

A modifier that enables the easy dispersion of alkyl-coated nanoparticles in an epoxy network

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Abstract Nanoparticles (NPs) coated with alkyl chains cannot be dissolved in diglycidylether of bisphenol A (DGEBA), which is a typical monomer used in the synthesis of epoxy networks. We show that adding small amounts of the linear amphiphilic polymer obtained by reaction of DGEBA with dodecylamine, produced a stable dispersion of dodecanethiol-coated gold NPs in DGEBA. The anionic homopolymerization of this blend initiated by a tertiary amine led to a nanocomposite with a uniform dispersion of gold NPs. The selected crosslinking chemistry allowed covalent bonding of the modifier to the matrix, avoiding phase separation and enabling easy tuning of the thermal properties of the matrix.

Keywords Nanocomposites · Gold nanoparticles · Epoxy network · Compatibilization

Introduction

The ability to control the distribution of nanostructures in a polymer matrix is a powerful tool for the design of advanced functional materials with unique and sophisticated properties [1–3]. In particular, successful strategies to uniformly disperse metal nanoparticles (NPs) in polymer matrices are potentially interesting in the development of materials for

sensing, actuation, catalysis, optoelectronics, etc., with applications in areas such as energy, biomedicine, textiles, and building, among many others [4–7]. In this sense, one of the greatest challenges is to avoid the typical nonuniform particle aggregation process that takes place when polymers and NPs are mixed [1]. The excellent mechanical, dielectric, and chemical properties of epoxy resins make them ideal polymer hosts for the development of advanced nanocomposites [8, 9]. However, homogeneous dispersion of NPs in these matrices usually requires especial surface modification with polymers or stabilizers to avoid chemical incompatibility [10–12]. This proper functionalization of NPs surface usually requires the use of very specific synthetic routes or additional time-consuming steps consisting in the replacement of the original coating by a specially designed stabilizer affine with the polymer matrix [1]. However, large-scale production and application of nanocomposites is strongly based on the possibility to find cost-effective and straightforward procedures for NPs synthesis, functionalization, and compatibilization with the host. There are many well-established, scalable techniques conducting to the synthesis of high-quality metal and oxide NPs stabilized by alkyl chains. However, these techniques are based on the use of fatty acids, amines, or thiols and produce hydrophobically coated colloids that are incompatible with conventional epoxy monomers.

A different strategy to obtain uniform dispersions of NPs with hydrophobic coatings in epoxy matrices consists in the modification of the epoxy precursors to make them compatible with the hydrophobic coating. For example, alkyl chains may be incorporated to an epoxy network by reacting diglycidylether of bisphenol A (DGEBA) with a small amount of a fatty acid, in the presence of a tertiary amine, followed by the homopolymerization of the excess of epoxy groups to generate an amphiphilic network [13]. This strategy was used to produce a uniform dispersion of oleic acid-coated magnetic NPs in an epoxy matrix [14].

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In this work, a new strategy to produce a uniform dispersion of as-synthesized alkyl-coated nanoparticles in an epoxy network is proposed. The pre-reaction of the epoxy monomer with a fatty acid is replaced by the simple addition of a small amount of an adequate linear amphiphilic polymer. But in order to avoid phase separation of the linear polymer during polymerization [15], it is necessary to use a reactive polymer that can be covalently bonded to the epoxy network by multiple bonds (telechelic linear polymers such as commercial carboxyl-terminated acrylonitrile-butadiene rubbers (CTBNs) undergo a phase separation process in the course of the polymerization of epoxy precursors) [15]. The use of a reactive modifier avoids phase separation processes and maintains optical clarity of the nanocomposites [12]. The approach proposed in this study is based on the use of a linear amphiphilic polymer easily obtained by reaction of stoichiometric amounts of DGEBA and dodecylamine (DA), as a compatibilizer of a blend of alkyl-coated NPs and DGEBA. This polymer has a brush-like structure with a linear chain compatible with the epoxy monomer and equally spaced dodecyl branches, which confer compatibility with the NP coating. Secondary hydroxyl groups arising from the epoxy-amine reaction are present in the structural unit of the amphiphilic linear polymer. These groups may be used to produce multiple covalent bonds of the linear polymer in the resulting epoxy network, avoiding its phase separation from the blend and the resulting partitioning of NPs between both phases. Covalent bonding can be achieved by employing the anionic homopolymerization of epoxy groups initiated by tertiary amines. In this chemistry, OH groups participate in the reaction through chain transfer reactions of propagating alkoxide anions [16]. It is shown that the use of the amphiphilic linear polymer combined with the anionic homopolymerization of epoxies allows generating a uniform dispersion of alkyl-coated nanoparticles in the resulting epoxy network.

