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SWELLING BEHAVIOR OF Ag/PVA HYDROGEL NANOCOMPOSITE SYNTHESIZED BY γ-IRRADIATION

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Abstract

In this study, the Ag/PVA hydrogel nanocomposite was synthesized using γ-irradiation. Incorporated Ag NPs were less than 10 nm in diameter with face centered cubic (*fcc*) crystal structure. Incorporation of Ag NPs into PVA hydrogel significantly affects the characteristic parameters of swelling process.

Introduction

Hydrogels are polymeric three-dimensional networks having the ability to swell, but not to dissolve. They are rendered insoluble by chemical or physical crosslinks, which provide the network structure and physical integrity. Due to characteristic properties such as swellability in water, hydrophilicity, biocompatibility and lack of toxicity, hydrogels have been utilized in a wide range of biological, medical, pharmaceutical and environmental applications.

The materials having metal nanoparticles (NPs) incorporated into polymer network have been widely investigated due to their unique properties induced by the synergy of two different materials. Silver nanoparticles (Ag NPs) have been proved to be effective antimicrobial agent and enhanced antibacterial properties have been demonstrated both *in vitro* and *in vivo*. Recent research efforts are directed towards exploiting the *in situ* synthesis of Ag NPs within polymeric network architectures and products of these approaches are new hybrid nanocomposite systems. Hydrogels in the swollen state provide free spaces within the network, which can serve for nucleation and growth of NPs. In this way, the carrier-hydrogel system acts as a nanoreactor that immobilizes NPs and provides easy handling. Among different synthesis route, γ-irradiation induced synthesis has been recognized as highly suitable tool for production of hydrogel nanocomposites due to formation and sterilization of material in one technological step [1, 2].

In this work the Ag NPs were radiolyticaly synthesized within poly(vinyl alcohol) (PVA) hydrogel, previously obtained by γ-irradiation induced crosslinking. Optical and structural analyses of synthesized hydrogels were performed as well as of their swelling kinetics behavior.

Experimental

PVA aqueous solution (5 wt%) was aerated for 30 min with argon (Ar), in order to remove oxygen and then γ-irradiated at a dose rate of 0.33 kGy/h, up to absorbed dose of 25 kGy. The obtained hydrogel was immersed in deionized water, for one week, to remove uncrosslinked PVA and dried at room temperature. PVA hydrogel was equilibrated in the solution containing $16 \cdot 10^{-3}$ M $AgNO_3$ and 0.2 M 2-propanol. Swelling of Ar-saturated gel was carried out for 48 h at room temperature, in the dark. Reduction reaction was performed by γ-irradiation to the absorbed dose of 30 kGy, at a dose rate of 10 kGy/h. γ-irradiation was performed at ^{60}Co radiation source, under ambient condition.

The optical properties of synthesized Ag/ PVA hydrogel nanocomposite were investigated by UV-Vis absorption spectroscopy using Thermo Scientific Evolution 600 spectrophotometer, while the microstructural analysis was performed by XRD measurement on Bruker D8 Advance Diffractometer (Cu $K_{\lambda 1}$ radiation, $\lambda = 0.1541$ nm).

Dynamic swelling studies were performed in deionized water at temperature of 25 ± 1 ^{o}C, using dry gels (xerogels). Hydrogel discs (diameter d = 10 mm, thickness δ = 5 mm) were cored out, dried to the constant weight and then used in swelling investigations. The swelling process was observed gravimetrically.

Results and Discussion

After the γ-irradiation, the yellow colored Ag/PVA hydrogel nanocomposite was obtained. Yellow color is characteristic of silver nanoparticles (Ag NPs). Formation of NPs was confirmed by UV-Vis spectroscopy and X-ray diffraction. Absorption spectrum of Ag/PVA hydrogel shows plasmon absorption band at 392 nm (characteristic of Ag NPs), while XRD pattern confirmed that Ag NPs were less than 10 nm in diameter, with face centered cubic (*fcc*) crystal structure [2, 3].

