



*Dedicated to Professor Valer Farcasan
on the occasion of his 95th anniversary*

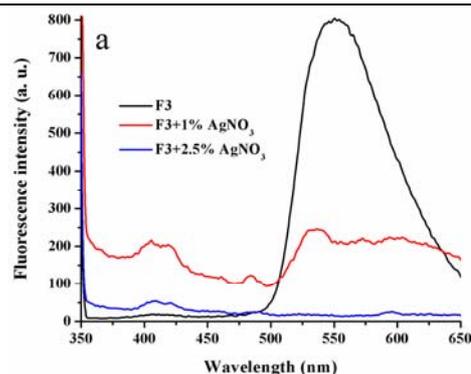
HYBRID POLYMER COMPOSITES CONTAINING SILVER NANOPARTICLES FOR (THERMO)PHOTOSENSITIVE COATING MATERIALS

Viorica E. PODASCA, Florentina JITARU and Emil C. BURUIANA *

“Petru Poni” Institute of Macromolecular Chemistry, 41 A Grigore Ghica Voda Alley, 700487, Iași, Roumania

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In the present paper, we report the preparation of hybrid composites based on (photo)thermosensitive monomers (N-isopropylacrylamide, N-methacryloyloxyethyl-N'-fluoresceinyl urea) besides other co-monomers and silver nanoparticles in situ photogenerated using Irgacure 819 as photoinitiator. Infrared spectroscopy monitors the evolution of the double bond conversion during the photoprocess, while photo-differential scanning calorimetry gave us information on the rate of polymerization and conversion. The photopolymerization rates of the formulations are in the range of $0.075\text{-}0.12\text{ s}^{-1}$, and the conversion degree after 3 min of UV irradiation is over 60%. The creation of the nanoparticles into a fluorescent polymer matrix has been confirmed with UV-vis and fluorescence spectroscopies, energy-dispersive X-ray spectroscopy analysis, and transmission electron microscopy (TEM), the absorption maxima originated from the resonance plasmon of silver nanoparticles being observed between 405 and 450 nm. A decrease of the fluorescence intensity was recorded due to the interaction between photopolymer and silver nanoparticles.



INTRODUCTION

In recent years, the concept of using light in the development of multifunctional materials with improved properties has attracted a great interest because their wide range of applications including nanotechnology.^{1,2} For this purpose acrylates, methacrylates, urethane monoacrylates and dimethacrylates with controlled functionality are among the most investigated structures, since the materials photocrosslinked in the presence of suitable photoinitiators find applications in the field of coatings,^{3,4} adhesives,⁵ microlithography,⁶ dental materials,^{7,8} tissue engineering,⁹ and many others.¹⁰⁻¹² One of the goals of polymer science is

to understand the contribution of each partner and role of the formed polymer for a given application, for which is useful knowing and correlating the structure, properties and kinetics of photoprocess that take place in such materials. For modern applications, the photochemistry of hybrid polymeric composites containing silver/gold nanoparticles open the possibility of preparation of new types of nanostructured materials with designed properties, which can be used in physical, biological, biomedical, and pharmaceutical applications.¹³⁻¹⁷

The objective of this research was the obtaining of hybrid polymer composites starting from *p*-acryloyloxybenzaldehyde (AcrBzA),

* Corresponding author: emilbur@icmpp.ro

N-isopropylacrylamide (NIPA) or poly(propylene glycol) dimethacrylate (PO-UDMA) and silver nanoparticle precursor followed by their characterization through specific methods (transmission electron microscopy (TEM), UV-vis spectra and energy-dispersive X-ray (EDX) spectroscopy analysis). It is expected that the introduction N-methacryloyloxyethyl-N'-fluoresceinyl urea into a formulation to affect the fluorescence properties of the final hybrid films.

