# PHYSICAL CHEMISTRY 2014

12[th] International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

The Conference is dedicated to the
25. Anniversary of the Society of Physical Chemists of Serbia

September 22-26, 2014
Belgrade, Serbia

**ISBN 978-86-82475-30-9**
**Title:** PHYSICAL CHEMISTRY 2014 (Proceedings)
**Editors:** Ž. Čupić and S. Anić
**Published by**: Society of Physical Chemists of Serbia, Studenski trg 12-16, 11158, Belgrade, Serbia
**Publisher**: Society of Physical Chemists of Serbia
**For Publisher**: S. Anić, President of Society of Physical Chemists of Serbia
**Printed by**: "Jovan" Priting and Publishing Company; 200 Copies;
**Number of pages**: 6+ 441; **Format**: B5; Printing finished in September 2014.

**Text an Layout**: "Jovan"



200 - *Coppy priting*

PHYSICAL CHEMISTRY 2014

*12th International Conference on Fundamental and Applied Aspects of Physical Chemistry*

*Organized by*
*The Society of Physical Chemists of Serbia*

*in co-operation with_*

*Institute of Catalysis Bulgarian Academy of Sciences*

*Boreskov Institute of Catalysis of Siberian Branch of the Russian Academy of Sciences*

*Faculty of Physical Chemistry, University of Belgrade, Serbia*

*Institute of Chemistry Technology and Metallurgy, University of Belgrade, Serbia*

*Vinča Institute, University of Belgrade, Serbia*

*Institute of General and Physical Chemistry, Serbia*

*Faculty of Pharmacy, University of Belgrade, Serbia*

# Ag-PVA/CMC BLEND HYDROGEL NANOCOMPOSITE SYNTHESIZED BY γ-IRRADIATION FOLLOWED BY FREEZE/THAWING METHOD

J. Krstić*, J. Spasojević, A. Radosavljević,
N. Abazović, U. Jovanović and Z. Kačarević-Popović

*Vinča Institute of Nuclear Sciences, University of Belgrade, P.O. Box 522, 11001 Belgrade, Serbia (*jelenak@vinca.rs)*

## ABSTRACT

Poly(vinyl alcohol)/carboxymethyl-chitosan (PVA/CMC) blend hydrogels were synthesized by γ-radiolysis followed by freeze/thawing (FT). Previous, the water-solubility of chitosan (CS) was obtained by γ-radiolytic acidic degradation. CMC molecular weight characterization was performed by a Zetasizer. The fluorescence measurements confirmed the presence of CMC in the PVA/CMC blend hydrogels. *In situ* preparation of Ag nanoparticles (AgNPs) in PVA/CMC blend hydrogel matrices has been performed exposing hydrogels, swollen in $AgNO_3$ solution, to γ-irradiation. The mathematical models applied for determination swelling kinetics showed that the initial concentrations of CMC and AgNPs directly have influence on the swelling parameters of Ag-PVA/CMC nanocomposites. Diffusion characteristics, determined by different diffusion models (Early Time (ET), Late Time (LT) and Etters (E)) are less due to the presence of AgNPs.

## INTRODUCTION

Derivation of CS followed by graft modification (by alkyl or carboxymethyl groups), improve water solubility, antibacterial and antioxidant properties, without affecting its cationic character [1]. On the other hand, blending the CS with PVA improves tensile strength, flexibility, bulk and surface hydrophilicity. Therefore, combination of CMC with PVA as hydrogel blend stabilizer of AgNPs creates materials which will be useful in the range of applications [2].

In this investigation, AgNPs where synthesized *in situ* by γ-irradiation in previously obtained radiolytically crosslinked PVA/CMC blend hydrogel matrices followed by FT. The water-solubility of CS was obtained prior to crosslinking by radiolytic acidic degradation. The post irradiation FT procedure for the matrix preparation is performed in order to prevent dissolution of ungrafted CMC during *in situ* synthesis of AgNPs. Namely, at the lower concentrations, such as in the tested system, the grafting of CMC chains is likely process. The aim of this investigation was to examine the influence of AgNPs and the concentration of CMC on the optical properties, morphology, structure and the swelling behavior of thus obtained nanocomposite blend hydrogels.

