Study on the activation of styrene-based shape memory polymer by medium-infrared laser light

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This paper demonstrates the feasibility of shape memory polymer (SMP) activation by medium-infrared laser light. Medium-infrared light is transmitted by an optical fiber embedded in the SMP matrix, and the shape recovery process and temperature distribution are recorded by an infrared camera. Light-induced SMP exhibits potential applications in biomedicines and flexible displays. © *2010 American Institute of Physics*. [doi:10.1063/1.3353970]

Shape memory polymers (SMPs) are responsive to external stimulus (e.g., heat,[1,2] light,[3,4] electricity,[5–8] magnetism,[9,10] and solution[11,12]) and then recover to their original shape. According the form of stimulus, SMPs can be classified as thermoresponsive, light-induced, electroactive etc. Among these shape memory polymers, thermoresponsive SMPs are the most common. This type includes polyurethane, cross-linked polystyrene, and styrene-butadiene copolymers. The transition temperature may be tailored from about 30 to 120 °C, and the maximum recovery strain may approach 400%.[1,2]

The external heat source should be in contact with SMPs to activate SMP recovery from a predeformed shape to its original shape. However, this type of activation is not suitable in a sheltered or nontouched environment, such as inside human body. The nontouched actuation polymers include the electroactive SMPs and light-induced SMPs. Some electrically conductive particles (e.g., nickel powders,[5,7] carbon nanotubes[6,8]) can be blended into the SMPs to realize the shape recovery by Joule heating under a relatively low voltage. However, the electrical current may generate electromagnetic waves and may be harmful to the human body. Therefore, this paper investigates the SMP activated by medium-infrared laser light. Our aim is to extend the potential application of SMPs in the human body or tissues for biomedical applications, actuators for flexible displays, or for morphing the external skin on smart aircraft.

In this paper, medium-infrared laser light is used to trigger the shape recovery of SMP based on the light-thermal transition mechanism. In order to improve the transition efficiency of light, the surface of the infrared optical fiber is chemically treated and placed in a special location. In this case, the core of fiber is directly in contact with the SMP. Then, the light emitted by a laser source is coupled into the optical fiber, and induced Joule heating triggers the shape recovery of the SMP. The shape recovery and temperature distribution are recorded by an infrared camera.

The SMP is polymerized by styrene, vinyl compound, and cross-linking agent (bifunctional monomer). Benzoperoxide was used as the reaction initiator, the polymerization temperature is 70 °C, and the reaction time is 24 h.

The middle infrared optical fiber is made by the Beijing Glass Research Institute, and it is multimode arsenic trisulfide (As_2S_3) fiber. The working wave band is 1–6 μm with a diameter of 340 μm, and a core of diameter 270 μm. The refractive index of fiber core is 2.8, and the cladding of optical fiber was corroded by 10 wt % sodium hydroxide (NaOH) water solution for 30 s. After corrosion, the diameter of the optical fiber is 250 μm. The corroded optical fiber was inserted into a capillary (diameter: 1 mm) with one end closed. The capillary was filled with mingled monomers, and both the optical fiber and the capillary were placed into an oven according to the synthesis procedure of our SMP. After heating and air-cooling, the capillary of the laser actuator is immersed into hydrofluoric acid solution for 24 h. After the capillary was totally corroded, the laser actuator was placed into a vacuum oven for another 24 h (vacuum degree $<2\times10^{-4}$ Pa, temperature: 35 °C). The infrared laser is the activation source, with a working wave band of 2–4 μm, and output power of 2 W. The source was coupled into the optical fiber by a coupler and transmitted into the polymer by the optical fiber. After absorbing the laser, the polymer was activated by the energy of the laser and recovered its original shape. The shape recovery of the optical fiber actuator and the temperature distribution during the shape recovery process was recorded by a video recorder and infrared camera, respectively.

The synthetic polymer is a thermal responsive thermoset styrene-based SMP. The absorbed laser energy can be transformed into heat and activated by Joule heating. After the temperature approaches the glass transition temperature (T_g), the deformed SMP may recover to its original shape. In this study, the T_g of the SMP was analyzed by a dynamic mechanical analyzer. Shown as Fig. 1, the temperature at the peak location is T_g.

