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Remote activation by green-light irradiation of shape memory epoxies containing gold nanoparticles

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ABSTRACT

Shape memory epoxies (SMEs) that can be remotely activated by the use of green light, are described. An epoxy matrix based on on diglycidylether of bisphenol A (DGEBA cured with a mixture of *n*-dodecylamine (DA) and *m*-xylylenediamine (MXDA), exhibits excellent shape memory properties as described in a previous paper (Leonardi et al., 2011). Au NPs with an average diameter close to 5 nm could be uniformly dispersed in this matrix using poly(ethylene oxide) (PEO) chains as stabilizer. These NPs showed a significant photothermal effect even at very low concentrations (0.01 wt% as metallic gold), when irradiated with a 532 nm laser at a power close to 2 W/cm^2. Under these conditions, a bended bar (1.4-mm thickness) recovered its initial shape in a few seconds. This formulation may be used to build up devices with the necessary mechanical strength and with the possibility to produce shape recovery by remote activation using green light. A second example was analyzed employing an amphiphilic epoxy matrix to produce a uniform dispersion of Au NPs stabilized with dodecyl chains (average diameter close to 3 nm). A bar (1.4-mm thickness) of the SME with 0.04 wt% Au NPs (as metallic gold) showed a fast recovery of its initial shape by irradiation with a 532 nm laser at a power close to 2 W/cm^2. This example shows the feasibility of adapting the epoxy chemistry to disperse Au NPs stabilized with different ligands and obtained through robust synthetic methods.

1. Introduction

Among the families of shape memory polymers, shape memory epoxies (SMEs) are receiving increasing interest for practical applications due to their excellent mechanical and thermal properties, easy processability, very good shape fixing and fast recovery, and the versatility to vary the location of the glass transition temperature (T_g) [1–14]. In SMEs a temporary shape is produced at temperatures above T_g by exerting a force, it is fixed by cooling below T_g while keeping the force, and the initial shape is recovered by removing the force and heating again above T_g.

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While direct heating is the usual way to activate shape recovery, some applications need remote activation. Photothermal and photochemical methods, induction heating and ultrasound activation, employed for this purpose, have been discussed in a recent review [15]. Among these methods, photothermal activation is a general approach that requires the dispersion of appropriate light absorbers in the polymer, capable of converting photons into heat. Different types of absorbers can be employed such as inks and organic dyes [16,17], gold nanoparticles or nanorods [18–23], graphene [24–26], carbon nanotubes [27], and metal complexes [28,29]. The excitation wavelength depends on the absorber type and can vary from the near IR, the visible or the UV range. One important aspect of photothermal activation is that it can produce a spatially controlled recovery toward the initial shape [16,19,22].

There are few reports of remote activation of SMEs in the literature. Puig et al. reported the synthesis of a SME containing a uniform dispersion of magnetite nanoparticles that was remotely activated in an alternating magnetic field [30]. He et al. synthesized an epoxy-based nanocomposite containing both carbon nanotubes and magnetite nanoparticles, located in different microphases [31]. As carbon nanotubes and magnetite nanoparticles responded to different radiofrequencies, both microphases could be independently activated leading to a multiple shape memory behavior. Wu et al. recently reported the synthesis of an UV/heat dual responsive SME incorporating an UV-heat transfer compound into the epoxy matrix [32]. However, no references of SMEs responsive to visible light were found. These materials can be obtained by dispersing Au nanoparticles (NPs) in the epoxy matrix. Due to the high extinction coefficient of Au NPs [33], photothermal activation would need a very small concentration of these nanoparticles [27]. In turn, this assures good transparency and improved light penetration.