## EXPERIMENTAL

1M acetic CS ($M_w$=94.8±8.74 kDa) solution (5% w/w) was γ-irradiated up to 100 kGy, to reduce molecular weight down to $M_w$=31.3±4.73 kDa. After neutralization with 1M NaOH, CMC molecular weight characterization was performed using a Zetasizer Nano ZS. The initial processing step in synthesis of Ag-PVA/CMC blend hydrogels was irradiation-induced crosslinking of PVA/CMC blend matrices (8%/2% w/w and 8%/4% w/w, samples S1 and S2 respectively) at a dose rate of 0.33 kGy/h up to an absorbed dose of 75 kGy, followed by FT up to 4 cycles. *In situ* synthesis of AgNPs in PVA/CMC was performed exposing samples (S1, S2) swollen in solution containing 8 mM $AgNO_3$ and 0.2 M 2-propanol (saturated with Ar) to γ-irradiation. The obtained nanocomposites were labeled as S3 and S4, respectively. Characterization of these systems was carried out by FTIR, fluorescence and UV-Vis spectroscopy, SEM and swelling measurements in water at 25 $^oC$. Swelling process was monitored gravimetrically by measuring weights of swollen hydrogel at predetermined time intervals ($t$), until the initial weights were equilibrated. The swelling degree is $SD=(W_t-W_0)\times 100/W_0$, where $W_t$ is weight of swollen hydrogel, and $W_0$ is the initial weight of the xerogel. Equilibrium swelling degree ($SD_{eq}$) was determined by getting the weight of hydrogel in equilibrium state ($W_{eq}$) instead the weight of swollen hydrogel in predetermined time intervals ($W_t$). The mathematical models (Power Law (PL), First-Order (FO) and Second-Order (SO)) were applied for determination of kinetics parameters of hydrogel swelling. For the initial stage ($SD/SD_{eq}\leq 0.6$), PL approach, $SD/SD_{eq}=kt^n$ ($k$ is the kinetic constant, $n$ is diffusion exponent) and FO equation, $SD/SD_{eq}=1-exp(-kt)$, were used. SO kinetics was used for extensive stage of swelling, $t/SD=A+Bt$, ($B=1/SD_{eq}$, $A=1/v_0$ is the reciprocal of the initial swelling rate). Diffusion coefficients ($D$) were determined by the models based on solutions of Fick's law, using three aproximations: ET (valid for the first 60% of sorption), LT (valid for the latter 40%), and E (valid for the whole range of swelling).

## RESULTS AND DISCUSSION

Figure 1(a) shows the FTIR spectra of CMC and the initial CS. The two peaks at 1593 $cm^{-1}$ and 1418 $cm^{-1}$ of CMC are the characteristic absorption bands of the carboxyl group ($v_{as}$ –$COO^-$ and $v_s$ –$COO^-$), which indicate that the carboxymethyl group is grafted onto the molecular chain of CS [3]. Figure 1(b) shows that PVA/CMC blend xerogel served as stabilizing agent for AgNPs. Decreasing in intensity and blue-shift of observed bands indicates possible formation of a coordination bond between AgNPs and –$COO^{-}$, –$NH_2$ and –OH groups in PVA/CMC matrix.

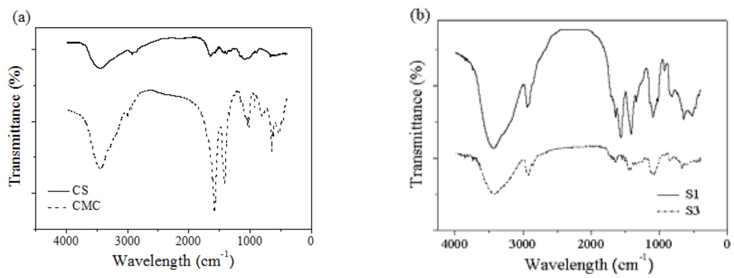


**Figure 1.** FTIR spectra of (a) pure CS and CMC, and (b) nanocomposite xerogel, S3, in comparing with pure S1 xerogel.

Fluorescence spectroscopy was employed to investigate the emission of crosslinked PVA/CMC blend after extraction in water (Figure 2(a)). Figure 2(b) shows UV-Vis spectra of Ag-PVA/CMC, experimentally obtained (solid line) and obtained by applying Mie theory (dashed line) [4]. AgNPs radii were determined by applying the computational analysis using the "MiePlot v.3.4" (http://www.philiplaven.com/mieplot.htm). In Figure 2(c) the micrographs of network (sample S4) and spherical particles (sample S3), obtained by scanning electron microscopy (SEM), are shown.

