also been reported^[23, 24]. Recently, our group has designed and implemented a traffic sensor based on the FAQTCs for long-term and real-time traffic parameter detection^[6]. However, these applications usually use the FAQTCs as “all or nothing” switches. Also, effects on the pressure-sensitivity of FAQTCs, especially for rubber-based composites such as conductive filler amount, dimension and morphology of conductive fillers, polymer matrix viscoelasticity, interface between fillers and polymer, loading forms, as well as factors associated with time-dependent electrical behavior have been rarely reported. It is very necessary to provide a deeper understanding of the conduction processes and characterize the FAQTCs in depth for promoting other applications that related to quantifying,

such as long-term and accurate traffic monitoring.

This paper aims to systematically study the effect of conductive fillers and silicon rubbers on the pressure-sensitive behaviors of the FAQTCs. The electrical properties of the composites prepared under different curing conditions are studied first, followed by the study of its surface topology and the inner structure using scanning electron microscopy. Then, different loadings including the monotonic compressive loading, cyclic compressive loading and static compressive loading are performed. Finally, based on the experimental results, the mechanisms of pressure-sensitivity of the composites are investigated and a mathematical model describing pressure-sensitivity is accordingly developed.

2 Experimental details

2.1 Materials

Two types of spiky spherical nickel powders with different diameters (type 123 and type 255, Inco Ltd, CA) were used as conductive fillers, the typical physical characteristics of which are given in Tab. 1. Three types of silicon rubbers differ in viscosity (in liquid phase) were used as matrices, as shown in Tab. 2. Polydimethylsiloxane (PDMS, SYLGARD 184) and Silicon T4 coupled with curing agent were supplied by Dow Corning Corporation, USA. Silicon RTV 615 and catalyst (dibutyltin dilaurate, CP) were obtained from Shenzhen Hongyejie Technology Co., Ltd. Dimethyl silicon oil ($\eta = 100 \text{ mPa}\cdot\text{s}$, 25°C) was from Beijing Hangping silicon and chemical Co., Ltd. Deionized water was used in all the experimental processes. All chemicals were used as received without further purification.

Tab. 1 Typical physical characteristics of spiky spherical nickel powders

Type	Type 123	Type 255
Fish sub-sieve size (μm)	3-7	2.2-2.8
Bulk density (g/cm^3)	1.8-2.7	0.5-0.65
Typical specific surface area (m^2/g^{-1})	0.4	0.7
Density (g/cm^3)	8.9	8.9
Electrical resistivity ($\Omega\cdot\text{cm}$)	6.84×10^{-4}	6.84×10^{-4}

Tab. 2 Types and the characteristics of silicon rubber after curing

Silicon type	Density (g/cm^3)	Viscosity ($\text{mPa}\cdot\text{s}$)	Hardness (A°)	Tensile strength (MPa)
T4	0.96	70000	40	6.7
PDMS	1.03	51000	43	6.7
R615*	1.08	15000	15	2.5

*For R615, a 50 vol % of dimethyl silicon oil was mixed to reduce the viscosity of silicon R615 matrix in the liquid phase.

2.2 Composite preparation

According to the solution mixing process as described previously ^[27], liquid silicon rubber and spiky spherical nickel powders were mixed and carefully stirred for about 15 min. For samples prepared by silicon R615, dimethyl silicon oil (50% in weight ratio) was first mixed and mechanically stirred for 10 min before introducing nickel particles to control the mixture viscosity. Subsequently, the curing agent (for silicon R615, called catalyst), which accounted for 10% (for silicon R615, it is 3%) in weight ratio of silicon rubber, was added to the above mixture and thoroughly mixed for 5 min, before the degassing process in vacuum and the subsequent extrusion in the poly(methyl methacrylate)(PMMA) mold with a diameter of 20mm. The mold has two different effective depths of 1mm and 4mm, with an uncertainty of 10%. The whole mixing process should avoid injuring sharp protrusions on the surface of spiky spherical nickel powders ^[20]. Two electrode plates were inserted into the mold (see Fig. S1) and then the mixture was cured

in an oven at 60°C for 8h. For the ordered-structure FAQTCs samples preparation, the mixture was simultaneously subjected to a constant magnetic field of 300mT during the curing process as shown in Fig. S1. All samples were prepared in duplicate or triplicate and the data presented were average values.

For the convenience of discussion, in this paper, for instance, sample was denoted as T4/123-3M representing the composite prepared by silicon T4 and type 123 spiky spherical nickel powders with a weight ratio of nickel powder to silicon rubber of 3:1 and cured under a magnetic field.

2.3 Characterization

The experimental setup is shown in Fig. 1. The electrical resistance under compression was directly measured by a two-electrode method at room temperature, using a Keithley 2100 digital multimeter with a measurement range of 100M Ω under constant voltage of 1 V (Keithley Instruments Inc., Cleveland, OH, USA). Therefore, samples with a resistivity above 100M Ω are considered as nonconductive due to the limitation of current set-up. The compressive testing under displacement control was conducted using an Instron 5567A universal mechanical testing machine with a load cell of 1000N (Instron Inc., Norwood, MA, USA). Two PMMA thin plates were placed between the specimen and the loading plate to eliminate electrical interference between the samples and the testing machine. All of the measurements from the universal mechanical testing machine and the multimeter were taken simultaneously and automatically into a computer to record the real-time resistance under compression as illustrated in Fig. 1. Ten loading-unloading cycles between a specific strain range with a loading rate of 0.2mm/min were conducted for each composite to investigate the dynamic pressure-sensitivity. For stress relaxation

behaviors test, the specimen was compressed at an instantaneous rate of 2 mm/min to a given strain and then the loading head kept constant. All the measurements were performed at room temperature.

