Polymer Bulletin 58, 271–279 (2007)
DOI 10.1007/s00289-006-0593-4

Polymer Bulletin

Fabrication of Ag-PVA hydrogel nanocomposite by γ-irradiation

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Received: 15 July 2005 / Revised version: 4 November 2005 / Accepted: 20 November 2005

Summary

The radiolytic formation of Ag nanoparticles in crosslinked PVA hydrogel was investigated. The reduction of Ag^+ ions was performed using strongly reducing species such as hydrated electrons, propan-2-ol and PVA radicals. Ag^+ ions were efficiently reduced in swollen PVA matrix by PVA radicals. Thermal and thermooxidative properties of radiolytically obtained nanocomposites were affected by the content of nanofiller as well as by different routes of preparation.

Introduction

The preparation of metal particles at nanoscale has received increasing attention due to unique properties of such particles which result from size effects. The radiolytic method is particularly suitable for generating metal particles in solution. The radiolytically generated species, solvated electrons and secondary radicals, exhibit strong reducing ability, so the metal ions are reduced at each encounter. Therefore, the atoms formed by reduction reactions are distributed homogeneously through the solution. Metal atoms then tend to coalesce into oligomers which progressively grow into larger clusters. In order to suppress growth of nanoparticles, the coalescence is restricted by adding a polymer as stabilizer [1]. It was found that solid or swollen polymers are able to stabilize small crystallites to spontaneous growth via aggregation [2]. Swollen gels contain liquid-filled cavities, which were anticipated to restrain fast growth and aggregation of metal crystallites [3]. As a result, new properties can arise from interactions between macromolecules and particles. Thus, investigation of formation pathways of small metal crystallites in polymers can yield the knowledge useful in advancing the synthesis of novel materials.

Although γ-irradiation has proven to be a powerful tool for synthesis and modification of materials [4], not many studies have been reported concerning the radiolysis formation of metal nanoparticles in hydrogel matrix. In the present work, the radiolytic formation of Ag nanoparticles in PVA hydrogel, previously obtained by γ-irradiation, was investigated. Radiation chemistry has proven to be a very effective

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Presented at 44th P.M.M. Microsymposium "Polymer Gels and Networks", Prague, 10–14 July 2005 method to construct three-dimensional polymer networks [5] offering advantages over conventional physical or chemical methods of network formation: mild reaction conditions, negligible formation of by-products, fast gelation and no need for catalysts. Physicochemical properties of the radiation-crosslinked polymer network and the swelling ability of radiation-crosslinked hydrogels can be tailored by changing the irradiation time. PVA as a matrix component is selected because it is an optically transparent material and its macromolecular backbone is able to donate electron and reduce metal ions [2]. On the other hand, size-dependent properties of silver are of technological significance.

The aim of the work is to compare the influence of different reducing species formed by γ-irradiation (hydrated electrons, propan-2-ol and PVA radicals) on the properties of Ag nanoparticles itself, and consequently, of Ag-PVA nanocomposites. Moreover, we intend to check the ability of this polymer in the hydrogel system to serve as an exclusive electron donor in the reduction of metal ions. In N_2O-saturated aqueous solutions, N_2O quantitatively converts the radiolytically obtained hydrated electrons into hydroxyl radicals which produce the polymeric PVA radicals [6].

Experimental

Materials

All the chemicals used were of analytical grade and they were used as received. Water from Millipore Milli-Q system was used. $AgNO_3$, propan-2-ol and PVA of molecular weight 72000 and degree of hydrolysis min. 99 %, were the products of Merck. Ar and N_2O gases were of high purity (99.5 %).

Instruments

Perkin-Elmer Lambda 5 spectrophotometer was used to record UV-Vis spectra. A dispersive spectrophotometer, IR Perkin-Elmer 983 G was used to record IR spectra of neat PVA and Ag-PVA nanocomposite.