RESULTS AND DISCUSSION

Synthesis and characterization

A series of hybrid composites were prepared by the free-radical photopolymerization of various acrylate monomers in the presence of silver salt, according to previously reported method by Sangermano and Yagci.¹⁸⁻²⁰ Thus, a mixture of *p*-acryloyloxybenzaldehyde (AcrBzA) and N-isopropylacrylamide (NIPA) or a new urethane dimethacrylate (PO-UDMA) along with metal precursor were chosen as initial components for the synthesis of hybrid composites (F1, F2) upon exposure to UV irradiation. Other two formulations (F3, F4) incorporating N-methacryloyloxyethyl-N'-fluoresceinyl urea (MA-FI) as a fluorescent co-monomer were also taken into account to investigate the effect of silver

nanoparticles on the fluorescence behavior of such hybrid composites. Polymerization of monomers using Irgacure 819 as the photoinitiator was carried out at room temperature in the presence of 1 wt% and 2.5 wt% AgNO₃. The structures of monomers used in our study and the formulation composition are given in Fig. 1, and Table 1, respectively. It should be noted that for the urethane dimethacrylate synthesized from poly(propylene glycol) and 2-isocyanatoethyl methacrylate the spectral data confirmed the expected structure (see experimental section for details).

Photopolymerization study

To evaluate the photoreactivity of acrylate monomers, the conversion kinetics of polymerization was evaluated by FTIR spectroscopy. Fig. 2 presents the spectral changes that occur in the infrared spectra of the formulation F2 composed of AcrBzA (80 wt.%) and PO-UDMA (20 wt.%) to UV irradiation, observing that the stretching vibration of polymerizable C=C double bond at 1638 cm⁻¹ decreases gradually with increasing irradiation time. The conversion of the double bond attained after 100 seconds of irradiation of F2 is 69%, while in the F1 formulation (AcrBzA:NIPA, 20:80 wt.%) conversion was of 98%.

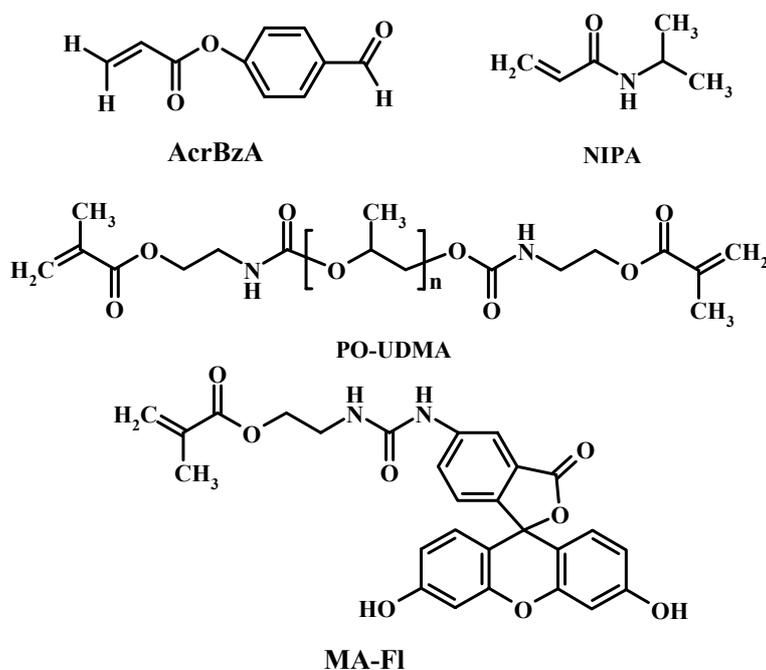


Fig. 1 – Structure of acryloyloxybenzaldehyde (AcrBzA), N-isopropylacrylamide (NIPA), poly(propylene glycol) dimethacrylate (PO-UDMA) and N-methacryloyloxyethyl-N'-fluoresceinyl urea (MA-FI) monomers.

Table 1
Composition of the formulations used in photopolymerization reactions

Sample	AcrBzA (wt%)	NIPA (wt%)	MA-FI (wt%)	PO-UDMA (wt%)
F1	20	80	-	-
F1+1% AgNO ₃	20	80	-	-
F1+2.5% AgNO ₃	20	80	-	-
F2	80	-	-	20
F2+1% AgNO ₃	80	-	-	20
F2+2.5% AgNO ₃	80	-	-	20
F3	15	55	30	-
F3+1% AgNO ₃	15	55	30	-
F3+2.5% AgNO ₃	15	55	30	-
F4	55	-	30	15
F4+1% AgNO ₃	55	-	30	15
F4+2.5% AgNO ₃	55	-	30	15