Fig. 1 Photograph (a) and schematic diagram (b) of the compression test apparatus

The morphological characterization of the FAQTCs was carried out by a field emission scanning electron microscope (FESEM; model Nova NanoSEM 450, American FEI Ltd, USA) with an accelerating voltage of 10 kV. Fig. S2 shows the FESEM photos of the two spiky spherical nickel powders, nano-scale projections can be observed on the surface of the spiky spherical nickel particles

3 Results and discussion

3.1 Electrically conductive behaviors

The electrical resistances of each composite with and without magnetic field experience were

measured and compared before compression. Without magnetic field experience, all the composites using silicon T4 and PDMS as the matrix presented an insulating behavior with a value higher than $100\text{M}\Omega$ in the uncompressed state even if the weight ratio (denoted by w) of type123 (type255) to silicon rubber is up to 4:1(3:1), indicating that nickel particles are well separated each one from the others, confirming the absence of conductive paths. It can be verified from Fig. 2 that the nickel particles are intimately coated with thin film and well distributed inside the insulating matrix, resulting in no formation of large or long-range conductive aggregates throughout the composite. This phenomenon is similar with the results previously reported by Bloor^[20] and Stassi^[28], which provides the endorsement for field-assisted tunneling conduction between neighbouring nickel particles. Differently, the composites using silicon R615, which has relative low viscosity compared with the two other silicon rubbers, show measurable electrical resistance as listed in Tab. 3. The conductivity for the silicon R615-based FAQTCs increases with increasing nickel particle content, even exhibiting percolation behavior when $w=8:1$, whereas decreases with increasing nickel particle diameter. This phenomenon agrees with the fact that since silicon R615 has a lower viscosity in the liquid phase, it is able to produce a thinner insulating layer around the nickel particles. In this condition, the conduction regime is dominated by contacts among nickel particles, which shortens the conductive path across metallic aggregates^[29]. Therefore, there is an important role of the insulating material with aspects to the conductivity of the composites.

Fig. 2 SEM images of (a) PDMS/123-3. (b) PDMS/255-3. (c) PDMS/123-4 and (d) T4/123-4 FAQTCs

Tab. 3 Electrical resistivity of the silicon R615-based FAQTCs with different types and contents of nickel particles

Sample	R615/123-3	R615/123-6	R615/123-8	R615/255-4	R615/255-6
Electrical resistivity ($\Omega \cdot \text{cm}$)	1.20×10^{10}	9.42×10^6	145.70	3.37×10^9	1.33×10^6

On the other hand, it is reasonable to assume the determination of the distances among conductive fillers along the direction of electrical current. Further, the role of magnetic field in providing ordered chain structures in PDMS/255 FAQTCs was investigated by comparing the electrical resistivity of PDMS/255 FAQTCs and PDMS/255-M FAQTCs, as shown in Fig. 3. Composites curing under magnetic field show much lower electrical resistivity than those without magnetic treatment. SEM analysis (see Fig. S3) showed that large numbers of relatively ordered

chain structures composed of conductive nickel particles align along the applied magnetic field, attributing to the significant decrease in the electrical resistivity of PDMS/255-M FAQTCs. This result suggests that highly conductive polymer composites with relatively a small quantity of conductive fillers can be achieved by controlling the inner structure or precisely, the distance among conductive fillers. We have also investigated the effect of magnetic field on the electrical resistivity of R615/123 FAQTCs and R615/255 FAQTCs (see Tab. S1). It can be seen that magnetic field treatment could also reduce the electrical resistivity of the R615/123 FAQTCs and R615/255 FAQTCs. Some other factors affecting the order structure, such as curing condition, magnetic field intensity and nickel particle diameter should be studied deeply in the future.

Fig. 3 Comparison of electrical resistivity of PDMS/255 FAQTCs with different nickel particle contents, curing under magnetic field and under no magnetic field experience. Note that w denotes the weight ratio of type 255 to silicon PDMS, and M denotes under magnetic field.

3.2 Pressure-sensitive behaviors

Prior to sets of measurements performed to describe the pressure-sensing behavior of the FAQTCs, it is necessary to introduce the characteristic curve of pressure-sensitivity in consideration of convenience. As shown in Fig. 4, the electrical resistivity can be initially measured only when the stress reaches σ_a . Then, the change trend of the electrical resistivity as a function of applied compressive stress show exponential decreasing until the stress reaches a certain value σ_b , which may be a small range. Above σ_b the resistivity decreases gradually and is expected to become almost constant, corresponding to less sensitivity to pressure. Therefore, $\Delta\sigma_b = \sigma_b - \sigma_a$ can be defined as pressure-sensitive zone. In addition, the variation of electrical resistivity due to mechanical deformation can be quantified through determination of equivalent sensitivity $S_{p_i}^* = \ln\Delta\rho_i/\Delta\sigma_i$, which is herein, defined to characterize pressure-sensitivity of the FAQTCs, where i refers to the value of the stress, $\ln\Delta\rho_i = \ln\rho_i - \ln\rho_a$, and $\Delta\sigma_i = \sigma_i - \sigma_a$.

