



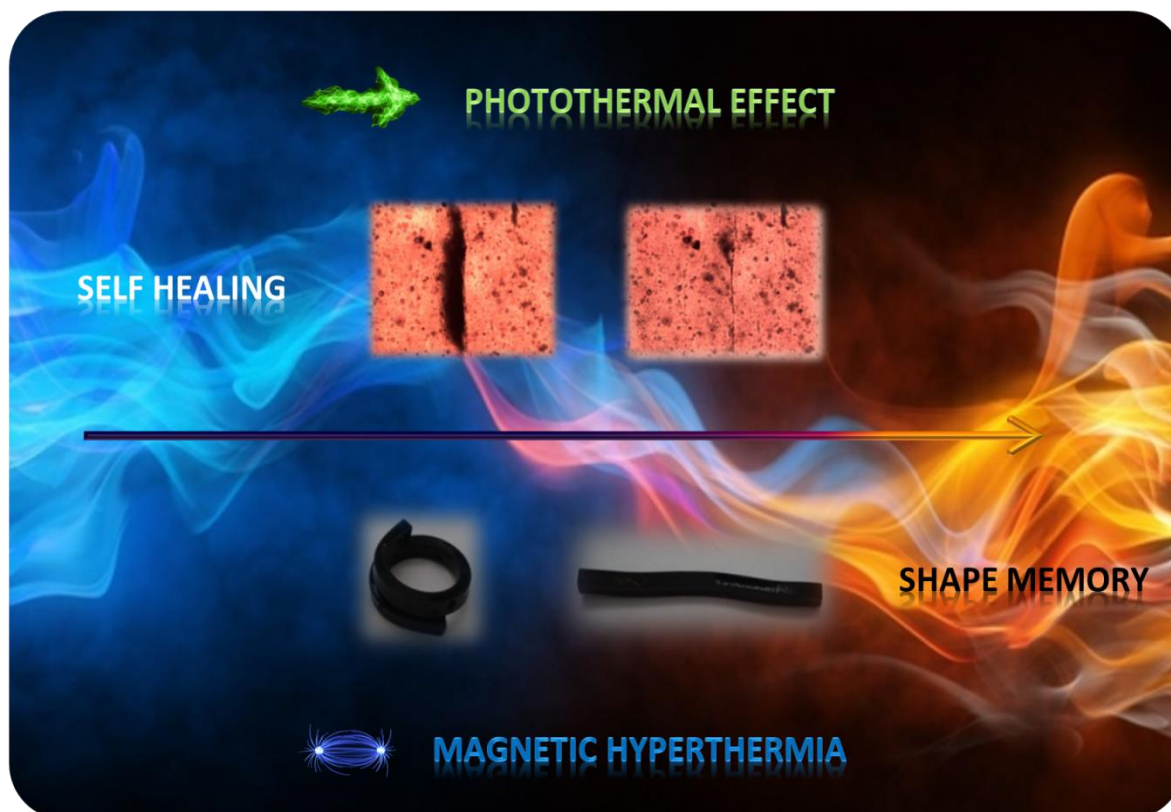
REMOTE ACTUATION OF EPOXY NANOCOMPOSITES WITH FUNCTIONAL PROPERTIES

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Resumen Gráfico - Graphical abstract



Resumen

Las redes epoxi son una familia de compuestos con uso extensivo en aplicaciones tales como recubrimientos, adhesivos y materiales compuestos avanzados. Exhiben diferentes propiedades funcionales tales como la capacidad de modificar su forma en respuesta a estímulos externos (epoxi con memoria de forma o SME por sus siglas en inglés), o su capacidad para intercambiar segmentos en su estructura química cuando se calientan a temperaturas superiores a la temperatura crítica (vitrimeros epoxi o EV). Los vitrimeros constituyen uno de los descubrimientos más importantes en el campo de los polímeros de los últimos años. Se comportan de diferente manera según se varíe la temperatura por encima o debajo de la temperatura crítica. Por encima de la misma pueden fluir e intercambiar segmentos de cadenas elásticas sin modificar la densidad de entrecruzamiento. Esto es lo que precisamente les otorga propiedades de auto-curado, reciclado y soldado. Los SME y EV se activan en ciclos de

calentamiento/enfriamiento. La incorporación de nanopartículas capaces de convertir radiación IR o visible en calor (efecto fototérmico) hace posible la actuación remota de estos materiales inteligentes. Similarmente, la incorporación de nanopartículas magnéticas hace posible el mismo efecto por medio de la hipertermia magnética. La síntesis de materiales inteligentes a partir de nanocompuestos basados en matrices de epoxi requiere la funcionalización apropiada de las nanopartículas para producir una dispersión homogénea en la matriz de epoxi. En este artículo discutiremos los desarrollos más recientes en los nanocompuestos EV y SME que pueden ser activados.

Abstract

Epoxy networks are one of the most important families of thermosetting polymers with an extensive use as adhesives, coatings and matrices of advanced composites. In recent years, smart materials based on epoxy formulations were developed. They exhibit different functional properties such as the capacity of modifying their shape in response to an external stimulus (shape-memory epoxies, SME) or the capacity of interchanging segments of their chemical structures when heated above a critical temperature (epoxy vitrimers, EV). Vitrimers are one of the most important recent discoveries in the field of polymers. They behave as conventional thermosets below the critical temperature but they can flow at higher temperatures interchanging segments of elastic chains while keeping a constant crosslink density. This enables their self-healing, recycling and welding as well as the relaxation of strained chains. SME and EV are activated by adequate heating/cooling cycles. Incorporation of specific nanoparticles (NPs) capable of converting IR or visible light radiation into heat (photothermal effect) makes it possible the remote actuation of these smart materials. Similarly, incorporation of magnetic NPs can be used to produce the remote heating by exposure to an alternating magnetic field (magnetic hyperthermia). The photothermal effect provides also the possibility of local heating and, therefore, a local response (e.g., localized shape recovery or the self-healing of a localized area). Besides, the synthesis of smart epoxy nanocomposites requires the appropriate functionalization of NPs to produce their uniform dispersion in the epoxy matrix. In this article, we review recent selected papers dealing with the development of EV and SME nanocomposites that can be remotely activated.

Palabras Clave: *Vitrimeros epoxi, activación remota, epoxis con memoria de forma.*

Keywords: *epoxy vitrimers, remote activation, shape memory epoxies.*

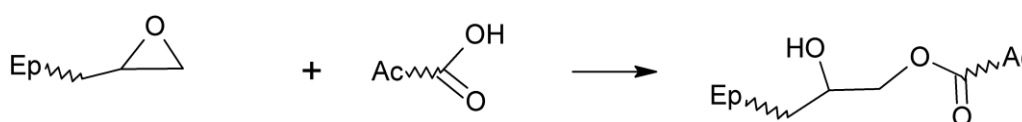
1. Introduction

Epoxies are one of the most important families of thermosetting polymers with conventional uses as adhesives, coatings and matrices of composites for advanced applications. In recent years, their applications have been expanded to the new field of stimuli-responsive materials. This is a consequence of the versatility of epoxy formulations for designing networks with a large variety of controlled physicochemical properties. In the present article we will place the focus on two of these new families of advanced materials: shape memory epoxies (SME),¹⁻³ and epoxy vitrimers (EV).⁴⁻⁷

