SELF-HEALING USING SHAPE MEMORY POLYMER

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State-of-the-art of self-healing

Self-healing of structural damage has been a tremendous interest in the scientific community recently [1,2]. The ability to heal wounds is one of the truly remarkable properties of biological systems. A big challenge facing the materials science community is to design 'smart' synthetic systems that can mimic this behavior by not only 'sensing' the presence of a 'wound' or defect, but also actively re-establishing the continuity and integrity of the damaged area. Such 'self-healing' materials would significantly extend the lifetime and utility of a vast array of manufactured structures [1,2]. We believe that for an effective self-healing, four criteria must be met: (1) the systems should undergo repair in a relatively autonomous fashion, with as little external or human intervention as possible; (2) the systems should be able to repair damage more than once, so that as new cracks or damage appear, these can also be automatically repaired; (3) the healing must be at molecular level, i.e., re-establishment of material continuity by molecule entanglement or chemical bond (covalent bond, hydrogen bond, etc.); and (4) the healing efficiency should be high, i.e., the original capacity should be fully or almost fully recovered. For polymers, thermoplastics are capable of autonomously and repeatedly self-healing damage at molecular level by simply heating the materials above their melting temperature and cooling down through mechanisms such as molecular interdiffusion, recombination of chain ends, etc. Therefore, self-healing of thermoplastics is relatively simple. Also, thermoplastics are not used as widely as thermosets in structural applications due to their low stiffness and thermal instability. Therefore, thermoplastics will not be further discussed in this paper. This paper will be focused on thermoset polymers.

It is well known that thermoset polymers are chemically or physically cross-linked polymers (chemical bonds between polymer chains, intermolecular van der Waals bonds, dipole-dipole interactions, and molecular entanglement). These cross-links serve as molecular anchorages which prevent molecular motion of the polymer chains. This is how thermoset obtains its strength, stiffness, and thermal stability and why it behaves in a brittle manner under mechanical loading. Once one chain factures, the force is transferred to its neighbors through the cross-linked network, leading to crazing, cracking, and ultimate macroscopic fracture at a relatively small strain. In summary, the special molecular structure suggests that the failure of thermoset under mechanical loading such as impact is brittle and involves molecular-length scale fractures such as cross-links or chemical bonds in the main polymer chains. Compared to thermoplastics, thermosets do not possess the chain mobility that is so heavily utilized in the self-healing of thermoplastics. As a result, the development of self-healing thermosets has followed distinctly different routes and represented real challenge.

Some early versions of self-healing schemes obviously cannot satisfy the above four criteria simultaneously. For example, the first self-healing material utilized either hollow glass fibers [3] or microcapsules [4] which enclosed a monomeric fluid, and catalysts were dispersed throughout the matrix material. When a propagating crack encounters one of the dispersed capsules or hollow glass fibers, the capsule/fiber bursts/fractures and the encased fluid flows into the cracked region. Catalyst in the vicinity initiates an *in-situ* polymerization reaction such as ring-opening metathesis polymerization (ROMP) and thus patches the crack. While this repairing scheme leads to high efficiency in an autonomous fashion and at molecular level, it cannot repair damage more than once [5]. Some modified versions of this idea such as a self-healing system that simulates the human circulatory system [6], which may heal damage more than one time, suffer from new challenges such as the microcapsules are driven to burst and discharge their entire payload at a damaged region, thereby delivering a high concentration of healing agents to a small area.

Recent development in self-healing thermosets includes thermo-reversible covalent bonds or addition of thermoplastic particles. The first generation of a highly cross-linked and transparent polymer was synthesized via the Diels-Alder (DA) cycloaddition of furan and maleimide moieties, and the thermal reversibility of the chemical bonds was accomplished via the retro-DA reaction [7]. The use of thermally reversible covalent bonds to heal cracks eliminates the need to incorporate self healing agents, catalysts, etc. in the polymer system. Another important advantage is the repeatability of the healing process. However, this scheme is a very lengthy process. It needs first to heat the damaged material to high temperature to decouple the covalent bond so that the component can flow into the damaged space; after that, it needs cooling down to re-develop the covalent bond so that the material can be healed. The re-establishment of covalent bond at room temperature usually takes several days. Also, the healing efficiency is still low. For example,

the healing efficiency was only 80% for the first crack healing process, with a continuous reduction for subsequent healing cycles [7].