Fig. 4 Characteristic curve of pressure-sensitivity for the T4/123-4 FAQTC.

The pressure-sensitivity of the FAQTCs was investigated by uniaxial compression with a loading rate of 0.2mm/min as shown in Fig. 5a. In spite of different starting points due to different composites, the general trend demonstrated that the electrical resistivity of all samples decreases logarithmically with stress as described in characteristic curve above. However, it is clearly seen that the variation of electrical resistivity increases as the conductive filler content increases, especially for the initial compression part from 0~0.1MPa, indicating that more sensitive FAQTCs can be obtained by increasing the weight ratio of nickel particle to silicon rubber. Moreover, Fig.5b shows the electrical resistivity of the FAQTCs at $\sigma=0.6$ MPa. The electrical resistivity of the PDMS/123-2 FAQTC at $\sigma=0.6$ MPa is nearly 3 orders of magnitude higher than that of the PDMS/123-3 FAQTCs, and 5 orders of magnitude higher than that of the PDMS/123-4 FAQTC due to the less distribution density of nickel particles in composites (see Fig. 2a, c).

Fig. 5 (a) The electrical resistivity changes with applied stress under uniaxial compression for silicon PDMS-based FAQTCs with different sample thickness and different types and diameters of nickel particles. (b) The electrical resistivity at $\sigma=0.6$ MPa.

The dependence of pressure-sensitivity with respect to the sample thickness is also provided in Fig. 5a, from which it can be seen that pressure-sensitivity of the PDMS/123 FAQTCs slightly

decreased with decreasing sample thickness from 4mm to 1mm. By further comparing the electrical resistivity at $\sigma=0.6$ MPa (see Fig. 5b), the differences of electrical resistivity as thickness decreasing are shortened with increasing nickel particles content. It is therefore concluded that sample thickness shows little effect on the pressure-sensitivity of the FAQTCs. In sensory applications for robotics, structural health monitors, wearable communication devices and other systems, lightweight, tiny and thin architectures are preferred ^[30]. Therefore, an appropriate sample thickness can be selected to gain a desirable sensitivity for FAQTCs' sensing applications. In the following tests, sample thickness was chosen as 1mm unless otherwise stated.

Fig. 5a also shows the variation of pressure-sensitivity as a function of diameter of nickel particles, which indicates that the PDMS/123-3 FAQTC is less sensitive when compared to the PDMS/255-3 FAQTC. When $\sigma=0.6$ MPa, $S_{p_{0.6}}^*$ of the PDMS/255-3 FAQTC is ~ 26.63 , which is larger than that of PDMS/123-3 FAQTC (~ 24.24). This results can be explained by the higher distribution density of nickel particles in composites with type 255 nickel powders than that in the composites with the same content of type 123 nickel powders as obviously shown in Fig. 2a, b. However, different result was demonstrated by our previous work, in which different diameters of spiky spherical nickel particles were dispersed into cement-based composites. The sensitivity of cement-based composites decreases with decreasing particle size of nickel particles due to the lower initial electrical resistivity ^[31]. Such differences between different matrixes might originate from different interfacial interactions between the nickel particles and the insulating matrix ^[32]. Therefore, the effect of the insulating matrix on the pressure-sensitivity of the FAQTCs was further investigated as shown in Fig. 6.

Fig. 6 The effect of the insulating matrix on the pressure-sensitivity of the FAQTCs fabricated with different silicon rubber. (a) The electrical resistivity changes with applied stress under uniaxial compression for the T4/123-4 FAQTC and PDMS/123-4 FAQTC. (b) The electrical resistivity and strain (insert) change with applied stress under uniaxial compression for the R615/123-6 FAQTC.

For the T4/123-4 FAQTC, the electrical resistivity can be initially obtained when $\sigma=0.6$ MPa (i.e. $\sigma_a=0.6$ MPa), which is $\sim 7.55 \times 10^8 \Omega \cdot \text{cm}$. This value is even higher than that of the PDMS/123-4 FAQTCs ($\sim 6.41 \times 10^7 \Omega \cdot \text{cm}$) at $\sigma_a=0$ MPa. By increasing the stress, the electrical resistivities of the two FAQTCs are both significantly decreased, reaching their saturation resistivity at a stress (σ_b) of ~ 0.31 MPa and of ~ 3.48 MPa for the PDMS/123-4 FAQTC and the T4/123-4 FAQTC, respectively. This indicates that each pressure-sensitive zone of the PDMS/123-4 FAQTC is much narrower than that of T4 based FAQTCs. Interestingly, the two FAQTCs have comparable electrical resistivity variation within each pressure-sensitive zone, namely comparable equivalent sensitivity but different working range. Such difference may be explained with the accepted idea of the pressure-sensitivity of conductive polymer is generated by the translation and rotation of conductive fillers caused by the deformation of the polymer matrix under compression. This can induce rearrangement and orientation of conductive fillers, leading to the formation of effective conductive path across the matrix [33, 34]. In addition, thin polymer layer