An epoxy matrix based on diglycidylether of bisphenol A (DGEBA) cured with a mixture of *n*-dodecylamine (DA) and *m*-xylylenediamine (MXDA), was selected for this study. Its shape memory properties were analyzed in a previous publication [8]. This formulation exhibited interesting properties to constitute the basis of an SME. Its glass transition temperature (T_g) could be varied in a broad range by changing the DA/MXDA ratio. It varied from 14 °C (neat DA) to 120 °C (neat MXDA). The particular formulation synthesized with a molar ratio DA/MXDA = 4, with $T_g = 41$ °C, could be strained up to 75% in repeated shape memory cycles with tensile stresses close to 3 MPa. This formulation combined large strains with relatively large stresses, a desirable property for an SME. Shape fixity and shape recovery values were close to 98% and 96%, respectively. In order to produce remote activation of shape recovery it was necessary to disperse Au NPs in this epoxy matrix.

There are considerable challenges in achieving uniform dispersions of Au NPs in cured epoxies. One possible way is the use Au NPs with stabilizing ligands that assure solubility in the initial formulation and throughout the polymerization. In some cases, Au NPs are soluble in the monomers but segregate during reaction by a polymerization-induced phase separation process [34,35]. In order to avoid phase separation, the stabilizing ligands must be extremely soluble during the whole conversion range. Poly(ethylene oxide) (PEO) exhibits this behavior, particularly with typical epoxies based on diglycidylether of bisphenol A (DGEBA) [36–39]. Therefore, Au NPs stabilized with PEO chains were synthesized and dispersed in the epoxy monomers. The quality of the dispersion of Au NPs in the cured specimens was analyzed as well as their remote activation by irradiation with a 532 nm laser.

A second formulation was analyzed employing an amphiphilic epoxy matrix to produce a uniform dispersion of Au NPs stabilized with dodecyl chains. These NPs were synthesized with the Brust–Schiffrin classic method [40]. The amphiphilic epoxy host was described in a previous publication [41]. In this case, only the remote shape recovery by irradiation with a 532 nm laser will be reported, without any analysis of shape memory properties of the epoxy matrix. The aim of this second example was to show the feasibility of obtaining remotely activated SMEs by adapting the epoxy chemistry to disperse Au NPs stabilized with different types of ligands.

2. Experimental section

2.1. Synthesis of Au NPs coated with PEO chains (Au@PEO)

Au NPs coated with PEO chains (Au@PEO) were synthesized using a technique reported by Rucareanu et al. [42]. Briefly, a solution of tetraoctylammonium bromide (TOAB, Sigma–Aldrich) in toluene (56 mM) was contacted with an aqueous solution of $HAuCl_4 \cdot 3H_2O$ (Sigma–Aldrich, 37 mM). This mixture was stirred at room temperature until the latter was phase-transferred to the organic phase (evidenced by the decoloration of the previously yellow aqueous phase). A fresh sodium borohydride aqueous solution ($NaBH_4$, Sigma–Aldrich, 462 mM) was then added as reducing agent. After stirring overnight at room temperature, the organic layer was extracted and washed with Millipore water (three times) and then dried over anhydrous sodium sulfate. The solution was then diluted to 250 mL. The ligand (TOAB) was immediately exchanged by 4-(dimethylamino)pyridine (DMAP, Sigma–Aldrich) by adding an aqueous solution of DMAP (0.1 M) to the solution of Au@TOAB nanoparticles in toluene. Phase transfer of the particles occurred spontaneously, and the wine red aqueous solution of DMAP-stabilized Au nanoparticles (Au@DMAP), was isolated. The solution, stored at 4 °C, was stable for months. Finally, same volumes (about 125 mL) of aqueous solution (0.45 mM) of thiol-terminated poly(ethylene oxide) (PEO-SH) ($M_n = 2100$ g/mol) and aqueous solution of Au@DMAP were contacted overnight to promote the exchange. The volume was reduced by roto-evaporation, thereby obtaining a concentrated solution of nanoparticles. Dialysis was performed to purify the nanoparticles, using a Sephadex LH-20 membrane (MWCO 12-14000). Once the purification process was finished, Au@PEO NPs were dried combining roto-evaporation with freeze drying.