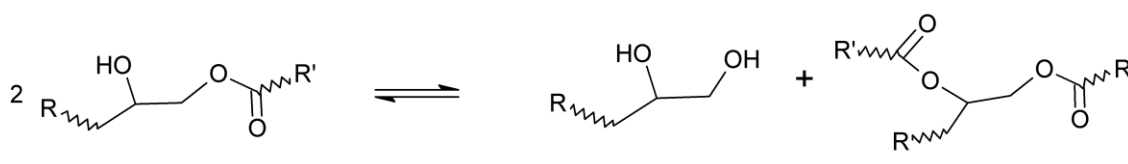
The shape memory is a characteristic feature of polymer networks. When they are heated above the glass transition they can be deformed to a temporary shape by employing an adequate tension. If they are cooled under tension to temperatures below the glass transition, the temporary shape is frozen with elastic energy stored in the strained chains. If tension is removed and the material is heated again above the glass transition, the elastic chains turn back to their equilibrium conformations and the material recovers its initial shape. If the change of shape is

prevented by a constraint, the material exerts a tension equivalent to the one used to produce the initial deformation. Materials that can change their shapes in a desired way or that can exert a force on an external constraint have found several practical applications. SME are one of the most important families of shape memory polymers due to their high versatility for tuning the location of the glass transition temperature, their excellent mechanical properties at temperatures below and above the glass transition and the high values of shape fixity and recovery. Formulations can include liquid crystalline monomers that introduce a new thermal transition enabling the generation of multiple-shape materials exhibiting two or more different temporary shapes frozen either by the glass transition or by an isotropic-liquid crystal transition. This gives new possibilities for practical applications.

The discovery of epoxy vitrimers (EV)⁴⁻⁶ has completely changed the usual description of thermosetting polymers as materials that cannot be reprocessed or welded like thermoplastic polymers. The most important family of epoxy vitrimers is based on the reaction of carboxylic acids with epoxy groups generating β -hydroxyester groups (Scheme 1). Under the action of specific catalysts and at temperatures above a specific temperature (usually called topology freezing transition temperature, T_v , arbitrarily defined by a timescale adapted for practical applications), these groups can undergo transesterification reactions as shown in Scheme 2. This allows the interchange of chain segments enabling the material to flow and keeping a high viscosity associated to its crosslinked structure. The rheological behavior of vitrimers is equivalent to the one of inorganic glass with the same capacity of being thermoformed (the name vitrimers given to these materials derives from this property). This new family of materials behaves as a typical thermosetting epoxy network at temperatures below T_v . However, above this temperature the material can be recycled, welded, self-healed or thermoformed. As strained chains can be relaxed to equilibrium configurations by transesterification reactions, the temporary shape of an SME can be converted to a permanent shape by a simple thermoforming process. This enables to produce complex shapes out of a mold. Besides transesterification reactions, several other chemistries were recently proposed to produce a similar behavior in different types of polymer networks. However, epoxy vitrimers keep their position at the frontier of practical applications.



Scheme 1. Reaction of a carboxylic acid with an epoxy group generating a β -hydroxyester group.



Scheme 2. Transesterification reactions of β -hydroxyester groups.

Remote triggering of the actuation of these smart epoxy networks requires the dispersion of adequate nanoparticles (NPs) that can respond to external fields generating heat. Herein we will discuss examples of the use of the photothermal effect or magnetic hyperthermia to produce the remote heating of nanocomposites based on SME or EV. The photothermal effect consists on the conversion of light into heat by electrically conductive nanostructures, such as metal NPs and nanowires (NWs), carbon nanotubes (CNTs) and graphene, when they are irradiated with light of a wavelength matching that of its surface plasmon resonance (SPR).^{8–11} At SPR the population of “hot electrons” that can couple with the phonons of the lattice significantly increases giving place to a fast increase of the lattice temperature.¹² The low thermal conductivity of the polymeric matrix surrounding the NPs prevents the generated heat to be quickly transferred to the environment, and therefore a significant temperature increase is produced. The whole process displays a very fast dynamics, related to the relatively small volume fraction of NPs in the material.^{9,12}

Magnetic hyperthermia is based on the generation of heat due to losses during magnetization reversal process of the magnetic NPs, under exposure to an alternating magnetic field.^{13,14} This mechanism has found applications in: electronics,¹⁵ energy,¹⁶ and biomedicine,^{17,18} and has been already approved for brain cancer therapies.^{17,19} Transformation of the magnetic energy provided by the external magnetic source working in the radio-frequencies range, RF ($f = 3$ KHz – 300 GHz), into heat by magnetic NPs can be produced by three potential mechanisms: Néel (inner fluctuation of the magnetic moment) and Brown (rotation of the whole particle) relaxation mechanisms for single-domain super-paramagnetic (SPM) NPs, or due to hysteresis losses (magnetic domain and domain wall motion processes) for multi-domain ferro-magnetic (FM) NPs respectively.²⁰ In systems formed by magnetic nanofillers dispersed in rigid substrates, rotation is forbidden and Neel relaxation is the only mechanism enabling heating of the material. In this review article we describe some selected articles from the recent literature dealing with the remote heating of EV and SME nanocomposites produced by the photothermal effect or by magnetic hyperthermia.

2. Remote Activation of EV and SME Nanocomposites by the Photothermal Effect

Remote activation of transesterification reactions in EV nanocomposites was first reported by Yang et al.^{21,22} They added 0.1-3.0 wt% multi-walled carbon nanotubes (MWCNTs) to a vitrimer synthesized from a commercial epoxy resin based on diglycidyl ether of bisphenol A (DGEBA) crosslinked with adipic acid and with 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as a transesterification catalyst.^{6,23} Though the reaction between a difunctional epoxy resin and a difunctional acid leads to linear chains, a crosslinked structure is obtained due to transesterification reactions.²⁴ These CNT-vitrimers could be efficiently welded by irradiating them with infrared light ($\lambda=808$ nm; 3.8 W/cm²) for times varying from 30 s to 3 min depending on the MWCNTs content. Vitrimers containing only 1% of MWCNTs reached a temperature of about 180 °C when infrared light was applied for 20 s with a power of 0.84 W/cm². Figure 1 shows experiments that illustrate the remote activation of properties by the photothermal effect. Figure 1a shows the welding of two ribbon-shaped specimens using infrared light. Lap-shear tests proved that 30 s of irradiation (0.84 W/cm²) provided a better bonding than 10 min of direct heating in an oven at 180°C. Figure 1b shows that bonding can be restricted to selected areas by simply using a mask. Figure 1 (c and d) shows the healing of damaged samples and the mechanical tests for as-synthesized, cut and healed samples, respectively. Good levels of healing were in all cases obtained by triggering the materials response by infrared light. However, the authors found, unexpectedly, that direct heating at 180 °C in an oven produced lower levels of healing, even after 1 h.