between the nickel particles where the mobility of the molecular polymer chains is restricted to some extent due to filler-polymer interaction, depending on the type of the polymer and the filler to filler distance. For the silicon PDMS-based FAQTCs, as silicon PDMS has a lower viscosity in the liquid phase, it is able to produce a thinner insulating layer around the particles during their dispersion inside silicone and the nickel particles, on turn, can easily rotate disposing closer together (see Fig. 2c, d). At the same time, the filler reinforcement effect in the elastomer matrix is also reduced. Therefore, when the silicon PDMS-based FAQTCs is slightly deformed, the particles come together, exhibiting extremely high pressure-sensitivity^[35-37]. This explanation is further scrutinized by comparing with the R615/123-6 FAQTC, which has narrower pressure-sensitive zone than the previous two FAQTCs regardless of higher nickel particles content. More study is still needed to understand the mechanism. It is therefore concluded that tailored sensitivity to satisfy various application scenarios can be achieved by selection of different silicon rubbers.

As discussed in the Section 3.2, the applied magnetic field can form ordered chain structures inside the matrix, thus causing the conductivity of the FAQTCs effectively improved. In addition, the effect of magnetic field on enhancement of the pressure-sensitivity of the FAQTCs was also examined by comparing PDMS/255 FAQTCs with PDMS/255-M FAQTCs as a function of nickel particle content (see Fig. 7). The change of electrical resistivity with applied stress of PDMS/255 FAQTCs is shown to increase with increasing concentration of nickel particles, suggesting that the pressure-sensitivity of the PDMS/255 FAQTCs increases with added nickel particles, which is in good agreement with the result presented in Fig. 5. However, an entirely opposite trend was observed for the PDMS/255 FAQTCs after magnetic field treatment (see Fig. 5b). The equivalent sensitivity at $\sigma=0.3\text{MPa}$ of the PDMS/255-M FAQTCs nearly halved with increasing nickel

particles from $w=1:1$ to $w=3:1$, in spite of much lower initial electrical resistivity (see Fig. 3). Interestingly, the PDMS/255-1M FAQTCs shows the highest equivalent sensitivity at $\sigma=0.3\text{MPa}$ (~ 51.937), even slightly higher than that of the PDMS/255-1M FAQTCs (~ 51.437). This difference may be attributed to more ready-to-continuously preformed pathways for electron transport along the direction of magnetic field, leading giant electrical resistivity change induced by stress. Considering that the PDMS/255-1M FAQTC is much lighter in weight than the PDMS/255-3 FAQTC, this result suggests the external magnetic field during curing process allows better adjustment of the pressure-sensitivity of the FAQTCs with fewer nickel particles. Moreover, the smoother curves obtained for the PDMS/255-1 FAQTC indicate stable and correct collection under lower electrical resistance, thus low equipment requirements [38].

Fig. 7 The effect of magnetic field on the pressure-sensitivity of the FAQTCs. (a) The electrical resistivity changes with applied stress under uniaxial compression for PDMS/255 FAQTCs and PDMS/255-M FAQTCs with different nickel particles content. (b) The equivalent sensitivity at $\sigma=0.3\text{ MPa}$.

3.3 Reproducibility of pressure-sensitivity

Generally, the pressure of tires on the ground caused by a passing vehicle is about

0.7~2.0MPa^[39]. Therefore, the T4/123 FAQTCs is more suitable to be developed as a traffic sensor for traffic parameter detection. To evaluate the reliability of the T4/123 FAQTCs, the dynamic pressure-sensitivity was investigated with a cyclic compressive between a specific strain range for each composite, subjected to ten loading-unloading cycles with a loading rate of 0.2mm/min, as shown in Fig. 8. It is observed that the electrical resistivity generally decreases with increasing stress/strain and increases with decreasing stress/strain in one cycle, producing a series of successive and regular peaks (i.e. minimum electrical resistivity value). Much smaller peak values are observed for the T4/123-4 FAQTC, which has higher filler content than the T4/123-3 FAQTC, indicating higher pressure-sensitivity under dynamic deformation. This phenomenon agrees well with the observations discussed in Section 3.2. In addition, upward shift between each adjacent peak is clearly noted, i.e. the reduction of pressure-sensitivity. Moreover, FAQTCs with lower filler contents have a more obvious drift during cyclic stretching compression. This shift comes to disappear after several cycles, which means good stability. More obvious result could be found in Fig. S5. This is thought to be caused by the competition between destruction and reconstruction of conductive pathways during cyclic loadings^[40-42]. The transverse deformation of composites caused by compression induces the orientation of nickel particles and rupture of nickel-rubber bonds axially, i.e. variations in the conductive networks, which come into a stable state after several repeated cycles. Previous work of Kost et al. has suggested that cyclic preconditioning strain could be utilized for stabilization of the electrical resistivity of the conductive rubber-based composites^[41], which is in good agreement with our observations. Fig.S6 shows cyclic stress-strain curves of the T4/123 FAQTCs, which have considerably obvious hysteresis loops due to internal friction generated by the motion of polymer molecular chains and nickel particles^[43, 44]. When the strain comes to the specified value in unloading process, offset

($\sim 1.33\text{MPa}$ for the T4/123-3 FAQTC and $\sim 1.18\text{MPa}$ for the T4/123-4 FAQTC) occurs between the stress value of the first cycle and that of the other nine cycles, for which the values are nearly constant, indicating the production of plastic deformation under the high stress ^[45]. Moreover, similar hysteresis loops are also observed in the cyclic stress-electrical resistivity curves as shown in Fig. S5, which means that the response of the conductive networks to applied stress exists hysteresis in the forward and backward curves. This phenomenon therefore provides evidence that the viscoelastic behavior of silicon rubber matrix has a significant influence on the pressure-sensitivity of the FAQTCs ^[18, 46]. Therefore, the time dependence of pressure-sensitivity of the FAQTCs was accordingly investigated in the next section.

