RECENT PROGRESSES IN POLYMERIC SMART MATERIALS

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Smart materials can be defined as materials that sense and react to environmental conditions or stimuli. In recent years, a wide range of novel smart materials have been developed in biomaterials, sensors, actuators, etc. Their applications cover aerospace, automobile, telecommunications, etc. This paper presents some recent progresses in polymeric smart materials. Special emphasis is laid upon electroactive polymer (EAP), shape memory polymer (SMP) and their composites. For the electroactive polymer, an analysis of stability of dielectric elastomer using strain energy function is derived, and one type of electroactive polymer actuator is presented. For the shape memory polymer, a new method is developed to use infrared laser to actuate the SMP through the optical fiber embedded within the SMP. Electrically conductive nanocarbon powders are utilized as the fillers to improve the electrical conductivity of polymer. A series of fundamental investigations of electroactive SMP are performed and the shape recovery is demonstrated.

Keywords: Smart materials; electroactive polymer; shape memory polymer.

1. Introduction

Smart materials are materials that have one or more properties that can be significantly changed in a controlled fashion by external stimuli, such as, temperature, moisture, pH, electric or magnetic fields [1-3]. Various smart materials have already existed, and are being researched extensively. These include piezoelectric materials, shape memory materials, magneto-rheostatic materials, electro-rheostatic materials and so on. The property that can be altered influences what types of applications the smart material can be used for [1-2]. In the last decade, a wide range of novel polymeric smart materials have been developed in biomaterials, bioinspired materials, functional nanomaterials [4], sensors, actuators [5, 6], etc. The applications cover aerospace, automobile, telecommunications, such as actively moving polymers, neural memory devices, smart micro-/nanocontainers for drug delivery, various biosensors, dual/multi-responsive materials, biomimetic fins [1, 7, 8].

This paper presents some recent advances in polymeric smart material, including electroactive polymer, shape memory polymers and their composites. For EAP, the stability of dielectric elastomer is derived, and two types of electroactive polymer actuators are proposed. For SMP, a new method is developed to use infrared laser to actuate the SMP. Additionally, the electrically conductive fillers are incorporated into SMP to improve the electrical conductivity.
2. Electroactive Polymers

Electroactive polymers (EAPs) are polymers whose shape is modified when a voltage is applied to them. EAPs can be used as actuators or sensors. Generally, EAPs present the ability to induce strains that are as high as two orders of magnitude greater than the movements possible with rigid and fragile electroactive ceramics (EACs). EAPs have attracted much attention from engineers and scientists from diverse disciplines. In particular, dielectric elastomer actuators have been intensely studied in recent years. Most of the attentions are focused on the theory of mechanical properties and the stability of the dielectric elastomer actuators. Using the large deformation theory hyperelastic model, the mechanical properties of the planar actuator is analyzed. The electromechanical coupling effect and the nonlinear field theory analysis are considered. An electric energy density function model with varying dielectric constant is proposed. Because the dielectric elastomer film is very thin, an applied high voltage may result in an electrical breakdown. Based on the stability theory of dielectric elastomer actuator, a new method on the stability of the dielectric elastomer actuator using the strain energy function with two parameters and the electric energy density function with varying dielectric constant is derived in our recent study (Figure 1).

Furthermore, using the acrylic film VHB 4910 (3M) the actuator is developed, including a wound roll dielectric elastomer actuator and an inflated dielectric elastomer actuator (see Figure 2). We tested the overall performance of these actuators and actuated an artificial muscle arms and artificial bio-mimetic eyeball respectively. Based on the silicone elastomer (BJB, TC5005A/B-C) we fabricated a planar film actuator and folded dielectric elastomer actuator, and tested the performance of the actuator in terms of actuation strain, breakdown voltage and the deformation. An agonist-antagonist actuator was studied to mimic the actions of the lateral rectus-type human ocular muscles, with an aim to enable bi-directional rotations of the eyeball around an axis.
Additionally, Barium titanium oxide ferroelectric (BaTiO$_3$) powder was used to develop a particular filled composite based on a silicone elastomer matrix, with an improved dielectric permittivity. Characterizations of the physical and chemical properties of the dielectric elastomer are currently being conducted.

3. Infrared-Laser Activated Shape Memory Polymer

Shape memory polymers (SMPs) are one kind of novel smart material, which are able to recover their original shape upon applying an external stimulus, such as heat, light$^{12}$, electricity$^{13-17}$, and solvent, etc. In our study, the actuation of shape memory polymer is realized by an embedded optical fiber transmitting infrared laser$^{12}$. The SMP used in this study is a thermoset SMP, which is synthesized based on styrene copolymer. The glass transition temperature ($T_g$) of this SMP is about 53.7 °C, characterized by a dynamic mechanical analysis (DMA). Figure 3 shows the schematic of the SMP embedded with optical fiber. In order to increase transmission efficiency of the optical fiber, the surface of the optical fiber was etched by the aqueous solution of sodium-hydroxide and consequently the coating is removed. During the curing process of SMP, the treated infrared optical fiber was embedded in the shape memory polymer. After curing of SMP, an infrared laser at a special range of wavelength is coupled into optical fiber, transmits to the end area of fiber, finally transmit into SMP through the bare fiber and subsequently heat the SMP.