The test model selected was a stretching model with a frequency of 1 Hz. The scanning range is from −20 to 140 °C with a heating rate of 2 °C/min. During heating, as the temperature approaches T_g, the inner macromolecular morphology of the material changes. Hence, the material viscosity also changes, which is reflected in the storage modu-

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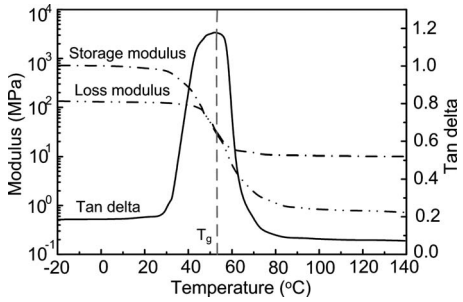

FIG. 1. Storage modulus, loss modulus, and tan delta of the shape memory polymer.

lus, loss modulus and tan delta. During the experiment, the temperature corresponding to the peak of the tan delta is measured as the T_g of the SMP (T_g=53.7 °C).

The shape recovery process of the SMP relies on thermal energy in the material, which is transformed from laser energy. An infrared light demonstrated the best performance for activating the SMP in our study. The vibrational manner of the molecules in materials that can change its dipole distance is different and therefore, various types of materials absorb infrared light at different wavelengths. Thus, infrared analysis was proposed determine a proper infrared wavelength for the SMP in this study.

Figure 2 shows the infrared absorption spectrum of the SMP. Clearly, a strong absorption peak of the polymer appears at 3000 cm^{-1} (λ=3270–3410 nm), which corresponds to the stretch vibration of C–H bonds in the benzene ring. Therefore, the wavelength of the infrared laser for the actuator was set between 3 and 4 μm.

According to our infrared spectroscopy experiment, an infrared light with a working wave band of 2–4 μm was coupled into the fiber in the SMP to study the realistic actuating effect of the infrared laser. The shape recovery of the optical fiber actuator and temperature distribution during the shape recovery process was recorded by a video recorder and infrared camera, respectively. The actuating experiment is shown in Fig. 3, where the silvery white belt is the SMP and the red thin stick is the infrared optical fiber. Clearly, the shape of the SMP is actuated gradually from a curved shape [Fig. 3(a)] to a relatively flat shape [Fig. 3(g)]. Hence, it demonstrates that the infrared light in the selected wavelength can activate SMP shape recovery. The final shape was close to the original rod with some residual flexion due to the influence of gravity on the soft SMP.

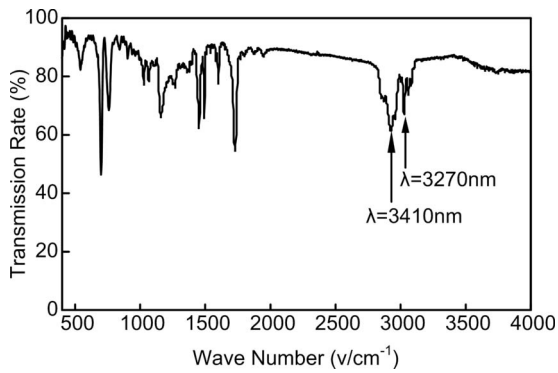

FIG. 2. The IR spectra of the thermoset shape memory polymer.

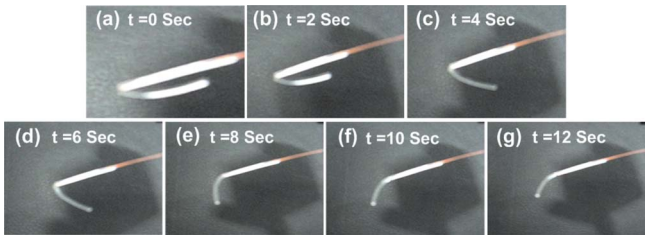

FIG. 3. (Color online) Shape recovery snapshots of the SMP induced by infrared light. (a) Initial predeformed configuration; (b)–(g) Deployment sequence of the actuator at t=2, 4, 6, 8, 10, and 12 s, respectively.