Fig. 8 Time-history relationship between electrical resistivity and cyclic compressive stress/strain. (a) and (b) 10 cycles at a strain between 22.5% and 37.5% for T4/123-3 FAQTC. (c) and (d) 10 cycles at a strain between 15% and 30% for T4/123-4 FAQTC.

3.4 Electrical resistance relaxation behavior

Silicon rubber is a typical elastomer, which shows marked viscoelastic behavior. Under a constant stress or strain, the silicon rubber based FAQTCs will exhibit the time-dependent mechanical behaviors, including stress relaxation and creep. Besides, the interparticle separation change of the polymer matrix is also performed as a function of time, which can be interpreted by the creep of polymer, causing the conductive particles time-dependent movement, thus pressure-sensitivity time-dependent of the FAQTCs. Similarly, the phenomenon of the electrical resistivity of the FAQTCs changes with time under constant external strain is named electrical resistance relaxation behavior^[43, 47, 48].

Fig. 9 shows stress relaxation behaviors of the T4/123-4 FAQTC at an instantaneous rate of 2mm/min to different constant strains. It can be seen that the stress shifts followed a logarithmic decrease with increasing time, whereas the amplitudes of the shifts were increased with increasing strain. The stress relaxation behaviors of polymer composites can be favorably described by Cotton equation^[49]:

$$\sigma_t = \sigma_1 t^{-n} \quad (1)$$

where σ_t and σ_1 represent the value of the stress at the moment t and $t = 1$ s, respectively, n is defined as the stress relaxation rate. As shown in Fig. 9, the fitted data from Eq. (1) coincides well with the experimental data.

Fig. 9 Stress relaxation behavior of the T4/123-4 FAQTC. (a) $\varepsilon=20\%$. (b) $\varepsilon=25\%$. (c) $\varepsilon=28\%$ and (d) $\varepsilon=30\%$.

The fitted relaxation rate n plotted in Fig. 10 as a function of the given strain was found to increase with increasing strain due to the accelerated adjustment of chain reformation inside the composites when subjected to a larger strain/stress. The viscoelastic behavior is generally studied and modelled by using Burgers' model, in which the viscous term in Maxwell's (in-series spring, E and dashpot, η) viscoelastic model is replaced by a Kelvin's model (in-parallel spring, E and dashpot, η)^[43, 50](see Fig.11a). Fig.11b shows the change process of the microstructure of the percolation network for composite under static compression. Initially, the silicon rubber molecules are highly frizzled with the lengths of springs E_1 , E_2 and dashpot η are L_0 , l_0 and d_0 , respectively. The instantaneous strain would then cause the elastic deformation of the composite, whereas

without the response of the viscous part (in-parallel element), i.e. the length of springs E_1 changes from L_0 to L_1 , while l_0 and d_0 keep constant. At this moment, the system is in an unstable state, each element moves coordinately to maintain stress equilibrium. The adjustment of molecular configuration of silicon rubber chains through thermal motion may lead to the relative slippage between the chains, resulting in the reconversion of frizzled configurations. During this process, the viscous part move time-dependently, i.e. the length of springs E_2 extends from l_0 to l_1 , dashpot η changes from d_0 to d_1 , while E_1 shrinks from L_1 to L_2 to eliminate interior stress and finally the stress relaxation is likely to stop when the whole system has a new equilibrium state ^[51]. This transformation from elastic deformation to viscoelastic deformation can be facilitated by the increasing strain, manifesting as stress relaxation rate increases as the applied strain is increased (see Fig.10) ^[47].

Fig. 10 Fitted stress relaxation rate as a function of strain.

Fig. 11 Schematic diagrams of (a) Burger's model and (b) the change process of the microstructure of the percolation network for composite under static compression

In the whole process of stress relaxation, not only the movement of molecules and segments occurs, but also the slippage of nickel particles is generated, resulting in the alteration the local microstructure of the conductive network, i.e. electrical resistance relaxation behavior (see Fig. S7). The electrical resistance of the composite decreased over time to a steady state during the stress relaxation. Based on the above analysis, similarly, the Burgers' model can be applied to describe the electrical resistance relaxation behavior of the FAQTCs^[52, 53].

$$\frac{\Delta R}{R_0} = \frac{R - R_0}{R_0} = a + b \exp\left(-\frac{t}{\tau_R}\right) + ct \quad (2)$$

where R_0 represents the electrical resistance at the moment $t = 0$, R represents the electrical resistance at the any moment t , $\Delta R/R_0$ represents the electrical resistance fractional change, τ_R is

the mean relaxation time, and a , b and c are constants depending on the level of strain, in which $b \cdot c < 0$ and $b > 0$.