Thermogravimetric measurements were carried out using a Perkin-Elmer TGS-2 instrument in nitrogen or oxygen atmosphere (flow rate 30 ml min^{-1}) from ambient temperature to 600 °C, at a heating rate of 10 °C min^{-1}. Nanocomposite samples were prepared by drying Ag-PVA hydrogel in vacuum oven at 40 °C for 24 h.

Synthesis of Ag-PVA nanocomposites

The polymer was completely dissolved in boiling water. In order to remove O_2, the PVA solutions were bubbled with Ar in sealed air-tight containers before being exposed to γ-rays.

The γ-irradiated PVA samples were aged at 50 °C for 24 h in oxygen-free atmosphere to complete any post-irradiation crosslinking. Gels were prepared by swelling the crosslinked polymer samples with solutions of $AgNO_3$ in water and in water with 0.2 mol dm^{-3} propan-2-ol for 24 h. Swelling of Ar-saturated and N_2O-saturated gels was carried out in tightly closed containers for 24 h at room temperature in the dark; longer swelling periods had no effect. Only gels free of voids were employed. γ-irradiation was performed in ^{60}Co radiation facility, at room temperature and a dose rate of 0.5 kGy h^{-1} up to the total radiation doses 25 kGy for crosslinking of 5 % PVA solution and 6.6 kGy, 13.0 kGy and 26.3 kGy for reduction of 3.9 x 10^{-3} mol dm^{-3}, 7.8 x 10^{-3} mol dm^{-3} and 1.6 x 10^{-2} mol dm^{-3} Ag^+ respectively, at a dose rate of 15 kGy h^{-1}.

Gel fraction and equilibrium degree of swelling

The weight fraction of gel, W_g in %, was calculated as:

$$W_g\,(\%) = W_g / W_0 \times 100$$

where W_g is the weight of dry gel after extraction and W_0 is the initial weight of the dry gel. The equilibrium degree of swelling (EDS) was calculated as:

$$\mathrm{EDS} = W_e / W_i$$

where W_e is the equilibrium mass of the swollen gel and W_i is the initial mass of the dried gel.

Results and Discussion

The primary products of water radiolysis are shown in Eq. (1)

$$H_2O \rightarrow e_{aq}^{-}\,(2.7),\ OH^{\bullet}\,(2.7)\ H^{\bullet}\,(0.6),\ H_2\,(0.45),\ H_2O_2\,(0.7) \qquad (\mathbf{1})$$

The numbers in parentheses represents the respective *G* values. The *G* value for a given irradiated system is the absolute chemical yield expressed as the number of individual chemical events occurring per 100 eV of absorbed energy [7]. Thus the *G* (e_{aq}^-), *G* ($OH^\bullet$), etc. are the number of solvated electrons, hydroxyl radicals, etc., formed per 100 eV of absorbed energy.

In the presence of alcohol, the $OH^\bullet$ and $H^\bullet$ radicals abstract hydrogen from the alcohol to produce an alcohol radical [6].

It is well known that the radiation crosslinking of PVA molecules is mainly induced by $OH^\bullet$ radicals in aqueous medium (with the *G* value of irradiation-induced intermolecular crosslinking 0.48 [8])

$$2\mathrm{PVA}\,(H) + 2OH^{\bullet} \rightarrow \mathrm{PVA—PVA}\ (\text{crosslinked polymer}) + 2H_2O \qquad (\mathbf{2})$$

Under the given experimental conditions the Ag^+ ions are reduced with strongly reducing hydrated electrons, propan-2-ol and the polymeric PVA radicals formed by H atom abstraction from PVA chains by hydroxyl radicals.

$$nAg^{+} + n\,e_{aq}^{-} / \mathrm{PVA}^{\bullet} \rightarrow (Ag)_n \qquad (\mathbf{3})$$

During γ-radiolysis of N_2O-saturated aqueous solution the hydrated electrons are quantitatively converted into hydroxyl radicals

$$N_2O + 2e_{aq}^{-} \rightarrow N_2 + 2OH^{\bullet} \qquad (\mathbf{4})$$

The formed hydroxyl radicals are consumed in reaction (2) to produce the polymeric PVA radicals.

