New Design of Shape Memory Polymers: Mixtures of an Elastomeric Ionomer and Low Molar Mass Fatty Acids and Their Salts

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Introduction. Shape memory polymers (SMP) are materials that can change shape when exposed to an external stimulus, such as temperature. SMPs have a permanent shape that is provided by a cross-linked network, but they can be deformed above a critical temperature (T_c) of a second, reversible network and fixed into a temporary shape when cooled under stress to below T_c. When reheated above T_c without stress, the material assumes its permanent shape. SMPs have applications as medical devices (e.g., stents and sutures), actuators, sensors, artificial muscles, switches, smart textiles, and self-deployable structures.[1]

All previous work on SMPs has involved synthesizing new polymers or modifying existing polymers, though many applications include fillers and additives to adjust the modulus and/or strength of the material. The permanent networks are either covalently cross-links or physical cross-links with sufficiently long relaxation times that, mechanically, the "bonds" behave as permanent above T_c. The temporary networks typically rely upon vitrification, melting, or some other physical interaction such as nanophase separation that is reversible with temperature (or another external stimulus, such as photosensitivity[2]). There are currently four classes of SMPs:[3] (1) covalently cross-linked glassy polymers, (2) covalently cross-linked semicrystalline elastomers, (3) physically cross-linked glassy polymers, and (4) physically cross-linked semicrystalline block copolymers.

Ionomers possess a strong physically cross-linked network due to nanophase separation of ion-rich domains that can persist to relatively high temperatures.[4] Ionomers have been used to design SMPs, but either the shape memory properties were poor or the ionomer was used primarily to vary the stiffness of the hard segments or melting point of a polyurethane.[5–9] This paper describes a new type of SMP based on blends of an elastomeric ionomer and low molar mass fatty acids or their salts. Nanophase separation of the ionomer was used to develop the permanent network, and fatty acids (salts), FA, were used to produce a secondary network where T_c was related to the melting point of the FA, T_m.

Experimental Details. Sulfonated EPDM (SEPDM) is a thermoplastic elastomer that was developed by Exxon in the mid-1970s.[10] It possesses properties characteristic of a cross-linked rubber but exhibits viscous flow at temperatures >150 °C. Poly{ethylene-*r*-propylene-*r*-(5-ethylidene-2-norbornene [ENB])}, EPDM (Royalene 521: Mooney viscosity = 40 (ML (1 + 4)/100 °C) and composition of 49% ethylene, 46% propylene, and 5% ENB), was obtained from Crompton Chemical Co. The zinc salt of sulfonated EPDM (ionomer) with a zinc sulfonate concentration of 0.03 mequiv/g was prepared

by sulfonating EPDM with acetyl sulfate (see Scheme 1) and neutralizing the product with zinc acetate.[11] Although SEPDM can flow at elevated temperatures, the melt viscosities are too high to be practical for any conventional melt-processing operation, e.g., extrusion or injection molding. This problem can be resolved by adding a polar plasticizer such as zinc stearate (ZnSt), which not only lowers the melt viscosity but when the compounds are cooled to below 100 °C, the ZnSt crystallizes and acts as a reinforcing filler.[12] Zinc stearate (ZnSt)/ionomer composites were prepared by dispersing the ZnSt in a solution of the ionomer, flashing off the solvent with steam, and drying. Film samples were compression-molded at 200 °C. Shape memory cycles to assess fixation and recovery of the SMPs were measured with a TA Instruments dynamic mechanical thermal analyzer (DMTA) 2980 using the tension mode and a frequency of 1 Hz.

Results and Discussion. Figure 1 shows the shape memory characteristics of a 33.3 wt % ZnSt/ionomer composite. The film (a) was heated to 100 °C and stretched to 47% strain and cooled to room temperature to fix a temporary elongated shape (b). The temporary shape was stable below ∼80 °C, but when reheated to 100 °C, the film recovered to the permanent shape (c). The length recovery was ∼92%.