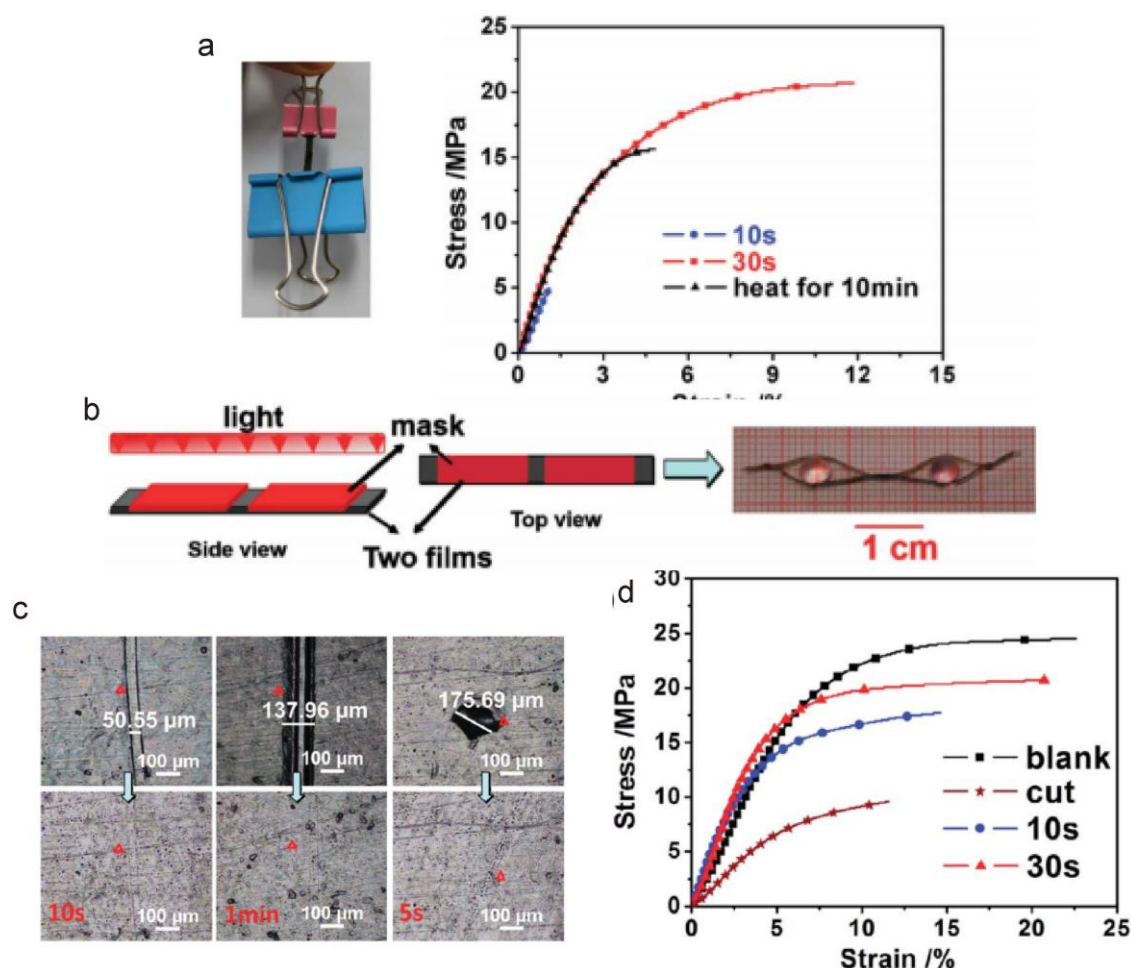


Figure 1. (a) Healed CNT-vitrimer specimen of 6 mg holding a weight of 14 g, and the corresponding lap shear tests. (b) Different figures that can be obtained using masks and irradiating with infrared light. (c) Healing of damaged samples of CNT-vitrimer composites with infrared light with an intensity of 15.2 W/cm^2 . From left to right: a razor blade cut ($50 \mu\text{m}$ width) healed for 10 s, a wider cut ($130 \mu\text{m}$) healed for 1 min and a needle pierce ($140 \mu\text{m}$ in diameter), healed for 5 s. (d) Stress-strain curves of virgin, cut and healed CNT-vitrimer. Repr. from Ref. [21] with permission from the Royal Society of Chemistry.

The incorporation of metallic NPs constitutes another route for the light-triggering of the self-healing of EV. We successfully employed polyvinylpyrrolidone (PVP)-capped gold NPs, (Au@PVP) NPs, with a mean diameter of 13.1 nm to activate transesterification reactions by visible light irradiation.²⁵ The polymeric network was obtained by crosslinking epoxidized soybean oil (ESO) with citric acid (CA), whose self-healing ability was previously demonstrated⁷. One remarkable advantage of Au NPs over carbon-based nanostructures is that even very low amounts of gold lead to significant temperature increases, and thus the material remains with a high degree of transparency in wide regions of the visible spectrum. ESO-CA-Au@PVP nanocomposites with 0.02 and 0.08 wt% Au displayed a SPR band centered at 538-545 nm. Upon illumination with a green laser ($\lambda=532 \text{ nm}$; 1.74 W/cm^2) the bulk temperature measured within the sample (at about 1 mm of the irradiated surface) increased quickly (3-4

minutes) from 22°C to more than 80°C for nanocomposites with 0.02wt% Au and to around 130°C for 0.08 wt% Au. Moreover, nanocomposites with 0.08 wt% Au underwent thermal degradation on the surface, indicating that temperature reached values above 200°C. Figure 2a and b shows, respectively, optical micrographs of a cracked sample before and after irradiation and the stress-strain curves for tensile tests of the neat matrix, and virgin and healed nanocomposites with 0.02 wt% Au. Due to the lack of a transesterification catalyst, reactions were relatively slow. An additional advantage of photothermal heating is that thanks to the confined thermal expansion of the irradiated area, the fracture surfaces become in close contact without the need of external pressure.^{25,26} This is probably the explanation for the poor healing observed by Yang et al. when their CNT-vitrimers were subjected to direct heating.²¹

Using a similar concept based on the use of Au NPs, Wang et al. introduced polydopamine-modified Au microspheres (averaging 1300 nm in diameter) in a vitrimer matrix based on DGEBA, sebacic acid and TBD²⁷. They used infrared light ($\lambda=808$ nm; 3.5 W/cm²) to trigger self-healing, and found that 120 s of infrared irradiation yielded a more effective healing than direct heating in an oven for 10 min at 180°C (Figure 2c and d).

In another study, we developed two different SME nanocomposites that could be remotely activated by green light irradiation.²⁸ AuNPs were incorporated in two different epoxy matrices as photothermal fillers. In the first strategy, PEO (poly(ethylene oxide)) was used as stabilizing ligand of NPs to minimize aggregation. This polymer was selected due to its high solubility in epoxy networks based on DGEBA. DGEBA was cured with a mixture of n-dodecylamine (DA) and m-xylylenediamine (MXDA) to give a shape memory thermoset with excellent recovery and fixation ratios.³ This formulation combined large strains with relatively large stresses, a desirable property for an SME. Activation temperature was 41 °C (the glass transition temperature T_g of the matrix), a value located near room temperature that is useful for practical applications. Incorporation of a very low amount of Au@PEO NPs (0.01, 0.05 and 0.1 wt%) did not produce any significant change in the thermal or mechanical properties of the polymer. The temperature increase of the nanocomposites under green light irradiation (DPSS laser at 532 nm), is shown in Figure 3. The three samples showed high temperature increases after 400 s irradiation (power density close to 2 W/cm²), reaching 140°C for the highest NPs loading (0.1 wt%). A bar of the sample containing 0.01 wt% Au@PEO NPs was bended above T_g and cooled to room temperature (temporary shape). As shown in Figure 4, recovery of the initial shape occurred after a few seconds irradiation with the green light laser.