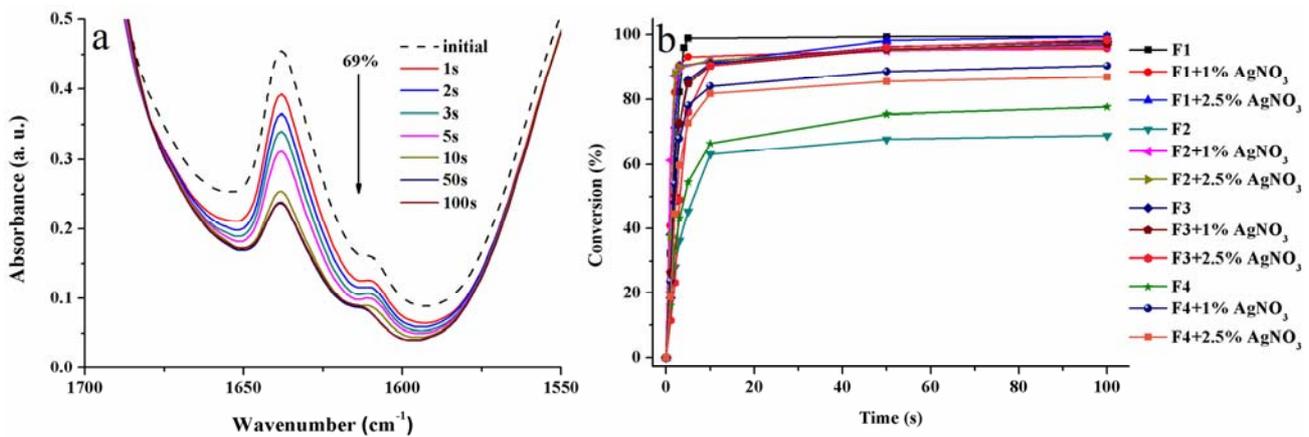


Fig. 2 – Evolution of the absorption band characteristic to the double bond from F2 (a) and the conversion evolution for monomer mixtures monitored in the FTIR spectra as a function of UV irradiation time (b).

Comparison of the kinetic parameters of the formulations with 1 wt.% AgNO₃ or 2.5 wt.% AgNO₃ shows that the photopolymerization process and reduction of silver salt induced by UV light depend on the formulation composition and the monomer structure (Fig. 2b), but in all cases the conversion degree is over 69%.

In connection, the time to achieve the maximum heat of polymerization, the degree of double bond conversion and the rate of polymerization were determined by photoDSC. As can be seen in Fig. 3a–b all formulations exhibited fast photopolymerization response (0.075–0.12 s⁻¹) reaching the highest polymerization rate in about 7 s of UV irradiation.

When F1 contains different amounts of metal precursor (F1+1% AgNO₃, polymerization rate: 0.086 s⁻¹; F1+2.5% AgNO₃, polymerization rate: 0.11 s⁻¹) the photopolymerization rate decreases compared to the formulation without the metal salt

in the system (F1, polymerization rate: 0.12 s⁻¹). Surprisingly is the fact that F2+1% AgNO₃ (polymerization rate: 0.097 s⁻¹) and F2+2.5% AgNO₃ (polymerization rate: 0.105 s⁻¹) presented a slight increase in the rate of photopolymerization (F2, polymerization rate: 0.075 s⁻¹), most probably due to the composition effect and crosslinking oligodimethacrylate PO-UDMA.

The degree of conversion (DC) determined after 3 min of UV irradiation is represented in Fig. 3 inset, and provides information on whether conversion is affected by silver salt. Indeed, F1+1% AgNO₃ achieved a DC value of 73% and on increasing the AgNO₃ content to 2.5%, the DC turn out to be lower (60%). A similar trend in the conversion evolution has been observed in the case of F2+1% AgNO₃ (82%) that indicates a higher DC than that of F2+2.5% AgNO₃ (73%) and pure F2 (80%).