A shape memory cycle[1,3] for a composite containing 33.3 wt % ZnSt is shown in Figure 2. The film was heated to 120 °C with a preload of 0.005 N to maintain tension (step 1) and held at 120 °C to equilibrate, during which the length shrunk to a strain of about −4% (step 2). The film was then stretched to 29% strain and cooled under load at constant strain to 0 °C (step 3). After equilibrating at constant temperature and strain, the force was reduced to 0.005 N at constant strain (step 4). Shape recovery was achieved by reheating the film at 2 °C/min (step 5). Recovery began at ∼80 °C (T_c). After reaching 120 °C, the film was cooled quickly to 50 °C (step 6).

The strain recovery in the cycle shown in Figure 2 was >100%; this is discussed later in this Communication. T_m of ZnSt in the composite was 120 °C, which is lower than that of the neat ZnSt (∼130 °C). This was due to improved miscibility of the ZnSt in the ionomer because of strong interactions between the sulfonate groups of the ionomer and the metal stearate groups. The melting point depression of fatty acids (salts) mixed into Zn−SEPDM are given in Table 1. Although no direct evidence of the interactions, e.g., by spectroscopy, was obtained, strong interactions between the ionomer and ZnSt are supported by the observation that composites containing as much as 33 wt % ZnSt were stable and relatively clear, while the addition of <1 wt % ZnSt to non-sulfonated EPDM produced a white, opaque sample with noticeable phase separation and exuding of the ZnSt.[13]

The permanent network in these composites arises from strong intermolecular associations of the Zn−sulfonate groups in the ionomer, which produce nanophase separation of ion-rich
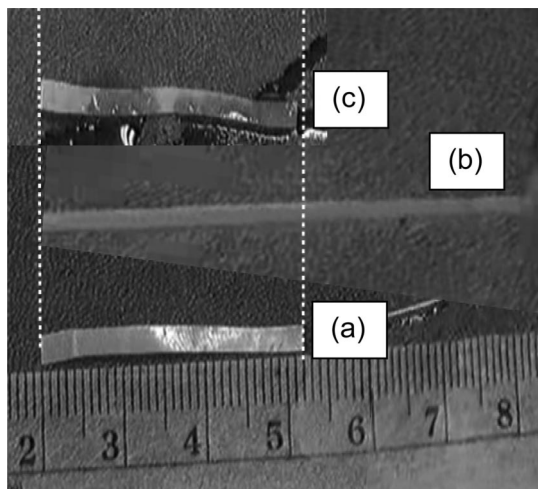
Scheme 1. Synthesis of SEPDM (DCE = Dichloroethane)
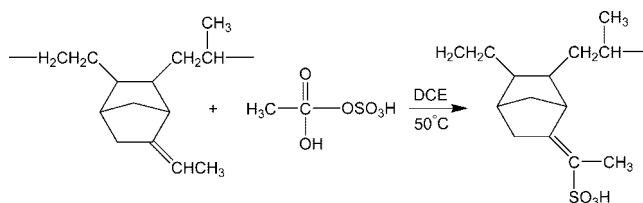
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Figure 1. Shape memory behavior of a Zn-SEPDM containing 33.3 wt % ZnSt: (a) compression-molded rectangular strip (permanent shape); (b) strip heated to 100 °C, stretched, and cooled to room temperature under stress (temporary shape); (c) strip reheated to 100 °C without any external stress (recovery back to permanent shape). The dotted lines indicate the original length of the strip (permanent shape). The length recovery was 92%.

domains that persist to >200 °C.[14,15] The characteristic relaxation times for the ionic aggregates in other sulfonate ionomers was reported to be greater than 5 orders of magnitude greater than the relaxation time associated with the glass transition, which indicates that the physical cross-links in these polymers should behave as permanent for the experiments described above. The temporary network is due to very small imperfect ZnSt crystals that interact strongly with the Zn−SEPDM and act as cross-links below the softening of the ZnSt crystals (T_c).[11]