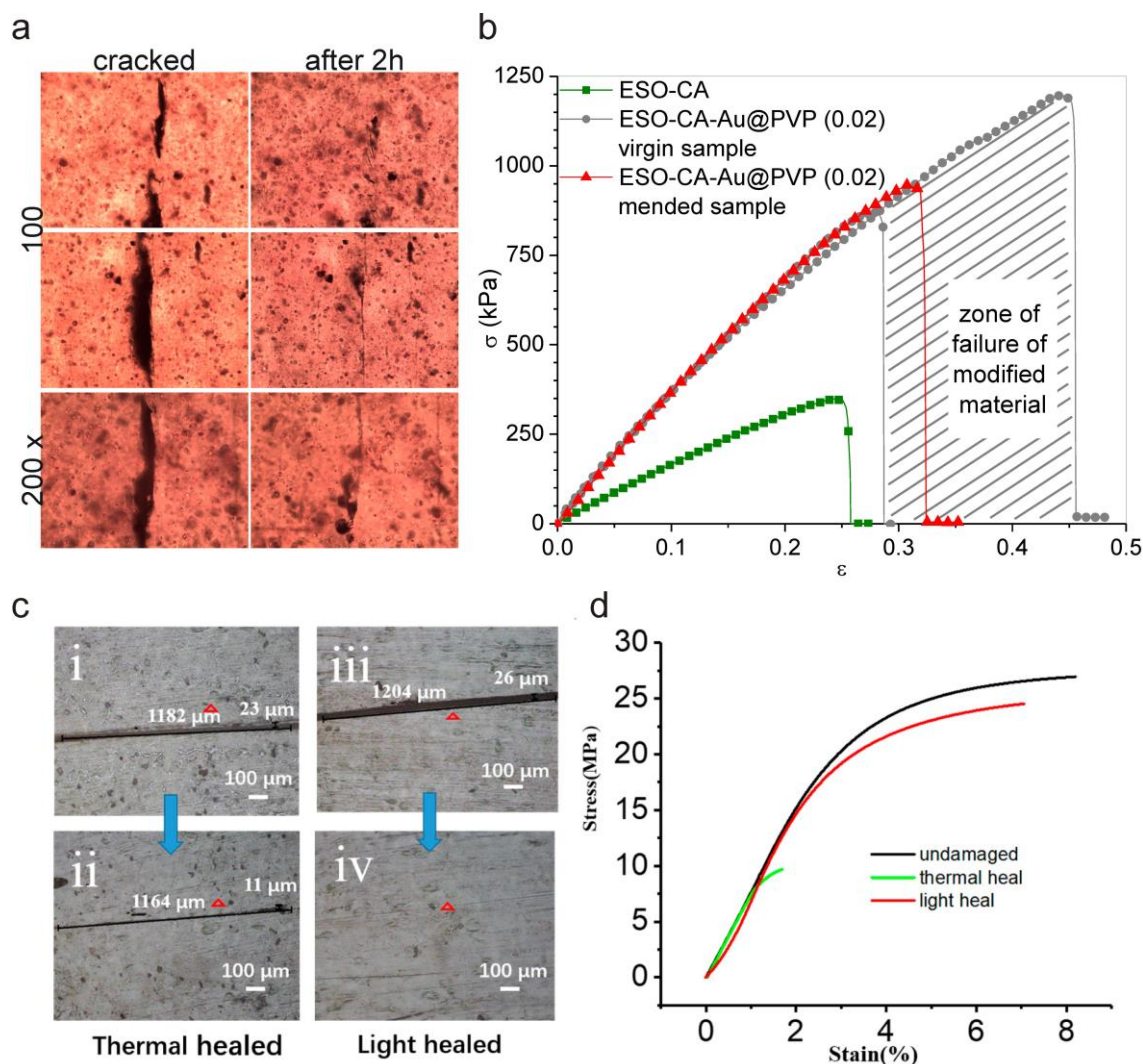


Figure 2. (a) Optical microscopy images of a healed crack after irradiation with a green laser with an intensity of 1.74 W/cm^2 . Scale bars lengths represent 0.2 mm . (b) Strain-stress curves of the neat polymer and the virgin and healed (after complete cut through) nanocomposite. (c) Comparison between direct (10 min, 180°C) and photothermal (infrared light, 120 s, 3.5 W/cm^2) heating for the vitrimer with gold microspheres. (d) Strain-stress curves of the virgin material and samples healed through direct heating and infrared radiation. (a) and (b) repr. with permission from Ref. [25] (©2016 IOP Publishing LTD.) and (c) and (d) repr. from Ref. [27] (©2018 Multidisciplinary Digital Publishing Institute)

The second strategy was to employ an amphiphilic epoxy matrix to generate a uniform dispersion of Au NPs coated with dodecyl chains (Au@DD NPs).²⁹ An epoxy matrix was obtained by homopolymerization of DGEBA with benzyldimethylamine (BDMA) in the presence of 5 wt% of a linear polymer (LAP) containing pendant dodecyl chains. This LAP was obtained by reaction of DGEBA with dodecylamine in stoichiometric ratio. During homopolymerization of DGEBA, the LAP was covalently bonded to the network by chain-transfer reactions, generating a transparent material with a T_g of 43°C .²⁹ Au@DD NPs (0.04 wt%) could be uniformly dispersed due to the compatibility between the alkyl chains of the

network and those stabilizing the Au NPs. The temperature increase was recorded with an embedded thermocouple (Figure 5). About 38 % of the maximum power and less than 20 s were needed to increase the temperature above T_g . A bar of the SME nanocomposite was bended in three different sections to demonstrate the localized shape recovery under exposure to green light (Figure 6). The first irradiation step was carried out for 15 s at the first bended section; the second step was performed for 19 s at the second bended section, and the last step for another 18 s at the third bended section. This enabled a complete recovery of the initial shape. This work demonstrated the possibility of local control on actuation with very low concentrations of Au NPs.

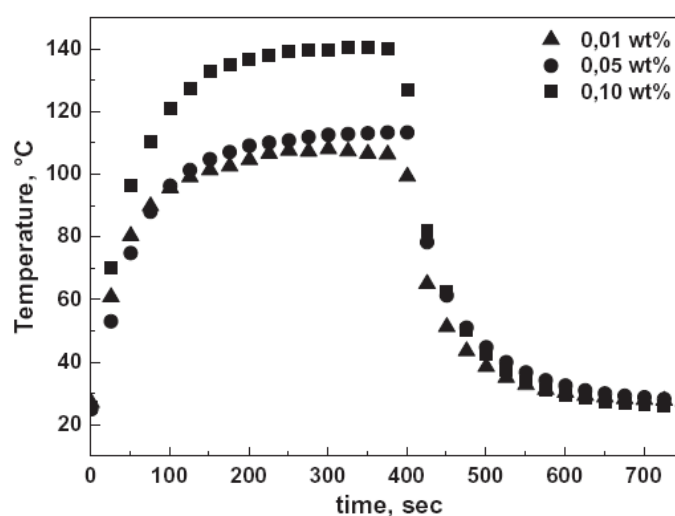


Figure 3. Temperature increase of SME containing different amounts of Au@PEO NPs. Temperature was recorded with a thermocouple inserted in the material before polymerization. Reprinted from ref [28]