As shown in Fig. 12, the fitted data obtained from Eq. 2 coincides well with the experimental data. Therefore, it can be concluded that the Burgers' model is suitable to explain the electrical resistance relaxation behavior of the FAQTCs, including the instantaneous response of the conductive network to the applied strain (the first constant part in Eq. 2) and the time-dependent response related with the mechanical behaviors of the polymer matrix (the second exponential part and the third linear part in Eq. 2) ^[51]. The fitted mean relaxation time τ_R is plotted in Fig. 13 as a function of the given strain, which shows different change trend with the stress relaxation (see Fig.10). This is likely due to the rigid structure of nickel particles. The electrical resistance of the composite can be as low as several ohms when high strain was applied (see Fig.S7). This near-metallic conducting characteristic provides the proof that a number of physical contacts may be generated between nickel particles, which may lead to higher sliding friction inside the composites. Finally, the slippage of nickel particles responding to the driving of silicon rubber molecules and segments movement would be weakened, leading to longer electrical resistance relaxation time. Therefore, it is postulated that the electrical resistance relaxation behavior of the FAQTCs is not only related to mechanical relaxation behavior of the matrix, but also influenced by the conductive network responding to the adjustment of dispersion state of each nickel particle under deformation. More study is still needed to focus on the stress relaxation behavior of the composites.

Fig. 12 Fractional electrical resistance change $\Delta R/R_0$ as a function of time t during stress relaxation at different strains for the T4/123-4 FAQTC. (a) $\varepsilon=20\%$. (b) $\varepsilon=25\%$. (c) $\varepsilon=28\%$ and (d) $\varepsilon=30\%$.

Fig. 13 Fitted mean relaxation time as a function of strain.

3.5 Modeling and mechanism

Generally, pressure-sensitivity can be considered as percolation brought by the deformation-induced volume fraction change of conductive fillers^[29, 32, 54]. As shown in Fig. 4, using an analogy with percolation curve, the electrical resistivity as a function of stress can be divided into three characteristic zones: Insulation zone A, percolation zone B and conductive zone C. Low values of the applied stress (lower than σ_a) correspond to an insulating state, at which the percolation networks come to appear but have not formed, and gradually develop with the increasing stress, thus the conductivity of the composites strongly relies on the microstructure of the percolation networks, i.e. the insulating thin films remaining in the contact zone between the nickel particles^[29]. Here, σ_a is defined as stress percolation threshold. By increasing the value of the stress, the proximity between particles increases the number of contact spots, which enables the formation of long-range percolation cluster. The percolation regime is now achieved when the stress reaches σ_b . The width of percolation zone (i.e. $\sigma_b - \sigma_a$) is closely related to composition of the composites, such as the nickel particles content and the silicon rubber viscosity (see Section 3.2). In this case, the conductivity is governed by tunneling the thin films between the nearest metallic particles. In addition, the sharp nano-tips on the surfaces of nickel particles generates field emission effect conduction, which increases the potential energy of electrons through tunneling barrier between the nickel particles, thus causing the enhancement in tunneling conduction^[7, 19, 20, 55, 56]. This may contribute to the ultrahigh pressure-sensitive of the FAQTCs responding to the applied external force or deformation. Above σ_b , a continuous path between particles is established, the composite is now governed by the metallic conductivity through the contact spots between the nickel particles. The above-mentioned three processes are schematically described in Fig. 14. This analysis suggests that the electrical resistivity as a function of stress can be described

by the percolation scaling law:

$$\rho \propto (\sigma - \sigma_p)^{-t} \quad (\sigma > \sigma_p) \quad (3)$$

where σ_p represents the stress percolation threshold, i.e. σ_a and t is the percolation exponent.

The electrical resistivity ρ of the T4/123-4 TAQTC was found to scale linearly as a function of $\sigma - \sigma_p$, as shown in Fig. 15. The t value is higher than that calculated for a 3D random network in content-related percolation theory ($t \approx 2$)^[57]. This may be explained by the destruction of the conductive networks under compression^[9, 40].

Fig. 14 Schematic diagram of the percolation conduction mechanism in FAQTCs under compression

Fig. 15 Electrical resistivity ρ as a function of $\sigma - \sigma_p$ for the T4/123-4 FAQTC

In order to further explain the pressure-sensitivity mechanism of the FAQTCs qualitatively, effective conductive path model was used to analyze the changes in the inner structure of the composite during compression [8, 58, 59]. According to the effective conductive path theory, the applied stress leads to changes in the gap between conductive fillers. Electron can flow between the adjacent fillers by the tunneling effect if the gap is small enough, leading to the formation of local conductive path (see Fig. 16a). If local conductive path penetrates insulating matrix, an effective conductive path is formed, contributing to the decreasing electrical resistivity of the composite (see Fig. 16b). Also, compression would cause the transverse slippage of conductive fillers, leading to the destruction of effective conductive path (see Fig. 16c). Therefore, pressure-sensitivity is regarded as the change in the number of effective conductive paths during compression. For the FAQTCs, the increase of the number of effective conductive paths plays a dominant role in terms of pressure-sensitivity.

Fig. 16 Schematic diagram of effective conductive path model. (a) Tunneling the thin film between the nearest metallic particles. (b) Formation of effective conductive path. (c) Destruction of effective conductive path.

