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Intelligent Shape Memory Polymers and Application

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1. Introduction

Recently shape memory polymers have received much attention as one of important intelligent polymers. They can recover their original shape by being heated above their transition temperature, which are defined by their different phases in the materials. In particular, the shape memory effect of polyurethane block copolymer (PU) has been extensively researched due to its superior material properties, which arises from the phase-separated structure of its hard and soft segments. The hard segments form physical crosslinks due to polar interaction, hydrogen bonding, and crystallization in the hard domain, while the soft segments form the reversible phase due to molecular motion in a rubbery state. This shape memory effect is usually induced by thermal stimulation due to heating above the transition temperature of polymers, such as glass transition temperature or melting temperature. However, some other stimulating sources, such as pH, electric field, and chemicals may also be available for actuating polymers with shape memory.

The shape recovery of conducting PU composites using carbon nanotubes was investigated by applying voltage as well as thermal heating. This achievement may lead to application of shape memorypolymer as an electroactive actuator, which is important in many practical applications such as smart actuator for controlling micro aerial vehicle. To obtain conducting shape memory polymer, multi-walled carbon nanotubes (MWNTs) were usually used via functionalization such as chemical modification in mixed solvents of hydrochloric acid and sulfuric acid and grafting for improvement of interfacial bonding between polymers and nanotubes. An improvement of the dispersion of MWNTs in PU matrix was also tried by grafting of poly(ε-caprolactone)diol (PCL) onto the surface of MWNTs.

An interesting water-responsive shape memory effect could be also created in the recent years by introducing hydrophilic and hydrophobic groups in the soft and hard segments, respectively. Polyhedral oligomeric silsesquioxane (POSS) is one of potential candidates as the hydrophobic group. It is composed of a polyhedral siliconoxygen nanostructured skeleton with intermittent siloxane chains, and has novel mechanical properties due to its cage-like molecule. Polyurethane containing POSS molecule to the polymer chain has a largely enhanced tensile modulus and strength due to presence of POSS molecules as nano-scale reinforcement agents as well as formation of well phase-separated hard segment domains from soft segments. Block copolymers containing poly(ethylene oxide) (PEO) as hydrophilic block like Pluronic polymers have high solubility in water due to its excellent hydrophilicity.

In this work, an overview on shape memory polymers and their potential application is presented.

2. Experimental

2.1. Synthesis of shape memory PU

PU containing 40% hard segments was synthesized through a prepolymerization method by controllingamounts of polycaprolactonediol (PCL), 4,4'-methylene bis (phenylisocyanate) (MDI), and 1,4-butanediol (BD). The PCL works as the soft segment, whereas the MDI and BD do as the hard segments. First, the prepolymer was prepared from a reaction of MDI (Junsei Chemical) and PCL (Solvay Co., MW=3,000 g/mol) at 80°C for 90 minutes in a four-neck cylindrical vessel equipped with a mechanical stirrer. Second, a chain extender of BD (Duksan Chemical) was gradually added to the prepolymer at 110°C for 150 minutes, and was reacted. Final PU was used after washing with water and drying completely in an oven.

2.2. Preparation of PU-CNT nanocomposites

PU composites were prepared by mixing PU and MWNT. MWNT of a diameter of 10-20nm and a length of 20m was supplied by Iljin Nanotech Co, Korea. MWNTs were used after surface-modification in mixed solvents of nitric acid and sulfuric acid (3:1 molar ratio) at 140°C for 10 minutes, followed by high-energy sonication in ethanol for two hours. Final PU composite films were obtained by casting PU-MWNT solution in mixed solvents of tetrahydrofuran and dimethylforamide.

3. Results and Discussion

3.1. Electroactive PU/CNT nanocomposites

Electric-field-triggered shape recovery was observed by recording images using a video camera as a constant voltage was applied to sample. The sample was initially a rectangular strip that was deformed into a helix at 60°C and cooled to room temperature. Its electro-active shape recovery behavior was demonstrated for the sample containing 5 wt% surface-modified MWNT. The original shape of the sample was almost completely recovered in at least 10 seconds when an electric field of more than 40V was applied. The rate of shape recovery was strongly dependent on the magnitude of applied voltage and the MWNT content of the samples (Figure 1). The unreacted MWNT composites could be heated more rapidly to a higher temperature with voltage application than the surface-modified MWNT composites could due to higher conductivity, as described previously. It was, however, difficult to control the temperature of sample due to its rapid rise above the melting temperature of hard segments of PU. Therefore, its shape recovery behavior could not be well developed compared with that of surface-modified MWNT composite. Consequently, the composites with surface-modified MWNT could give better electro-active shape recovery as well as mechanical properties.

