博 士 論 文 の 内 容 の 要 旨

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論文題目	Synthesis and characterization of two-way shape memory polymers （双方向形状記憶ポリマーの創製と性能評価に関する研究）

（博士論文の内容の要旨）

Shape memory polymers (SMPs) are smart materials that can significantly change their shape upon exposure to an external stimulus, such as temperature, water, light, electricity, magnetism, and pH. SMPs can be formed into soft materials that have the advantage of being light weight and low cost, excellent active deformation with potential uses in a wide range of applications, including as actuators and sensors, and in aerospace technology, textiles, and biomedical applications. One-way shape memory polymers only remember their shape upon external stimulus and programming once leads to only one shape memory cycle, which limits their application as actuators and for artificial intelligence. In recent years, two-way shape memory polymers (2W-SMPs) have attracted considerable interest because they are fully reversible following exposure to external stimuli without the necessity of reprogramming. The aim of this research is to synthesize a novel two-way shape memory materials using thermal crosslinking reaction which exhibits the full two-way shape memory reversibility following exposure to external stimuli of temperature. The findings in this study will contribute to their applications as soft material actuators and artificial muscles in various fields.

The three significant parts in this dissertation are given as follows:

(1) PEVA/BPO two-way (reversible) chemically crosslinked semi-crystalline shape memory polymers with various crosslinking densities from poly(ethylene-co-vinyl acetate) (PEVA) and various contents of benzoyl peroxide (BPO) were synthesized by thermally crosslinking reaction via micro twin-screw extruder and hot-pressing machine, where PEVA containing various contents of BPO--i.e., 0wt% to 14wt%, are indicated by PEVA-B0 to PEVA-B14. The network properties related to the two-way shape memory behavior of PEVA/BPO samples were determined by the gel content. The developed materials were capable of reversible shape change by “switch on” temperature, which triggers shape change within a reasonable temperature range. The recovery ratio (R_{rec}) increased markedly as when the BPO content increased from 4 wt% to 10 wt%. PEVA-B10 (PEVA with 10wt% BPO) sample had optimal actuation performance and an excellent recovery ratio of over 99%. The non-crosslinked sample (PEVA-B0) did not recover during the heating, and did not exhibit two-way shape memory behavior. PEVA-B1 demonstrated weak two-way shape memory behavior and did not exhibit good thermomechanical recyclability. These results indicate that the crosslinking using BPO plays an important role in ensuring samples return to their original shape, and the PEVA/BPO compositions with high crosslinking densities had significantly elevated recovery ratios. As a result, the developed PEVA/BPO materials were adequately soft and had good mechanical properties, even at large deformation.

(2) The two-way shape memory effect (2W-SME) of PEVA/BPO has been achieved under both constant stress and stress-free conditions. The relationship between the initial prestretching strain ($R_{prestretch}$) and recovery strain (R_{rec}) was the main reason for achievement of the stress-free 2W-SME of PEVA/BPO polymers. Furthermore, three different types of stress-free two-way shape memory behavior were observed during the TMA cycles: the ideal stress-free 2W-SME ($R_{rec} = R_{prestretch}$), the weak stress-free 2W-SME ($R_{rec} > R_{prestretch}$), and no stress-free 2W-SME ($R_{rec} < R_{prestretch}$), which can be controlled by varying R_{rec} using different

setting temperature (T_{set}) during the recovery process. More importantly, the two-way shape memory driving force and recovery force, as the one of key indicators for two-way shape memory materials, was investigated, and they significantly change depending on the BPO content. The clear two-way shape memory performance with clear driving and recovery force was observed for PEVA-B10. The sample with high BPO content shows excellent high-temperature creep resistant performance. A highly crosslinked structure can suppress viscous flow and provides sufficient force to allow the sample to recover its initial shape after crystal melting. Therefore, the PEVA/BPO samples are able to contract during heating. 2D-WAXS and DSC tests indicated that the crystalline structure led to oriented growth of crystals under applied stress, and crystallization led to elongation upon cooling.

(3) Two-way reversible shape memory PEVA/BPO foams with porous three-dimensional structures were fabricated using a salt-leaching and thermo-crosslinking technology. Various pore sizes of PEVA/BPO porous foam were obtained using different NaCl particle sizes. The different reversible shape changes in various pore sizes of PEVA/BPO foams upon exposure at low/high temperature under constant compression conditions were investigated using thermomechanical analysis (TMA). The ideal two-way shape memory performance can be clearly observed in the large pore size sample PEVA/BPO-450 under the same prestretching strain at the crosslinking temperature of 200 ℃. The morphology was characterized by scanning electron micron microscopy (SEM) and X-ray microcomputed tomography scanning (μCT) analysis. The compression behavior of PEVA/BPO foam was also investigated. These properties of two-way reversible shape memory PEVA/BPO foams could qualify their use as lightweight porous actuators in artificial intelligence and aerospace applications.