Experimental

Materials

The diepoxy monomer was based on diglycidyl ether of bisphenol A (DGEBA, DER 332, Aldrich), with a mass per mole of epoxy groups equal to 174.3 g/mol ($n=0.03$ in the chemical structure shown in Fig. 1). The initiator of the homopolymerization reaction was benzyldimethylamine (BDMA, $\geq 99\%$, Aldrich, boiling point 183 °C). DA, 98 wt%, Fluka, melting temperature in the range 27–29 °C), was used to synthesize the linear amphiphilic polymer.

Dodecanethiol, hydrogen tetrachloroaurate (III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $\geq 49\%$ as Au), tetraoctylammonium bromide, sodium borohydride were purchased from Aldrich and

used as received. Tetrahydrofuran (THF), acetone, and toluene, used as solvents, were P.A.-grade.

Synthesis of the linear amphiphilic polymer

Stoichiometric amounts of DGEBA and DA were mixed by vigorous stirring at approximately 100 °C. The polymerization was carried out in bulk at 100 °C for 3 h, leading to a linear polymer with $M_n=16,800$ g/mol and $M_w=42,000$ g/mol, based on polystyrene standards [17]. The polymer was a transparent material, soluble in different solvents like THF, chloroform, toluene, acetone, dimethylformamide, and dichloromethane [17]. Figure 1 shows the chemical structure of its repeating unit. In order to arrest structuration processes leading to physical gelation [17, 18], the linear polymer was stored at -5 °C, a temperature located below its glass transition temperature (comprised between 10 °C and 14 °C).

Synthesis of nanoparticles (NPs)

The 2 nm gold NPs coated with dodecyl chains were obtained by the Brust–Schiffirin method [19]. Briefly, 0.1 mmol of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was mixed with 244 mg of tetraoctylammonium bromide in 10 ml of toluene. The two-phase mixture was stirred until no coloration was observed in the aqueous phase. Then, 0.1 mmol of dodecanethiol (DDT) was added to the organic solution. An excess of a freshly prepared sodium borohydride aqueous solution was then added as reducing agent. The as synthesized DDT-coated gold NPs were separated from unattached DDT by precipitation with ethanol (in a volume ratio with respect to toluene solution of 7:1), followed by centrifugation (8,000 rpm). The wet product was dried at 40 °C and stored as a waxy solid at room temperature. A transmission electron microscopy (TEM) micrograph of as-synthesized NPs is shown in Fig. 2.

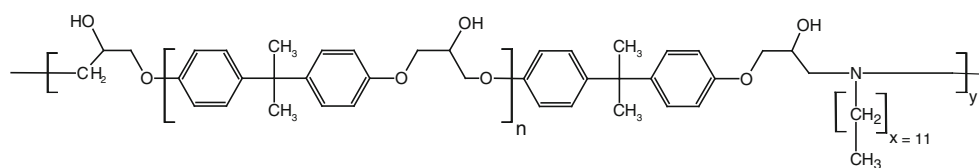
Synthesis of nanocomposites

Selected amounts of DGEBA, BDMA (0.06 mol/mol of epoxy groups), dodecanethiol-coated gold NPs, and the linear amphiphilic polymer were dissolved in the minimum amount of THF, at room temperature. The solution was heated to 100 °C, allowing removal of the solvent and cast into polypropylene moulds (commercial 1-ml vials) or between two glass covers coated with Teflon® using a 1-mm rubber cord as spacer. The cure was performed in an oven held at 100 °C for 4 h. Under these conditions, a complete conversion of epoxy groups takes place as determined by near-infrared spectroscopy [20].

Techniques

Cloud point curves for the DGEBA/linear polymer blend were determined by visual inspection during cooling in a

Fig. 1 Chemical structure of the repeating unit of the linear amphiphilic polymer



thermostatic bath. Different amounts of the amphiphilic linear polymer were dissolved in DGEBA using dichloromethane as common solvent at room temperature, and cloud point temperatures were recorded after solvent evaporation on a hot plate at 50 °C.

Fourier-transformed near-infrared spectroscopy was used to check the conversion degree of epoxy groups in final samples. A Nicolet 6700 FTIR device was used to identify the absorption band of epoxy groups centered at $4,530\text{ cm}^{-1}$ (assigned to the conjugated epoxy CH₂ deformation band with the aromatic CH fundamental stretch) [20].

TEM images were obtained using a Philips CM-12 microscope operated at an accelerating voltage of 100 kV. Ultrathin sections were cut with an ultramicrotome.