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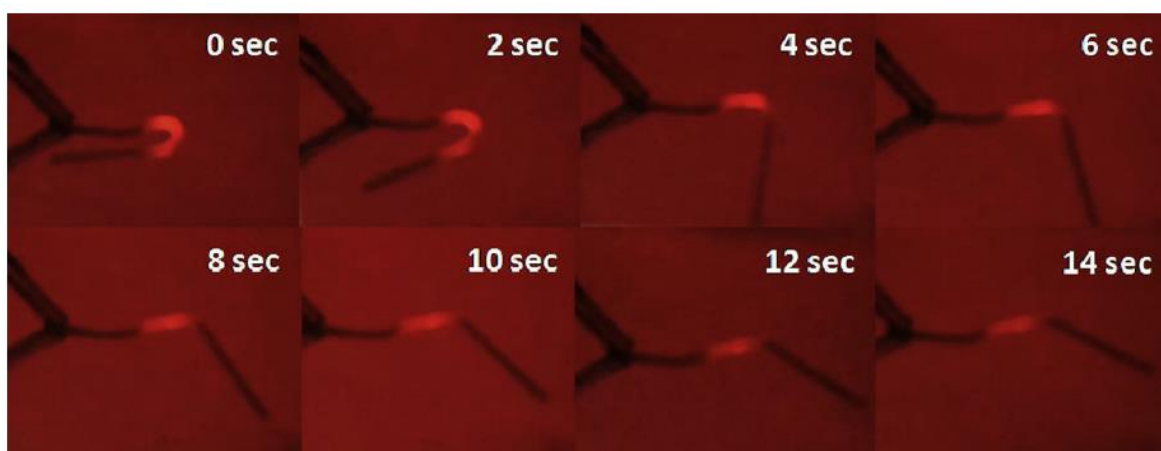


Figure 4. Shape recovery of an SME nanocomposite containing 0.01 wt% Au@PEO NPs, previously folded at 180° , when irradiated with green light at the bended section (photos were taken with a red filter). Reprinted from ref [28] ©2015 with permission from Elsevier.

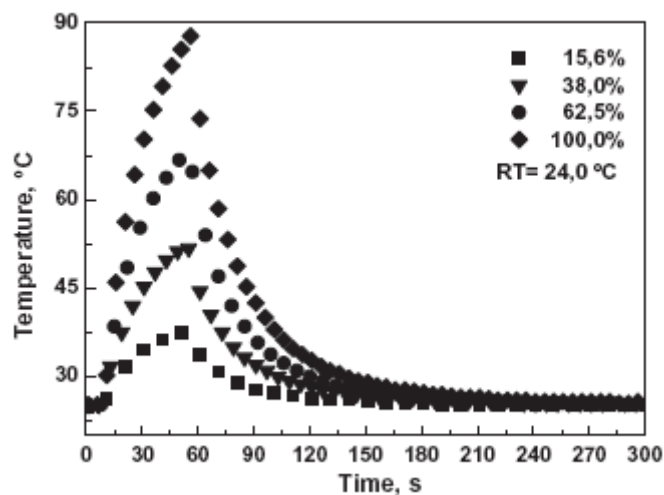


Figure 5. Temperature increase in the SME nanocomposite containing 0.04 wt% Au@DD NPs, recorded with an embedded thermocouple. The irradiation started at 10 s and was stopped at 52 s. Curves correspond to different irradiation powers (100% corresponds to about 700 mW). Reprinted from ref [28]

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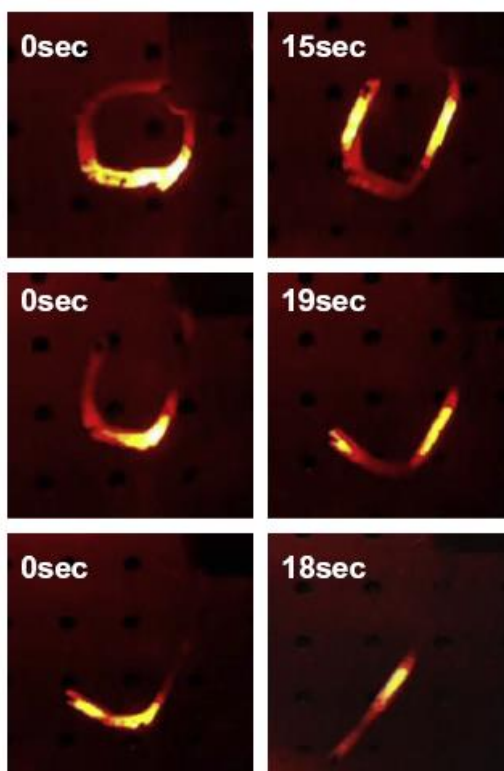


Figure 6. Shape recovery of a SME containing 0.04 wt% Au@DD by irradiation with green light at the previously bended section (photographs were taken with a red filter). Reprinted from ref [28] ©2015 with permission from Elsevier.

Pei et al. first realized that the remote actuation of shape memory of epoxy vitrimers enables access to complicated architectures that would hardly be possible to obtain by other means.³⁰

They used three different diepoxide precursors, sebacic acid and TBD as catalyst of the transesterification reactions, for obtaining the three EV with different T_g values, comprised between 30 °C and 50 °C. Two of the EV were liquid crystalline networks with isotropic-liquid crystal transition temperatures (T_i) of 65 and 100°C. They were used to weld parts of different networks, giving place to shape memory structures with different shape recovery temperatures, where the original permanent shape could be recovered in steps of increasing temperature (Figure 7a).

The incorporation of CNTs offered the possibility of locally heating the samples by infrared light irradiation ($\lambda=808$ nm; 0.28 W/cm²), obtaining a remote shape recovery of one of the segments of the strip while the others were sequentially activated by direct heating (Figure 7b).