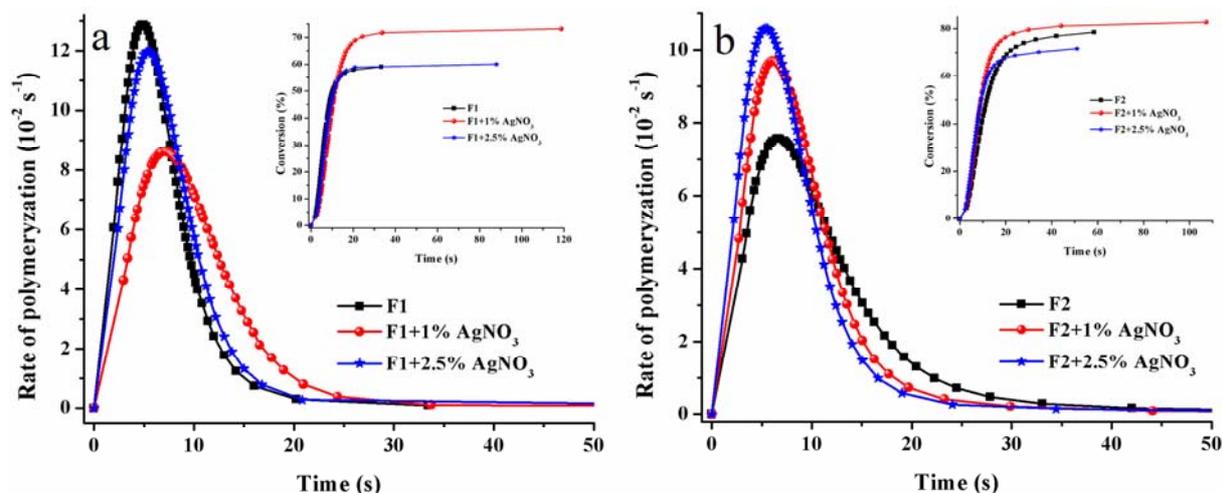


Fig. 3 – PhotoDSC rate profiles for the formulations F1 (a) and F2 (b) with and without Ag salt (inset double bond conversion with UV irradiation time).

Formation and distribution of nanoparticles

Reduction of silver ions and in situ formation of Ag nanoparticles (NPs) were confirmed by the UV-Vis spectroscopy, fluorescence and energy-dispersive X-ray (EDX) spectroscopy analysis, and transmission electron microscopy (TEM). Following the photopolymerization process of the monomers in the presence of silver nanoparticle precursors (F1+2.5% AgNO_3) through UV-Vis spectroscopy, the appearance of the surface plasmon band around 409 nm (after 500 seconds of irradiation) under the adopted experimental conditions (Fig. 4a) is noticeable. From the UV-Vis absorption spectra registered for formulation F3+2.5% AgNO_3 (Fig. 4b) the addition of the fluorescent monomer like N-methacryloyloxyethyl-N'-fluoresceinyl urea (MA-FI) before photopolymerization, led to a plasmonic

band shifted towards red, associated with the silver nanoparticles photogenerated in the organic matrix containing fluorescein molecules. It should be noted that the absorption peak at 447 nm for the formulation F3+2.5% AgNO_3 is narrower than that for F1+2.5% AgNO_3 .

Similar results have also been found in the formulations containing both monomers and 1 wt% AgNO_3 (Fig. 5a-c). Therefore, the formation of silver nanoparticles occurs more rapidly in systems where there is the fluorescent monomer than in the rest of the formulations. From this point of view, the absorption maxima originated from the resonance plasmon of silver nanoparticles were observed at 405 nm (F1+1% AgNO_3), 446 nm (F2+1% AgNO_3 and F3+1% AgNO_3) and at 450 nm (F4+1% AgNO_3).