Gel fraction values, X_{gel}, were determined gravimetrically from samples cut in squared pieces of approximately $1 \times 1 \times 0.2\text{ cm}^3$ (initial weight = W₀). After 24 h immersion in THF at room temperature, the supernatant was removed and slices dried to constant weight (weight = W_d). The gel fraction was defined by the ratio W_d/W₀.

Results and discussion

Blends of DGEBA and the linear polymer

Modifiers of thermosetting networks can dissolve, phase separate, and/or covalently be attached to the network during the crosslinking reaction. Which situation is attained

depends on the presence of reactive groups in the structure of the modifier, the curing conditions, and the nature of the crosslinking reaction. For a selected modifier, curing temperature and composition can be selected to start with a homogeneous or phase-separated blend. This requires previous determination of the equilibrium phase diagram of the system.

Binary blends of the linear amphiphilic polymer and DGEBA showed an upper critical solution temperature behavior (Fig. 3). The threshold temperature of the cloud-point curve is close to 70 °C. Below 3.5 wt% of the modifier, samples were homogeneous at room temperature. It has to be noted that initial solubility does not preclude the existence of a phase separation process in the course of polymerization of the reactive solvent. The increase in the homopolymer molecular weight that takes place in the course of the reaction produces a decrease in the entropic contribution to the free energy of mixture that can induce a phase separation process [15]. However, in the present system, no evidence of phase separation during polymerization was observed. The reason is the participation of the linear amphiphilic polymer in the crosslinking reaction through chain transfer reactions of terminal alkoxide ions to the OH groups present in its constitutional repeating unit (Fig. 1) [12]. The covalent bonding of the modifier to the network precludes phase separation giving place to cured homogeneous materials. Incorporation of the modifier to the network was confirmed by determining THF gel fractions in systems modified with 0, 5, and 10 wt% of the linear

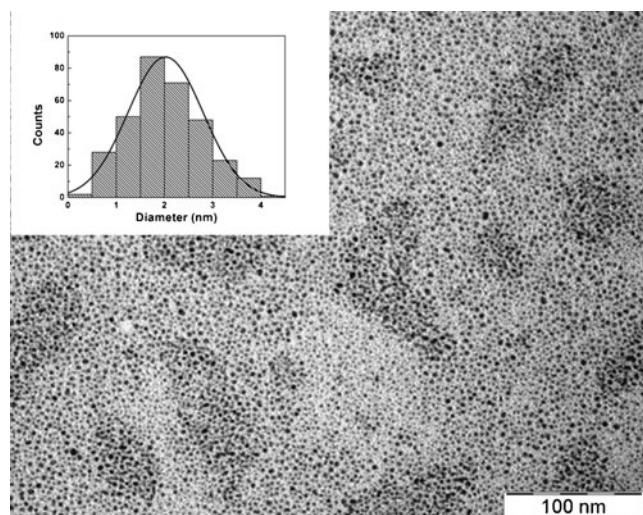


Fig. 2 TEM micrograph of dodecanethiol-coated gold NPs

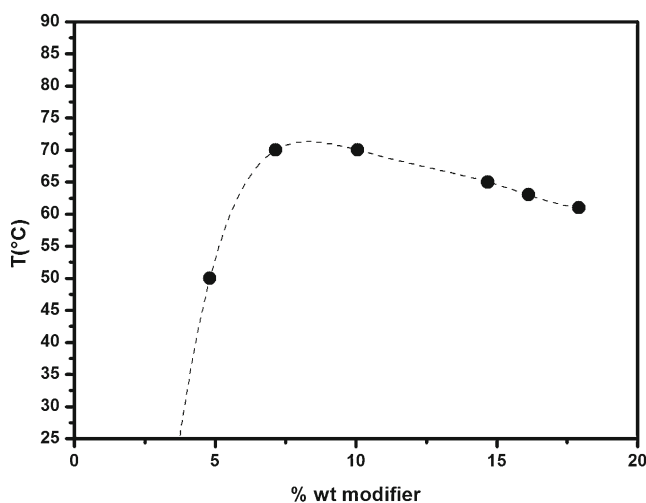


Fig. 3 Cloud-point curve of the DGEBA/linear polymer system

polymer. In all cases, X_{gel} , after prolonged immersion in THF, was higher than 0.995, indicating complete incorporation of the linear polymer to the final material.