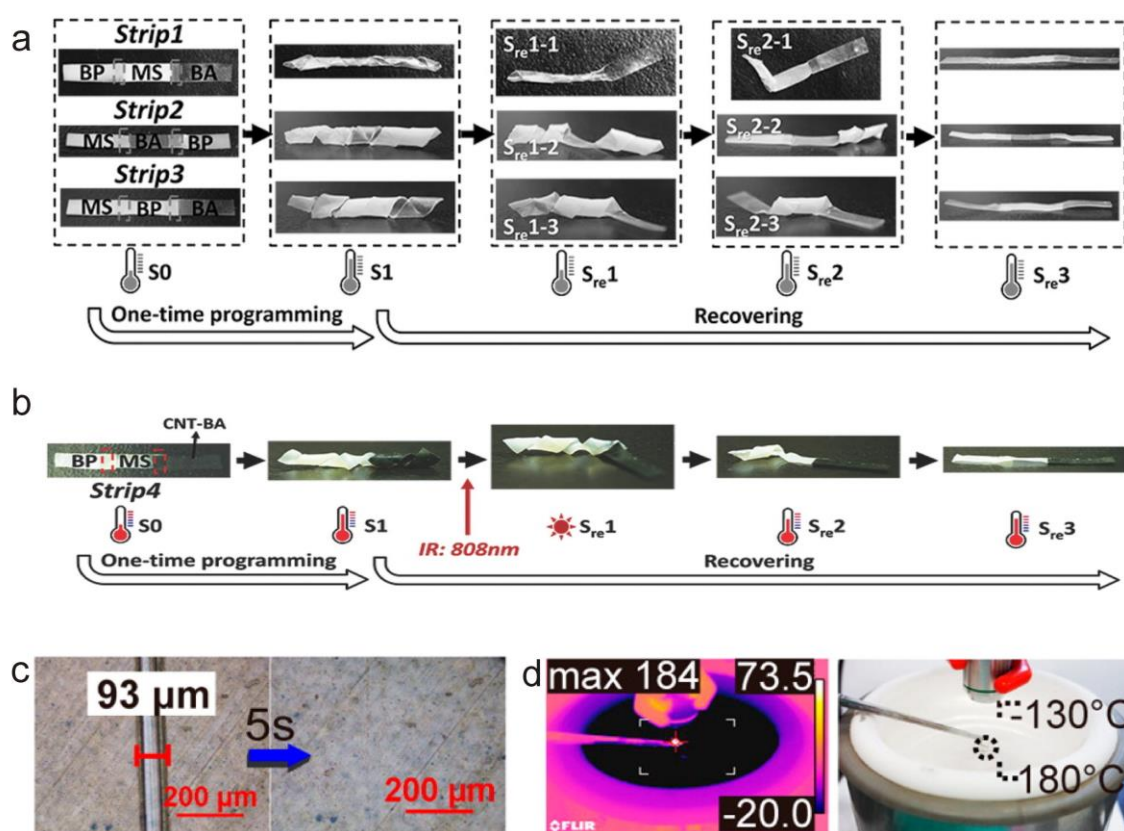


Figure 7. (a) Demonstration of the multi-shape memory behavior of strips formed by three vitrimers with different shape recovery temperatures activated sequentially by a temperature increase; (b) Demonstration of multi-SM behavior of a strip with CNTs in one of its three segments that is first activated through infrared radiation; (c) Healing of a cut (93 μm width) in the EV nanocomposite by infrared light irradiation; (d) IR and optical images of the liquid crystalline vitrimer nanocomposite irradiated in a nitrogen vapor atmosphere at -130°C . (a) and (b): Reproduced from Ref. [30]. Copyright 2016 ©-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) and (d): Reprinted with permission from Ref. [31]. ©2016 American Chemical Society.

The same research group synthesized an EV nanocomposite with an isotropic-liquid crystal transition temperature, adding MWCNTs to a matrix based on diglycidyl ether of 4, 4'-dihydroxybiphenol (DGE-DHBP) crosslinked with sebacic acid and employing TBD as transesterification catalyst.³¹ Figure 7c shows the light induced ($\lambda = 808$ nm) self-healing of a 93 μm crack, and Figure 7d depicts the high temperatures (enough to activate the shape recovery) reached through the photothermal effect, even when the surroundings are in a nitrogen vapor atmosphere at -130°C .

Yang et al. described the utilization of graphene for the remote heating of an EV nanocomposite based on DGEBA-sebacic acid and TBD as transesterification catalyst.³² The photothermal effect produced by graphene enabled shape recovery by infrared light irradiation ($\lambda = 808$ nm; 0.1 W/cm^2)³². They clearly showed how shape memory could be combined with the stress relaxation produced by transesterification reactions to produce a box that could be deployed and closed by an adequate thermal cycle (Figure 8). The first sequence shows a simple shape recovery sequence. The bar was deformed at 70°C , cooled to freeze the temporary shape and heated again to 70°C to recover the permanent shape. The second sequence shows the reconfiguration of the permanent shape by a thermoforming step at 200°C . At this temperature, transesterification reactions are active and relax the initially strained elastic chains to their equilibrium values, fixing the new permanent shape. Then temperature was decreased to 70°C , a new temporary shape was created that was frozen by cooling to room temperature. By a new heating at 70°C , the permanent shape produced at 200°C was recovered. The third sequence shows the generation of a new permanent shape at 200°C , the generation of a temporary shape at 70°C (similar to the permanent shape generated in the previous sequence), its fixation by cooling to room temperature and the recovery produced by a new heating at 70°C . The final sequence shows the possibility of generating a box using the properties of the EV. The box may be first formed by welding four faces to a central face. By folding these faces at 70°C , an open box is generated. Heating at 200°C for 30 min eliminates residual tensions and the box becomes the permanent shape. The box may be opened again by reducing temperature to 70°C and cooling to room temperature to freeze the temporary shape.

Heating to 70°C produces the folding of faces to obtain again the box (permanent shape). As the nanocomposite contains MWCNTs, the heating steps to 70°C may be performed by the photothermal effect employing IR radiation.

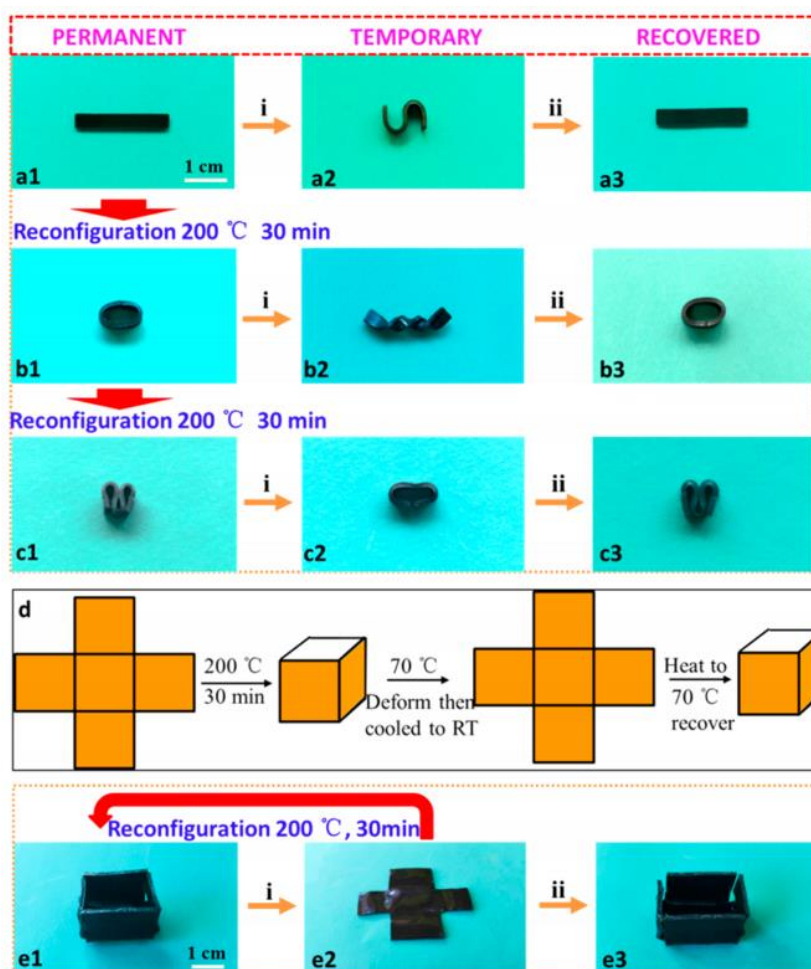


Figure 8. Permanent and temporary shapes of an EV nanocomposite containing MWCNTs (explanation of different shapes is given in the text). Reprinted with permission from Ref. [32]. ©2016 American Chemical Society..