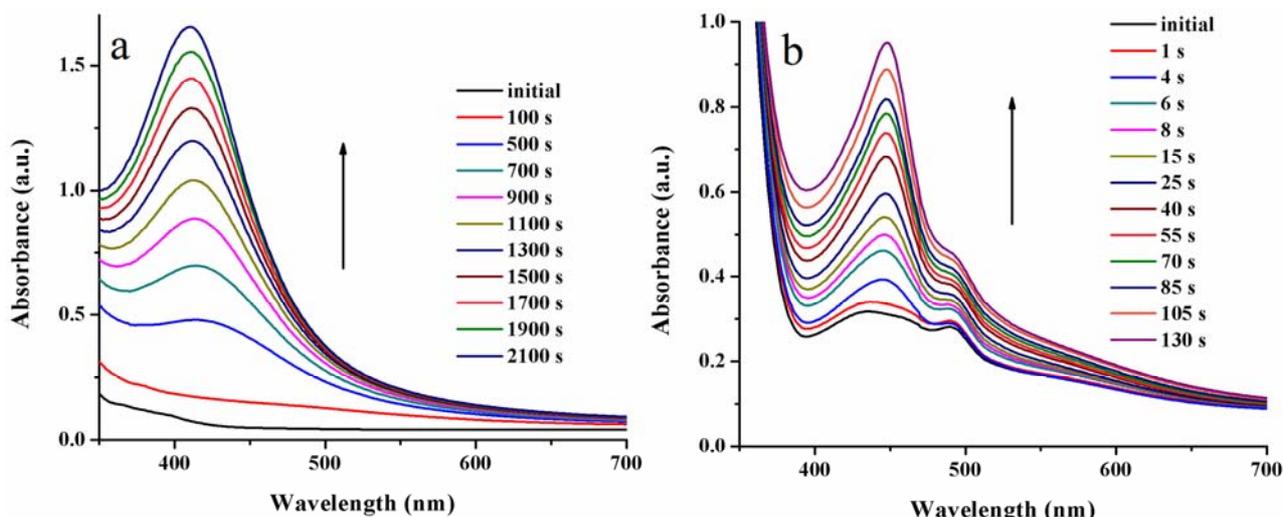


Fig. 4 – The UV-Vis spectra for the absorption monitored at different irradiation time for the formulations F1+2.5% AgNO_3 (a) and F3+2.5% AgNO_3 (b).

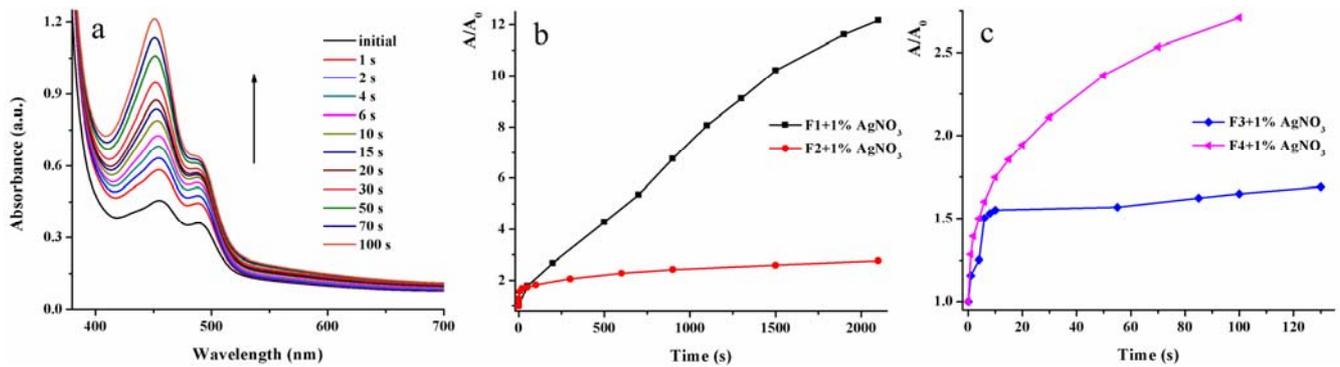


Fig. 5 – The UV–vis spectra for F4+1% AgNO₃ (a) and increase of the absorption monitored at different irradiation time for formulations F1–F4 with 1% AgNO₃ (b, c).

EDX and TEM analysis

Elemental and spatial distribution of the silver atoms formed within the photopolymerizable matrix was investigated by energy dispersive X-ray spectroscopy (EDX). In the resulting EDX pattern (Fig. 6), the existence of characteristic peaks for C, O, N, and Ag elements are visible, demonstrating that the silver nanoparticles were prepared by one-pot process. Besides, a uniform distribution of the atoms inside the polymer matrix is suggested in the EDX images of the films (Fig. 6a and 6b).

