Biodegradable Shape-Memory Polymers

Peixi Yuan Literature Seminar September 30, 2010

Shape-memory polymers (SMPs) have attracted significant attention from both industrial and academic researchers due to their fascinating functionality and applications.[1,2] SMPs are an emerging class of polymers with applications spanning various areas of everyday life, such as: temperature sensor,[3] smart films for packaging[4], light responsive materials[5,6] and multifunctional SMPs.[7,8] Besides these, there is a very promising field of biomedicine applications, [9,10,11] in which SMPs can be the enabling technology for future applications. And one of the most notable works is biodegradable SMPs, involving implants, [10] drug-delivery system[11] and smart sutures.[12]

SMPs are stimuli-responsive "smart" polymers that have dual-shape capability, which depends on application of an external stimulus. First, SMP is conventionally processed to receive its permanent shape. Afterwards, the polymer is deformed and the intended temporary shape is fixed. This process is called programming. Finally, the permanent shape is now restored while SMP goes through the recovery process.[4] A change in shape caused by a change in temperature is called a thermally induced shape-memory effect (SME), which is the most common method for inducing SME.

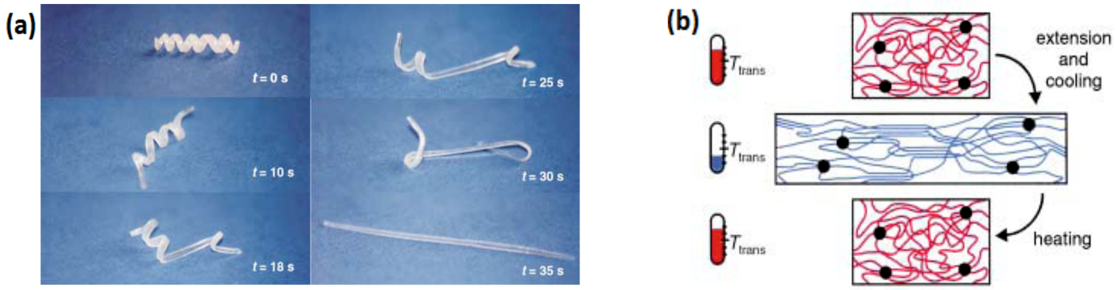

Figure 1: (a) A recovery transition from the temporary shape (Spiral) to permanent shape (Rod) for a polymer synthesized from poly (ε-caprolactone) dimethacrylate in 35 seconds at 70°C.[3] (b) Schematic representation of molecular mechanism of thermally induced SME for a covalently cross-linked polymer with $T_{tran(thermal\ transition)}=T_{m(melting)}$.[1]

In Fig.1 (a), a picture sequence demonstrates impressively the performance of SMPs. The permanent shape of the polymers formed from 1 and 2 is that of a rod, which has been deformed to a spiral (temporary shape) during the programming process. Under the influence of hot air having a temperature of 70°C the permanent shape is recovered as soon as the switching temperature or thermal transition temperature (T_{tran}) is reached. And the molecular mechanism of SME is shown in Fig.1 (b). SMP polymer systems consist of two segments, one of them is a fixed phase or hard segment (black dots) and another is a reversible or switching segment (red/blue lines).[1] The permanent shape is given by physical/chemical crosslinks between hard segments, and switching segments enable SMP to be programmed through applying stress while cooling down under T_{tran}, and recover by heating up above T_{tran}.

Currently, approaches for surgical medical devices, many of which are polymeric in nature, often require complex surgery followed by device implantation. But with the help of SMP, there is possible creation of biocompatible/degradable SMPs with appropriate mechanical properties might enable the development of novel types of medical devices. [13,14,15]

In the work of A. Lendlein[12], et al., oligo(ɛ-caprolactone)diol (OCL) was chosen as the precursor for the switching segments having a melting transition temperature (T_m) around 40°C. Crystallizable oligo(p-dioxanone)diol (ODX), with a higher T_m(~80°C) than OCL was chosen as a hard segment to provide the physical crosslinks to determine the permanent shape of this block copolymer.

To record the change in elongation during the SME, another cyclic thermo mechanical experiment was performed, as shown in Fig. 2(a). Step 1 is the deformation of the permanent shape and corresponds to a standard stress-strain test. After maintain this strain for 5 min to allow relaxation for chains, the stress is then held constant while the sample is cooled (step 2), whereby the temporary shape is fixed. Then stress is completely removed after waiting for 10 mins (step 3), and the sample is now in its temporary shape. Heating in step 4 (2K min^{-1}) actuates the SME. The contraction of the sample can be observed on the strain axis, and the fastest shape change is recorded at 40°C, which is the T_{tran} of this material.

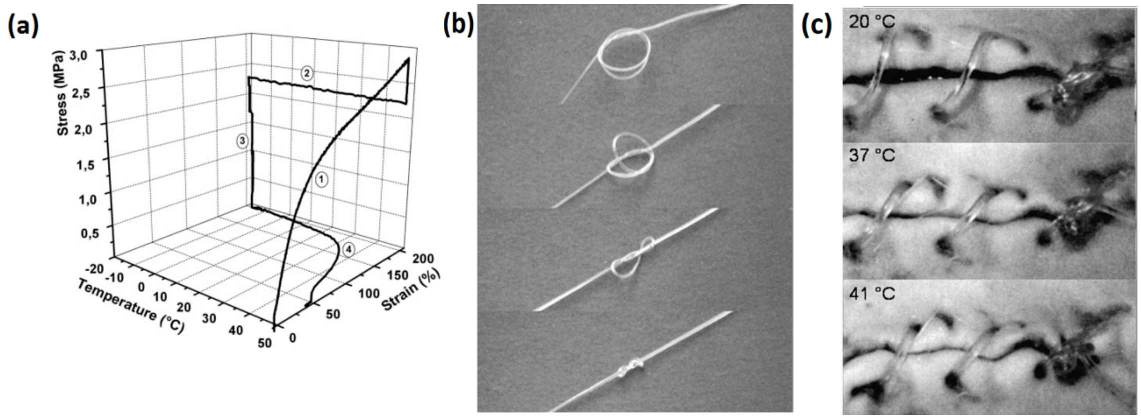

Figure 2: (a) Cyclic thermomechanical experiment of this degradable material.[12] (b) A fiber of thermoplastic SMP was programmed by stretching about 200%. After forming a loose knot, both ends of the suture were fixed. The photo series were taken in 20 seconds at 40°C. (c) Biodegradable shape-memory suture for wound closure.

One of the challenges in endoscopic surgery is tying a knot with proper stress applied on. As shown in Fig. 2 (b), this suture could be applied loosely in its temporary shape; when the temperature was raised above T_{tran}, the suture would shrink and tighten the knot, applying the optimum force. Based on the unique T_{tran}, which is close to human body temperature and biodegradable ability of Poly(ɛ-caprolactone) series polymer, this SMP can generate promising biocompatible application. Furthermore, this smart suture was tested in animal (rat), which is shown in Fig.2 (c). The wound was loosed sutured over an incision of the rat's abdominal muscle. When temperature was increased to 41°C, the SME was actuated.

This feasibility study suggests that this type of material has the potential to influence how implants are designed and could enable new surgical devices in the future.

Biodegradable SMPs have been successfully synthesized and demonstrated for biomedical applications. Suitable biodegradable SMPs can be designed with an optimum biodegradability and with adjusted recovery temperatures by selecting copolymer composition. Unique design of biodegradable SMPs may create considerable and promising evolution in surgical application and biomedical field.

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