



Properties and shape-memory behavior of compounds of a poly(ethylene-co-methacrylic acid) ionomer and zinc stearate



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ABSTRACT

The mechanical properties and shape memory behavior of compounds formed from a commercial poly(ethylene-co-methacrylic acid) ionomer and zinc stearate (ZnSt) are described. For compounds containing less than 10 wt% ZnSt, the components were miscible. Although the components were only partially miscible above 10 wt% ZnSt, the compounds were compatible, as judged by their macroscopic homogeneity and the improvements of the mechanical properties. The addition of 30 wt% ZnSt produced ductile materials and improved the room temperature tensile modulus by ~50% and the stress at yield by ~30%. The strain at yield, however, decreased by ~45%. Compounds with 40 or 50 wt% ZnSt improved the modulus of the ionomer by nearly 100%, but the compounds were relatively brittle and broke before yielding. Shape memory behavior was demonstrated with a compound containing 50 wt% ZnSt where nanophase-separated ionic aggregates acted as a *permanent* network and a phase-separated ZnSt crystalline phase was a reversible, temporary network. The shape memory behavior was repeatable over five consecutive shape memory cycles with shape fixity and shape recovery values of ~92% and ~97%, respectively.

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1. Introduction

Shape memory polymers (SMP) are an emerging class of polymers that can change shape when exposed to an external stimulus such as heat, light, electric or magnetic fields, change in pH, or the presence of specific ions [1]. Thermally activated SMPs have a permanent shape as a consequence of having a crosslinked network, but they can be deformed and fixed into a temporary shape when heated above a *switching temperature*, T_c , of a second, reversible network. The temporary shape remains unchanged until the material is reheated above T_c , which in the absence of an external stress produces a recovery of the material to its original, permanent shape. A variety of thermal SMPs have been reported with a wide range of switching temperatures and applications such as medical devices, mechanical actuators, sensors and self-deployable structures. A number of recent reviews have surveyed the progress in the development and understanding of SMPs and their applications [2–5].

We recently reported a new concept for designing a shape

memory polymer that involves compounds of a low molecular weight crystal, e.g., a fatty acid or fatty acid salt (FAS), and an ionomer where there is a very strong supramolecular bond between the two components [6–10]. That approach was used to develop soft, elastomeric SMPs from composites of FASs and an elastomeric ionomer [6–8], the zinc salt of sulfonated poly(ethylene-co-propylene-co-(5-ethylidene-2-norbornene)), Zn-SEPDM and a high temperature thermoplastic SMP from sulfonated poly(ether ether ketone), SPEEK [9,10]. For those compounds, the permanent network was formed by physical crosslinks due to microphase-separated ionic nanodomains within the ionomer phase, covalent crosslinks and/or a crystalline phase, while the temporary network was due to microscopic crystals of the FAS. Strong dipolar interactions between the carboxylic acid or metal carboxylate groups of the FAS crystals and the metal sulfonate groups of the ionomer provided a strong supramolecular bond that was capable of supporting a load. The switching temperature was the melting point of the FAS crystals, which generally was lower in the shape memory compound than for the pure FAS due to the strong intermolecular interactions.

The novelty of that SMP design is that strong intermolecular interactions between the low molecular weight crystals and the ionomer allow microdomains of the FAS to support stress and

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function as temporary crosslinks in these systems. Although the ionic associations within the ionomer can be used as the permanent network, the main role of the ionomer is to facilitate dispersion of the FAS and to provide a complementary functionality to the matrix polymer that stabilizes the FAS dispersion and develops the strong intermolecular interactions. The versatility of this approach is that one can create a family of SMPs with different transition temperatures from a single ionomer simply by melt compounding it, using conventional plastics processing equipment, with a variety of FAs or FASs with different melting points [6]. Thus there is no need to develop and synthesize new polymers for each application.

The previous work that has been done with this SMP design of a polymer/fatty acid compound used amorphous ionomers, an elastomer (Zn-SEPDM) [6–8] and a high temperature plastic (SPEEK) [9,10]. The present study assessed the applicability of this approach with a semi-crystalline poly (ethylene-co-methacrylic acid) ionomer, PEMA. We previously demonstrated tunable shape memory effects with PEMA ionomers [11], where T_c could be varied over a wide temperature range that fell within the broad melting transition of the ionomer. Note that the first SMP reported was cross-linked low density polyethylene (XLDPE) [12], which is still widely used commercially as shrinkable film and tubing. PEMA is similar to crosslinked LDPE except that in PEMA the crosslinks are supra-molecular bonds between metal-neutralized methacrylic acid groups instead of covalent bonds. The advantage of the ionomer compared to conventional XLDPE as a SMP is that the ionomer can be molded into complex shapes by conventional melt processing methods and does not require a post-molding crosslinking reaction. Another important distinction between physically-crosslinked PEMA and XLDPE is that the ionomer is significantly tougher, because of the energy dissipation that occurs with reversible, supra-molecular crosslinks.

