A.L. TOLSTOV,
Institute of Macromolecular Chemistry NAS of Ukraine, 48, Kharkivske shose, Kyiv, 02160, Ukraine,
E-mail: a.tolstov@ukr.net
ORCID: 0000-0001-6016-9308

V.F. MATYUSHOV,
Institute of Macromolecular Chemistry NAS of Ukraine, 48, Kharkivske shose, Kyiv, 02160, Ukraine,
ORCID: 0000-0002-0524-5862

E.V. LEBEDEV,
Institute of Macromolecular Chemistry NAS of Ukraine, 48, Kharkivske shose, Kyiv, 02160, Ukraine,
ORCID: 0000-0002-5674-5306

D.A. KLIMCHUK,
N.G. Kholodny Institute of Botany NAS of Ukraine, 2, Tereshchenkivska str., Kyiv, 01601, Ukraine,
ORCID: 0000-0002-7076-8213

FORMATION AND CHARACTERIZATION OF SILVER-CONTAINING COMPOSITES BASED ON IONOMERIC POLY(URETHANE-ACRYLATE)S PREPARED VIA DIFFUSION/SORPTION APPROACH

Silver containing composites were prepared via diffusion/sorption of silver ions into previously synthesized functionalized poly(urethane-acrylate) matrices. The peculiarities of coordination of Ag+ ions by carboxylate groups of the polymer chains followed by its reduction was observed by FTIR, UV-vis, SEM and lyophilicity measurements. Interactions between silver moieties and the functionalities of polymer matrices were identified by spectral studies. A high-temperature shift of relaxation transition temperature of PPO segments of silver-containing polymers in accordance with DMA studies is an additional evidence of coordination of different forms of silver (ions, clusters etc) by helix oligoether structures. The conditions of sorption process as well as chemical structure of the matrices and reactivity of Ag+ ions provide a transformation of ionic silver into reduced metal moieties and its immobilization within surface layer of polymer matrices as nano- and submicron size aggregates. Nanoparticulate silver even in aggregated form demonstrates a strong surface plasmonic resonance with a maximum position depends on functionality of the matrix (mainly near 400 and 500 nm).

Keywords: polyurethane, acrylics, ionomers, silver, composite, interaction, structure, properties.

Introduction

Polyurethanes and acrylic polymers of various structure attract a great attention of scientists and industrial engineers for a long time because of their valuable characteristics for medicine, optical materials and specific adhesives for wide and specific modern applications [1, 2]. Generally a combining polyurethane and acrylics into poly(urethane-acrylate)s (PUA) copolymers provides a exceptional biocompatibility, enhanced optical characteristics, controlled lyophilicity of new materials obtained. Today commercially available poly(urethane-acrylate)s are successfully used as preservation layers [3], functional coatings [4], carriers for drug delivery [5], contact lens [6] etc. Additional introducing silver

A.L. Tolstov, V.F. Matyushov, E.V. Lebedev, D.A. Klimchuk

(ions, nanoparticles) into PUA materials imparts to the composites a high conductivity, plasmonic characteristics and high bactericidal activity of the composites [7]. Recently a producing of bactericidal materials was successfully combined with inkjet printing technology for elaboration of high performance silver-based nanocomposites for medical application [8]. An idea of using silver nanoparticles/thermoresponsive acrylic polymer core-shell nanohybrids with enhanced plasmonic, luminescent and volume thermoresponsive properties as potential biomedical platform for advanced materials engineering has been demonstrated in novel studies [9]. Ex-situ hybridization approach applied for silver nanostructures and conjugated polymer provides highly selective sensor activity towards to gaseous compounds of different nature [10].

Thus the aim of the present work is a preparation of silver-containing PUA composites by cost-effective sorption approach, detailed characterization of the materials obtained to evaluate their exploitation properties.

Experimental

Materials.
Poly(propylene oxide) (PPO) of different molecular weights (Mw = 2000 for dihydroxy- and Mw = 5000 for trihydroxy-terminated polyethers, which were identified as PPO2000 and PPO5000, correspondingly) were taken as polyether constituent. Commercially available tolylene diisocyanate (TDI), as a mixture of 2,4-/2,6-isomers with a weight ratio of 80/20, and hexamethylene-1,6-diisocyanate (HMDI) were used as isocyanate component. 2-Hydroxyethyl methacrylate (HEMA), acrylic acid (AA) and methyl methacrylate (MMA) monomers were purchased from Aldrich Chemicals. All reagents were purified accordingly to pre-synthesis protocols (drying, distillation etc). Silver nitrate (AgNO$_3$) was used as received.

