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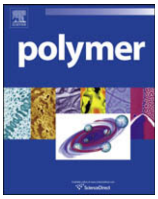

Polymer Communication

A visible light photochemical route to silver–epoxy nanocomposites by simultaneous polymerization–reduction approach

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ABSTRACT

The *in situ* synthesis of silver–epoxy nanocomposite by visible light photoinduced processes was described. The visible light photoinitiator, camphorquinone (CQ) (2,3-bornanedione), was used to generate electron-donating radicals upon photolysis. Subsequent oxidation of these radicals to the corresponding cations in the presence of silver hexafluoroantimonate ($AgSbF_6$) leads to the simultaneous formation of silver nanoparticles and initiation of cationic polymerization of epoxy resin, 1,3-bis-(3,4-epoxycyclohexylethyl)tetramethyldisiloxane (EPOX) present in the formulation. The cured nanocomposites were characterized by FT-IR, DSC and TEM measurements.

1. Introduction

Nanocomposite materials containing noble metal nanoparticles dispersed into a polymer matrix may exhibit novel physical and chemical properties that are of high scientific and technological importance [1,2]. They have been proposed for optical [3], electrical [4] and medical [5] applications as well as for data storage [6]. In particular silver nanoparticles are very important for their excellent electrical conductivity [7], anti-microbial effect [8] and optical properties [9]. Typical examples of polymer silver nanocomposites [10] include, but are not limited, polyvinyl alcohol [11,12] and polyimide [13,14] based systems. In such applications, the homogeneous dispersion of these thermodynamically unstable nanoparticles is a key challenge due to their easy agglomeration arising from their high surface free energy. A possible approach of this problem is the *in situ* generation of the silver nanoparticles during polymerization through a reduction process of a precursor silver salt. However, both polymer and silver nanoparticle simultaneous formation in the same reaction media has rarely been employed [15,16]. Previously, simultaneous synthesis of silver nanoparticles and polymer constituting the nanocomposite film was achieved by thermal means [17,18]. In these cases, while the some portion of the radicals generated from the well-known initiator 2,2′-azobisisobutyronitrile (AIBN) initiated polymerization of vinyl monomers present in the system, the remaining portion underwent electron transfer reaction with the silver salt to form silver nanoparticles. Photochemical simultaneous reduction/polymerization route was also used for the preparation of polymer silver nanocomposites. Polyacrylonitrile (PAN) silver nanocomposites were *in situ* synthesized by ultraviolet irradiation of a mixture of silver nitrate and acrylonitrile monomers [19]. It was proposed that the reduction of the silver salt occurred through the photolysis of the complex formed between silver salt and acrylonitrile monomer. The selection of the polymeric matrix for the nanocomposite materials is important for the optimization of the systems. Usually, polymers act as both protecting, and dispersing and stabilizing media for the nanoparticles formed. Polymers containing polyether segments were found to be quite suitable for this purpose. Polymerization of epoxides by either cationic or anionic modes essentially yields polyethers. We previously reported an efficient synthetic methodology for *in situ* generation of silver nanoparticles during photoinduced cationic curing of bisepoxides [20]. In this case, photochemically generated electron donating radicals reduce the silver salt to form silver nanoparticles. As a consequence of such redox reaction, the radicals are concomitantly oxidized to the corresponding cations capable of initiating cationic ring-opening polymerization of the epoxides present in the system. Depending on the radical concentration rather stable silver nanoparticles were

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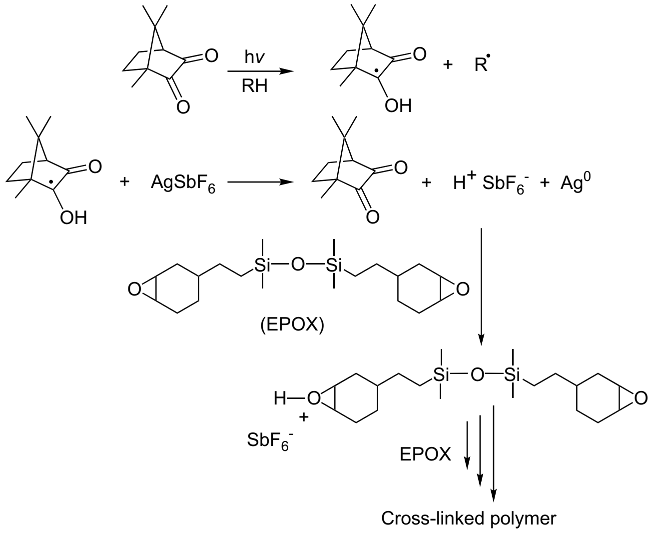

Scheme 1. Visible light-induced synthesis of silver–epoxy nanocomposites.

formed in the polymerizing medium. Many photolytically formed radicals can be oxidized [21–23] by suitable oxidants. Although widely used in free radical promoted cationic polymerization, benzoin and derivatives bear the risk of interfering with the absorption of silver salt itself or their complexes with the monomers. At least in principal, a variety of photoinitiator/photosensitizer systems may be used to produce silver nanoparticles and initiating cations upon absorption of near UV and visible light. However, many of these systems suffer from various disadvantages, including toxicity and limited solubility in a wide variety of monomers.