5% PVA aqueous solution was pre-irradiated in order to form the gel. The obtained weight fraction of gel was 86 %, the equilibrium degree of swelling of hydrogel was 7. After irradiation of PVA hydrogel loaded with Ag^+ ions a yellow gel was obtained as a result of electron transfer. Reduction of Ag^+ in PVA hydrogel matrix induced formation of Ag nanoparticles with a typical surface plasmon absorption band at λ_{max} around 410 nm (see Figs. 1-3).

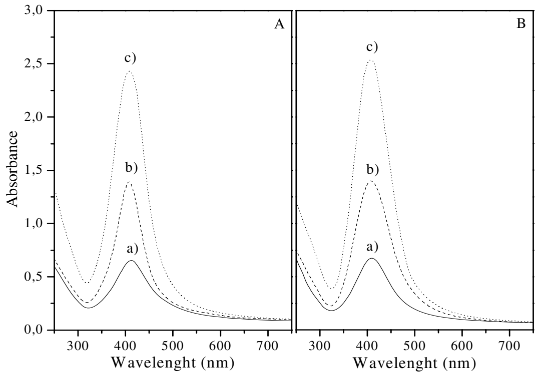

Figure 1. The UV-Vis absorption spectra of Ag nanoparticles formed in Ar-saturated PVA hydrogel with (A) or without (B) propan-2-ol; a) 3.9 x 10^{-3}, b) 7.8 x 10^{-3}, and c) 1.6 x 10^{-2} mol dm^{-3} Ag.

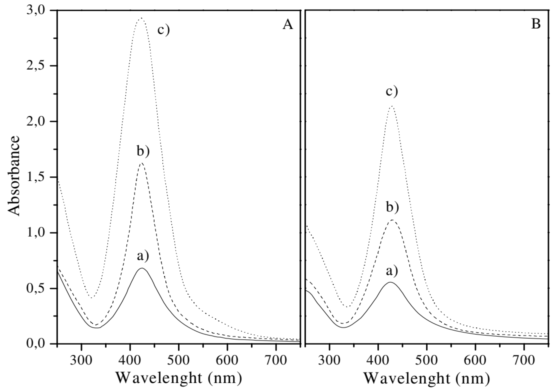

Figure 2. The UV-Vis absorption spectra of Ag nanoparticles in the dry PVA matrix. Concentration of Ag nanoparticles is the same as in Fig. 1.

Figure 1 depicts the concentration dependence of the surface plasmon absorption band of Ag nanoparticles obtained in the presence (Fig. 1A) or absence (Fig. 1B) of propan-2-ol. The reduction of Ag^+ ions occurred under the action of solvated electron as well as propan-2-ol and PVA radicals. In dry polymer matrix, as shown in Fig. 2, position of peak maxima (425 nm) is shifted towards longer wavelengths compared to that in hydrogel (see Fig. 1) due to change of the dielectric permitivity of the environment [9]. Figure 3 shows the evolution of the plasmon absorption bands for Ag nanoparticles obtained by three different radiation-chemical routes. To the best of our knowledge, the reduction of Ag^+ ions exclusively with PVA radicals formed radiolytically in the hydrogel matrix, has not been reported in literature.

These UV-Vis spectra indicate that besides hydrated electrons and propan-2-ol radicals, PVA radicals have sufficient reducing ability to produce Ag nanoparticles in swollen polymer gels.

