Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Supporting Information

1. Materials and Methods

1.1. Preparation of Memory Polymer

The segmented semi-crystalline MP was synthesized using poly(1,6-hexanediol adipate) (PHA; UBE industries, Japan) having molecular weight of 3000 g.mol^{-1} as a reversible phase (soft segment), 4,4′-diphenylmethane diisocyanate (MDI; Aldrich Chemical Company, USA), and chain extender 1,4-butanediol (BDO; Acros Organics, USA) as a fixed phase (hard-segments). All experimental glass apparatus was dried in an oven at 400^{O}C for 8 hrs prior to synthesis. First, PHA-3000, MDI, and BDO were separately degassed at 80 ^{O}C in vacuum condition before the use. The polyurethane was synthesized via pre-polymerization method. Then, PHA-3000 and MDI were mixed in a three-necked flask and the reaction was continued for 3 hrs at 80^{o}C under nitrogen environment. The chain extension process was done by adding the cross-linker BDO to the pre-polymer and ensured to have a homogeneous blend using mechanical stirrer. The hard segment content (HSC) of the synthesized MP was at 28.5% based on weight. The prepared polymer bulk was poured into a pre-heated (100^{o}C) PTFE mold for curing process up to 24 hrs. Synthesized MP is a melting transition type and Differential Scanning Calorimetry (DSC) thermograph indicated the endothermic peak at 41.7 ^{O}C.

1.2. Preparation of Memory Polymeric Film

The bulk polymer chips was dissolved in a solvent N,N'-dimethylformamide (DMF; Aldrich Company, USA) and the mixture was stirred for 6 to 8 hrs at 80^{O}C using magnetic stirrer. The weighted ratio of 1:9 was maintained for chips and solvent. Rectangular Teflon mold (20cm x 20 cm) was used to cast the film and dried for 24 Hrs at 100^{O}C in a vacuum oven (10 mmHg) to eliminate the thermal history and residual solvent in the film. The film was having thickness around 0.4 to 0.5 mm.

1.3. Thermo-mechanical Cyclic Test

Thermo-mechanical cyclic testings were carried out using INSTRON-5566 tensile tester equipped with controlled heating chamber. The tensile load and displacement of gauge length was measured from load cell (500N) and moving cross-head respectively. The specimen dimensions of film were 80 mm x 10 mm x 0.4 mm and 100 filaments/bundle for MPFs. Gauge length of 80 mm was maintained during testing. The total strain was 100% with an extension ramp of 10 mm.min^{-1}. The cooling at ambient temperature and heating at 60^{o}C was done at a thermal ramp of 5^{o}C/min. The detailed steps of the thermo-mechanical testing are given below and also can be found from our recent work.[6] The shape fixity (R_f) and shape recovery ratio (R_r) were calculated from the below equations. (ε_u: fixed strain; ε_m: maximum strain; ε_p: plastic or residual strain)

$$Shape\ fixity\ (\%) = \frac{\varepsilon u}{\varepsilon m} \times 100 \tag{1}$$

$$Shape\ recovery\ (\%) = \frac{\varepsilon m - \ \varepsilon p}{\varepsilon m} \times 100 \tag{2}$$

The thermo-mechanical cycle includes:

1) Stretching of the MP above T_{trans};

2) Holding the MP under constraint;

3) Cooling the SMP under constraint;

4) Relaxing the employed constraint;

5) Reheating the MP for shape recovery. No plastic strain was observed after repeating 5 cycles. More details are provided in our previous work.[7] This finally ensure the structural integrity of the polymeric network for its prolonged and repetitive use with no plastic deformation.

2. Switch-spring-frame model and mechanism

Memory polymer constitutes a physically cross-linkable hard segment and a crystallizable soft segment (also termed as switch). At low temperature, the switch represents the well-aligned dense crystalline domain (off state) and at high temperature the crystals are molten into free molecular chains (on state). At this step, the deformation strain was kept constraint (20%, 40%, 60%) assuming same number of corresponding switches with variable temperature levels for melting. As the temperature is raised, the switches start to release the stored stress by melting of the newly formed crystallites in the soft segment. This results in breaking of strong internal bonds to allow conformational motions of polymer molecular chains. Thus, enable to increase the entropic elasticity in the molecular chain network which favors contraction of the MP and thereby releases the stored stress under constraint strain condition. At lower temperature (i.e. 20 to 30^{o}C), the number of active (ON) switches are less resulting in partial melting of crystallites and contributing to achieve recovery of less memory stress. Similarly, at high temperature (i.e. above the transition temperature), more number of crystallites are molten to release more stored stress. The maximum change in memory stress was seen around the transition temperature which is due to rapid melting of crystallites. The significant crease in the molecular attraction occur around transition temperature resulting in faster transformation of the switches from OFF state to ON. Melt spinning has caused orientation of molecular chains in the filaments with closed polymer packing leading to high crystallinity which helps to store and retrieve maximum memory stress than film. Number of crystallites (switches) increases with strain and this is significant as confirmed by DSC exothermic (Figure 7b) and WAXD diffraction crystalline peaks (Figure 8).