A different possibility of introducing alkyl chains to the epoxy network would be to add an amount of dodecylamine to the initial formulation equal to the one added as part of the linear polymer. In this case, a fast end-capping of the amine by the DGEBA excess would take place, leading to DGEBA-DA-DGEBA species including a small amount of (DGEBA-DA-DGEBA) $_n$ oligomers. These reaction products will then take part in the homopolymerization reaction, leading to an almost uniform distribution of the alkyl chains in the resulting polymer network. But, due to the large excess of DGEBA, the alkyl chains will be present in a uniform small concentration in the polymer network. As a counterpart, the use of the large-mass linear polymer enables to generate hydrophobic domains with equally spaced alkyl chains. These hydrophobic domains are presumably more effective to interact with the ligands of the Au NPs, preventing their segregation from the polymer network.

Nanocomposites containing alkyl-coated Au NPs

Blends of DGEBA and alkyl-coated Au NPs (in contents as low as 0.1 wt%) were immiscible. NPs settled to the bottom of the vial, and the initial brownish color was changed to a bluish color as a consequence of aggregation (see the beaker on the left in Fig. 4a). This effect is typically associated to the shift and broadening of the NPs plasmon band that occurs by aggregation of NPs [21].

A very different behavior was observed when low amounts of the amphiphilic polymer were added to the initial formulations. In this case, the color of the sample was almost the same as the color observed for the colloidal dispersion of NPs (see the beaker on the right in Fig. 4a), indicating a successful transfer to the reactive system.

Blends including the tertiary amine and that polymerized at 100 °C led to uniform nanocomposites that retained their initial color and clarity (Fig. 4b). Special care was taken in

the selection of the curing temperature to avoid prolonged heating above 100 °C that could induce coalescence and increase in the size of the very small gold NPs [17, 22–26].

Successful dispersion of variable amounts of NPs was attained for both low and high contents of the modifier. Figure 5 shows TEM images of ultrathin cuts for nanocomposites containing 0.05, 0.5, and 1.0 wt% of NPs in formulations containing 2.0 and 10.0 wt% of the amphiphilic polymer. In all cases, nanocomposites showed individual NPs dispersed in the polymer matrix without any evidence of agglomeration. Reactive samples prepared with 2 wt% modifier were clear at room temperature, whereas those prepared with 10 wt% modifier were initially homogeneous only above the cloud point temperature 70 °C (see Fig. 3). However, evidences of phase separation during polymerization were not found for any of the analyzed compositions. This is due to the covalent incorporation of the modifier to the network by chain transfer reactions occurring during curing. As can clearly be observed in Fig. 5, addition of only 2 wt% of the amphiphilic polymer was efficient for compatibilization of up to 1 wt% of NPs.

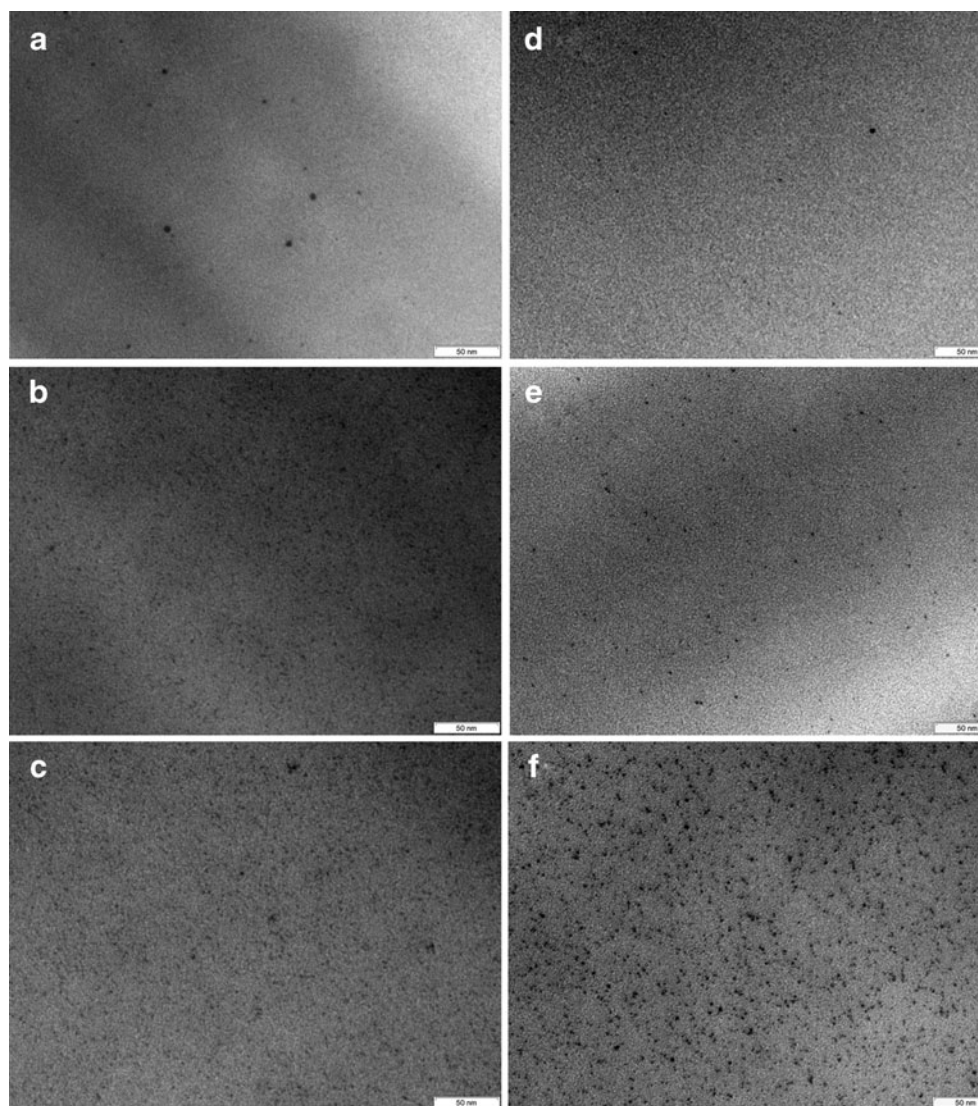
The effect of the addition of the amphiphilic polymer on the thermal properties of the network was analyzed by DSC. As observed in Fig. 6, T_g decreases markedly with the addition of the amphiphilic polymer, reaching values near 40 °C for 10 wt% of modifier. Covalent incorporation of long, flexible alkyl chains to the epoxy network is expected to diminish T_g values of the final materials. The decrease of crosslink density by chain transfer reactions can also account for the observed decrease of the glass transition temperature. On the contrary, T_g values were not profoundly influenced by the presence of low concentrations of alkyl-coated NPs (Fig. 6).

