Synthesis and characterization of poly(2-hydroxyethyl methacrylate)/silver hydrogel nanocomposites prepared *via in situ* radical polymerization

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ABSTRACT

Nanocomposites of poly(2-hydroxyethyl methacrylate), PHEMA, hydrogels with silver nanoparticles (Ag NPs) were produced using an *in-situ* bulk radical polymerization technique. The reduction of Ag^+ precursors to Ag NPs took place during the reaction exclusively by the hydroxyl and carbonyl groups present in HEMA monomer. The formation of silver nanoparticles was identified using XRD characteristic peaks and the surface Plasmon resonance vibration, from UV–vis spectra. FTIR data showed that the inclusion of Ag NPs in the polymer matrix affects the chemical bonds present in the polymer matrix. The thermal stability of the nanocomposites was slightly decreased compared to neat PHEMA, whereas their thermo-mechanical properties (*i.e.* elastic modulus) and the glass transition temperature were increased with the amount of the Ag NPs. The polymerization activation energy of the nanocomposites, as calculated from differential isoconversional methods using non-isothermal DSC experiments, was found to vary with conversion in a different way compared to neat PHEMA. These observations were explained based on the destruction of the hydrogen bonds between the hydroxyl and either hydroxyl or carbonyl groups originally existing in neat PHEMA from the formation of the silver aggregates and their binding to the macromolecular chain.

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1. Introduction

During last decade research related to the synthesis of new intelligent materials with specified nano-properties has had an incredible and remarkable increase. In this context, intelligent hydrogels have attracted the attention of several researchers due to their hydrophilic character and their potential biocompatibility [1,2]. Poly(2-hydroxyethyl methacrylate) (PHEMA) is such a polymer hydrogel that has been widely used in the biomedical field because of its nontoxicity, antigenicity, and excellent compatibility with living organism tissue. Indeed, hydrophilic polymers based on HEMA have been used as substitutes for metals, to suppress corrosion and inflexibility, as well as in soft contact lenses. PHEMA was also applied in the field of tissue engineering as matrix for repairing and regenerating a wide variety of tissues and organs, in artificial skin manufacturing and burn dressings, as it ensures good wound-healing conditions [3,4].

One of the major disadvantages of polymers when used in bio-medical applications is that they are susceptible to microbial attack. Incorporation of bioactive agents including antimicrobials into polymers has been commercially applied in drug and pesticide delivery, household goods, textiles, surgical implants and other biomedical devices. Among different antimicrobial agents, silver (Ag) is the most widely used as polymer additive since it is active against a wide range of microorganisms and non-toxic to cells. Therefore, the introduction of silver nanoparticles (Ag NPs) into conventional polymers results in new materials with improved properties. However, the challenge is how to incorporate the Ag NPs into the polymeric matrix in a uniform way.
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he preparation of silver nanoparticles using a variety of methods has been the subject of a number of papers in literature [5–10]. However, their incorporation into a polymeric matrix, in order to form a nanocomposite polymeric material, has only

found limited research interest since now [11–16]. Poly(methyl methacrylate), PMMA, was mainly used as a polymer matrix and DMF as a solvent/reduction agent [11,13], whereas for the reduction of Ag^+ to Ag^0, butylated hydroxytoluene was also employed [14]. Vodnik et al. [15] were the only researchers who prepared silver/PMMA nanocomposites *via* a purely *in-situ* polymerization technique using $NaBH_4$ as a reducing agent. In a subsequent publication by the same the authors, the glass transition and polymer dynamics of silver/PMMA nanocomposites were investigated [16]. Su et al. [12] prepared nanocomposites materials of silver with poly(2-hydroxyethyl methacrylate) using $AgNO_3$ in DMF solution. Moreover, the gamma radiolysis method was used to fabricate silver nanoparticles *via in situ* reduction of $AgNO_3$ embedded in swollen poly(2-hydroxyethyl methacrylate/itaconic acid) hydrogels [17]. The same copolymer matrix was used to examine the antimicrobial properties of silver. Excellent antimicrobial potential was maintained during the entire release time [18]. Recently, Henriquez et al. used $AgNO_3$ as a source for silver nanoparticles formation which were embedded into a photopolymerized hydrogel based on HEMA and a dimethacrylate monomer [19,20]. For the reduction of Ag^+ to Ag^0 irradiation with a UV lamp at 365 nm was employed.

In our laboratory we have prepared in the past nanocomposites materials based on a polymer matrix *via* the *in situ* bulk polymerization technique [21–24]. Lately, we extended this technique in the incorporation of Ag NPs in PMMA based nanocomposites [25]. As a continuation, in this work we present the synthesis and characterization of PHEMA hydrogels with silver nanoparticles using the *in-situ* polymerization technique, where the reduction of Ag^+ takes place during the reaction. The effect of silver on the properties of the PHEMA/Ag nanoparticles hybrids was measured using a variety of techniques including, X-Ray diffraction, FTIR and UV–vis spectrometry, thermogravimetric (TG) analysis, differential scanning calorimetry (DSC) and dynamic thermo-mechanical analysis (DMA). According, to our knowledge this is the first approach to synthesize PHEMA based hydrogels with Ag NPs formed *in situ* during the reaction.

