Silver rubber-hydrogel nanocomposite as pH-sensitive prepared by gamma radiation: Part I

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Abstract: Silver rubber-hydrogel nanocomposite based on silver/styrene butadiene rubber/polyvinylpyrrolidone/methacrylic acid (SBR/PVP/MAA)/Ag was prepared by gamma radiation-induced crosslinking. During the radiation crosslinking of SBR/PVP/MAA solution containing silver nitrate AgNO3 (0.01 mol), in situ reduction of Ag+ ions was performed under the radiolysis of water. The properties of silver rubber-hydrogel nanocomposite were investigated by FT-IR, XRD, TEM, SEM, DSC and TGA techniques. Transmission electron microscope (TEM) reveals that AgNPs have uniform distribution and spherical shape with mean diameter in the range of 8–10 nm. Differential scanning calorimetry (DSC) results of the nanocomposite showed one phase suggesting the miscibility between rubber and hydrogel phases. The swelling measurement of the synthesized silver rubber-hydrogel nanocomposite in different pHs at room temperature was performed. The results showed that it has pH-sensitivity.

Subjects: Chemistry; Material Science; Materials Science; Composites; Polymers & Plastics

Keywords: rubber; hydrogel; nanocomposite; AgNPs; gamma irradiation; pH-sensitive

1. Introduction

Recent advances in the design and synthesis of hydrogels for a wide range of applications have been made by introducing other compatible materials with them. Hydrogels have high degrees of swelling, environmental sensitivity and high permeability (Gupta & Shivakumar, 2012). Hydrogels can be defined as polymeric networks that can retain a significant amount of water within their structures, and swell without dissolving in it. Relatively high water content, hydrophilicity, expandability, selective permeability, soft rubbery consistency and low interfacial tension are among the advantages of hydrogels which enable them to resemble soft living tissues.

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Specialist: 1-nanotechnology applications 2-specific interest, Ionic Polymer Metal Composite (IPMC), as electroactive polymer (EAP) and magnetic polymer. 3-application of radiation chemistry for synthesis of polymer and hydrogel with a wide range biomedical application. Another kind of polymeric materials like (Organogel, fabric polymer and grafted films for different applications like self cleaning and self healing hydrogel.

PUBLIC INTEREST STATEMENT

- Uses of radiation technology for prepare silver rubber-hydrogel (styrene butadiene rubber/polyvinylpyrrolidone/poly methacrylic acid)/silver nanocomposites.
- In situ reduction of Ag+ ions was performed under the radiolysis of water.
- The swelling behavior of (SBR/PVP/PMAA)/Ag nanocomposites as a function of pH at room temperature was performed.
- Ag nanoparticles were in the range of 8–10 nm.
A hydrogel is a crosslinked polymer that may be synthesized in a number of chemical ways. These include one-step procedures like polymerization and crosslinking of multifunctional monomers, as well as multiple step procedures involving synthesis of polymer molecules having reactive groups with suitable crosslinking agents. The polymer design and synthesize of polymer networks with molecular-scale control over structure such as crosslinking density and with tailored properties, such as biodegradation, mechanical strength, and chemical and biological response to stimuli (Burkert, Schmidt, Gohs, Dorschner, & Arndt, 2007).

Ionizing radiation has been used as an initiator to prepare the hydrogels. This includes gamma rays (Elbarbary & Ghobashy, 2017; Ghobashy & Khafaga, 2016; Karadað, Saraydin, & Guven, 2001) and electron beams (Ajji, Mirjalili, Alkhatab, & Dada, 2008). On the other meaning, Gamma irradiation is a promising technique to fabricate a wide scale of different materials especially polymeric materials (Ghobashy & Abdeen, 2016; Ghobashy & Ehab, 2016; Ghobashy & Elhady, 2017). The irradiation of an aqueous polymer in the presence of vinyl monomers solutions leads to the formation of radicals on the polymer chains and/or on the vinyl groups. The recombination of the radicals on different molecules results in the formation of covalent bonds or crosslinked structure.

Hybrid hydrogel with other materials exhibited high stiffness for different applications (Ahmad & Al-Malaika, 2014; Zheng, Sun, Yuan, Duan, & Tian, 2016) such as polypeptide–polyethylene glycol for extracellular matrix (ECM) mimics (Wang, Cai, Paul, Enejder, & Heilshorn, 2014), graphene oxide-hybrid hydrogels for bio-inspired smart actuator (Wang et al., 2015), chitin/hydroxylapatite hybrid hydrogels as scaffold nano-materials (Chang et al., 2013) and laponite/alginite hybrid hydrogels as pH-sensitive (Li et al., 2011) and amino clay hybrid hydrogel which act as novel supramolecular scaffolds for light-harvesting (Venkatarao, Datta, Eswaramoorthy, & George, 2011).

The response of hydrogels to environmental parameters is an active area for researchers such as pH (Ghobashy, 2017; Wang, Turhan, & Gunasekaran, 2004), temperature, electric field (Ali, El-Rehim, Hegazy, & Ghobashy, 2006), ionic strength (El-Hag Ali, El-Rehiem, Hegazy, & Ghobashy, 2007), etc. A pH-sensitive hydrogel is a gel structure that is sensitive to the changes in pH. Depending on the nature of functional groups, the hydrogel will swell or contract in response to a change in the local chemical environment. These pH-sensitive hydrogels have applications in controlling valves that are sensitive to a change in pH such as in systems that can release a compound (Peterson, 2014), controlled drug delivery systems (Kim & Peppas, 2003), and in membrane separations.

Metal nanoparticles such as gold, silver, iron, zinc and metal oxide nanoparticles have been of interest in bioapplications (Bhattacharya & Mukherjee, 2008). Silver nanoparticles (AgNPs) can be prepared by several methods such as chemical reduction (Lorestani, Shahnazav, Mn, Alias, & Manan, 2015), electrochemical reduction (Hadipour-Goudarzi, Montazer, Latifi, & Aghaji, 2014), photochemical reduction (Kim & Lee, 2015), UV irradiation (Yang, Zhai, Wang, & Wei, 2014), ultrasonic method (He et al., 2014) and γ-irradiation (Akhavan, Sheikh, Khoylou, Naimian, & Ataeiavari, 2014; Malkar, Mukherjee, & Kapoor, 2014). Recently, radiolytic method was used in the preparation of metal nanoparticles in which the hydrated electrons produced during γ-irradiation can reduce metal ions to metal particles of zero valences (Li, Park, & Choi, 2007). Radiolytic in situ formation of AgNPs is rarely described in previous literature with extended analysis (Jovanović et al., 2011), such as radiolytic synthesis of AgNPs within poly(N-vinyl-2-pyrrolidone) (PVP) hydrogel for biomedical application (Kacarevic-Popovic et al., 2010), rubber composite fibers containing AgNPs were prepared through combination of electrospinning and in situ chemical crosslinking (Hu, Wu, Zhang, Fong, & Tian, 2012).

Rubber is a soft material that has glass transition temperatures lower than room temperature, and due to the high flexibility of rubber. It could be used for enhancing the elasticity of much composite materials (Fong & Reneker, 1999; Sarkawi, Kaewsakul, Sahakaro, Dierkes, & Noordermeer, 2016; Yong, 2015; Yong & Mustafa, 2014). Styrene-butadiene rubber (SBR) describes families of synthetic rubbers derived from styrene and butadiene. These materials have good abrasion resistance and good aging stability when protected by additives (Ansarifar, Wang, Yoong, Osman, & Pappu, 2010).
Poly(N-vinyl-2-pyrrolidone) (PVP) has important applications in various biotechnology areas such as tissue engineering, controlled drug release, separation of bio-macromolecules as well as biosensor (Ding, Kamulegeya, Chen, Chen, & Liu, 2007; Wan, Xu, Huang, Huang, & Yao, 2007). Poly(methacrylic acid) (PMAA) hydrogels can undergo a volume change in response to pH stimuli; due to this unique property, PMAA-related polymers have been developed to design pH-sensitive hydrogels that can modulate drug release by change in pH (Liu, Fan, Kang, & Sun, 2004; Liu, Liu, Chen, Sun, & Zhang, 2007; Mullarney, Seery, & Weiss, 2006).

The compatibility was expected between SBR and hydrogel matrices, whereas the latter would be reactive with the SBR matrix due to the polar groups. The pH sensitivity of rubber-hydrogel matrices was carried out to evaluate the compatibility between them. A high miscibility was observed between the MAA/PVP hydrogel and the matrix of SBR. This study is the first step in preparing a hydrogel-rubber with a pH-sensitive material.

In this study, silver rubber-hydrogel (SBR/PVP/MAA)/Ag nanocomposite was prepared by mixing SBR and copolymer hydrogel (polyvinylpyrrolidone –co-methacrylic acid) crosslinked by gamma irradiation in the presence of silver nitrate (AgNO₃) (0.01 mol). The changes in hydrogel properties due to SBR rubber matrices and/or AgNPs were investigated by FT-IR, XRD, TEM, SEM, DSC, and TGA. The swelling of rubber-hydrogel matrices embedded and non-embedded AgNPs in water or in different buffers at various pH’s were investigated.

2. Experimental

2.1. Materials

Emulsion of styrene butadiene rubber (E-SBR) including styrene and butadiene monomers, water, emulsifier, initiator system, modifier, shortstop and a stabilizer system was used as it is. E-SBR is commercial grades (BUNATM SB 1502-Schkopau), the percentage of styrene is 23.5, the glass transition temperature (Tg) of SBR is −50°C and this material has been supplied from Trinseo, USA. Polyvinyl pyrrolidone (PVP) with molecular weight (100 kDa), methacrylic acid monomer (MAA) 99% and silver nitrate (AgNO₃) were provided by Sigma-Aldrich. Other chemicals and solvents were used without further purification.

2.2. Preparation of (SBR/PVP/MAA)/Ag nanocomposite

Firstly, SBR/PVP/MAA was prepared by dissolving 0.5 g of PVP in 10 ml solution of (30/70) (methanol/distilled water) followed by adding 0.5 ml of MAA. Secondly, 10 ml of commercial solution of SBR was mixed well with the above mixture solution and stirred for 30 min. The reactant mixtures were placed into test tubes (Scheme 1), deaerated by bubbling with nitrogen gas for 3–5 min, sealed, and then subjected to γ-radiation at dose of 20 kGy. The preparation of (SBR/PVP/MAA)/Ag nanocomposite was carried out by repeating the above steps by adding 1.7 mg AgNO₃ (0.01 mol) after the polymerization process has been carried out. The resulting rubber-hydrogel samples were cut into disks (10 mm in diameter). Then, the disk of samples were soaked in distilled water for 24 h to remove the unreacted molecules, the water has been renewed three times every 24 h and then the samples were dried in oven at 50°C for 24 h.

2.3. Gamma irradiation cell

The polymerization process of rubber-hydrogel was carried out in the cobalt-60 gamma cell at a dose rate of 2.05 K Gy/h. The irradiation facility is located at the National Center for Radiation Research and Technology (NCRRT), Atomic Energy Authority of Egypt.

2.4. Determination of swelling ratio

A dried sample of a known weight was immersed in distilled water or in buffers of different pHs for 24 h, the equilibrium swelling ratio was determined by the amount of water absorbed by samples after 24 h ($W_s - W_d$) divided by the weight of dried samples $W_d$, the swelling ratio was calculated as follows:
where, $W_s$ and $W_d$ are the weights of wet and dry rubber-hydrogel, respectively. Note: the measurement of swelling was repeated three times with error $\pm 5\%$.