2. Experimental details

2.1. Materials

The PEMA ionomer, Surlyn[®] 9520, was obtained from DuPont de Nemours Co. It had a melt index of 1.55 g/10min, measured at 190 °C and 2.16 kgf with a Dynisco Polymer Test D4003x melt indexer, and a nominal methacrylic acid concentration of 10 wt% that was 70% neutralized to the zinc methacrylate [13]. Zinc stearate (ZnSt), 99% purity, was purchased from Acros Organics. Both materials were used as received.

Composites of the ionomer with as much as 50 wt% ZnSt were prepared by melt mixing the two components with a Haake MiniLab II Micro Compounder (ThermoFisher Corp.). Films, ~0.5 mm thick, were prepared by compression molding at 140 °C using a Carver Hydraulic Press, Model #3912. Although the PEMA films were semi-crystalline, they were optically clear, which is due to the very small crystallite sizes that occur in this ionomer [14]. For low ZnSt concentrations, the films remained clear, which indicated that the FAS crystals were also microscopic or the ZnSt dissolved in the ionomer. As the ZnSt concentration increased above ~30 wt%, the films became less clear and for the highest ZnSt concentrations, they were translucent, as would be expected if the ZnSt crystals grew to sizes greater than ~0.5 μm. The films for all concentrations appeared homogeneous, which indicates that the two components were well dispersed. Samples with the highest ZnSt concentrations, however, were brittle, which was probably due to either the high crystallinity or large crystallites of the ZnSt at high ZnSt concentration. The sample notation used in this paper is PEMA(x), where x denotes the ZnSt concentration in wt%, i.e., PEMA(20) is a compound of the ionomer and 20 wt% ZnSt. A covalently cross-linked PEMA(50) compound was prepared by exposing a

compression molded film to electron beam (EB) radiation in air at NEO Beam Alliance Ltd. (Middlefield, OH) using a radiation dose of 200 kGy.

2.2. Materials characterization

The thermal stability of the compounds was measured using a TA Instruments TGA Q50 thermogravimetric analyzer (TGA) by heating the sample under a dry nitrogen atmosphere from room temperature to 600 °C with a heating rate of 10 °C/min. Thermal transition temperatures were measured with a TA Instruments differential scanning calorimeter (DSC), Model Q200, by scanning between –70 °C or 50 °C and 150 °C using cooling and heating rates of 10 °C/min. The samples were crimped inside aluminum pans and blanketed with a dry nitrogen atmosphere. The temperature and enthalpy were calibrated with an indium sample. The crystallinity of the components was calculated by the ratio of the measured heat of fusion (normalized by the mass fraction of the component of interest) and the heat of fusion of a perfect crystal of polyethylene, 278 J/g [15] or a crystal of stearic acid, 199 J/g [16].

A TA Instruments Q800 dynamic mechanical analyzer (DMA) with a tensile film fixture was used to study the viscoelastic properties of the compounds. The samples were rectangular films (20 mm × 5 mm × 0.5 mm) and the DMA measurements were performed using a constant frequency of 1 Hz, a 0.01 N preload force and a strain amplitude of 20 μm. Measurements were made from –75 °C to 150 °C using a heating rate of 2 °C/min.

The shape memory properties of the ionomer and its blends were evaluated by shape memory cycles (SMC) carried out with the DMA using a tensile film fixture and the same sample preparation procedure described above for dynamic mechanical measurements. The DMA's controlled force mode was used to deform the sample with a fixed heating and stretching protocol. A preload force of 0.0015 N was used to prevent sagging of the sample. The sample was first heated at 5 °C/min to a temperature above T_c , at which point it was stretched isothermally to a stress of 1.5 kPa. The sample was then cooled with a constant tensile stress to fix the temporary shape, after which the applied stress was removed. Shape *fixity* (F), i.e., the effectiveness at fixing the temporary shape, was defined by equation (1),

$$F = \frac{\epsilon_f}{\epsilon_s} \times 100\% \quad (1)$$

where ϵ_f was the strain of the fixed temporary shape after removing the stress and ϵ_s was the strain after stretching the sample, i.e., before the stress was removed. The original, permanent shape of the sample was recovered by reheating the unconstrained sample to above T_c . The effectiveness of the shape recovery, R , was defined by equation (2),

$$R = \frac{\epsilon_s - \epsilon_r}{\epsilon_s - \epsilon_0} \times 100\% \quad (2)$$

where ϵ_r was the residual strain of the sample at the completion of the SMC and ϵ_0 was the initial strain of the sample at the beginning of the experiment (usually zero). For an ideal shape memory material, $F = R = 100\%$.

The melt index of PEMA(0) and PEMA(30) at 190 °C, and 2.16 kgf was measured with a Dynisco Polymer Test D4003 melt indexer following ASTM Standard D-1238 [17]. Tensile properties were measured with an Instron 5567 universal testing machine using a 10 N load cell and a cross-head speed of 5 mm/min. Tensile specimens were dog-bone shaped with dimensions of the gauge-length region of 7.62 mm × 3.18 mm × 0.50 mm. A Bruker D8 Discover X-ray diffractometer with a general area detector diffraction system

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