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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.

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

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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} Ω 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 Table 1. Three types of silicon rubbers differ in viscosity (in liquid phase) were used as matrices, as shown in Table 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 (η = 100 mPa 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.

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 20 mm. The mold has two different effective depths of 1 mm and 4 mm, 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°Cfor 8 h. For the ordered-structure FAQTCs samples preparation, the mixture was simultaneously subjected to a constant magnetic field of 300 mT 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

Table 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 (Ω•cm)	6.84 × 10^{-4}	6.84 × 10^{-4}