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Effect of gamma ray on magnetic bio-nanocomposite

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HIGHLIGHTS

- PVA and Fe_3O_4 nanocomposite films and hydrogels were prepared.
- Gamma-irradiated hydrogels showed high saturation magnetization.
- The nanocomposite films had excellent mechanical properties.
- Magnetic hydrogels showed high equilibrium water content.

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ABSTRACT

Magnetic polyvinyl alcohol (M-PVA) films were prepared via solution casting filled with surface modified superparamagnetic nanoparticles (M-NPs). The M-NPs were coated with citric acid during synthesis. The chemical interaction between the citric acid and M-NPs was confirmed by Fourier transform infrared spectroscopy (FTIR). The average hydrodynamic diameter of M-NPs was 19.7 nm measured by dynamic light scattering DLS and appeared almost spherical in scanning electron microscopy (SEM). The M-NPs were uniformly dispersed in polyvinyl alcohol (PVA) matrix and showed high optical transparency with good mechanical properties. M-PVA hydrogels were synthesized using gamma irradiation. The characteristic XRD peak of PVA at 19.4° was split after irradiation indicating formation of different crystallite sizes. The M-PVA hydrogel showed higher saturation magnetization compared to un-irradiated M-PVA. Also the presence of M-NPs enhanced the crosslinking of PVA by irradiation.

1. Introduction

In the past decade responsive polymeric nanocomposites whose properties can be controlled by applying magnetic field are of great interest due to their wide application as bio-membranes, biomedical materials, biosensors, artificial muscles and drug delivery devices [1–4]. For drug delivery purposes, a material that can control dose and release of drug in the presence of magnetic field is desirable. In this regard PVA hydrogels filled with magnetite nanoparticles are an excellent choice because of their biocompatibility, high equilibrium water content and superparamagnetic behavior. Among various physical and chemical methods of fabricating PVA hydrogels, irradiation of aqueous solutions with γ-ray forms clean hydrogels without any initiators and/or chemical crosslinking agents such as glutaraldehyde that are possibly harmful or difficult to remove for biomedical applications [5,6]. In addition, irradiation of polymers in aqueous solutions is easier to control and study. The incorporation of magnetic nanoparticles such as iron oxide into hydrogels creates tunable nanocomposites that could be controlled by a magnetic field [7,8]. Temperature-responsive magnetic poly N-isopropyl acrylamide hydrogels were developed for controlled-drug release application [9]. The compatibility of magnetic nanoparticles with polymeric matrix can be enhanced by its surface modification [10]. Magnetic PVA gel beads were fabricated by freezing-thawing method for drug release purposes [11].

It has been shown that PVA coated superparamagnetic iron oxide nanoparticles can be used as drug delivery targeting in synovial membrane tissue [12]. Using magnetic hydrogels in cancer treatment via hyperthermia, generating heat in cancerous tissue upon exposure of magnetic particles to an external alternating magnetic field (AMF), also has received many attentions. Exposing the cancerous tumor tissue, embedded magnetic nanoparticles, to an external alternating magnetic field (AMF) led to increase of the

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temperature inside the tumor tissue [13]. Synthesis and characterization of PVA composite films with different fillers for different purposes have been reported by many investigators. PVA nanocomposite films filled with hematite nanoparticles were fabricated by Z. Guo et al. [14] using drop casting method and physicochemical properties of PVA were explored. A. A. Novakova et al. [15] investigated magnetic behavior of polymer nanocomposite films containing Fe_3O_4 nanoparticles in polyvinyl alcohol by means of Mossbauer transmission, conversion electron spectroscopy and magnetic measurements. In addition, chemical crosslinking and freezing-thawing methods for preparing hydrogels are widely used by researchers. J. Chatterjee et al. [16] synthesized a bio-magnetic PVA gel film incorporated with $\gamma - Fe_2O_3$ nanoparticles and crosslinked by glutaraldehyde. The results showed that particles are in the size of 7–10 nm and have uniform distribution in polymer matrix. Also magnetization measurements revealed that both magnetic nanoparticles and magnetic gel films are superparamagnetic. In a more resent work J.S. Gonzalez et al. [17] synthesized filled PVA hydrogels with freezing-thawing method. In order to improve mechanical and tribological properties hydroxyapatite was used in PVA matrix and bentonite was added for improving water vapor permeability and antimicrobial properties. Furthermore to obtain responsive hydrogels for use as drug delivery system, magnetic iron oxide was in situ synthesized in PVA matrix. The results showed that fillers substantially improve the specific properties required for biomedical applications with respect to neat PVA matrix. Also magnetic PVA gel beads were made by Li Zhou et al. [18] using freezing-thawing method and the drug loading and release properties of them were investigated in details. In order to achieve dual or multi-responsive gel beads magnetic PVA-PNIPAM (Poly N-isopropyl acrylamide) gel beads that simultaneously possess temperature and magnetic responsibilities were prepared and their drug delivery behaviors at different temperatures were also explored. Surprisingly no report was found on the mechanical properties of surface treated Fe_3O_4 nanoparticles/PVA nanocomposites and also on magnetic properties of Fe_3O/PVA hydrogels prepared by gamma irradiation.