According to the number of reports concerning the size-dependent position of surface plasmon absorption band, described by the Mie theory or effective medium theories, we estimate that the diameter of Ag particles is in the size range from 10 to 20 nm

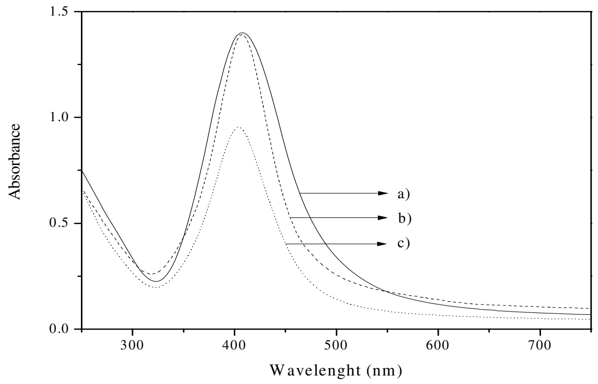

Figure 3. The UV-Vis absorption spectra of Ag nanoparticles formed in Ar-saturated PVA hydrogel containing 7.8 x 10 $^{-3}$ mol dm^{-3} $AgNO_3$ in the absence (a) and in the presence (b) of propan-2-ol; The UV-Vis absorption spectra of Ag nanoparticles formed in N_2O-saturated hydrogel (c).

[10-13]. The peak positions for sample a and b (see Fig. 3) are slightly shifted towards longer wavelengths compared to the sample c indicating that Ag particles prepared using only PVA radicals are slightly smaller.

For the synthesis of the particles, the most accepted mechanism suggests a two-step process, i.e., nucleation followed by successive growth of the particles [14]. In the first step a part of the metal ions in solution is reduced with a suitable reducing agent. The atoms thus produced act as nucleation centers and catalyze the reduction of remaining metal ions present in the bulk solution. In the case of the reduction Ag^+ by PVA radicals only, the action of the produced atoms as nucleation centers and their catalytic activity in the reduction of the remaining metal ions is probably constrained due to lower mobility of the reducing species.

In order to understand interactions between nanoparticles and the polymer matrix, thermal properties of the composite were investigated. The TG curves of thermal decomposition of nanocomposites and corresponding derivative TG curves are shown in Figs. 4-6. The TG traces in both nitrogen and oxygen show the weight loss occurring in several steps during thermal degradation, indicating the complexity of degradation process. In general, the chemical composition of a degrading polymer is the function of an enormous number of competing paths and sequences. The rate constants have their individual functional relationships with variables such as temperature. The rates of evaporation of species from the condensed phase are also temperature- and pressure-dependent.

The onset of degradation and temperature of maximal rate of degradation in nitrogen of crosslinked films as well as the crosslinked films filled with Ag nanoparticles are higher compared with the film obtained by evaporation of the solvent (Fig. 4). The introduction of nanofiller into the matrix has changed the degradation path of the polymer decreasing the temperature of maximal degradation from 364 °C to 325 °C. On the other hand, the rate of degradation is lower compared with the neat matrix.

The main decomposition product in the first step of thermal degradation of PVA are polyenes generated by the chain-stripping elimination of H_2O, as well as cis and trans allylic methyls that can be formed by random chain scission reactions that accompany elimination [15]. In the second degradation step the polyenes are converted into