Shape memory polymer for self-healing

Among the various shape memory materials such as shape memory alloy (SMA, for instance Ni–Ti alloy), shape memory ceramic, and shape memory polymer (SMP), SMPs have drawn increasing attention because of their scientific and technological significance [8]. The driving force for shape recovery is the conformational entropy of the molecular segments in terms of micro-Brownian thermal motion. Thermodynamically, the molecular segments experience a change from a temporary and ordered configuration to its random and coiled configuration during the shape recovery process. Since this process is accompanied by an increase in entropy, it is an autonomous process. It is the recovery in strain and in stress that makes SMP a viable choice as sensors and actuators. In order to make the polymer smart, it usually experiences a typical four-step thermomechanical cycle called programming; see Fig. 1 for a 1-D tensile stress (σ), tensile strain (ε), and temperature (T) relationship during the programming cycle. The programming starts at a temperature above the glass transition temperature (T_g) of the SMP. It involves a high-strain deformation in the rubbery state, which is called ''pre-deformation'' or ''pre-strain''. Step 2 is a ''strain storage'' process by maintaining the pre-strain constant while cooling down to below T_g. Because of the thermal contraction of the SMP during cooling, the tensile stress needed to maintain the pre-deformed shape increases as the temperature drops. The third step is a ''low temperature unloading'' process, which is defined as the removal of the stress in the glassy state. The low temperature unloading process may be accompanied by ''springback'', i.e., some pre-strain may be rebounded. In step 4, which involves reheating to its starting temperature (above T_g) without applying any constraint, sometimes called ''free strain recovery'' or ''unconstrained recovery'', brings the pre-strain back to zero (if the recovery rate is 100%).

The efficiency of a shape-memory polymer is empirically controlled by its composition, as defined by the polymer's chemical structure, molecular weight, degree of cross-linking, and fraction of amorphous and crystalline domains [8]. The energy that is restored with shape recovery is a growing function of the energy supplied during the deformation at a high temperature [9,10]. A critical science and technological implication of SMP is that we can utilize its shape memory functionality for self-sealing purposes.

A shape memory polymer based syntactic foam was developed by Li and John [11]. The syntactic foam cored sandwich was prepared and the sandwich was subjected to seven rounds of impact-healing cycles. It is found that the impact response remained almost the same and the residual strength was almost fully recovered after each healing cycle. Figure 2 shows the ultrasound C-scan images of the original sandwich, the sandwich after seventh round impact and the same sandwich after seventh round healing. Obviously, the impact damage (white spot) was healed after healing.

Acknowledgement

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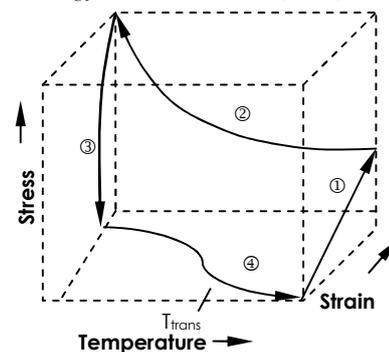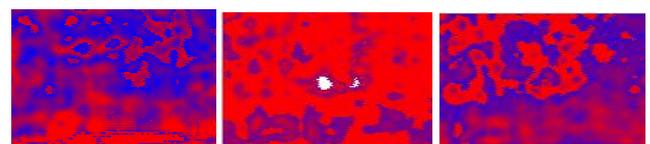11. Li G and John M. *Composites Science and Technology*, 68: 3337-3343, (2008).

Fig. 1 Schematic of four-step strain controlled programming

(a) Original   (b) After 7th impact   (c) After 7th healing

Fig. 2 Ultrasound C-scan images