In summary, the use of the amphiphilic modifier enabled the dispersion of alkyl-coated NPs in an epoxy network and, at the same time, allowed tuning the thermal properties of the matrix, which could be of interest in the design of materials for technological applications. For example, magnetite NPs with



Fig. 4 **a** Blends of DGEBA and alkyl-coated Au NPs (0.1 wt%) without (*left*) and with (*right*) 3 wt% of amphiphilic polymer; **b** nanocomposites prepared with 3 wt% of the amphiphilic polymer and 0.1 wt% gold NPs: The test tube shows the aspect of a dispersion of gold NPs in THF

Fig. 5 TEM images corresponding to samples prepared with 2 wt% (*left*) and 10 wt% (*right*) of the amphiphilic polymer and **a, d** 0.05; **b, e** 0.5; **c, f** 1.0 wt% of NPs



hydrophobic coatings might be dissolved in DGEBA modified with a convenient amount of the amphiphilic

linear polymer, to generate shape memory epoxies with a controlled T_g and offering the possibility of remote activation.

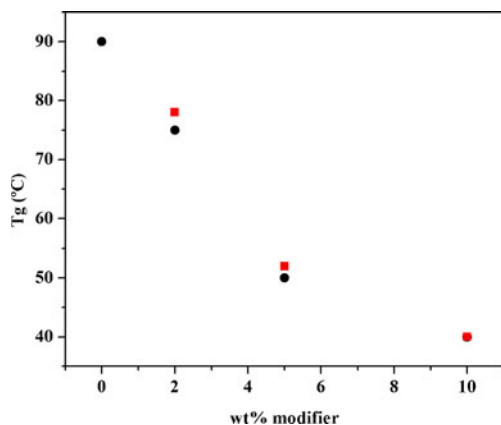


Fig. 6 T_g values for materials obtained with variable amounts of the amphiphilic polymer, without (*circles*) and with (*squares*) alkyl-coated NPs (0.05, 0.1, and 0.1 wt% of NPs for 2.0, 5.0, and 10.0 wt% of modifier, respectively)

Conclusions

A linear amphiphilic polymer synthesized by reaction of stoichiometric amounts of DGEBA and DA was used as a modifier of blends of alkyl-coated NPs and DGEBA. In the absence of modifier, alkyl-coated NPs and DGEBA were immiscible. By adding only 2 wt % of modifier, a homogeneous stable dispersion could be obtained. The addition of BDMA as initiator of the anionic homopolymerization of DGEBA produced a nanocomposite with NPs homogeneously dispersed in the epoxy matrix. The selected crosslinking chemistry produced the incorporation of the modifier to the epoxy network through chain transfer reactions to hydroxyl groups. This prevented its phase separation from the matrix and allowed tuning the thermal properties of the matrix, which

could be of interest for the design of materials with technological applications.

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