Camphorquinone (CQ), (2,3-bornanedione) as a 1,2-diketone seemed to overcome such limitations. CQ possesses good optical absorption properties in the visible region and exhibits excellent solubility and low toxicity [24]. Furthermore, CQ is widely used in conjunction with hydrogen donors as visible light free-radical photoinitiators in dental applications [25].

Following this line on photopolymerization, we report here the *in situ* synthesis of silver–epoxy nanocomposites by visible light-induced simultaneous electron transfer and polymerization processes. The overall photopolymerization process has been investigated and the cured films are characterized.

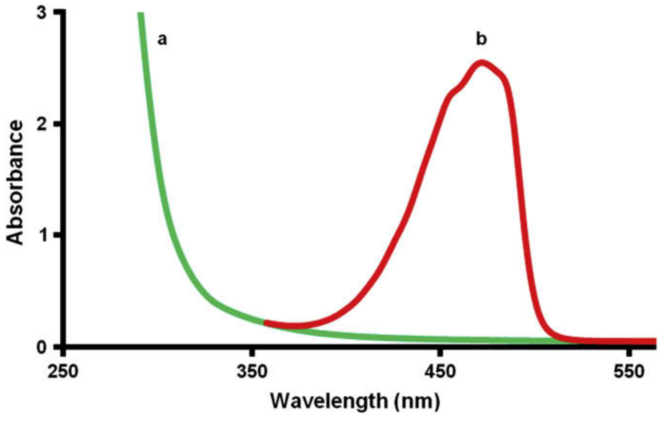

Fig. 1. UV–vis spectra of 1 wt% $AgSbF_6$ (curve a) and 1 wt% CQ (curve b) in 1,3-bis(3,4-epoxycyclohexylethyl)tetramethyldisiloxane resin.

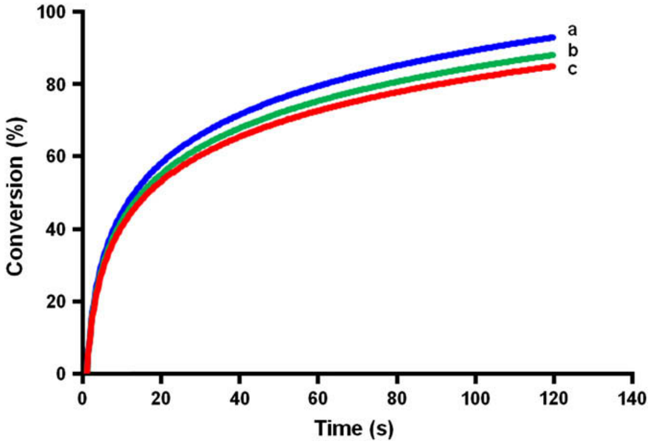

Fig. 2. Real-time FT-IR kinetic conversion curves for the visible light induced curing of 1,3-bis(3,4-epoxycyclohexylethyl)tetramethyldisiloxane resin containing different concentrations of $AgSbF_6$ and camphorquinone (2 wt%). 0.3 wt% $AgSbF_6$ (curve a), 0.5 wt% $AgSbF_6$ (curve b), 1 wt% $AgSbF_6$ (curve c).

2. Experimental

2.1. Materials

The epoxy based resin, 1,3-bis(3,4-epoxycyclohexylethyl)tetramethyldisiloxane (**EPOX**) was purchased from ABCR, Germany. Camphorquinone (**CQ**, maximum wavelength absorption at 478 nm) and silver hexafluoroantimonate ($AgSbF_6$) were purchased from Aldrich. All materials were used as received.

2.2. Sample preparation

The photocurable samples were prepared by dispersing the silver salt into the epoxy resin in the range between 0.5 and 1 wt%. Camphorquinone was added at a concentration of 2 wt%. The formulations were cured, under nitrogen, with a blue light (wavelength emission above 450 nm) using an Astralis 5 lamp, a flexible handy high-performance halogen lamp, with an intensity output of 530 mW/cm^2. The samples were irradiated for 2 min and cured transparent films of about 100 μm were obtained.