To build a mathematical model of the pressure-sensitivity mechanism of the FAQTCs succinctly, only the tunneling conduction is taken into consideration. Based on the tunneling theory [60], the tunnel current $I(\varepsilon)$ as a function of the strain ε can be given by:

$$I(\varepsilon) = \frac{3a^2\sqrt{2m\varphi}}{2d(\varepsilon)} \left(\frac{e}{h}\right)^2 V \exp^{\gamma d(\varepsilon)} \quad (4)$$

where V is the applied voltage, m is the electron mass, φ is potential barrier height, e is the electron charge, h is Plank's constant, $d(\varepsilon)$ is the thickness of the tunneling film as a function of the strain ε , $\gamma = -\frac{4\pi}{h}\sqrt{2m\varphi}$. Then, the electrical resistance of a single effective conductive path $R_s(\varepsilon)$ can be calculated by ^[59]:

$$R_s(\varepsilon) = (M(\varepsilon) - 1) \frac{2h^2 d(\varepsilon)}{3e^2 a^2 \beta \sqrt{2m\varphi}} \exp^{\gamma d(\varepsilon)} \quad (5)$$

where $M(\varepsilon)$ represents the number of nickel particles forming a single effective conductive path. The total electrical resistance $R(\varepsilon)$ of the composite is approximated as the parallel electrical resistance of $N(\varepsilon)$ effective conductive paths, which can be calculated by ^[61]:

$$R(\varepsilon) = \frac{(M(\varepsilon) - 1)}{N(\varepsilon)} \frac{2h^2 d(\varepsilon)}{3e^2 a^2 \beta \sqrt{2m\varphi}} \exp^{\gamma d(\varepsilon)} \quad (6)$$

For convenience, the normalized electrical resistance of the composites $R_r(\varepsilon)$ is defined by:

$$R_r(\varepsilon) = \frac{R(\varepsilon)}{R(0)} = \frac{R_s(\varepsilon)/N(\varepsilon)}{R_s(0)/N(0)} = \frac{d(\varepsilon)/N(\varepsilon)}{d(0)/N(0)} \exp^{\gamma[d(\varepsilon)-d(0)]} \quad (7)$$

where $R(0)$ and $R_s(0)$ are the initial electrical resistances of a single effective conductive path and the composite, respectively, $N(0)$ is the initial number of effective conductive paths, $d(0)$ is the initial thickness of the tunneling film. This variation in the thickness is caused only by the deformation of the polymer since the nickel particles result incompressible compared with the silicon rubber. Therefore, the thickness of the tunneling film $d(\varepsilon)$ can be calculated as:

$$d(\varepsilon) = d(0)\left(1 - \frac{\sigma}{G}\right) = d(0)(1 - \varepsilon) \quad (8)$$

where G is the compressive modulus of the composite. To assume all nickel particles as spherical with the same diameter and arranged in a cubic lattice structure, $d(0)$ can be estimated as ^[62]:

$$d(0) = D \left[\left(\frac{\pi}{6\phi} \right)^{\frac{1}{3}} - 1 \right] \quad (9)$$

where D is the nickel particle diameter, ϕ is the nickel particle volume fraction, which is given by:

$$\phi = \frac{w\rho_s}{\rho_n + w\rho_s} \quad (10)$$

where ρ_s and ρ_n are the density of silicon rubber and nickel particle, respectively. As discussed above, three characteristic zones in Fig. 4 have different change rate in the number of effective conductive paths: in insulation zone A, no effective conductive path is formed; in percolation zone B and conductive zone C, the number of effective conductive paths is exponential changed with different rates as a function of the stress/strain. Therefore, only zone B and zone C will be considered. The normalized numbers of effective conductive paths in zone B, $N_r^B(\varepsilon)$ and zone C, $N_r^C(\varepsilon)$ as a function of ε are modeled as follows ^[39, 63]:

$$N_r^B(\varepsilon) = \frac{N^B(\varepsilon)}{N(a)} = \exp^{(A\varepsilon + B\varepsilon^2 + C\varepsilon^3 + D\varepsilon^4)} \quad (11)$$

$$N_r^C(\varepsilon) = \frac{N^C(\varepsilon)}{N(b)} = \exp^{(A_1\varepsilon + B_1\varepsilon^2 + C_1\varepsilon^3 + D_1\varepsilon^4)} \quad (12)$$

where $A, B, C, D, A_1, B_1, C_1$ and D_1 are fitting parameters. The substitution of Eqs. 11 and 12 into Eq. 7 yields the normalized electrical resistances of the composites $R_r^B(\varepsilon)$ and $R_r^C(\varepsilon)$:

$$R_r^B(\varepsilon) = \frac{R(\varepsilon)}{R(a)} = \frac{R_s(\varepsilon)/N^B(\varepsilon)}{R_s(a)/N(a)} = (1 - \varepsilon) \exp^{-(A^* \varepsilon + B \varepsilon^2 + C \varepsilon^3 + D \varepsilon^4)} \quad (13)$$

$$R_r^C(\varepsilon) = \frac{R(\varepsilon)}{R(b)} = \frac{R_s(\varepsilon)/N^C(\varepsilon)}{R_s(b)/N(a)} = (1 - \varepsilon) \exp^{-(A_1^* \varepsilon + B_1 \varepsilon^2 + C_1 \varepsilon^3 + D_1 \varepsilon^4)} \quad (14)$$

where $A^* = \gamma d(a) + A$ and $A_1^* = \gamma d(b) + A_1$. Taking logarithm of Eqs.13 and 14:

$$\ln(R_r^B(\varepsilon)) = -(A^* \varepsilon + B \varepsilon^2 + C \varepsilon^3 + D \varepsilon^4) \ln(1 - \varepsilon) \quad (15)$$

$$\ln(R_r^C(\varepsilon)) = -(A_1^* \varepsilon + B_1 \varepsilon^2 + C_1 \varepsilon^3 + D_1 \varepsilon^4) \ln(1 - \varepsilon) \quad (16)$$