Another strategy to obtain a multi-stimuli responsive EV was described by Chen et al.³³ Instead of nano- or microstructures, they used an amino-capped aniline trimer (ACAT) and/or the absorption of a Cu^{+2} salt to produce the photothermal effect using IR radiation ($\lambda=808$ nm). The neat EV was synthesized using DGEBA, suberic acid and TBD as transesterification catalyst. Formulations modified with ACAT not only allowed using infrared light to generate heat, but also provided the material with other functional properties such as electrochromism, metal ions sorption ability and pH and voltage responsiveness. Moreover, it was found that ACAT could also exert a catalytic effect, speeding up the transesterification reactions thanks to the presence of amino groups. Temperature increases from room temperature to more than 200°C were measured in the EV with an ACAT content of 10 mol %, for an irradiation power density of 0.9 W/cm². The shape memory behavior of different EV is shown in Figure 9. As expected, the unmodified EV was not responsive to IR radiation (sequence I). After absorption of Cu^{+2} , the EV exhibited shape recovery for an irradiation power of 0.19 W/cm² (sequence II). The EV modified with

ACAT showed shape recovery using a lower light intensity (0.09 W/cm^2 , sequence III). The EV modified with ACAT and with absorbed Cu^{+2} exhibited shape recovery at a still lower light intensity (0.06 W/cm^2 , sequence IV).

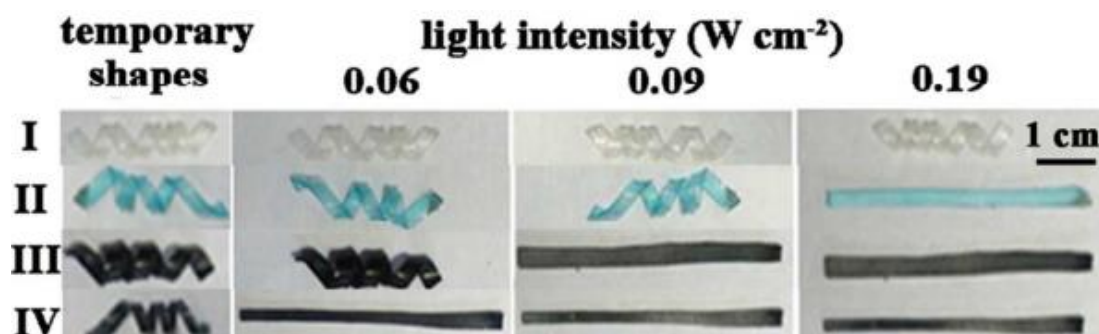


Figure 9. Shape recovery at different light intensities of the neat EV (I), EV after absorbing Cu^{+2} (II), ACAT-modified EV (III), and ACAT-modified EV after absorbing Cu^{+2} (IV). Reproduced from Ref. [33]

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3.Remote Activation of SME Nanocomposites Using Magnetic Hyperthermia

Instead of employing light, the remote heating may be produced by introducing magnetic NPs in the formulation and using an alternating magnetic field (magnetic hyperthermia). Vialle et al. investigated the remote activation of SME nanocomposite foams.³⁴ A commercial epoxy formulation was modified with the addition of different magnetic fillers: a) Magsilica (silica with embedded iron oxide) with a particle size between 5-30 nm and b) magnetite NPs with an average size of 250 nm.

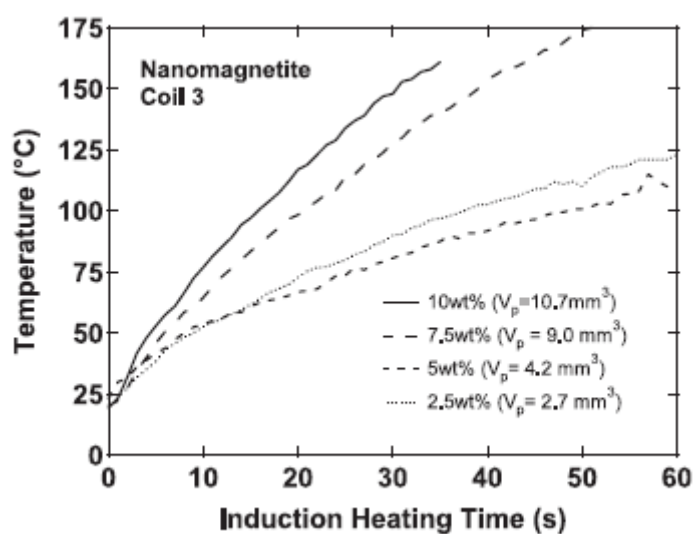


Figure 10. Heating response of a SME foam containing different concentrations of magnetite NPs, exposed to a RF magnetic field. Reproduced from Ref. [35]. Copyright 2009 IOP PUBLISHING, LTD.

The heating response of various formulations was monitored using different magnetic coils and configurations. Nanocomposites obtained with magnetite NPs performed significantly better than those obtained with silica embedded-iron oxide NPs. Figure 10 shows the heating response of SME nanocomposites with different contents of magnetite filler (from 2.5 to 10 wt %) in a 330 kHz magnetic field. The heating rate increased with the filler content enabling fast recovery rates (less than 20 s) for SME foams containing 10 wt % magnetite NPs.

He et al.³⁵ described the synthesis of a bar of a SME with three segments of different compositions (Figure 11). The segment at the left was modified with 0.4 wt% CNT ($T_g = 59\text{ }^\circ\text{C}$), the central segment was made by the unmodified SME ($T_g = 60.7\text{ }^\circ\text{C}$) and the segment at the right contained 5 wt% magnetite NPs ($T_g = 44.7\text{ }^\circ\text{C}$). As magnetite NPs induce heat at a frequency of 296 kHz and CNTs at 13.56 MHz, both segments could be independently activated. Figure 11 shows the shape recovery of the multicomposite. When a deformed sample (temporary shape 1) was exposed to a 13.56 MHz RF field, only the region containing CNTs was heated, allowing a complete recovery of that segment (temporary shape 2). Subsequent exposure to 296 kHz RF field led to a selective heating and recovery of the magnetite/epoxy segment (temporary shape 3). Finally, by heating in an oven (temporary shape 3), the neat epoxy segment was recovered leading to the permanent shape. The multiple shape memory behavior could be selectively activated varying the frequency of the alternating magnetic field.

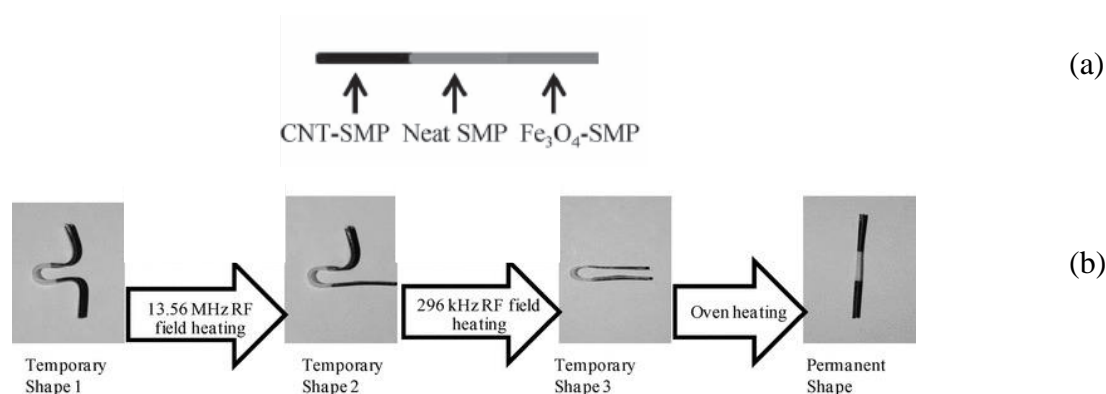


Figure 11. Selective shape recovery of a bar containing three segments of different composition, exposed to an alternating magnetic field of variable frequencies. Reproduced from Ref. [36]. Copyright © 2011 WILEY-VCH

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Achieving uniform dispersions of magnetic NPs in SME is not a trivial task. A common synthesis of magnetite NPs uses oleic acid (OA) as a stabilizing ligand. The resulting $\text{Fe}_3\text{O}_4\text{@OA}$ NPs are hydrophobic and difficult to disperse in polar epoxy formulations. By pre-reacting DGEBA with 20 wt% OA, the magnetite NPs could be uniformly dispersed in the epoxy matrix.³⁶ The unreacted epoxy functionalities were homopolymerized in the presence of BDMA

leading to a SME nanocomposite with $T_g = 51$ °C. A TEM image of the SME with 8 wt% of $\text{Fe}_3\text{O}_4@OA$ NPs shows the presence of a uniform dispersion of NPs (Figure 12).