Synthesis of acrylic-terminated oligourethanes (OUA).
Oligourethanes of different molecular structure with terminal acrylic functionalities (OUA) have been synthesized accordingly to conventional polyaddition procedure from polyether (PPO2000 or PPO5000), diisocyanate (TDI or HMDI) and acrylic (HEMA) constituents. The molar ratio of NCO/OH was 1/1 for all compositions. A composition of as-synthesized OUAs is showed in Table 1.

Synthesis of ionomeric poly(urethane-acrylate) (PUA) networks.
Functionalized poly(urethane-acrylate) matrices were synthesized from a mixture of OUA, MMA and AA by UV-induced photopolymerization procedure [11] and the polymer film samples with a thickness of 500±50 mm were produced. The OUA content for all compositions was taken as 60 wt%. A ratio of acrylic monomers in PUA recipes was taken as 40 wt%. Differentiation of a structure of polymer networks was performed by a shape of OUA macromolecules: linear (lPUA) and branched (bPUA). Detailed composition of PUA matrices was summarized in Table 1. Using AA as a comonomer in the composition of polymer matrices provides a presence of free pendant COOH groups along the macrochains for efficient complexation of ionic silver (Ag$^+$) and strong attachment of nanoparticulate silver moieties to the PUA networks. Non-ionogenic COOH-free PUA network was also prepared and tested.

Preparation of Ag-containing PUAs.
For preparation of silver-containing metal-polymer hybrids a diffusion/sorption approach has been applied. PUA films were dipped into 0.01 M aqueous AgNO$_3$ solution till an equilibrium sorption state achieved. A process of a saturation of polymers by Ag$^+$ ions was continuously controlled by measuring of silver content in an eluent. When an equilibrium is reached the swelled polymer composite films were

Table 1. **Recipes of polymer matrices**

Polymer matrix	PUA composition, wt%						
	OUA composition, wt%					MMA	AA
	PPO^{2000}	PPO^{5000}	TDI	HMDI	HEMA		
lPUA-1	51,7	-	6,0	-	2,3	40,0	-
lPUA-2	51,7	-	6,0	-	2,3	30,0	10,0
lPUA-3	46,0	-	8,0	-	6,0	30,0	10,0
bPUA-4	-	53,7	-	4,2	2,1	30,0	10,0

taken out, thoroughly washed with distilled water and dried in the dark conditions at ambient temperature for 12 hrs followed by drying at elevated temperature (60 °C) for 5 hrs to a constant weight. Drying procedure provides a completion of Ag^+-matrix complex formation reactions and partial autocatalytic transformation of Ag^+ into silver clusters and nanoparticles moieties.

Characterization techniques.

Chemical changes in the composites synthesized were observed by FTIR spectroscopy using Bruker TensorTM 37 FTIR analyzer in the spectral region of 4000–600 cm⁻¹. For characterization of heterogeneous structure and morphology of the composites a JEOL JSM 6060 LA Scanning Electron Microscope (accelerating voltage of 30 kV) was used. Before testing the samples were sputtered with gold film of 5–10 nm thickness. Morphology analysis was accompanied with Energy Dispersive X-ray Scattering analysis for quantitative determination of the elements in composite samples. Lyophilicity of neat and silver-containing PUAs films was measured by both water sorption behavior and contact angle measurements. Kinetics of water sorption process was observed gravimetrically. Contact angle determination was occurred using horizontal optical microscope scheme and a volume of water drop of 40 mL. Dynamic mechanical testing was performed using Q800 DMA analyzer at a tensile mode in a temperature range of −100 … +200 °C and a heating/cooling rate of 20 °C per minute. UV-vis spectrometry studies of thin films were carried out using ULAB 108UV spectrometer in a spectral region of 300–700 nm.

Results and Discussion

Polyurethane materials are widely used for many applications due to enhanced exploitation characteristics – high mechanical strength, stability, biocompatibility etc. Introducing active additives into the polymers attaches them other valuable properties, as antimicrobial and optical activity, transport properties. Producing silver-containing polymer composites by diffusion/sorption process is a very efficient approach from economical as well as exploitation viewpoints. It provides an appropriate distribution of active constituent mainly in a surface layer of the polymer matrix and prevents an inefficient distribution of silver in a bulk of composite materials. For these purposes we have used aqueous $AgNO_3$ solution for introducing Ag+ ions into a surface layer of the composites. Reactivity of ionic silver (coordinating and oxidative ability) and chemical nature of PUA matrix (electron donor functionality efficiently coordinates mono- and polyvalent metal ions) may result in partial reducing Ag^+ ions to metallic nanostructures and their efficient immobilization in surface layer of functionalized matrix followed by formation of metal-containing nanostructurized polymer systems.

Swelling behavior

Lyophilicity of the polymer matrix and the nanocomposites was evaluated by water uptake experiments for demonstration of peculiarities of structural changes while the composites form (Table 2). As it could be seen COOH-free network is characterized by lowest water uptake (2.5 %) and hydrophilicity. Other polymer matrices demonstrate better water sorption ability and the water uptake values reach

Table 2. **Characteristics of neat and silver-containing PUAs**

Sample	DMA			UV-vis		SEM/EDX		Water uptake, %	Contact angle Θ,
	T_{g1},	T_{g2},	T_{g3},	λ_{max1},	λ_{max2},	d,	$C_{Ag-surf}$,		
	°C	°C	°C	nm	nm	μm	wt%		degree
lPUA-1	−78,2	−29,8	-	-	-	-	-	2,5	71
lPUA-1^Ag	−75,8	−30,3	-	-	425	0,95	8,1	3,1	66
lPUA-2	−73,1	−24,1	−8,7	-	-	-	-	7,6	74
lPUA-2^Ag	−71,3	−23,9	−4,2	390	492	0,71	11,6	10,4	57
lPUA-3	−69,9	−19,9	−8,7	-	-	-	-	7,0	84
lPUA-3^Ag	−66,6	−22,0	−5,4	398	520	0,74	12,0	8,5	52
bPUA-4	−76,6	−29,9	−16,5	-	-	-	-	14,0	71
bPUA-4^Ag	−78,7	−31,8	−14,9	379	493	0,66	16,4	14,1	54
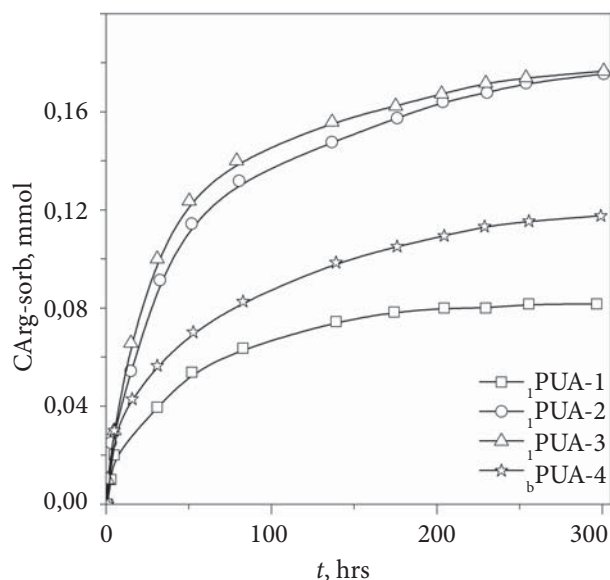
Figure 1. Kinetics of Ag+ ion sorption by PUA film samples

Figure 2. Fourier-Transformed IR spectra of neat lPUA-2 (1) and lPUA-2Ag composite (2) samples

7–14 % (depend on its chemical structure and functionality). Introducing Ag^+ ions increases hydrophilicity of the networks by 24–36 % due to introducing inorganic constituent of ionic nature (Ag+ cations, NO_3^- counterions) into polymer matrices. Minor difference in lyophilicity of neat and Ag-containing bPUA-4 samples is observed due to disordered macromolecular structure of the matrix synthesized from branched OUA macromolecules and, as a result, introducing ionic component has no noticeable impact on water uptake behavior of the composite.

Ag⁺ sorption kinetics.