2. Experimental

2.1. Materials

The monomer used, 2-hydroxyethyl methacrylate (HEMA) with a purity ≥97% was purchased from Sigma-Aldrich and contained monomethyl ether hydroquinone (MEHQ) as inhibitor. The free radical initiator, benzoyl peroxide (BPO) with a purity >97% was provided by Alfa Aesar and purified by fractional recrystallization twice from methanol (Chem-Lab). For the formation of silver nanoparticles, solid silver nitrate ($AgNO_3$) was used from Mallinckrodt, which was dissolved in the monomer. All other chemicals used were of analytical grade and were used as received without further purification.

2.2. Synthesis of PHEMA/silver nanocomposites by in-situ bulk radical polymerization

In a 100 mL conical flask, the appropriate amount of $AgNO_3$ was dispersed in the monomer HEMA by adequate magnetic and supersonic agitation, so that to obtain mixtures containing 0.05, 0.1 and 0.2 wt-% of Ag to the monomer. Three different mixtures thus prepared and studied and were named PHEMA005, PHEMA010 and PHEMA020, respectively. In the final suspension, the initiator, BPO 0.03 M was added and the mixture was degassed by passing nitrogen and immediately used. It should be noted here that, since this product could be used in commercial applications, the actual

amount of Ag in the nanocomposites was rather low, in order to keep the final product cost at low levels as we already did in the case of PMMA/Ag nanocomposites [25]. Following, the flask with the mixture was placed into a pre-heated bath at 80 °C for a suitable time. After the completion of polymerization, all materials were dried to constant weight in a vacuum oven at room temperature. Experiments were repeated thrice and average values are reported. Throughout the polymerization, all solutions were kept in a dark place to avoid any photochemical reactions.

Exactly the same experiment was repeated using only the monomer HEMA and the initiator, without adding any amount of $AgNO_3$.

2.3. Polymerization kinetics

In order to study the polymerization kinetics, non-isothermal experiments were carried out in a DSC under various heating rates from 1 to 10 °C min⁻¹. Polymerization was investigated using the DSC, Diamond (from Perkin-Elmer) equipped with the Pyris software for windows. Indium was used for the enthalpy and temperature calibration of the instrument. The initial mixture was prepared by dispersing the appropriate amount of $AgNO_3$ in the monomer HEMA by adequate magnetic and supersonic agitation. In the final suspension, the initiator, BPO 0.03 M was added and the mixture was degassed by passing nitrogen and immediately used. The samples were weighted (approximately 10 mg) sealed and placed into the appropriate position of the instrument. The reaction exotherm was recorded as a function of temperature. The rate of heat release ($d(\Delta H)/dT$) measured by the DSC was directly converted into the overall reaction rate (dX/dt) using the following formula:

$$\frac{dX}{dt} = \left(\frac{dX}{dT}\right)\left(\frac{dT}{dt}\right) = \beta\left(\frac{dX}{dT}\right) = \frac{\beta}{\Delta H_T}\frac{d(\Delta H)}{dT} \qquad (1)$$

where ΔH_T denotes the total reaction enthalpy, β is the constant heating rate and X fractional conversion.

The polymerization enthalpy and conversion were calculated by integrating the area between the DSC curves and the baseline established by extrapolation from the trace produced after complete polymerization. After the end of the polymerization the pans were weighted again and a negligible loss of monomer (less than 0.2 mg) was observed only in a few experiments.

Exactly the same experiment was repeated using only the monomer HEMA and the initiator, without adding any amount of $AgNO_3$.

2.4. Measurements

2.4.1. Fourier-transform infra-red (FTIR)
The chemical structure of the neat PHEMA and PHEMA/Ag NPs was confirmed by recording their IR spectra. The instrument used was the Spectrum 1 spectrophotometer from Perkin Elmer with an attenuated total reflectance (ATR) device. ATR was necessary since the samples with high amounts of AgNPs were not transparent. Measurements were carried out using thin films prepared in a hot hydraulic press and spectra recorded over the range from 4000 to 600 cm⁻¹ at a resolution of 2 cm⁻¹ and 32 scans were averaged to reduce noise. The instrument's software was used to identify several peaks.

2.4.2. X-Ray diffraction
The crystalline structure of the prepared PHEMA/Ag NPs materials was characterized using X-ray diffraction (XRD) in a Rigaku Miniflex II instrument equipped with CuKα generator ($\lambda = 0.1540$ nm). The XRD patterns were recorded at the range $2\theta = 5$–$85°$ and scan speed of $2°$ min⁻¹.