### 2.5. Preparation of buffer
To investigate the effect of pH on the equilibrium swelling ratio, the samples were immersed in buffer solution at pH ranged from 1 to 11 at room temperature. Swelling at various pHs individual solutions with acidic and basic pHs were prepared as follows: pH 1 and 2 prepared by 0.1 M of HCl (dilute 4.23 ml of 36.5% HCl to a final volume of 500 ml with distilled water), and 0.1 M KCl (7.46 g + H2O to 1 liter). pH 1 was obtained by 97 ml of HCl mixed with 3 ml of KCl, and pH 2 was obtained by mixing 10.6 ml of HCl with 89.4 ml of KCl. pH 3, 4, 5 and 6 have been prepared by 0.1 M Citric acid: 19.21 g/l (M.W.: 192.1) and 0.1 M Sodium citrate dihydrate: 29.4 g/l (M.W.: 294.0). Citric acid and sodium citrate solutions were mixed in the proportions (46.5:3.5) ml for pH 3, (31:19) ml for pH 4 (20.5:29.5) ml for pH 5 and for pH 6 (7:43) ml. Mixing and adjusting the final volume to 100 ml with deionized water have been carried out to get the required pH 7, 8, 9, 10 and 11 made up the following solutions; 0.1 M disodium hydrogen phosphate (14.2 g/l), 0.1 M HCl and 0.1 M NaOH (4.0 g/l), mixed in the following proportions for pH 7 (75.6:24.4:0) ml, for pH 8 (95.51: 4.49:0) ml, for pH 9 (95.50:4.50:0) ml for pH 10 (96.64:0:3.36) ml and for pH 11 (96.53:0:34.7) ml, respectively.

### 2.6. Fourier-transform infrared spectroscopy (ATR-FTIR)
The chemical structure of samples was identified using attenuated total reflectance Fourier-transform infrared ATR-FTIR spectroscopy Vertex 70 FTIR spectrometer equipped with HYPERION™ series microscope, Bruker Optik GmbH, Ettlingen, Germany, over the 4000–400 cm$^{-1}$ range, at a resolution of 4 cm$^{-1}$ has been utilized. A software OPUS 6.0 (BRUKER) was used for data processing, which was baseline corrected by rubber band method with CO$_2$ bands excluded.
2.7. X-ray diffraction (XRD)
X-ray diffraction patterns were obtained with a XRD-6000 series, Shimadzu apparatus using Ni-filter and Cu-Kα target.

2.8. Transmission electron microscopy
The particle size distribution of AgNPs was investigated using a transmission electron microscopy (TEM), JEOL JSM–100 CX, Japan, with an acceleration voltage of 80 kV. For TEM observations, the samples were prepared by making a suspension from the Ag nanocomposite in distilled water using ultrasonic water bath. The silver rubber-hydrogel sample was frozen on liquid nitrogen and quickly ground to a fine powder. This powder was suspended in acetone solution and centrifuged to separate the aggregated large size particle. Then a drop of the suspension was put into the carbon grid and left to dry at room temperature.

2.9. Scanning electron microscopy
The surface morphology of the swelling sample was investigated using Scanning Electron Microscopy (SEM) which is a powerful technique to provide information about miscibility of both the rubber and hydrogel phases. The surface topology was measured by SEM JEOL JSM-5400, Japan, with accelerating voltage of 30 kV. The surfaces of dried samples were sputter-coated with gold for 3 min for forming ~3–5 nm of thick gold on the sample surface. Sputtering time 5 min., current of 10–40 mA (discharge power 3–15 W), total pressure about 5 Pa, and the electrode distance of 15 mm. The power density was 0.13 W cm⁻².

2.10. Thermal analysis
Thermal analysis was performed using differential scanning calorimetry (DSC) and Thermo gravimetric analysis- Derivative thermo-gravimetric (TGA-DTG) from TA Instruments Waters—LLC, 159 Lukens Drive, New Castle, DE 19720. The melting temperature (T_m) measured by heating the samples from 25°C up to 300°C with heating rate 10°C/min. All measurements were conducted under a nitrogen atmosphere (20 ml/min). The cell was calibrated using an indium standard. The weight of the sample was 5–10 mg and heated up to 600°C, at a heating rate of 10°C/min under N₂ atmosphere.

3. Results and discussion
Scheme 1 demonstrates the procedure of polymerization and in situ nanoparticle formation induced by gamma irradiation. From Scheme 1, it is clear that the color after polymerization has been changed. The color of silver salt (AgNO₃) changes from its original color to a golden yellow color due to the reduction process. Before and after polymerization process, it was observed that (1) the miscibility of both rubber and hydrogel phases took place. (2) Good dispersion of AgNPs colloid thereby indicated that the AgNPs have no tendency to agglomerate because of effective capping by rubber hydrogel matrices.

