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Radiation-crosslinking of shape memory polymers based on poly (vinyl alcohol) in the presence of carbon nanotubes

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HIGHLIGHTS

- SMPs were presented via a combination of chemical and radiation crosslinking.
- SMPs were developed containing PVA in the presence of CEA and MWCNTs.
- Radiation crosslinked SM-PVA demonstrated 100% gel fraction at 50 kGy.
- Radiation crosslinked SM-PVA exhibits good temperature responsive SM behavior.

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ABSTRACT

Shape memory polymers based on poly(vinyl alcohol) (SM-PVA) in the presence of 2-carboxyethyl acrylate oligomers (CEA) and multi-wall carbon nanotubes (MWCNTs) crosslinked by ionizing radiation were investigated. Chemical-crosslinking of PVA by glutaraldehyde in the presence of CEA and MWCNTs was also studied. The swelling and gel fraction of the radiation-crosslinked SM-PVA and chemically crosslinked systems were evaluated. Analysis of the swelling and gel fraction revealed a significant reduction in swelling and an increase in the gel fraction of the material that was chemically crosslinked with glutaraldehyde. The radiation-crosslinked SM-PVA demonstrated 100% gelation at an irradiation dose of 50 kGy. In addition, radiation-crosslinked SM-PVA exhibited good temperature responsive shape-memory behavior. A scanning electron microscopy (SEM) analysis was performed. The thermal properties of radiation-crosslinked SM-PVA were investigated by a thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). The ability of the material to return or store energy (E'), to its ability to lose energy (E''), and the ratio of these effects (Tanδ), which is called damping were examined via DMA. The temperature of Tanδ in the radiation-crosslinked SM-PVA decreased significantly by 6 and 13 °C as a result of the addition of MWCNTs. In addition, the temperature of Tanδ for SM-PVA increased as the irradiation dose increased. These radiation-crosslinked SM-PVA materials show promising shape-memory behavior based on the range of temperatures at which Tanδ appears.

1. Introduction

SMPs, defined as polymeric materials with the ability to sense and respond to external stimuli in a predetermined fashion, have been known since the mid-1980s. They can be stimulated by temperature, pH, chemicals, and light. Polymeric materials have various elasticity, ranging from hard glass to soft rubber (Jinsong et al., 2009). SMPs is capable of memorizing a permanent shape, while being temporarily programmed in another temporary shape. Upon exposure to an external stimulus, the SMP will spontaneously revert to its original permanent shape from its temporary geometry (Hu and Chen, 2010). Lendlein and Kelch (2002) found that the shape-memory-effect was controllable by a thermo-mechanical cycle. Fig. 1(a) shows the schematic representation of the thermally induced shape-memory effect (Takeru et al., 2004). The shapes of these thermally responsive SMPs can be readily changed at temperatures above the shape memory transition temperature (T_{trans}) and the deformation can be fixed below this temperature. When heated above T_{trans}, their original shape is automatically recovered. The shape-memory, transformation depends on the mechanism by which polymer molecules transpose between the constrained and random-entangled conformations (Behl et al., 2012). Chemical crosslinks, rather than physical crosslinks, can also be used in elastomeric SMPs. In terms of

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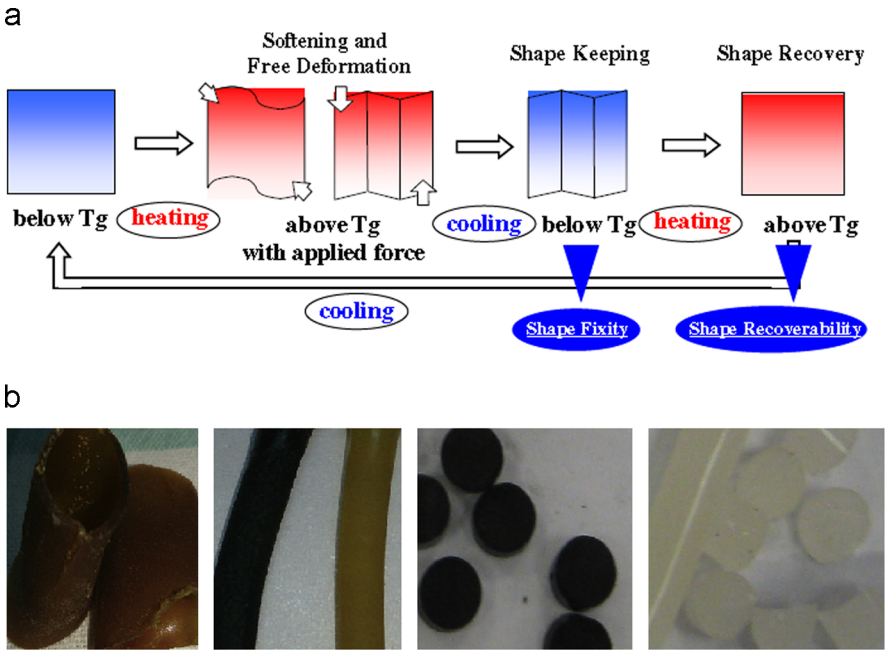