In this paper, only the experimental data of the T4/123-4 FAQTC was fitted with Eqs.15 and 16 as shown in Fig. 17, which demonstrates that the fitted data obtained from Eqs. 15 and 16 coincides well with the experimental data. Fitting parameters are listed in Tab. S2. The difference of the fitting parameters in different zones is mainly due to the different formation rates of the number of effective conductive paths during compression.

Fig. 17 Experimental data and fitted data of the T4/123-4 FAQTC. The inset shows normalized electrical resistivity changes with applied strain for the T4/123-4 FAQTC. Two transition zones are distinctly observed when $\varepsilon \approx 19\%$.

In addition, from Eq. 8, the normalized electrical resistances of the composites $R_r^B(\sigma)$ and $R_r^C(\sigma)$ as a function of σ can be expressed as:

$$R_r^B(\sigma) = \frac{R(\sigma)}{R(a)} = \frac{R_s(\sigma)/N^B(\sigma)}{R_s(a)/N(a)} = (1 - \frac{\sigma}{G}) \exp^{-(A^* \frac{\sigma}{G} + B(\frac{\sigma}{G})^2 + C(\frac{\sigma}{G})^3 + D(\frac{\sigma}{G})^4)} \quad (17)$$

$$R_r^C(\sigma) = \frac{R(\sigma)}{R(b)} = \frac{R_s(\sigma)/N^C(\sigma)}{R_s(b)/N(a)} = (1 - \frac{\sigma}{G}) \exp^{-(A_1^* \frac{\sigma}{G} + B_1(\frac{\sigma}{G})^2 + C_1(\frac{\sigma}{G})^3 + D_1(\frac{\sigma}{G})^4)} \quad (18)$$

It should be noted that compression modulus G of the FAQTCs rose with the applied stress. To increase the accuracy of the fitting models, the mechanical effects on compression modulus should be taken in account. The value of G can be estimated from the derivative of the experimental stress–strain curve and subsequently fitted as a function of the stress:

$$G(\sigma) = k_1 + k_2\sigma + k_3\sigma^2 \quad (19)$$

where k_1 , k_2 , and k_3 are fitting parameters. Therefore, the electrical resistivity-stress curve of the T4/123-4 FAQTC was simulated using the parameters in Tab. S2, comparing with the experimental data as shown in Fig. 18. The simulated data agrees well with the experimental data suggesting the proposed mathematical model can be used to describe the pressure-sensitivity mechanism of the T4/123-4 FAQTC. It also suggests that the quantum tunneling effect contributes to the pressure-sensitivity under compression. However, this proposed mathematical model is still not a universal model to describe the pressure-sensitive behavior of the FAQTCs completely due to the randomness of the system. This could be improved by adding effects such as the dimensions of the FAQTCs, polymer matrix viscoelasticity and the influence of pressure and temperature on the elasticity modulus and the dynamic viscosity of the FAQTCs.

Fig. 18 Experimental data and simulated data of the T4/123-4 FAQTC. The insert shows the stress-compression modulus curve for the T4/123-4 FAQTC.

4 Conclusions

Under different curing conditions, the FAQTCs were fabricated using different kinds of nickel particles, different dosages of nickel particles and different silicon rubber types. It was demonstrated that the composites act as an insulator without loading due to the silicon rubber wrapping on the surface of nickel particles, causing no formation of percolation conducting network in the composites. Magnetic field treatment can promote the generation of chain conductive structures effectively, thus causing a significant increase in the conductivity of the composites. In addition, the external magnetic field during curing process allows better adjustment of the pressure-sensitivity of the FAQTCs with fewer nickel particles. The composites with remarkable response to external force can be used to develop traffic detection sensors. The increase of the dosage of nickel particles can improve the stability and reproducibility of the pressure-sensitivity of the composites. Electrical resistance relaxation behavior of the composites

is partly controlled by the stress relaxation behavior. This study provides a guideline for the fabrication of the FAQTCs with tunable pressure-sensitivity and good cyclic electromechanical consistency. Finally, based on the theory of percolation conduction, the mechanisms of the pressure-sensitivity of the FAQTC composites under uniaxial load are discussed and further qualitatively explained by adopting effective conducting path model. The proposed mathematical model can be well described the pressure-sensitivity of the composites, suggesting the dominant mechanisms of the remarkable pressure-sensitivity of the composites under uniaxial load are the quantum tunneling effect. For further investigation, our future work will pay attention to charge storage in the composite on the resistance-strain characteristics. In addition, simulation will be applied to describe the effect of nickel particles with random shapes, sizes and distribution on the pressure-sensitive behavior of the FAQTCs.

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Electrical resistivity exponentially decreases with stress increasing

Relaxation

Mechanism

Modeling