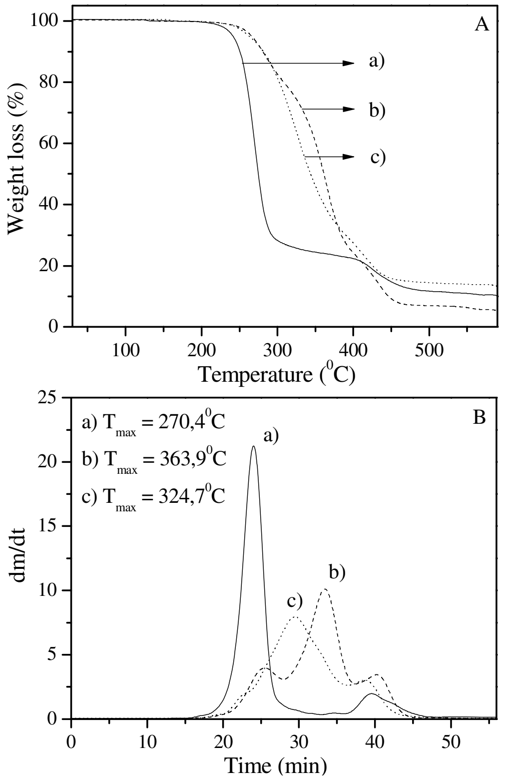

Figure 4. Thermogravimetric (A) and differential thermogravimetric (B) curves in nitrogen for a) PVA foil b) crosslinked PVA c) crosslinked PVA with 1.6 x 10^{-2} mol dm^{-3} Ag.

aliphatic groups. The Diels-Alder intramolecular cyclization and radical reactions are responsible for this conversion. In crosslinked polymer the gels result from the coupling of polymer radicals which were directly or indirectly produced by abstraction hydrogen atom(s) from the CH_2 and/or CH (OH) groups of PVA by the action of γ-rays [8]. Probably due to the network present in the polymer, the first degradation step splits into two stages, chain-stripping elimination (lower extent) is followed by scission of crosslinks and chain scission reactions. When Ag nanoparticles are present in crosslinked polymer, the interaction between nanoparticles and polymer can occur via lone electron pairs [10] inducing change in degradation mechanism of crosslinked PVA.

Figure 5 shows the thermal degradation in nitrogen of nanocomposites obtained by three different radiation chemical routes. It can be seen that degradation occurred at higher temperatures for nanocomposites obtained by reducing the Ag^+ ions with PVA radicals only, probably due to a slightly smaller size of nanoparticles and additional crosslinking of the polymer.

In Figure 6 it can be seen that the onset of thermooxidative degradation occurred at somewhat lower temperatures for higher contents of Ag nanofiller. But in general, thermooxidative degradation was almost complete and occurred at higher temperatures compared with the degradation in nitrogen atmosphere (see Fig. 5). Thermooxidative degradation is accompanied by adsorption of oxygen which caused an increase in temperatures of thermal degradation. On the other hand, the presence of nanoparticles in PVA matrix increased the rates of thermooxidative degradation.

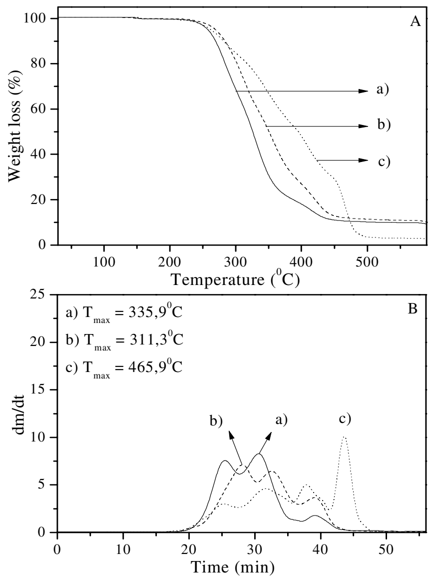

Figure 5. Thermogravimetric (A) and differential thermogravimetric (B) curves in nitrogen for Ag-PVA nanocomposites containing 7.8 x 10^{-3} mol dm^{-3} Ag prepared in Ar saturated crosslinked PVA without (a) or with (b) propan-2-ol, as well as N_2O-saturated crosslinked PVA (c).