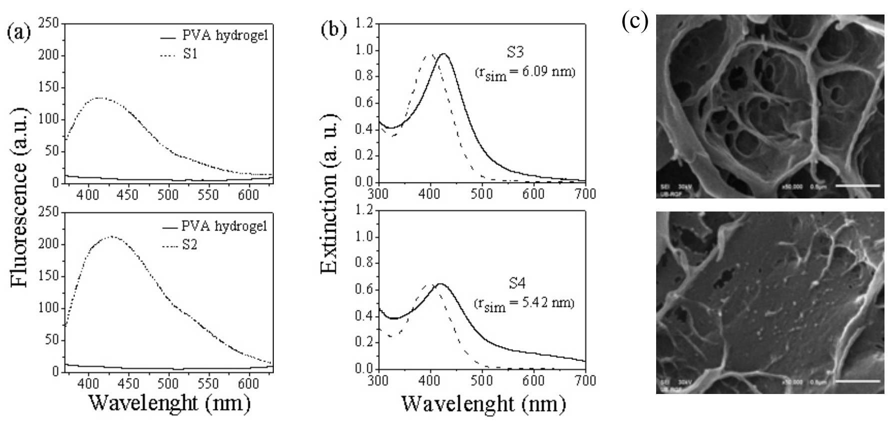


**Figure 2.** (a) Fluorescent spectra of PVA/CMC blend hydrogels; (b) UV-Vis spectra (solid line) and spectra obtained by applying Mie theory (dashed line); (c) SEM micrographs of S4 (up) and S3 (down).

The absorption of surrounding fluid by Ag-PVA/CMC blend hydrogel is affected by a simultaneous influence of the matrix and the presence of AgNPs. Doubly increasing of CMC concentration reduces swelling capacity. The water uptake in Ag-blend hydrogel increases comparing with pure PVA/CMC. At the initial stage of swelling, systems show Fickian diffusion ($n<0.5$) for all samples (S1-S4) [5], meaning that media transport is driven by a concentration gradient rather than by convective flux (not limited by polymer relaxation). The diffusion constants are less due to the presence of AgNPs. The kinetic parameters and diffusion constants are presented in Table 1.

**Table 1.** Kinetic parameters and diffusion constants.

| Sample | $SD_{eq}^{exp}$ | Power law kinetics | | First-order kinetics | | Second-order kinetics | | Early time | Late time | Etters model |
|---|---|---|---|---|---|---|---|---|---|---|
| | (%) | $k$ (1/h$^n$) | $n$ | $SD_{eq}$ (%) | $k_{FO}\times10^4$ (1/s) | $SD_{eq}$ (%) | $v_0$ (%/min) | $D\times10^7$ (cm$^2$/s) | $D\times10^7$ (cm$^2$/s) | $D\times10^7$ (cm$^2$/s) |
| S1 | 402±2 | 0.47 | 0.46 | 335 | 0.70 | 417 | 4.89 | 0.84 | 0.97 | 5.80 |
| S2 | 351±1 | 0.43 | 0.40 | 300 | 0.77 | 361 | 4.99 | 0.93 | 1.05 | 6.38 |
| S3 | 566±5 | 0.36 | 0.43 | 454 | 0.60 | 592 | 5.35 | 0.64 | 0.88 | 5.31 |
| S4 | 497±4 | 0.42 | 0.37 | 406 | 0.66 | 515 | 5.91 | 0.75 | 0.95 | 5.77 |

## CONCLUSION

Investigations show formation of a coordination bond between AgNPs and $-COO^-$, $-NH_2$ and $-OH$ groups of PVA/CMC matrix. Optical properties simultaneously depend on the concentration of CMC and on the presence of AgNPs. Swelling capacity decreases with increasing of CMC concentration, while the water uptake increases due to the presence of AgNPs. The media transport is driven by a concentration gradient (Fickian diffusion) while the diffusion constants are less due to the presence of AgNPs.

## ACKNOWLEDGEMENT

This work is financed by the Ministry of Education, Science and Technological Development of the Republic of Serbia (project III 45005) and International Atomic Energy Agency (IAEA), CRP: F22051/Contract No. 16733.

## REFERENCES

[1] W. S. Choi, et al., Polym. Degrad. Stabil., 2002, 78, 533–538.
[2] J. Krstić, et al., Rad. Phys. Chem., 2014, 96, 158-166.
[3] P. Liang, et al., J. Cryst. Growth., 2004, 261, 571-576.
[4] G.Mie, Ann. Phys., 1908, 25, 377–445.
[5] J. Krstić, et al., J. App. Polym. Sci., 2014, 131, 40321