3.1. Characterization of silver rubber-hydrogel nanocomposites
3.1.1. Chemical structure by FT-IR studies
The ATR-FT-IR spectrum (Figure 1(b)) for (SBR/PVP/PMAA)/Ag showed that there is a chemical bonding between rubber hydrogel matrices and silver nanoparticles (Sobczak-Kupiec, Malina, Wzorek, & Zimowska, 2011). This causes shifts of the main characteristic peak as shown in Figure 1(a) and (b). The stretching peak of (C=O) groups at 1,655 cm⁻¹ shifted to 1,675 cm⁻¹ with a slight broadening. C-N has a peak at 1,030 cm⁻¹ which shifted to 1,026 cm⁻¹, while no shift was observed in the peak attributed to C-H at 2,922 cm⁻¹. From the above-mentioned, N and O atoms in the molecule of function groups have affinity for Ag ions and metallic Ag coordination (Khanna, Gokhale, & Subbarao, 2004; Silvert, Herrera-Urbina, Duvauchelle, Vijayakrishnan, & Tekaia-Elhsissen, 1996). This results give spot about in situ chemical reduction of Ag⁺ ions to AgNPs were performed by rubber hydrogel compositions like PVP. The PVP reduction mechanism of AgNPs formation has been described by two steps. The first step involves the formation of coordinative bonds between Ag⁺ ions and the N and O atoms in polymer function groups, as a result of donation of lone pair electrons from O and N to empty
orbital of Ag⁺. The second step, the complex is then thought to promote nucleation of Ag⁺ atoms that are exposed to γ-irradiation are reduced to AgNPs (Chahal, Mahendia, Tomar, & Kumar, 2010; Malina, Sobczak-Kupiec, Wzorek, & Kowalski, 2012; Sadeghi, Sadjadi, & Pourahmad, 2008; Shin, Yang, Kim, & Lee, 2004; Zhang, Zhao, & Hu, 1996). The role of PVP in the irradiated solution considerably remains as one of the holding matrix beside COOH functional group of PMAA that may temporarily bind with the Ag⁺ ions this made stabilization of AgNPs.

3.2. XRD studies

Figure 2 shows the XRD pattern of SBR/PVP/PMAA and (SBR/PVP/PMAA)/Ag nanocomposite. The XRD of SBR/PVP/PMAA shows a strong and broad diffraction peak located at 2θ = 20°. The XRD of irradiated Ag (SBR/PVP/PMAA) nanocomposite shows the diffraction peaks at 2θ = 38.11°, 44.28°, 64.61° and 77.9° corresponding to (111), (200), (220), and (311), lattice planes of Ag is observed and compared with the standard powder diffraction card (silver file No. 04–0783) of Joint Committee on Powder Diffraction Standards (JCPDS). Silver file No. 04–0783. The XRD study confirms that the resultant particles are (FCC) AgNPs corresponding to Face Center Cubic (FCC) (Sulaiman, Mohammad, Abdul-Wahed, & Ismail, 2013).
3.3. Particle size measurements using TEM
A typical TEM image of AgNPs formed is displayed in Figure 3. The Ag nanoparticles were readily generated during gamma irradiation. The silver nanoparticles are well distributed in the rubber-hydrogel nanocomposite, where TEM image reveals that the uniform sphere structure shape of AgNPs was in the range of 8–10 nm.

3.4. Swelling characterization
Swelling is one of the most important parameters affecting the characteristic properties of the prepared rubber-hydrogel composite and, therefore, determines their applicability for practical use. The influence of the swelling time on the water uptake was investigated for SBR/PVP/PMAA without silver and silver rubber-hydrogel (SBR/PVP/PMAA)/Ag nanocomposite prepared as shown in Figure 4. The water uptake rapidly increases as the swelling time increases, reaching a certain limiting value after almost 4 h (25 and 24 (g/g), respectively). As a result, the diffusion and swelling properties are shown to be new features of rubber when hydrogel is introduced. However, in case of embedding AgNPs, this leads to a decrease in the swelling efficiency due to silver particles filling the network gaps of rubber hydrogel matrices.