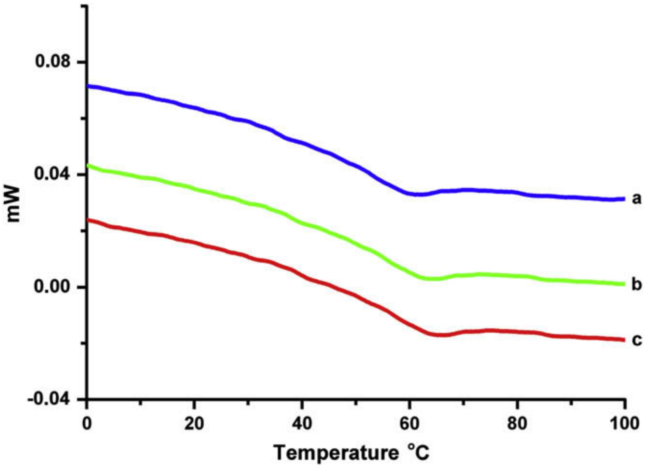

Fig. 3. DSC curves for the cured samples containing increasing silver salt concentration (0.3 wt% AgSbF6 (curve a), 0.5 wt% AgSbF6 (curve b), 1 wt% AgSbF6 (curve c)).

Table 1
Properties of UV cured films.[a]

Sample	Epoxy group conversion[b] (%)	Gel content[c] (%)	T_g[d] (°C)
EPOX + 0.3 wt% $AgSbF_6$	93	93	45
EPOX + 0.5 wt% $AgSbF_6$	88	95	52
EPOX + 1.0 wt% $AgSbF_6$	85	94	56

[a] Formulations containing 0.3–1.0 wt% $AgSbF_6$ and 2.0 wt% camphorquinone in the epoxy resin (EPOX) were irradiated at 450 nm for 2 min.
[b] Determined by FT-IR spectroscopy.
[c] Determined by gravimetrically.
[d] Determined by DSC measurements.

2.3. Analysis

The kinetics of the photopolymerization was determined by Real-Time FT-IR spectroscopy, employing a Thermo-Nicolet 5700. The formulations were coated onto a silicon wafer. The sample was exposed simultaneously to the visible light, which induces the polymerization, and to the IR beam, which analyze *in situ* the extent of the reaction. Epoxy group conversion was followed by monitoring the decrease in the absorbance, due to epoxy groups, in the region 760–780 cm^{-1}. The same blue light sources (Astralis 5 lamp) employed for samples curing was used during RT-FT-IR evaluation.

DSC measurements were performed under nitrogen flux, in the range between −10 °C and 80 °C, with a DSCQ 1000 of TA instruments equipped with a low temperature probe.

The gel content was determined on the cured films by measuring the weight loss after 24 h extraction with chloroform at room temperature, according to the standard test method ASTM D2765-84.

Samples were prepared for TEM observation by Argon ion polishing system GATAN PIPS, working at 3.5 keV at an angle of 7°. They were examined in a 300 keV transmission electron microscope (TEM) Philips CM30. TEM micrographs were processed with a slow scan CCD camera and analyzed with the Digital Micrograph program. The TEM observations were always performed using a very low electron flux in order to avoid any structural modification of the sample induced by the electron beam.

3. Results and discussion

The radical source CQ is active in the range of visible light and capable of generating radicals via Norrish type II reaction. A silicone epoxy resin was used as photocurable monomer. Usually additional hydrogen donor molecule should be included to the formulation, but it is possible to foresee that silicone epoxy resin could act both as monomer and hydrogen donor molecule. The two components of the initiating system (CQ and silver salt) are indispensable for the polymerization to occur; no polymer is formed in the absence of either compound under our reaction conditions. Visible irradiation of CQ will generate reactive radicals that in the presence of $AgSbF_6$ will be oxidized to initiating cations leading to silver salt reduction with rapid generation of metallic silver particles. Although at different rate, both CQ and monomer derived radicals may participate in the redox reaction. The overall process is represented in Scheme 1. It should be pointed out that, at the irradiation wavelength, silver salt is transparent and all the light is absorbed by CQ (Fig. 1).

In order to investigate the efficiency of the proposed mechanism the polymerization process was followed in real-time by FT-IR analysis. Epoxy group conversion as a function of irradiation time is reported in Fig. 2. While the slope of the curves gives an indication of the rate of polymerization, the plateau value gives the final conversion. From the curves reported in Fig. 1, it is evident that silver hexafluoroantimonate is quite efficient at converting photochemically generated free radicals into propagating carbocations which start cationic epoxy ring-opening polymerization with high reactivity. The epoxy group conversion is almost complete when 0.3 wt% of silver salt is present in the photocurable formulation. A slight decrease on the conversion is observed by increasing silver salt content. This effect could be due to two different reasons. First of all, the competing tail absorption of silver salt (as was shown by UV–vis spectra of silver salt in solution) could decrease the visible light availability and a lower amount of electron donor radicals, and in turn, initiating cations are formed with a consequent decrease on epoxy group conversion.