![Fig. 3. Illustration of infrared-laser activated shape memory polymer (a) Treated optical fiber with the bare coating at the end area; (b) The treated surface of optical fiber were embedded in the shape memory polymer.](image)

In order to determine the special absorption peak of the SMP copolymer, the IR spectra (Nicolet 60, SXR FI-IR Spetrometer) was used. As shown in Figure 4, an absorption peak of the SMP copolymer is significant around the wave number 3000 v/cm$^{-1}$ which is the characteristic absorbing peak of bond C-H of benzene ring.
Consequently, the working frequency of infrared laser was specified at 3-4µm, while the working band of optical fiber was 1-6µm. The optical fiber was embedded into the SMP to transmit 3-4µm laser for SMP activation. The trigger of the shape recovery is possible by a contactless and highly selective infrared laser stimulus.

![The IR spectra of the thermoset shape memory polymer.](image)

The shape recovery of SMP by infrared laser was demonstrated. Figure 5 shows a typical shape recovery sequence of infrared-laser activated shape memory effect. In the figure, the red wire is the infrared optical fiber and the curved white wire is the SMP. The increase in temperature of SMP indicated that the infrared laser is able to transmit into the SMP and then heat the SMP. It demonstrates that the infrared laser stimulus of SMP is a candidate to be use as an actuator.

![Temperature distribution of SMP heated by infrared laser (a) and shape recovery sequences of a shape memory polymer actuator embedded with a optical fiber (b).](image)

### 4. Electroactive Conductive Shape Memory Polymers

In order to get rid of external heaters, thermo-responsive SMPs composites incorporated with various types of electrically conductive fillers (e.g., carbon nanotubes, Ni powders \[13, 14\], nanocarbon powders \[16\], chopped or continuous carbon fiber \[17\] ) have been developed, so they can be actuated by means of Joule heating (i.e., by passing an electrical current, just like that of NiTi shape memory alloys). This section focuses on the progress in electro-activate SMP composites. Special emphases are given on the filler types that affect the conductive properties of these composites. Then, the mechanisms of electric conduction are addressed. A series of fundamental investigations of electroactive SMP are conducted. Electrically conductive nanocarbon powders are utilized as the fillers to improve the electrical conductivity of polymers. With incorporating conductive nanocarbon powders into SMP matrix, not only it mechanics properties improve a lot, but
also it can be actuated by passing an electrical current. We systematically compared the conductivity and performed the shape recovery properties of the SMP nanocomposite. This is a good foundation to improve the electroactive performances of SMP, which maybe become a more smart material.

An electroactive SMP nanocomposite filled with nanosized (30 nm) carbon black (CB) is presented. The thermoset styrene-based SMP shows a glass transition temperature ($T_g$) of about 65°C. The SMP composite filled with five different contents of nanocarbon powders were fabricated, namely pure SMP (CB0), composite with the volume fraction of nanocarbon powders 2% (CB2), 4% (CB4), 6% (CB6) and 10% (CB10), respectively. With an increase of the incorporated nanocarbon powders of the SMP composite, its $T_g$ decreases and storage modulus increases.

Figure 6 presents the experimental results of electrical resistivity of SMP composites filled with different volume fractions of nanocarbon powders. It shows that the electrical resistivity of composite with less than 3% volume fraction of nanocarbon powders is extraordinary high ($10^{14}-10^{15} \, \Omega \cdot \text{cm}^{-1}$). In contrast, a sharp transition of electrical conductivity occurs between 3% to 5%, which is a percolation threshold range. As the fillers contents is larger than 5%, the resistivity reduces to a low and stable level ($10^{-1}-10^{1} \, \Omega \cdot \text{cm}^{-1}$). Due to the high micro-porosity and homogeneous distributions of nanocarbon powders aggregations in SMP matrix (Figure 7), the SMP composite shows a good electrical conductivity with a percolation of about 3.8 %. This percolation threshold is slightly lower than that of many other carbon based conductive polymer composites.

Figure 8 shows the shape recovery of the sample CB10. The specimen was applied by a voltage of 30 V and it takes about 90 s for the whole shape recovery process. Due to the relatively high electrical conductivity, a sample filled with 10 vol% nanocarbon powders shows a good electroactive shape-recovery performance.
5. Conclusion

This paper concerns some recent progresses in polymeric smart material, including electroactive polymer, infrared laser induced shape memory polymer, and electrical conductive shape memory polymer nanocomposite. For the electroactive polymer, an analysis of stability of dielectric elastomer using strain energy function is derived, and one electroactive polymer actuator is successfully fabricated. For the shape memory polymer, a novel method is developed to use infrared laser to actuate the SMP through the optical fiber embedded into the SMP. Furthermore, electrically conductive nanocarbon powders are incorporated into SMP matrix to fabricate an electroactive SMP composite. Due to a high electrical conductivity of nanocomposite, this SMP composite presents good shape recovery performance.

References

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