

氏名	DONG YUBING
学位の種類	博士（工学）
学位記番号	甲 第 642 号
学位授与の日付	平成 27 年 9 月 30 日
学位授与の要件	信州大学学位規程第 5 条第 1 項該当
学位論文題目	Synthesis and properties of shape memory water-borne epoxy and its nanocomposites (形状記憶水性エポキシ及びそのナノコンポジットの創製と性能評価に関する研究)
論文審査委員	主査 教授 倪 慶清 教授 村上 泰 准教授 後藤 康夫 准教授 夏木 俊明 教授 邱 建輝 (秋田県立大学)

論 文 内 容 の 要 旨

Shape memory polymers (SMPs), which have attracted considerable attention in recent years and will come to play a significant role in all areas of human life because of their scientific and technological significance, are a new class of stimuli-responsive materials that can maintain a temporary shape and subsequently recover their original shape by external stimuli, such as heat, water, pH, light, electric field, and magnetic field. As smart materials, SMPs can be potential applied in aerospace structures, biomedical devices, sensors, textiles, dry adhesives, self-healing applications, and so on. Many recent studies have proven the favorable shape memory (SM) properties of epoxies. Shape memory epoxies (SMEPs) merit a special reference among the diverse SMPs such as polyurethane, cross-linked polyethylene, styrene rubbers and acrylate systems as they are unique thermosetting SMP systems with excellent thermal, thermo-physical and mechanical properties along with ease of processability into engineering components. Unfortunately, the processes involved in developing epoxy are very environmentally unfriendly, complex, and expensive. A vast majority of these products are still formulated with organic solvents. However, as environmental regulation become stricter, the requirement for the industries to switch to more ecological and safer systems is constantly growing. This thesis focuses on the development and investigation of SMEP and SMEP nanocomposites which prepared via latex technology.

The most significant results achieved in this dissertation are given as follows:

(1) We reported a facile and environmental-friendly method to prepare epoxy-based SM materials. In the first strategy, we synthesized epoxy-graft-polyoxyethylene octyl phenyl ether (EP-g-TX100), which is a novel reactive copolymer emulsifier for preparing of water-borne epoxy (WEP). The chemical structure and emulsifying ability of EP-g-TX100 were systematically characterized by Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM). In the second strategy, we synthesized WEP via phase-inversion technology. After that, the freeze-drying and hot-press molding technology was applied to preparing the samples. The results show that the as-synthesized emulsifier EP-g-TX100 exhibits the expected structure, can covalently react with the curing agent through the side chains, and has excellent emulsifying ability for epoxy. WEP particle has an average diameter of 137 nm, with particles ranging from 50 nm to 300 nm. Furthermore, the final epoxy products show excellent SM property.

(2) Carbon nanotube (CNT)/WEP SM nanocomposites were successfully synthesized via

freeze-drying and hot-press molding. CNTs were mixed directly with a WEP. CNT/WEP nanocomposites were obtained from these mixtures by freeze-drying and compressing under a pressure of 10 MPa at 120 °C for 2 h. The morphology and mechanical properties of the nanocomposites were investigated by TEM, SEM, dynamic mechanical analysis (DMA) and tensile testing. The SM properties of the nanocomposites were evaluated by fold-deploy SM testing. The effects of filler content and recovery temperature on the SM properties were revealed through systematic variation. Results confirmed that CNTs were homogeneously dispersed and incorporated into the WEP matrices. Thus, significant improvements in the mechanical and SM properties of the nanocomposites were achieved. Moreover, CNT/WEP SM foams were prepared. CNTs were first dispersed in WEP by intensive stirring and then mixed with curing agent and blowing agent at room temperature. CNT/WEP SM foams were obtained from these mixtures via freeze-drying and foaming under a vacuum at 100 °C. The SM properties of the foams were evaluated together with other physical properties. Compression and thermo-mechanical cycle tests were performed to measure the effects of the CNTs on the mechanical performance of the foams. The foams had a high shape recovery and fixity ratio of more than 90% even after several thermo-mechanical cycles with the addition of 1.0 wt% CNTs. The CNTs significantly enhanced the strength of the WEP SM foams.

(3) In-situ grown silica/WEP SM nanocomposites were successfully synthesized by hydrolysis of tetraethoxysilane (TEOS) within the WEP and prepared via freeze-drying and hot-press molding method. The silane coupling agent 3-triethoxysilylpropylamine (KH550) was introduced to improve the interfacial properties between the in-situ generated silica particle and epoxy matrix. The morphology structure and the effect of the content of the in-situ formed silica on the mechanical and SM properties of the silica/WEP composites were studied. The experimental results indicated that the silica particles were homogeneously dispersed and well incorporated into the epoxy matrix. Significant improvements were achieved in the mechanical property of the organic-inorganic hybrid materials. The silica/WEP composites exhibited high shape recovery and fixity ratio approximately 100% even after 10 thermo-mechanical cycles. Moreover, silica/WEP SM foams were synthesized and prepared without extra blowing agent. Silica was synthesized by hydrolysis of TEOS. Silica/WEP foams were obtained from the TEOS solution and WEP mixtures after freeze-drying and foaming in the presence of residual moisture as the blowing agent under a vacuum at 110 °C. The morphologies of the resulting foams were evaluated by SEM and TEM. Compression and thermo-mechanical cycle tests were performed to measure the mechanical and SM properties of the foams. The experimental results indicated that the micrograph and mechanical properties of the foams were closely related to the freeze-drying time. The final foams have excellent SM properties even after several thermo-mechanical cycles. The properties obtained in the epoxy foams may offer new opportunities for their use in future structural applications.

WEPS, as novel versatile environmentally-friendly materials, are being attached great importance in engineering field and mainly used in coatings, metal primers, epoxy cement concrete, glass fiber sizing, and wood adhesives, etc., and additional function of SM will be a good aspect for extending their further applications. Furthermore, our strategy for obtaining SM epoxy materials will pave the way for designing and developing the functional SM effect polymers. The proposed method is applicable to various host polymers and does not require organic solvents.