When the infrared light activates the polymer to recover its original shape, the absorbed optical energy of the polymer is transformed into thermal energy. Therefore, the investigation of the temperature distribution of the optical fiber is essential. On the other hand, the temperature distribution can also represent the absorption of optical energy in the optical fiber actuator. An infrared camera was selected to record the temperature distribution during the shape recovery process. Note that the snapshot at t=0 s was omitted in Fig. 4 because the infrared laser was not yet coupled and the polymer temperature was the same as the background.

In Fig. 4(a) (t=2 s), the only bright position is located at the end of the fiber, which indicates that the infrared laser is mainly refracted at that position. In subsequent snapshots, the actuator becomes brighter globally. The temperature of the SMP around the treated optical fiber rises to 21.4 °C with an increased temperature of 2.4 °C compared to the ambient temperature; in contrast, the temperature of the SMP at the end of the optical fiber increases to 48 °C with a temperature increase of 29 °C, The latter temperature increase is above T_g and thus activates the actuator. It indicates that during laser transmission, more light is refracted from the end of the fiber into the polymer. This experimental phenomenon can be explained as follows: The optical fiber is treated by chemical corrosion to remove the cladding, and the surface of the core is uneven. The refractive index of the fiber core (n_c) is 2.8, and the refractive index of polymer (n_p) is 1.4–1.46, where n_c is higher than n_p. Therefore, according to the principle of total internal reflection, during the refraction of the infrared laser, part of the laser is refracted back into the fiber. Laser energy absorbed at the treated position of the optical fiber is relatively small, so the increase of temperature is slow. However, when no laser is reflected at the end of the fiber, a higher temperature increase is observed as a result of more laser-energy absorption. Temperature at the

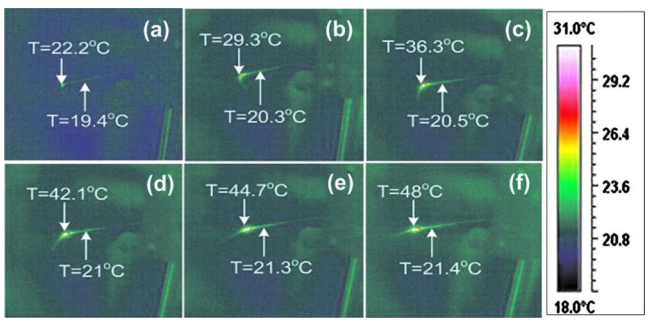

FIG. 4. (Color online) Temperature distribution snapshots of the SMP during the midinfrared laser-driven process. (a) t=2 s; (b) t=4 s; (c) t=6 s; (d) t=8 s; (e) t=10 s; and (f) t=12 s.

end and the treated positions of the fiber are denoted in Fig. 4. It shows that the SMP deploys promptly in about 12 s.

Note that, since the bent area may not fully recover to straight [Fig. 4(f)], the nonstraightened portion will somewhat reflect and absorb the light. This may limit its application to more complicated preprogramming with multiple twisted patterns. Our further characterization demonstrated that the absorption and reflection are acceptable, and therefore there are also enough light transmitted through this area and to trigger the shape recovery of SMP. Furthermore, we also have introduced some methods to decrease this unfavorable effect. The methods include coating on the polymer, decreasing the bending curve and reinforcing the strength of the polymer. We will put forward the systematically study, and the related results will be discussed in our next paper.

This infrared laser activation of SMP exhibits some unique characteristics. We have demonstrated remote-controlled activation, through the use of low density, high flexural, and easy implantable fibers. In addition, no electronic or magnetic interferences are generated, nor interfered with by external electronic or magnetic sources. Consequently, this method can be used as an actuator in flexible displays, without generating magnetic interference. In addition, it may be used to remove clots in a human blood vessel,[4] which requires remote-controlled actuation. The method may also be applied to actuate morphing skins since the fiber exhibit high flexibility and are easily deployed.

We have demonstrated that midinfrared light transmitted through a surface-treated fiber may trigger a shape memory effect by the use of a highly selective laser. A key step for the development of light-responsive SMPs is effective selection of the wavelength of the driving light. The sole light signal in the infrared-laser actuation system, without traditional electric and magnetic signal, without affecting the application environment. The activated method is of interest for actuator use in the human blood vessel in biomedicinal applications, as well for flexible displays or for morphing skins on smart aircrafts.

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