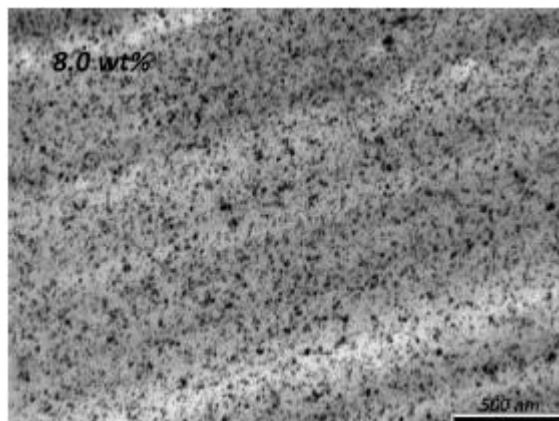


Figure 12. TEM image of an ultrathin cut of the SME nanocomposite containing 8 wt% $\text{Fe}_3\text{O}_4@OA$. Reprinted with permission from Ref.[36] ©2012 American Chemical Society.

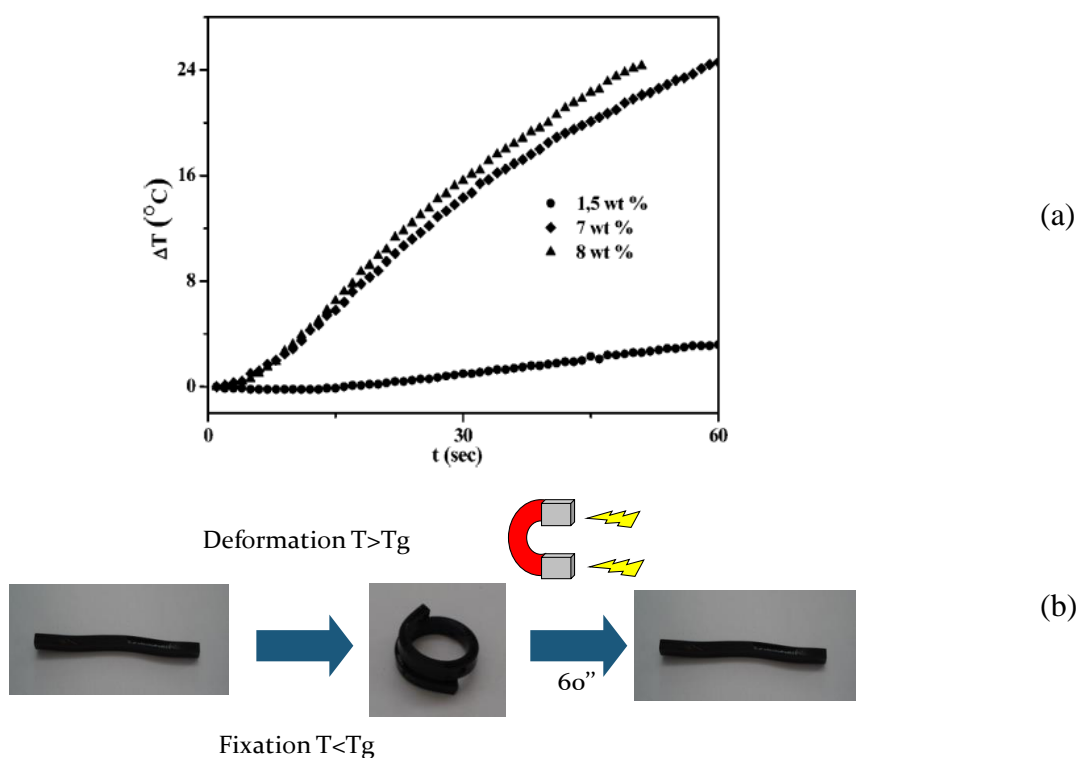


Figure 13. (a) Temperature increase for SME nanocomposites with different wt% magnetite NPs exposed to an alternating magnetic field. (b) Photographs showing the recovery process. Reprinted with permission from Ref.[36] ©2012 American Chemical Society

The magnetic heating of the SME nanocomposites was produced employing values of frequency and field strength in the range of biomedical applications (293 kHz and 30 mT). A maximum ΔT

~ 25 °C was recorded with a fiber optic sensor for nanocomposites with 7 and 8 wt% NPs after about 60 s, enough to produce the shape recovery (Figure 13).

Conclusions and Future Trends

Epoxy vitrimers (EV) containing NPs or compounds that generate heat when exposed to light or alternating magnetic fields of appropriate frequencies, can be remotely activated generating useful properties for practical applications. As described by the selected examples, these materials can be welded, recycled, self-healed and can relax stresses allowing thermoforming or the conversion of temporary shapes into permanent ones. Conventional SME can be also modified with a similar set of NPs enabling the remote activation of shape memory, necessary for some applications in medicine or in space. Key issues in the synthesis of these smart materials are related to the control of the dispersion level and the thermal response of the nano/microstructures embedded in the polymeric network. Variables as concentration, size, shape, and chemical nature of the stabilizing ligands influence the dispersion and response of the nanofillers employed to produce the remote actuation.

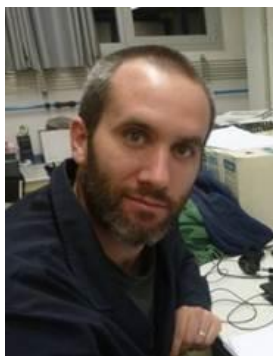
Publications and patents in this field have increased exponentially in recent years together with practical applications. Although the tremendous potential of these systems is clear, some points need further research work. Among them, precise mathematical models that can account for the heat transfer processes taking place in materials heated through magnetic hyperthermia or photothermal effect, are required. Thermal profiles in solid, stiff materials will depend on many variables related with both, the filler and the matrix, in a different way to that expected for colloidal dispersions or gels. A clear picture of this behavior will enable a more rational design of the required devices and a more delicate tuning of the activation rate without using high amounts of fillers and without affecting other important characteristics of the polymer, like transparency or mechanical properties. On the other hand, it will be necessary revising and adapting methods of incorporation of fillers in the polymeric matrix in order to control the dispersion level (models accounting for the influence of aggregation processes will be also necessary at this point) and avoid the use of organic solvents and high energy processing methods. Finally, possibilities of scaling-up, life-cycle analysis and costs associated with these technologies are important issues to consider for specific applications.

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