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Tailored and strong electro-responsive shape memory actuation in carbon nanotube-reinforced hyperbranched polyurethane composites

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ABSTRACT

Electro-active multi-walled carbon nanotubes (MWCNTs)-filled hyperbranched polyurethane (HPU) shape memory composites were prepared by a simple and efficient method. The highly crystalline poly(ε-caprolactone)-based HPU was synthesized in a one-step process, and the branched structure was very effective for the homogeneous dispersion of MWCNTs without any surfactant or surface modification. Enhanced mechanical properties in terms of tensile modulus and strength for the MWCNTs/HPU composites could be obtained due to the hyperbranched polymer-assisted dispersion of the MWCNTs. Young's modulus of the pure HPU film was 210 MPa, while the polymer with 7 wt% loading of nanotubes showed a modulus of 320 MPa. An increase in the concentration of MWCNTs from 0 to 7 wt% resulted in a non-monotonic trend with the breaking stress reaching a maximum at ~5 wt%. The MWCNTs/HPU composites showed more than 98% shape recovery and a rapid recovery time of 9 s in both thermal triggering and electrical actuating shape memory behavior. It is expected that the MWCNT-reinforced HPU composites can be used as potential material in various actuator applications.

1. Introduction

Shape memory materials have the capability to change their shape by being deformed and fixed into a temporary shape, and then to subsequently recover their original shape by initiation of various external stimuli, such as temperature [1], light [2,3], moisture [4], electro-magnetic fields [5], and electric [6,7] or pH [8]. Among the shape memory materials, shape memory polymers (SMPs) have received more attention owing to their low cost, low density, and easy processability, compared to shape memory alloys, ceramics, hydrogels, etc. Thus, SMPs show great potential for applications in sensors and actuators [9,10], biomedical devices [11,12], adaptive optical devices [13], and smart dry adhesives [14], and etc. Conventional SMPs have been usually activated by an external heat source. However, it is difficult to control actuation by heat-triggering because of slow heat transfer and response. In some applications, such as remote control of the actuator, voltage-triggering is a more convenient method than heat triggering. The demand to replace external heat-triggered actuation has led to development of conductive shape memory polymers, filled with a conducting filler such as carbon nanotubes (CNTs) [7,15], carbon nanopowder [16], and carbon black [17]. One of the carbon materials, carbon nanotubes (CNTs) have attracted enormous interest due to their excellent electrical, thermal, and mechanical properties [18–20]. Previously, we reported the preparation of conducting shape memory composite materials by the use of polymer and pristine or modified CNTs or conducting polymers [15,21]. However, the main difficulty of carbon nanotube-reinforced composites is the non-equivalent conductivity of composites due to poor dispersion of CNTs in the polymer. Although modified CNTs show good dispersion in the polymer matrix, but at the same time the conductivity decreases due to aggressive chemical functionalization that creates defects at the nanotube surface.

As an alternative approach, hyperbranched polymers may be employed to improve the dispersion of CNTs in the polymer matrix [22–24]. The controlled macromolecular architecture of hyperbranched polymers generally exhibits good solubility, lower melt and solution viscosity, the presence of empty internal cavities, and an extremely high density of functional groups at the surface [25,26]. However, it is well known that the hyperbranched polymers exhibit inferior mechanical strength due to the lack of entanglement and crystallinity, but this drawback can be overcome by the use of a simple oligomeric diol [22].

In this study, poly(ε-caprolactone) (PCL)-based hyperbranched polyurethanes (HPUs) were synthesized and employed to prepare nanocomposites with enhanced dispersion of multi-walled carbon

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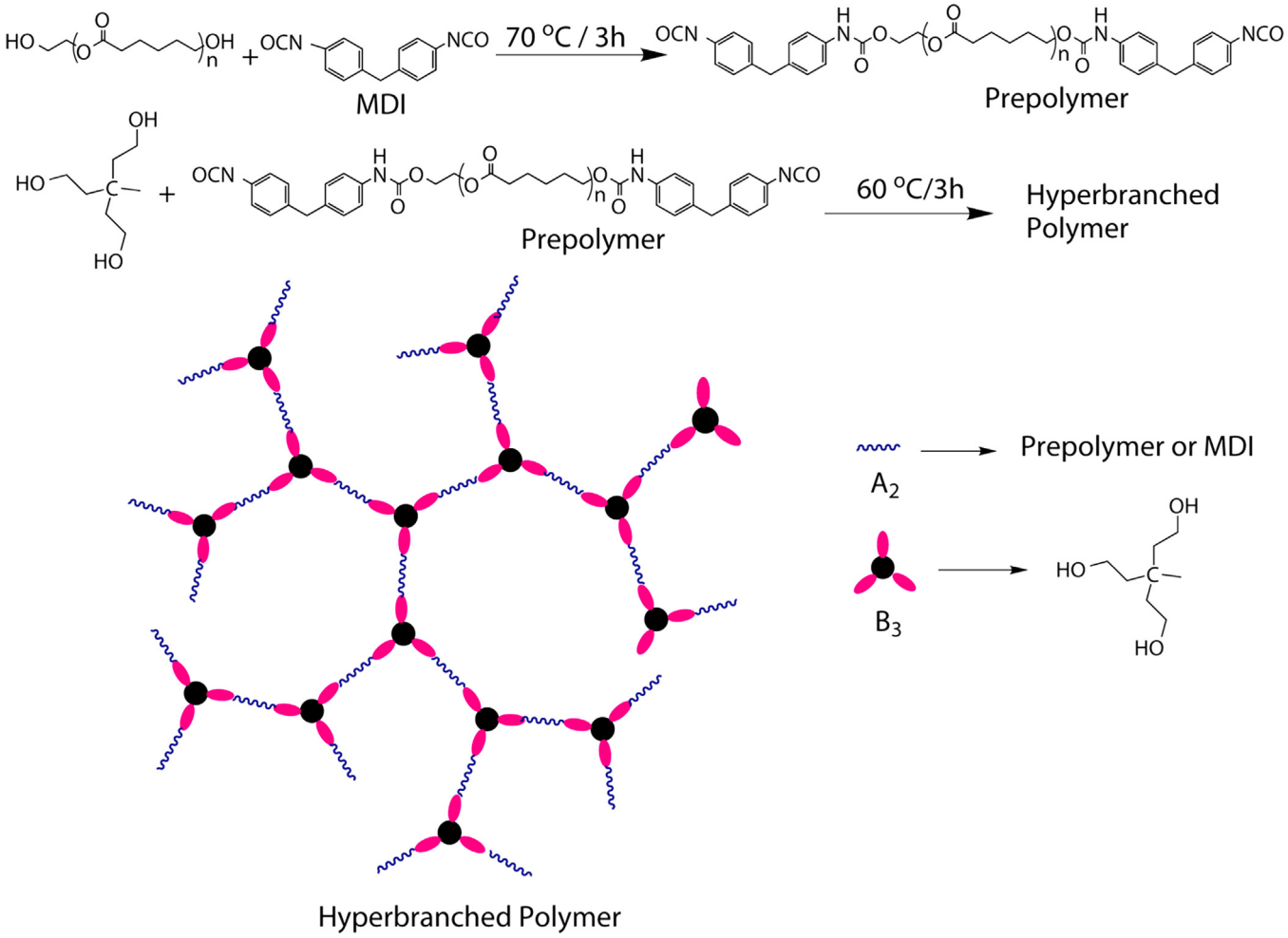

Scheme 1. Schematic representation of the synthesis of the hyperbranched polymer.

nanotubes (MWCNTs). The structural, thermal, mechanical, and electro-active shape memory properties as well as dispersion of MWCNTs for the nanocomposites were investigated.

2. Experimental

2.1. Materials

4,4′-Methylenebis(phenyl isocyanate) (MDI), 1,1,1-tris(hydroxymethyl)propane (THP), and dibutyltin dilaurate (DBTDL) were purchased from Aldrich Co. Poly(ε-caprolactone)diol with a molecular weight of 3000 g/mol was received from Solvay Co., UK. MWCNTs with diameter and length of about 10–20 nm and 20 μm, respectively, were purchased from Iljin Nanotech, Korea. N,N′-Dimethylformamide (DMF) was purified by drying overnight over magnesium sulfate followed by decantation of the drying agent, vacuum distillation, and stored over 4 Å molecular sieves before use.

2.2. Synthesis of hyperbranched polyurethane

The synthesis of the hyperbranched polyurethane was based on a procedure from our earlier report [22]. Briefly, in a 500 mL three-neck cylindrical glass reactor equipped with mechanical stirrer, PCL (6 g, 2 mmol) and MDI (2 g, 8 mmol) in 30 mL of freshly distilled DMF were stirred under a nitrogen atmosphere at 70 °C to prepare the pre-polymer. After 3 h, the pre-polymer synthesis was completed and the reaction vessel was cooled down to 0–5 °C. Then, THP (0.80 g, 6 mmol) and DBTDL (0.05 g) dissolved in 20 mL of dry DMF was added. The reaction vessel was slowly heated to room temperature, and then, the temperature was increased to 60 °C and stirring was carried out for 3 h. After completion of the reaction, the final product solution was dried in a hot-air oven at 50 °C to obtain the polymer films.

2.3. Preparation of HPU/MWCNTs nanocomposites

The HPU/MWCNTs nanocomposite films were prepared by solvent casting using HPU with 3, 5, and 7 wt% pristine MWCNTs loading. Prior to this, the required amount of MWCNTs was sonicated in DMF separately for 15 min with the use of 300 W 28 kHz ultrasonic generators to produce a homogeneous dispersion. The mixing beaker was maintained at 4 °C in a thermostatic bath for the duration of ultrasound irradiation. The MWCNTs–DMF solution was mixed with the HPU solution and stirred for 24 h at room temperature. The final product solution was poured into a glass Petri dish, and the solvent was evaporated in a hot-air oven at 50 °C to obtain the nanocomposite films with average thickness of 0.44 mm. The samples were denoted according to pristine MWCNTs loadings of 3, 5, and 7 wt%, as HPU/MWCNT(3), HPU/MWCNT(5), and HPU/MWCNT(7), respectively.