The size, distribution and shape of the silver nanoparticles into the organic matrix were further characterized by transmission electron microscopy (TEM), the typical TEM image of these nanoparticles derived from formulation F1+2.5% AgNO₃ is illustrated in Fig. 7. As can be seen from Fig. 7a, the silver NPs have spherical shape, interspersed with larger particles. In addition, the particle-size-distribution histogram of the silver NPs (Fig. 7b) confirms that the majority of the particles have sizes between 5 and 15 nm, the

generation of aggregates coming from silver nanoparticles aggregation.

Fluorescence study

When the F3 and F4 films are excited with a wavelength of 340 nm, it seems that the fluorescence intensity decreases due to specific interaction between the silver nanoparticles and photopolymer (Fig. 8). Further increase of the silver salt content in the photopolymerizable matrix subjected to UV light leads to a decrease of the fluorescence intensity. For instance, in the case of F3+2.5% AgNO₃, the fluorescence is quenched almost entirely, while the fluorescence intensity of the F4+2.5% AgNO₃ film is reduced by 75%. This difference in behavior of the quenching of fluorescence emitted by fluorescein molecules from the hybrid film could be caused by the nature of the polymer network achieved by including the PO-UDMA urethane dimethacrylate in the formulation F4, where the excited species have a diminished mobility.

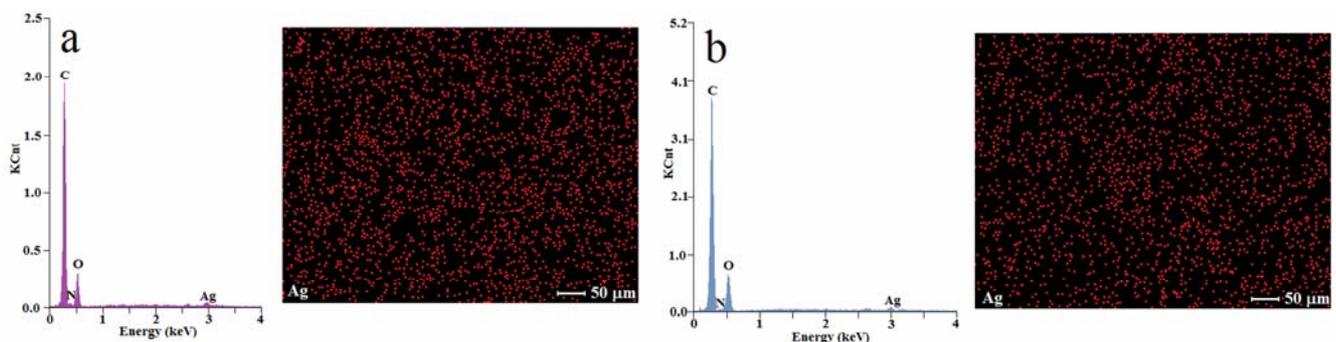


Fig. 6 – The EDX analysis results and the mapping images for silver atoms from F1+2.5% AgNO₃ (a) and F2+2.5% AgNO₃ (b) films.