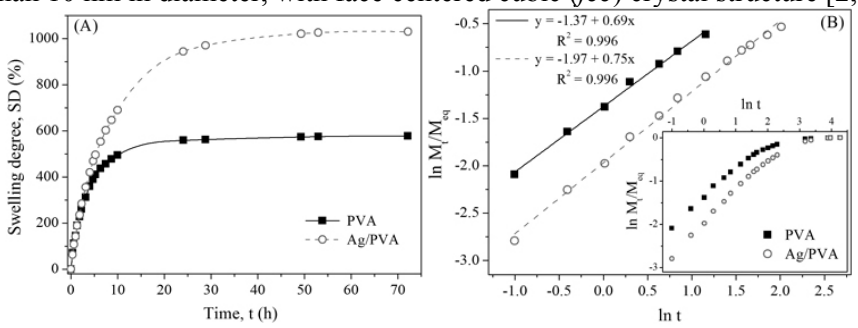

Fig.1. (A) Swelling curves of hydrogels, in deionized water at 25 ^{o}C. (B) Best linear fits of linear parts of swelling curves. Inset: Dependence $ln\ M_t/M_{eq}$ vs. $ln\ t$ in the whole investigated range.

The capacity of swelling is one of the most important parameters for evaluation the properties of hydrogels. Fig. 1(A) depicts the swelling curves of the investigated hydrogels in deionized water at 25 ^{o}C. As can be seen, the swelling isotherms are similar in shape, but incorporation of Ag NPs particles in the PVA

hydrogel has significant influence on the swelling properties. The equilibrium swelling degree (SD_{eq}) of Ag/PVA hydrogel nanocomposite was found to be 1.78 times higher in comparison with PVA hydrogel, and swells with the lower initial swelling rate (v_{in}) (Table 1). This can be ascribed to the existence of remnant Ag^+ ions in the *in situ* synthesized nanoparticles in hydrogel, which can be well dissolved in water thus altering the composition of swelling medium [3].

To analyze the model of water diffusion into the polymer network, the water sorption data was used. The logarithmic form of kinetic equation of swelling, $M_t/M_{eq} = k\ t^n$ (k is the kinetic constant, related to the structure of the network, t is time and n is the diffusion exponent), was presented as an inset on Fig. 1(B). The characteristic constant n and k was calculated from the slope and intercept, respectively, of the linear parts of initial stages of swelling (Fig. 1(B)), and they can be related to the specific transport mechanism. In this case, both hydrogel systems shows non-Fickian or anomalous diffusion ($0.5 < n < 1$) when the rates of diffusion and polymer chain relaxation are comparable [3]. The diffusion coefficient (D) can be calculated as $D = k^{1/n}\ \pi\ \delta^2/16$ (δ is thickness of the xerogel). The values for n, k and D were presented at Table 1. For extensive swelling of hydrogels the equation $t/SD = A+Bt$ was used (Fig. 2), and the linear dependence indicated the Schott second order kinetics ($dSD/dt = k_S(SD_{eq}-SD)^2$) [3, 4].

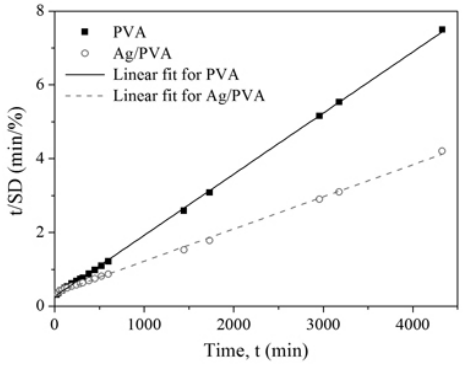

Fig.2. Relation *t/SD* vs. *t* for hydrogels, in deionized water at 25 °C.

Table 1. Characteristic parameters of swelling process for hydrogels, in deionized water at 25 °C.

	PVA	Ag/PVA
SD_{eq} (%)	575	1025
v_{in} (%/min)	2.49	2.29
k (1/s)	$7.1 \cdot 10^{-5}$	$3.9 \cdot 10^{-5}$
n	0.69	0.75
D (cm^2/s)	$5.58 \cdot 10^{-6}$	$2.15 \cdot 10^{-6}$

Conclusion

The Ag/PVA hydrogel nanocomposite was successfully synthesized by γ-irradiation. The obtained hydrogel nanocomposite had greater swelling capacity and diffusion coefficient, but it swells slowly, compared to PVA hydrogel, in deionized water at 25 °C. Both hydrogels show non-Fickian diffusion and Schott second order kinetics, at early and extensive stage of swelling, respectively

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