The typical relation between the surface temperature and applied voltage for the 5 wt% surface-modified MWNT composite was analyzed. The temperature of the samples was measured using digital multi-meters with a non-contact temperature measuring system. Assuming a simple relation between temperature (T) and applied voltage (V) as the following equation (1), an energy-conversion efficiency can be calculated.

$$C\ V' \ (T - T_o) = k\ t\ (V^2 / R) \qquad (1)$$

where denotes the density of sample, C the specific heat capacity, V′ the volume of sample, R the electrical resistivity, and t time. The factor k indicates energy-conversion efficiency. An energy-conversion efficiency of 10.4% was calculated. This is nearly the same as an order of 10% of efficiency in shape memory alloys actuators, though it is lower than that the 0.2 to 0.25 of human muscles. To achieve a higher efficiency as a shape memory polymer actuator, a higher electrical conductivity of composites may be required as described in the equation (1).

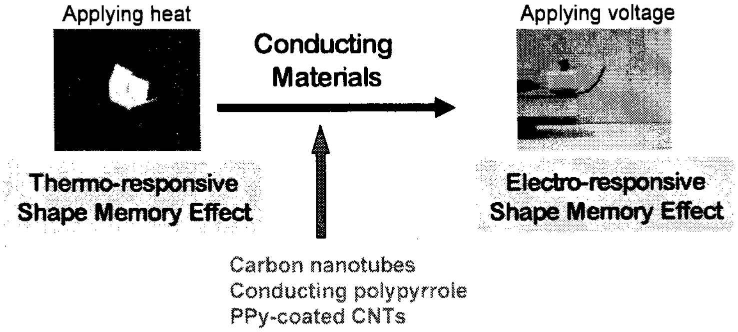

Figure 1. Scheme of thermo-responsive and electro-active shape memory behavior.

3.2. Water-triggered PU-POSS nanocomposites

The water-responsive shape recovery behavior of rectangular PU strip was demonstrated when it is immersed into water at 30°C (Figure 2). Initial straight shape of sample is fixed in a ring form after deforming at 60°C and cooling to room temperature. Original shape of sample is nearly recovered in 300 seconds when the ring sample is immersed into water at 30°C. It is also found that the water-responsive shape recovery is dependent on the temperature of water used. That is, as temperature of water is high, more rapid recovery appears, and above transition temperature, very high shape recovery occurs due to combined effects of water-absorption and thermal heating. The shape recovery higher than 70% is observed in the water-responsive shape recovery test. The best shape recovery of 85% is observed in the sample at a mole ratio of 5:1 POSS:PEG.

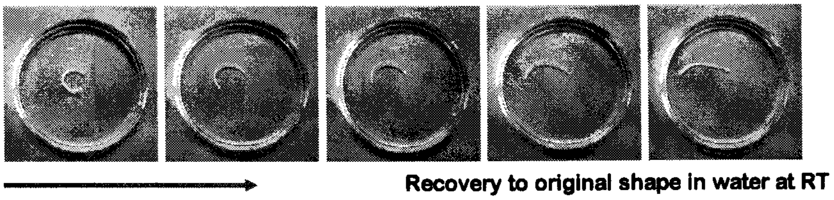

Figure 2. Water-triggered shape recovery for POSS-nanostructured polyurethane.

4. Conclusions

For the electro-active shape memory nanocomposites, the voltage-stimulated shape memory effect could be shown depending on the MWNT contentand degree of surface-modification of MWNT. With using surface-modified MWNT, the composites had an improved mechanical properties, and modulus and stress at 100% elongation increased with increasing surface-modified MWNT content. However, the electrical conductivity of the surface-modified MWNT composites was lower than that of the unreacted MWNT composites. An order of 10^{-3} S/cm was obtained in the samples with 5 wt% modified-MWNT content. The composites with surface-modified MWNT could show electro-active shape recovery with the energy-conversion efficiency of 10.4% as well as improved mechanical properties.

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