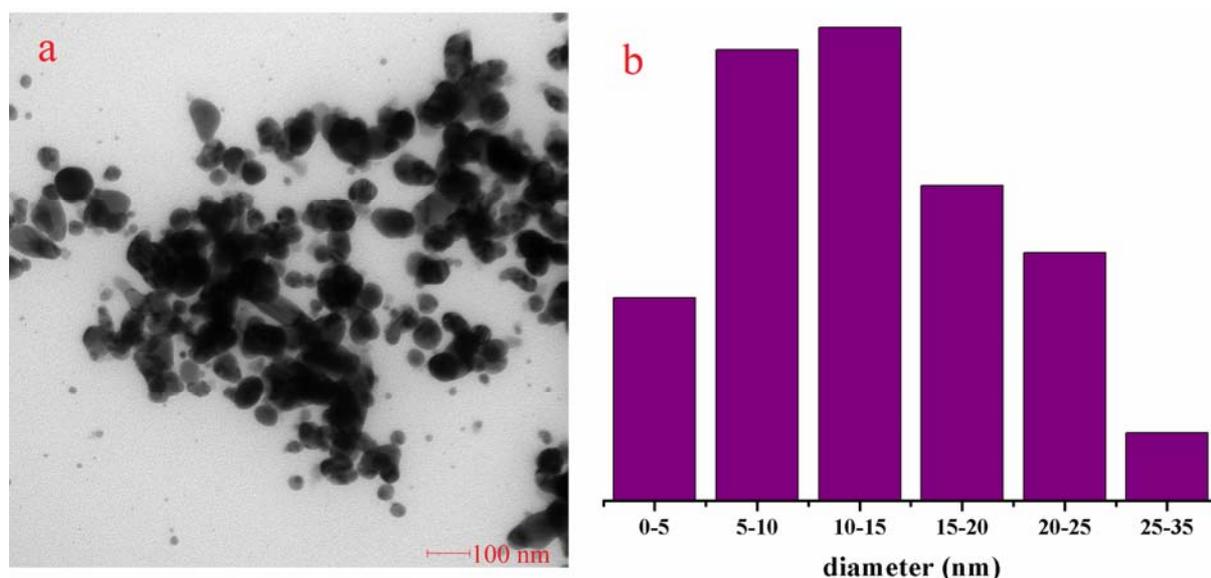


Fig. 7 – TEM image (a) and statistical size distribution (b) of the silver nanoparticles into F1+2.5% AgNO₃ formulation.

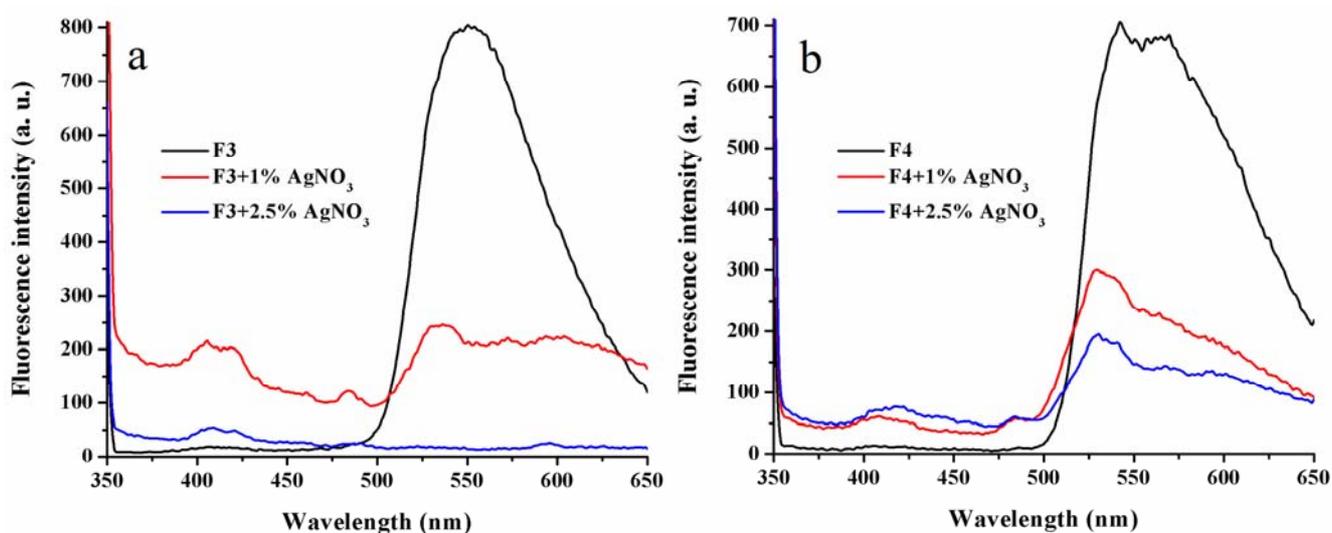


Fig. 8 – Fluorescence spectra for F3 (a) and F4 (b) films with and without silver nanoparticles.

However, considering the macromolecular characteristics, the use of N-isopropylacrylamide as co-monomer led to hybrid polymer films whose antimicrobial and thermosensitive potential follows to be investigated in a further study.

EXPERIMENTAL

Materials. Poly(propylene glycol) ($M_n = 1000$), 2-isocyanatoethyl methacrylate, dibutyltin dilaurat, N-isopropylacrylamide (NIPA), phenyl-bis(2,4,6-trimethylbenzoyl) phosphine oxide (Irgacure 819), silver nitrate (AgNO₃), deuterated chloroform (CDCl₃), tetrahydrofuran (THF), were used as received (Aldrich).

