Effects of carbon black nanoparticles on two-way reversible shape memory in crosslinked polyethylene

Lan Ma [a], Jun Zhao [b, **], Xiaoyan Wang [b], Min Chen [b], Yongri Liang [c, 1], Zhenwen Wang [b, 2], Ziniu Yu [a], Ronald C. Hedden [a, *]

[a] Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409, USA
[b] Department of Polymer Science and Engineering, School of Chemistry and Biological Engineering, University of Science and Technology Beijing, Beijing 100083, PR China
[c] Beijing National Laboratory for Molecular Sciences, Joint Laboratory of Polymer Science and Materials, State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China

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ABSTRACT

This work examines the effects of carbon black (CB) nanoparticles on two-way, reversible shape memory cycles in crosslinked polyethylene. The two-way shape memory effect is characterized by mechanical measurements, thermal analysis, and X-ray diffraction. For the first time, it is shown that there is an optimal loading of CB particles that maximizes the actuation ratio ($R_a \equiv (\varepsilon_2 - \varepsilon_1) \times 100\%$), where ε_1 is the initial strain under load above the crystal melting temperature and ε_2 is the strain following crystallization under load. Adding a small volume fraction of CB particles ($v^{CB} = 0.5$ to 1.0 vol. %) enhances R_a by more than a factor of 1.5. Through swelling experiments and mechanical testing, the CB nanoparticles are shown to act as physical crosslinkers, significantly decreasing ε_1. However, the observed ε_2 is barely affected by small amounts of CB, which are insufficient to disrupt the formation of highly oriented crystals. In contrast, the two-way shape memory effect is greatly reduced with higher CB loading ($v^{CB} = 20$ vol. %), which decreases both ε_2 and R_a. Addition of a small amount of CB is also shown to provide a simple means to lower the response temperature range of polyethylene-based shape memory polymers.

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1. Introduction

Shape memory polymers (SMPs) are smart materials that can recover from a temporary shape that is held after deformation to a permanent shape after applying an external stimulus [1–12]. SMPs have great potential to be used in sensors, actuators, and other devices. In contrast to the widely used shape memory alloys and shape memory ceramics, SMPs have advantages such as high extensibility (up to 500–800%), tunable elastic modulus, tunable response temperature, and low mass density. Generally speaking, SMPs contain chemical and/or physical crosslinking that defines the permanent shape, and they can undergo a reversible phase transition that triggers shape recovery.

In the past decade, many studies of SMPs focused on enhancing the mechanical and thermal properties or on achieving remote triggering [2,4,5,13–22]. Other studies have targeted SMPs with biocompatibility to be used in medical applications [23–25] and SMPs with multiple shape memory effects (SMEs) to provide complex actuation [16,20,26–31]. Compared with the well-documented one-way SMPs (1W-SMPs) that can only remember a high temperature shape, relatively few two-way reversible SMPs (2W-SMPs) that can remember both high and low temperature shapes have been reported [25,32–37]. 2W-SMPs could be very useful for achieving reversible actuation in devices such as artificial muscles. Reversible actuation triggered by temperature, light, or electric fields has already been demonstrated in several studies of oriented or "monodomain" liquid crystalline elastomers, for example [38–42]. However, there is still a driving force for design

* Corresponding author.
** Corresponding author.
   E-mail addresses: zhaoj@nanoctr.cn (J. Zhao), ronald.hedden@ttu.edu (R.C. Hedden).
   [1] Present address: College of Materials Science and Engineering, Beijing Institute of Petrochemical Technology, Beijing 102617, PR China.
   [2] Present address: Aerospace Research Institute of Material and Processing Technology, Beijing 100076, PR China.

of new 2W-SMPs based on economically attractive and readily processable polymeric materials such as polyolefins.

Recently, 2W-SMPs based on chemically crosslinked, semi-crystalline poly(cyclooctene) (PCO) were reported, and their shape memory behavior was attributed to stress-induced crystallization [32,35]. The same strategy has been used to achieve shape memory in some other semicrystalline polymers such as polyurethanes (PU), poly(ε-caprolactone) (PCL), and poly(ethylene-co-vinyl acetate) (PEVA) [25,33,34,36,37,43]. In our previous work, the preparation of 1W-SMPs from crosslinked polyethylene (cPE) and carbon black (CB) nanoparticles was described, and their self-healing behavior was studied [22]. The cPE and cPE/CB nanocomposites showed both high strain fixity ratio (R_f) and high strain recovery ratio (R_r). Crystallization-induced elongation was observed for all the SMPs prepared, but the effect became less remarkable with increasing volume fraction of CB nanoparticles (v^{CB}) [22].

CB is among many fillers that have been studied as modifiers for SMPs, including graphene, carbon nanotubes, clays, carbon fibers, glass fibers, Kevlar fibers, nano-SiC and nano-SiO$_2$. The fillers are normally intended to improve the mechanical properties, especially shape recovery stress. Improvements in mechanical response have been observed with graphene-reinforced hyperbranched polyurethane, polyimide or polyester/carbon nanofiber composites [44—47], carbon fiber or glass fiber-reinforced epoxy laminates [48—50], carbon nanotube or carbon nanofiber-reinforced polyurethane composites [51—55], and carbon nanoclay-tethered shape memory polyurethane nanocomposites [56]. A few studies have realized electroactive or photoactive SMPs by addition of carbon nanotubes [57,58] or carbon black [59,60].