Furthermore, an increase of T_g value was observed by increasing the silver precursor content. The T_g increase could lead to an early vitrification with a delay of the reactive species diffusion; as a result the reaction can stop before all the epoxy reactive groups will be consumed.

Thermal behavior of the cured films was evaluated by DSC measurements. The DSC curves are reported in Fig. 3 and the T_g values are collected in Table 1. A clear increase of T_g values by increasing silver salt content in the photocurable formulations was noted. The reason for such increase may be due to the infiltration of the *in situ* generated silver nanoparticles in the voids of polymer

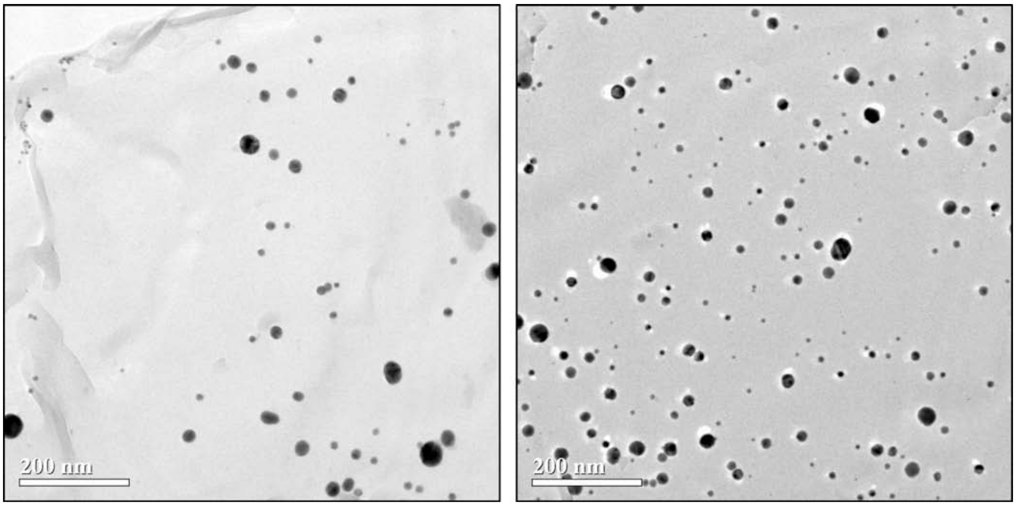

Fig. 4. Bright-field TEM micrograph the UV cured films obtained by irradiation of 1,3-bis(3,4-epoxycyclohexylethyl)tetramethyldisiloxane resin containing different concentrations of camphorquinone (2 wt%) and $AgSbF_6$ 0.5 wt% $AgSbF_6$ (left), 1 wt% $AgSbF_6$ (right).

network resulting in a decrease of the free volume. Additionally, a strong interaction between the silver nanoparticles and the polymeric chains is expected which impedes the mobility of the cross-linked epoxy network.

High gel content values (above 98%) are obtained in all cases (Table 1), indicating the formation of a highly cross-linked polymer network.

All the cured samples were transparent. This can be considered as visual evidence that the size of agglomerated silver particles, if any, was smaller than 400 nm. The nanometer range size of silver particles in the cured films was also verified by TEM analysis. In Fig. 4 the bright-field TEM micrographs for films cured in the presence of 0.5 and 1 wt% of silver salt are reported. It is evident that metallic particles are well dispersed with no significant macroscopic agglomerations. The observed features have a size distribution ranging between 20 and 40 nm. By increasing the silver salt content the size of the nanoparticles is not affected but a higher silver nanoparticle content is evident. These morphological results are in agreement with the T_g increase and the FT-IR measurements.

4. Conclusion

In situ synthesis of silver–epoxy nanocomposites was achieved by visible light polymerization through a simultaneous photoinduced electron transfer and cationic polymerization processes. CQ, which is active in the range of visible light, was used as radical source that, in the presence of $AgSbF_6$ leads to its reduction with rapid generation of both metallic silver and initiating cations. The overall process was investigated by means of RT-FT-IR analysis showing that silver salt is quite efficient at converting light-generated free radicals into propagating carbocations. An increase on T_g values was observed by increasing the silver precursor content in the photocurable formulations. This was ascribed to a decrease of free volume of the polymer network because of infiltration of the generated nanoparticles in the polymeric voids. The concept described here may also be used [26,27] for the preparation of network containing metal nanoparticles other than silver.

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