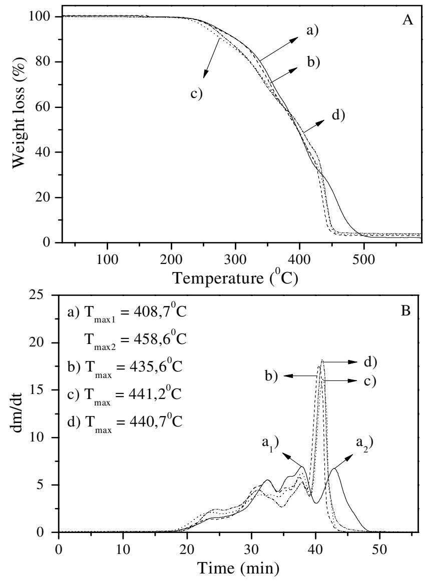

Figure 6. Thermogravimetric (A) and differential thermogravimetric (B) curves in oxygen for dry crosslinked PVA (a), as well as for nanocomposites containing 3.9 x 10^{-3} mol dm^{-3} Ag (b), 7.8 x 10^{-3} mol dm^{-3} Ag (c), and 1.6 x 10^{-2} mol dm^{-3} Ag (d).

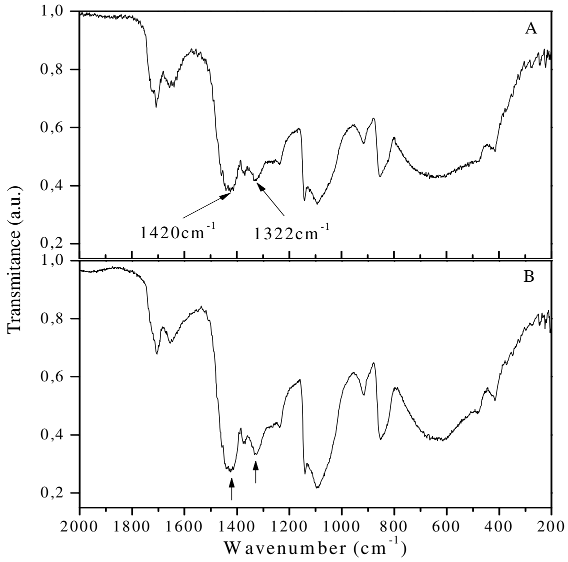

Figure 7. IR spectra of a PVA-Ag nanocomposite with 7.8 x 10^{-3} mol dm^{-3} Ag (A), and neat PVA crosslinked matrix (B).

According to IR spectra of a crosslinked PVA matrix and Ag-PVA nanocomposite, (Fig. 7), changes are observed for the band peaking at 1322 cm^{-1}. In alcohols this band is the result of the coupling of O-H in plane vibration (strong line at 1420 cm^{-1}) with C-H wagging vibrations. The decrease in the ratio of these bands with increasing content of the Ag indicates decoupling between corresponding vibrations and interaction of nanofiller with OH groups. According to previous investigation by FTIR spectroscopy, an interaction between Ag nanoparticles and the matrix takes place through the OH groups [9]. Also, attachment of the Ag nanoparticles to PVA chains prevents the out-of-plane oscillations of CH groups.

Conclusion

The study describes a novel and convenient way of preparation of colloidal silver stabilized by polymer. Water insoluble PVA films filled with Ag nanoparticles were prepared by a γ-radiolytic method. In the first step crosslinking of PVA was performed, while in the second step Ag^+ ions were reduced in PVA hydrogel using electron transfer reactions from radical species formed in water radiolysis. Three types of samples were investigated: two were prepared using a combined action of hydrated electrons and/or propan-2-ol and PVA radicals, and the third sample was prepared using exclusively PVA radicals. The size of silver particles estimated from the position of surface plasmon absorption bands was found to be 10-20 nm. The particles formed by the reduction of Ag^+ ions exclusively with PVA radicals are slightly smaller in diameter. The decomposition path of the crosslinked PVA matrix was affected by the presence of Ag nanoparticles. Thermal properties of the Ag-PVA nanocomposites were a function of the preparation route. The Ag-PVA nanocomposite prepared only with polymer radicals showed a higher temperature of the onset of thermal degradation. All Ag-PVA nanocomposites showed lower temperatures of the onset of thermooxidative degradation and increased rates of degradation compared with the neat crosslinked PVA matrix. Changes in thermal properties of PVA matrix were mainly induced by interactions between polymer functional groups and Ag nanoparticles as revealed by IR spectroscopy.

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