In the present work, M-NPs modified with citric acid were synthesized through co-precipitation and M-PVA films were prepared with different loadings of M-NPs by solution casting method. Also Co^{60} gamma-ray irradiation technique was used to make M-PVA hydrogels. Physical properties of hydrogels were measured and samples characterized with XRD, VSM, FTIR and mechanical measurements to evaluate applicability of these hydrogels and films for biomedical applications. This work provides some novel findings by investigating the effect of gamma ray on magnetic properties of polyvinyl alcohol/magnetite nanocomposites and also the effect of magnetic nanoparticles on the crosslinked structure of polyvinyl alcohol (PVA) matrix. Also the comparison between magnetic properties of un-crosslinked and radiation-crosslinked PVA nanocomposites are introduced.

2. Experimental

2.1. Materials

Polyvinyl alcohol (M_w = 72,000, Fluka), iron (III) chloride hexahydrate ($FeCl_3.6H_2O$, Merck), iron (II) chloride tetrahydrate ($FeCl_2.4H_2O$, Merck), ammonia solution (25% wt.) and citric acid were used to synthesis the samples.

2.2. Synthesis of surface modified magnetite nanoparticles (M-NPs)

Magnetite (Fe_3O_4) nanoparticles modified by citric acid (CA) were prepared by co-precipitation of $FeCl_2.4H_2O$ and $FeCl_3.6H_2O$ (1:2 M ratios) by the addition of NH_4OH. 0.86 g $FeCl_2.4H_2O$ and 2.35 g $FeCl_3.6H_2O$ were mixed in 40 ml deionized water and heated slowly to 80 °C in a flask under nitrogen atmosphere for 30 min and then 15 ml NH_4OH was added to the reaction mixture at the same temperature. After that, 1 g CA in 2 ml water was introduced as surfactant, the temperature raised up to 95 °C and the stirring continued for 60 min. The black colored precipitates were obtained and after cooling to room temperature, thoroughly washed with water. Finally samples were separated from the supernatant using a permanent magnet and dried in a vacuum oven at 50 °C.

2.3. Synthesis of magnetic polyvinyl alcohol films (M-PVA films)

Solution casting method was used to prepare M-PVA films according to the following procedure: PVA was dissolved in water at 90 °C. Various quantities of M-NPs were dispersed in water with the aid of ultrasound and were added to the PVA solution. The mixture was stirred for 24 h and a homogenous mixture was obtained. The mixture was transferred to a Petri dish and dried in a desiccator and vacuum oven for further characterization. Samples with M-NPs loadings of 1, 3 and 5% wt. were prepared. The films were of high optical transparency indication excellent dispersion of the M-NPs in PVA matrix.

2.4. Synthesis of magnetic PVA hydrogels using γ-ray irradiation (M-PVA hydrogels)

M-PVA aqueous solutions were prepared according to part 2.2 and were degassed to remove O_2 before being exposed to γ-ray. The γ-ray irradiation was performed with Co^{60} at 25 °C and the exposure dose rate of 3.44 Gy/s.

2.5. Analytical methods

Size distribution of nanoparticles was determined by Dynamic Light Scattering (DLS); MALVARN ZETA-SIZER Nano Series. The magnetic properties of samples at room temperature were evaluated on a magnetometer (Kavir Kashan Design Corporation, Iran). XRD patterns of samples were recorded with a STOE D-64295 X-ray diffractometer over the 2θ range from 10 to 70°, using Cu-Kα radiation (λ = 1.54 Å). SEM images were observed on a Hitachi model F-4160 scanning electron microscope with an accelerating voltage of 10–25 kV. Mechanical properties of samples were studied using a mechanical testing machine. Rectangular specimens were prepared according to ASTM D882 and tensile test was performed at the speed of 10 mm/min.

FTIR spectra were carried out on ABB BOMEM MB SERIES spectrometer using KBr method. For determining gel fraction (G %), M-PVA hydrogels were immersed in water (12 h) to remove the soluble fraction and then the samples were dried in a vacuum oven at 50 °C, until constant weight was obtained. G % in hydrogels was estimated by the formula:

$$G(\%) = \frac{W_f - W_F}{W_i - W_F} \times 100 \quad (1)$$

where W_i and W_f are the weight of the dried sample before and after removing sol and W_F is the weight of M-NPs in each sample.

Water swelling of M-PVA hydrogels was measured at 25 °C. Dry gels were immersed in distilled water for 48 h and after removing the superficial water, swollen samples were immediately weighed. The equilibrium water content W_{eq} in swollen samples was calculated as follows: