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学位論文題目	STUDY OF CAPACITIVE AND PIEZORESISTIVE FUNCTIONAL SILICONE ELASTOMERIC NANOCOMPOSITES FOR MECHANICAL SENSING APPLICATIONS （力学センサ用静電容量及びピエゾ抵抗特性を有するシリコーンエラストマーナノコンポジットに関する研究）
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論文内容の要旨

Mechanical Sensor is a significant device to convert different types of exterior mechanical stimulus, such as force, pressure, impact, vibration, and acceleration, to usable electrical signals. The demand for diverse types of sensors with smart property and low cost is growing rapidly as the development and widespread of many novel technologies. However, despite their various shapes and functionalities, traditional mechanical sensors are relatively expensive, limited by their fixed shapes, and sometimes even too fragile to measure the mechanical stimulus. Thus the demand of a variety of flexible mechanical sensors, which are cheap, sensitive, which can be applied to a flat or curving surface with large areas, is expanding fast. Such a flexible mechanical sensor has the ability of not only measuring an external mechanical stimulus, but also providing a protection to the inner device or apparatus. To develop a flexible mechanical sensor, silicone elastomer was utilized as a substrate, which is a special type of elastomer which possesses a lot of advantages, such as an extremely good flexibility, a very wide temperature tolerance range, an excellent insulation and an unparalleled excellent biocompatibility. Different types of particle-like functional additional materials can be integrated into the elastomer to provide their special functionalities, widen the areas of use, and overcome some drawbacks of the silicone elastomer matrix. This thesis aims to investigate the ability of different types of silicone elastomeric functional nanocomposites, including ferroelectric particles and conductive particles incorporated silicone elastomeric nanocomposites, to be applied as mechanical sensors, in other words, the ability of convert a mechanical stimulus to an electrical signal, with the efficiency and sensitivity as high as possible. This thesis includes 6 chapters as below:

Chapter 1 is a general introduction to the background of the research of this thesis. The basic introduction, the advantages and disadvantages of silicone elastomer were introduced. Then a brief introduction to the polymeric functional nanocomposites was made. Their characteristics and many related previous works were emphasized. As the mainstays of this thesis, the dielectric property, dielectric polymeric composites, electrically conductivity as well as electrically conductive nanocomposites was introduced in detail. Finally the object of the work was illustrated.

In Chapter 2, the extra-high dielectric properties of $BaTiO_3$, as well as its drawbacks were introduced. The potential of incorporate $BaTiO_3$ particles in an elastomer matrix to obtain a high mechanical sensing ability was demonstrated. A low dispersity, caused by the effects of incompatibility accompanied with the gravity during the curing procedure of silicone elastomer, was proved to be able to reduce the dielectric constant of the composites obviously. However, it is difficult to distribute $BaTiO_3$ nanoparticles into the silicone substrate due to the poor surface affinities between these two materials. The dielectric behaviors were found to be weakened by the incompatibility. To improve the dispersity of $BaTiO_3$ particles, a novel silicone coupling agent was used to modify the surface of particles. TG and FTIR results show that coupling agent was successfully coated on the surface. Raw $BaTiO_3$ particles and $BaTiO_3$ particles modified by silicone coupling agents were incorporated in the silicone elastomer to fabricate $BaTiO_3$/silicone membranes. Particle size distribution measurement and SEM observation show that $BaTiO_3$ particles get higher compatibility with silicone, dispersity of $BaTiO_3$ particles and the dielectric properties of $BaTiO_3$/silicone membranes were both improved by the surface modification.

In Chapter 3, the capacitive features of $BaTiO_3$/silicone nanocomposites were theoretically analyzed. To take advantage of the excellent insulation features as well as the excellent dielectric property, surface treated ferroelectric $BaTiO_3$ nanoparticles were added into the silicone elastomer to fabricate a flexible nanocomposite with a high dielectric constant. A measuring system containing the silicone coupling agent modified BT/silicone elastomeric membranes was assembled, connecting with a LCR meter and a Multimeter. Continuously increasing stresses and periodic varying stress (vibrations) were applied to the membranes, respectively. The changing capacities (equivalent to the generated currents) were evaluated by the LCR meter, while the generated instantaneous current was measured by the Multimeter. Clear and sensitive signals were obtained from both of the measurements even without a poling process during the fabrication or measurement. This type of materials is expected to have the applications in mechanical sensors due to its rapid response of instantaneous electric signals, simple structures and low costs.

In Chapter 4, in order to predict and elucidate the mechanisms of the factors and variation procedures of the resistance of flexible conductive nanocomposites, 3 types of theoretic piezoresistive models were introduced from different prospects. Each model was built considering both the solid and foamed conductive nanocomposite. A piezoresistive model was deduced based on the percolation threshold of conductive elastomeric nanocomposites, which is simple but can only be used for the calculation of the resistance variation in a conductive nanocomposite with a volume fraction near its percolation threshold. Another type of piezoresistive model was deduced based on the tunnel conductive theory for elastomeric nanocomposites, which is able to explain the resistance of flexible conductive nanocomposites with a wide range of volume fraction and with spherical conductive particles. To broaden the applicable scope of the model for a variety of particle shapes, a piezoresistive model based on the tunnel conductive theory for elastomeric nanocomposites considering the distribution, aspect ratio, and orientation of each fiber-like conductive particle was developed. Although with a high accuracy, its complexity reduced the practicality.

In Chapter 5, multi-walled carbon nanotubes (MWCNTs), with a high electrical conductivity and large relative surface areas, were integrated in the silicone elastomer to provide a high conductivity as well as a piezoresistive property. To raise the sensitivity and improve the piezoresistivity of the nanocomposite, a foaming procedure was introduced to reduce the viscoelasticity of the silicone elastomer. A series of conductive foamed nanocomposites were fabricated with different types of foaming agents to obtain a diverse porous structure. The porous structures of the foams, the distribution and orientation status of the multi-walled carbon nanotubes in the silicone matrix were observed/analyzed using laser microscope and SEM with/without a compression load.

The influences of the porous structure and porosity on the foam were studied. It was found that a different porosity and different voids structure affected the density, elastic modulus, resistivity as well as piezoresistive property significantly. This type of piezoresistive active nanocomposite was proved to have an obvious potentiality for utilizations in a mechanical sensor, such as a tactile sensor or an impact sensor. Applications of MWCNT/silicone elastomeric nanocomposites for mechanical sensing were investigated deeply. A mechanical sensing system was assembled with a piezoresistive MWCNT/silicone sponge-like sheet. It was found to have the ability of detecting not only a wide range of tactile pressure, but also a mechanically impact by measuring the variation of the resistive through a Multimeter.

In Chapter 6, a general conclusion of this work was made. It was concluded that a relatively precise and sensitive mechanical sensor can be easily developed from different prospects. It was found that a system containing a BT/silicone membrane and a Multimeter is appropriate for detection of a short-time mechanical stimulus, like an instantaneous impact or a vibration with a short period; a system containing a BT/silicone membrane and a LCR meter is able to measure a constant pressure; while a small pressure can be detected with a system containing MWCNT/silicone foamed nanocomposites. The directions for the future research were also mentioned, such as investigating the temperature dependent conductive property of MWCNT/silicone nanocomposites; enhancing the capacitive and piezoresistive property of the silicone elastomeric nanocomposites; expanding the versatility of the silicone elastomeric nanocomposite; and conducting the research of some practical applications using silicone elastomeric nanocomposites.

論文審査結果の要旨

近年技術の発展につれ力学センサの重要性が高まりつつある。しかし、従来型の力学センサはコストが高く、大型化が困難である。本論文では、シリコーンエラストマーと強誘電体チタン酸バリウム、または導電性を有する多層カーボンナノチューブ(MWCNT)のナノコンポジットを用いることで、広範囲な圧力刺激を探知可能な材料設計およびその作製方法が論じられていた。

第一章では、シリコーンエラストマーの特徴や、シリコーンエラストマーなどのポリマーを基材とするナノコンポジットの誘電性と導電性に言及し、その既往研究を紹介していた。こうした機能性ナノコンポジットを柔軟性力学センサとして応用する有用性が強く示されていた。

第二章では、チタン酸バリウム/シリコーン複合材料を作製した。チタン酸バリウム粒子とシリコーンエラストマーの表面親和性は悪く、機械的混合だけで良分散は得られなかった。また、計算モデルから、チタン酸バリウム粒子の沈降と凝集は複合材の誘電性能を下げる恐れがあることが示された。それらを解決するため、チタン酸バリウム粒子の表面を改質することで、チタン酸バリウム粒子とシリコーンの親和性を改善するに至った。その結果、シリコーン基材中へのチタン酸バリウム粒子の良分散に成功した。その後、チタン酸バリウム/シリコーンナノコンポジットの混合比を調整し、その誘電特性を解析した。その結果、良分散はナノコンポジットの高い誘電率に寄与することが示されていた。

第三章では、チタン酸バリウム/シリコーンナノコンポジットの静電容量が計算モデルにより解析されこれに基づき材料が作製されていた。作製したチタン酸バリウム/シリコーンナノコンポジットを電極に挟み、外部圧力を加えることで複合材を変形させ、ナノコンポジットの静電容量の変化、および静電容量の変化で生じる電流を捉えていた。その実験結果から、計算モデルが正確で材料設計に用いることができること、チタン酸バリウム/シリコーンナノコンポジット力学センサへの実用性が示されていた。

第四章では、導電性ナノコンポジットを力学センサに応用できることを導電性理論により証明していた。導電複合材料のパーコレーション閾値や導電性のトンネル理論に基づき、MWCNT/シリコーンナノコンポジットの発泡体に適した実用性の高いピエゾ抵抗モデルが提案されていた。

第五章では、前章の結果に基づき、発泡剤の種類を検討することでより優れたピエゾ抵抗性を持つMWCNT/シリコーンナノコンポジット発泡体を作製していた。作製したコンポジット発泡体中のMWCNT分布と気孔のモルホロジーを観察し，それが発泡体に対する影響を調べていた。発泡処理によりピエゾ抵抗性が改善されることが示された。さらに、前章で算出したピエゾ抵抗モデルが実測値との良い相関が有ることが示され、モデルの正当性とこれに基づく材料設計指針の正しさを証明していた。

第六章では、研究全体が総括され、今後の展望が述べられていた。

現在ロボットの人工皮膚やスマートスーツに柔軟性を有する力学センサの需要が高まっている。本研究はこの分野への応用展開可能であり、材料科学における工学的意義は大きい。以上より、本論文は、博士(工学)の学位授与に相当する内容であると認められる。