The monomers AcrBzA and MA-F1 used in this work were synthesized according to the procedure reported in literature.²¹

Synthesis of poly(propylene glycol) dimethacrylate (PO-UDMA): in a 50 mL three necked round bottomed flask fitted with a mechanical stirrer 4 g (4 mmol) of poly(propylene glycol) and 1.15 mL (8 mmol) of 2-isocyanatoethyl methacrylate were dissolved in 10 mL anhydrous THF, using dibutyltin dilaurat as catalyst. The reaction was followed through the infrared absorption of the isocyanate stretching band ($\sim 2260\text{ cm}^{-1}$) up to its disappearance. The reaction mixture was stirred at 38 °C for 24 hours, and then the solvent removed using a rotary vacuum evaporator.

¹H NMR in CDCl₃ (δ , ppm): 6.12 and 5.59 (H from H₂C=), 4.92(COOCH), 4.21 (-CH₂-OCO), 3.55 and 3.41 (-CH₂-OCONH), 1.94, 1.24 and 1.13 (CH₃-). ¹³C NMR in CDCl₃ (δ , ppm): 167.33 and 156.27 (-C=O), 136.13 (-C=CH₂), 126.04

(=CH₂), 75.64 and 70.72 (-CH-OCONH), 73.49 and 72.03 (-CH₂-OCO), 63.89 (-CH₂-NH), 40.16 (-CH₂-OCOC), 18.39 and 17.44 (CH₃-). FTIR (KBr, cm⁻¹): 3359 (urethane NH), 2972-2871 (-CH₂-), 1721 (carbonyl C=O), 1532 (amide II), 1638 and 815 (C=C), 1454 (CH₂-CO), 1297 (COO).

Measurements. The structure of all synthesized derivatives was verified by FTIR, ¹H NMR, ¹³C NMR, UV-vis and fluorescence spectroscopies. ¹H (¹³C) NMR and FTIR spectra were recorded on a Bruker 400MHz spectrometer at room temperature, and on Bruker Vertex 70 spectrometer, respectively. The UV-vis absorption spectra were measured with a Specord 200 spectrophotometer in film state. The fluorescence measurements were achieved with a Perkin-Elmer LS 55 spectrophotometer. The irradiations of the films containing 1 or 2.5 wt.% silver salt were carried out using UV light with intensity of 50 mW/cm² generated by a Hg-Xe lamp (Hamamatsu Lightningcure Type LC58, Model L9588). Differential scanning photocalorimetry studies were performed on a DuPont 930 apparatus with a double heat differential calorimeter 912. A standard high pressure mercury lamp with 4.5 mW/cm² light intensity (inserted in device) was used to irradiate the samples (1.5 ± 0.5 mg) in the presence of 1.5 wt.% Irgacure 819 as the initiator, using DSC DuPont standard pans. The measurements were performed in an isothermal mode under the ambient atmosphere, and irradiation started after 1 min of equilibration. A computer-controlled isothermal method was employed to determine the kinetic parameters (the time to reach the maximum polymerization heat (t_{max}), double bond conversion and rate of polymerization). TEM measurements were carried out at 100 kV using a Hitachi High-Tech HT7700 instrument. Microscopic investigations were performed on an environmental scanning electron microscope QUANTA200 coupled with an energy dispersive X-ray spectroscopy (ESEM/EDX).

CONCLUSIONS

A new urethane dimethacrylate macromer (PO-UDMA) has been synthesized and used along with AcrBzA, MA-FI or NIPA in the presence of a noble metal precursor (1% and 2.5% AgNO₃) to form hybrid nanocomposites with in situ created silver nanoparticles during photopolymerization. The existence of silver nanoparticles in the polymer matrix has been evidenced by UV-vis, energy-dispersive X-ray (EDX) spectroscopy analysis, and transmission electron microscopy (TEM). The silver nanoparticles embedded in the polymer matrix have as effect a fluorescence quenching, which suggests the use of these materials as biological sensors and in optoelectronics.

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