Fig. 1. (a) Schematic representation of shape-memory effect with four steps: (1) original shape after molding (2) softening and free deformation by heating over T_g and under an applied force; (3) shape fixity by cooling below T_g; and (4) shape recovery by heating over T_g under free load condition. The schematic representation was taken from a Takeru et al. (2004). (b) Photos of the various shaped PVA, PVA-MWCNT were molded via glass tubes.

chemical structure, SMPs may be considered phase-segregated linear block copolymers having a hard segment and a soft segment. The hard segment acts as the frozen phase, while the soft segment acts as the reversible phase. The reversible phase transformation of the soft segment is responsible for the shape memory effect (Weiss et al., 2008). When the material is heated above the melting point or glass transition temperature of the soft segment, stresses and strains are relieved as the material returns to its original shape. Mass market applications of SMP are foils for packaging and tubes for cables. Such materials with no nanotubes and no other nano fillers are well known and produced in many countries on a large scale by radiation technology. When being heated these materials shrink and are able to adapt to virtually any shape, providing mechanical protection and insulation.

High-energy ionizing radiation, predominantly in the form of gamma rays and electron beams, have been widely used in crosslink polymers, primarily because of their ability to efficiently produce a uniform crosslinked networks of a wide range of polymers. There have been many investigations on the development of radiation-processed polymer nano-composite materials and the analysis of their mechanical and physical properties. PVA has good a radiation crosslinking yield, and radiation processed PVA nano-composites have garnered interest in the development of implantable biomaterials and biodegradable plastics (Ramaraj, 2007; El-Mohdy, 2007). PVA can be spun from aqueous solutions, which provide a significant advantage in terms of production cost and environmental impact. PVA is known to interact strongly with nanotubes in aqueous solutions, inducing coagulation. Du and Zhang (2010) investigated the preparation of SMPs based on PVA (SM-PVA) crosslinked with glutaraldehyde. The influence of water content of the prepared materials was evaluated. As PVA is a hydrophilic polymer, it contains a small number of water molecules if exposed to air. These water molecules are beneficial in promoting shape-memory characteristics. The shape-memory behavior of SM-PVA, depending on the sequence of the chain segments, is normally observed around the material's T_g. The crosslinked network and undisturbed crystal domains in the PVA constitute the fixed phase, while the amorphous phase acts as the reversible phase. The good mechanical properties of SM-PVAs, along with their non-toxicity, bio-compatibility and biodegradability, indicate the potential for use in many fields (Hassan and Peppas, 2000). SMP compositions can hold more than one shape in memory, In other words, They can embed multiple shape memories in one object. Shape-changing polymeric medical devices offer advantages over traditional medical devices, including blood vessel stents and bone implants, and medical devices used in minimally invasive surgery. Importantly, SMPs may be surgically implanted in an impermanent, compact geometry and subsequently deployed into a different, long-lasting geometry to attain a specific surgical goal, such as the fastening of a suture or soft tissue to bone.

Carbon nanotubes (CNT) is a type of macromolecular systems. The structure of CNTs can be envisaged as rolled-up graphene sheets taking a cylindrical shape. These easily-obtained hollow structures may facilitate the flow and migration of metabolites or bioactive agents and may be used as convenient nanoscale drug carriers. PVA is known to provide good stress transfer of CNTs when used as a continuous matrix in CNT loaded constructs (Cadek et al., 2002).

Using carbon nanotubes may obtain higher performance than usual reinforcement due to the large surface area of carbon nanotubes. In the present study, the preparation and characterization of SMPs based on chemically crosslinked PVA in mixtures with CEA and two types of MWCNTs, followed by a subsequent exposure to ionizing radiation to complete the crosslinking process, mechanical properties, thermal properties and shape-memory behavior of PVA/multiwalled carbon nanotube was then studied in order to investigate the influence of MWCNTon mechanical properties and shape recovery behavior.

2. Experimental

2.1. Materials

CEA and PVA (MW 75,000), 98–99% hydrolyzed were purchased from Sigma-Aldrich (St. Louis, USA). MWCNT types 50 and 75 were procured from NanoKarbon, Korea nano IND. Co. The surfactant sodium dodecyl sulfate (SDS, C12H25SO4Na) was purchased from Sigma-Aldrich (St. Louis, USA) and used as received without further