3.5. Surface morphology (SEM)
Figure 5(a) and (b) shows SEM analysis of freeze-swelled rubber-hydrogel and Ag nanocomposite. SEM for rubber-hydrogel (Figure 5(a)) verified a uniform nature of surface morphology indicating good compatibility between the rubber and hydrogel materials. The porous structure affected by elasticity of SBR chains. SEM for silver rubber-hydrogel nanocomposite (Figure 5(b)) revealed a uniform dispersion of AgNPs in rubber-hydrogel matrix and no agglomerated regions were noticed.

3.6. Thermal analysis DSC and TGA-DTG
The TGA-DTG thermogram of dried samples of rubber hydrogel with and without AgNPs exhibits major one degradation steps from room temperature to 420°C which may be attributed to the higher thermal stability of SBR (Varkey, Augustine, & Thomas, 2000; Wang, Wang, & Cheng, 2009). Figure 6(a) and (b) shows that the decomposition occurred gradually for all polymer compositions (SBR, PVP and PMAA) at the same time. The same behavior observed in case embedded AgNPs. The results accounts for a single degradation step due to the higher miscibility and crosslink density of rubber-hydrogel matrices.
The DSC of the prepared rubber hydrogel without AgNPs (Figure 6(c)) shows a pure phase suggesting that these are fully miscible between rubber-hydrogel phases with a homogeneous amorphous phase. Glassy temperature ($T_g$) for SBR at $-56^\circ$C the glass transition temperature is shifted towards the higher temperature region upon $-51^\circ$C due to introduction of crosslinked (Radhakrishnan, Sujith, & Unnikrishnan, 2007). The major endothermic peak centered at about $252^\circ$C is due to the complex formation of a link between PVP and PMAA with weak H-bond interaction (Polacco, Cascone, Petarca, & Peretti, 2000). DSC curve of (SBR/PVP/PMAA)/Ag nanocomposite shows an endothermic peak at $226^\circ$C which is attributed to Ag particles causing removal of H-bond interaction between chains of polymer.

3.7. Swelling in different pH

The swelling behavior of any hydrogel network depends upon the nature of the functional groups of the hydrogel. Figure 7 shows the equilibrium swelling behavior as a function of pH at room temperature. At pH 1 the swelling degree was 40 (g/g) which decreased to 13 (g/g) when AgNPs are embedded, this is due to polyvinylpyrrolidone coated AgNPs that are negative in nature (El Badawy et al.,
Hence, protonation on the surface causes neutralization of AgNPs which leads to a decrease in the repulsion force between particles and so the water uptake will be decreased. While in case (SBR/PVP/PMAA) at pH1 the COOH groups are neutralized which leads to absence of H-bond interaction with PVP. This causes an increase in swelling degree at 40 (g/g). At pH 2, 3, 4 and 5 the swelling degree was 10, 16, 13 and 17 (g/g) for (SBR/PVP/PMAA), respectively, and was 11, 13, 9 and 16 (g/g), respectively, in case (SBR/PVP/PMAA)/Ag. The results revealed that Ag caused a decrease in the swelling efficiency. The pKa value of PMMA was 5.7 (Dai, Ravi, Tam, Mao, & Gan, 2003) exceeding this.
value causes a dramatic increase in domains of COO– groups and swelling degree to 63 (g/g) for (SBR/PVP/PMAA) and in case (SBR/PVP/PMAA)/Ag, the swelling degree increases to 73 (g/g). This is attributed to the negative charge of AgNPs which repels with COO– groups. While, the swelling of rubber-hydrogel samples decreases from pH 7 up to pH 11 as expected.

4. Conclusion
Preparation of pH sensitive rubber-hydrogel matrices using gamma irradiation gives a new material for appreciated applications related to pH effects. AgNPs (8–10 nm) are embedded into the prepared rubber-hydrogel to enhance its ability to be used as protecting agents to AgNPs with an average diameter of 8–10 nm. The DSC, TGA and SEM confirmed the one-phase formation of new matrices and ATR-FTIR confirmed the formation of complexes between PVP and PMAA. The new feature of SBR swelling improved in water and in different buffers solutions, this is due to incorporation with PVP/PMAA hydrogel.

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