The reason the final length of the SMP in the cycle shown in Figure 2 was less than the original length is believed to be a consequence of the nonequilibrium state of the original film. These were compression-molded above the dissociation temperature of the nanophase-separated domains, >200 °C,[11] and because of the long relaxation times of these ionomers, it is unlikely that an equilibrium chain conformation was achieved during the molding process. Prior work indicated that significant physical aging effects occur in these composites over a time period of a month.[14] Thus, during the shape memory cycle, it is possible that aging and stretching of the sample affected the "permanent network" and changed the "equilibrium" length of the sample. Multiple tests on different samples of the same material used in Figure 2 produced similar shape memory behavior, but differences in the final length which was always >90% of the original length.

Clearly, the lack of reproducibility of the recovered film length is troublesome for an SMP. But, the residual double bonds in the Zn−SEPDM can be covalently cross-linked during sample preparation to produce a covalently cross-linked network. Although the physical ionic associations were used for the "permanent network" in this study, the importance of the iono-mer is *not* to provide cross-links but, rather, to provide the strong interactions with the FA that allow it to provide a robust physical temporary network.

The novelty in this type of SMP is that the FA provides the temporary network, and a single elastomer can be used to create a family of SMPs with different T_c's by choosing FAs with varying melting points. T_c's for other FA/ionomer composites measured from shape memory cycles similar to Figure 2 are listed in Table 1. T_c was systematically lower than T_m, and these
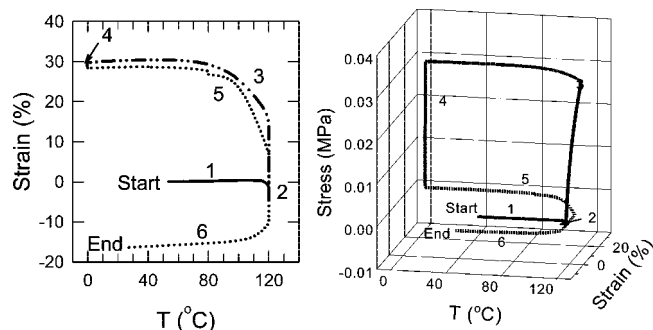
Figure 2. Temperature−strain and temperature−strain−stress plots for a shape memory cycle for a composite film of Zn-SEPDM containing 23.1 wt % ZnSt. The numbers denote the steps of the cycle described in the text.

Table 1. Melting Points of Fatty Acids (Salts) and Fixing Temperature of Fatty Acid (Salt)/Zn−SEPDM Shape Memory Polymers

		T_m (°C)		
fatty acid (salt)	concn in compd (wt %)	neat fatty acid (salt)	fatty acid (salt) in composite	T_c (°C)
decanoic acid	23.1	31	20	10
lauric acid	23.1	44	40	35
myristic acid	9.1	54	45	30
magnesium stearate	30.0	87	71	67
zinc oleate	33.3	88	77	70
zinc stearate	33.3	130	120	80

data show that with a judicious choice of FA the Zn−SEPDM/ FA composites provide SMPs with a ∼70 °C range of T_c's.

Conclusions. The feasibility of designing SMPs from mixtures of low molar mass fatty acids and their salts (FA) with an ionomer was demonstrated. The attraction of this type of SMP is that a family of SMPs with varying critical temperatures (T_c) can be easily developed from a single polymer by simply choosing FA's with different melting points. The role of the ionomer is to provide a strong intermolecular bond between the FA crystal and the polymer that will behave as a physical cross-link below T_c and allow reshaping of the material above T_c. Without the ionomer, interactions between FA crystals and polymers are not strong enough to provide a robust cross-link. Though not shown in this paper, the T_c is relatively independent of the amount of FA used above some critical amount, and the concentration of FA can be used to control the softness of the SMP.

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