High loadings of CB (>10 vol. %) were previously examined with polyurethane SMPs. Both Li et al. [61] and Jana et al. [52] found that CB could improve the strain fixity in polyurethane SMPs. However, CB addition decreased the shape recovery ratio and shape recovery speed, and it did not have much effect on the response temperature [52,61]. Vaia et al. [62] studied remote actuation in Morthane (polyester-polyurethane) SMPs, which were made sensitive to infrared light by addition of 1—5 vol. % of carbon nanotubes. Compared to CB-loaded polyurethane SMPs, a lower volume fraction of carbon nanotubes was required to achieve the same improvement in strain fixity. However, large volume fractions of CB nanoparticles are not always required to improve properties of SMPs. The results of Jana et al. [52] illustrate that low loadings (1—5 vol. %) of CB nanoparticles can have a significant impact on performance. In addition, the processing of CB into SMPs is straightforward, and CB does not suffer from the potential health risks associated with CNTs.

This work concerns the effects of CB nanoparticles on the 2W-SME in cPE, a polymer in which the 1W-SME is well-known [63—65]. These new investigations focus on characterizing the 2W-SME in our cPE materials and elucidating the effects of added CB nanoparticles on performance. Whereas studies of nanofillers in SMPs often focus on enhancing the modulus or toughness of the SMPs, the aim of this study is instead to examine the ability of CB nanoparticles to improve shape memory characteristics and alter the response temperature range. Using a series of samples having systematic variations in CB loading, the effects of CB particle loading on the actuation ratio (R_a) are reported. $R_a \equiv (\varepsilon_2 - \varepsilon_1) \times 100\%$, where ε_1 is the initial strain under load above the crystal melting temperature and ε_2 is the strain following crystallization under stress. In addition, the effects of CB nanoparticles on switch temperatures in heating and cooling steps are investigated, revealing a simple approach for lowering the response temperature range of cPE-based SMPs. The molecular and physical factors underlying the observed thermomechanical phenomena are elucidated through equilibrium swelling, differential scanning calorimetry, and X-ray diffraction experiments.

2. Experimental section

2.1. Materials

Low density polyethylene (type LD100BW) pellets (lPE) with density of 0.923 g cm^{-3} and melt flow index of 2.0 g (10 min)$^{-1}$ were supplied by Sinopec Beijing Yanshan Company (China). CB nanoparticles (Vulcan XC68) with diameter of 30—50 nm, iodine number of 68 mg g^{-1}, and dibutylphthalate number (DBP) of 123 mL (100 g)$^{-1}$ were purchased from Cabot Corporation (USA). 2,5-dimethyl-2,5-di-(tert-butylperoxy)-hexane (DHBP, 92%) was supplied by Acros Organics (Belgium).

2.2. Sample preparation

The preparation procedure is the same as in a previous work [22]. PE pellets and CB nanoparticles were dried completely in a vacuum oven at 80 °C before use. PE pellets were mixed with various volume fractions of CB nanoparticles in a Thermal Scientific Haake MiniLab II mixer (Germany) at 140 °C and stirred at 60 rpm for 10 min. The mixtures were extruded and cut into pieces before being soaked in DHBP in a hermetically sealed glass flask at room temperature for 72 h. The soaked pieces were subsequently molded by hot pressing at 200 °C and 20.0 MPa for 30 min to crosslink the PE component. The free-radical mediated crosslinking process has been described elsewhere [27,66]. Finally, thin films with a thickness of 0.5—1.0 mm were obtained by slow cooling in air.

2.3. Swelling experiments

Samples were immersed in large volume of 1,3-dichlorobenzene and stirred gently at 140 °C until an equilibrium mass was reached after about two days. During the swelling, the solvent was replaced several times in order to remove the extractable fraction. The extracted samples were dried completely in a vacuum oven at room temperature until their masses were invariant with time. The equilibrium mass swelling ratio (Q_s) was calculated according to eqn. (1).

$$Q_s = \frac{M_s}{M_{ex}} \tag{1}$$

In eqn. (1), M_s is the mass at equilibrium swelling and M_{ex} is the dry mass of the extracted sample. The gel mass fraction of the network (f_g) is defined by eqn. (2).

$$f_g = \frac{M_{ex}}{M_0} \tag{2}$$

In eqn. (2), M_0 is the initial dry mass of the sample prior to extraction.

2.4. Shape memory effect analysis

The cPE and cPE/CB samples having different volume fractions of CB nanoparticles (v^{CB}) were cut into rectangular strips with a width of ca. 3.0 mm and thickness of 0.5—1.0 mm. The shear storage moduli, $G'(\omega)$, were characterized in shear sandwich geometry on a dynamic mechanical thermal analyzer (TA Instruments Q800 DMTA, USA). Isothermal frequency scans from 0.1 Hz to 40 Hz were carried out with 0.5% strain amplitude at 130 °C.

1W-SME and 2W-SME analyses were performed on the DMTA in tension mode. The 1W-SME was characterized using a four-step program. In the 1st step, the samples were kept isothermally at