Ag-containing PUA composites as it mentioned above were prepared by diffusion/sorption approach and Ag^+ ions sorption kinetic curves for all PUAs films are shown in Fig. 1. COOH-free PUA film (lPUA-1) demonstrates low Ag+ sorption capacity because of lowest content of coordination active sites in macrochains of the matrix. Intermediate sorption ability was observed for bPUA-4 matrix because of higher content of coordination sites but disordered structure of coordination active oligoether chains. lPUA-2 and lPUA-3 polymer networks are characterized by maximum sorption capacity due to simultaneous combination of many factors: (i) presence of anionic COO– sites highly reactive against cations, (ii) enhanced segmental mobility of linear oligoether chains and (iii) ordering of TDI bonded neighbor oligoether fragments of PUA macrochains to helix structures with high coordination ability to monovalent ions [12]. Other electron donor groups of all
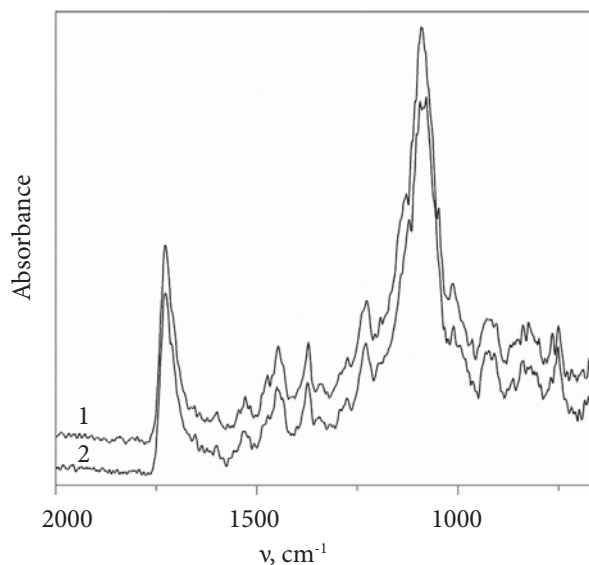
PUAs contribute similar coordination activity in overall silver uptake values.

EDX analysis.

The results of element analysis (Table 2) clearly reflect a reactivity of polymer matrices against oxidizing Ag+ ions. Accordingly to EDX scattering results the composites are characterized by moderate silver surface content with tendency to growing for higher reactive matrices. Less coordination active polymer network (lPUA-1) demonstrates lower Ag content in a surface layer. Otherwise, a highest silver content for bPUA-4Ag composite may explained by combination of both coordination and reducing ability of the matrix and increased free volume of the matrix (see Swelling behavior) due to branched disordered structure of OUA macrochains. Relatively high silver content at a surface layer of both lPUA-2Ag and lPUA-3Ag composites reflect enhanced segmental mobility of oligoether fragments, formation of coordination active helix structures and reducing activity of PUA matrices.

FTIR.

The spectral characteristics of all PUA compositions are very similar because of similarity of chemical composition. To demonstrate the peculiarities of a formation of the metal-polymer composites the FTIR spectra of neat lPUA-2 and its silver-containing system (lPUA-2Ag) are shown in Fig. 2 and analyzed in details. FTIR spectrum of lPUA-2 has characteristic bands of typical poly(urethane-acrylates). Namely, the most characteristic vibration bands are

C=O stretching vibrations at a region of 1750–1650 cm^{-1} (esters at 1728 cm^{-1}, COOH groups at 1709 cm^{-1}, urethanes at 1695–1680 cm^{-1}), C–O–C vibration bands of oligoether fragments at 1250–1000 cm^{-1}, and other less informative absorbance bands (C–H, C=C, N–H functions). Formation of Ag-containing PUA systems resulted in reducing integral intensities of some bands (C=O, C–O–C) and splitting an initially monomodal peaks to the few maxima. The C=O bands of acrylic esters at 1728 cm^{-1} split to two 1728 and 1721 cm^{-1} band. The C=O of COOH groups splits to 1709 and 1713 cm^{-1} bands. The C–O–C band at 1089 cm^{-1} splits to the bands at 1094 and 1086 cm^{-1}. These transformations are usually initiated by interactions between Ag$^+$ ions (or nanoparticles) and electron-donating functionality of PUA matrix. The facts of interactions were observed for C=O groups of acrylic esters and urethane functions, as well as carboxyl functionality of PUA. In regard to oxyalkylene groups the oligoether macrochains are able to create crown-like helix structures which coordinate Ag$^+$ ions or envelop silver nanostructures (clusters or nanoparticles). These interactions provide a shift of vibration frequencies of chemical bonds as a result of a redistribution of electron density of corresponding functional groups of the matrix.

SEM.

Morphology of the metal-containing composites was studied by SEM and quantitative analysis of heterogeneity level at the surface layer of polymer composites obtained was summarized in Table 2. A surface of all compositions is characterized by a presence of polydispersed silver structures of 0.66–0.95 μm in size with macroscale non-uniform distribution on a surface layer. Largest particles size was observed for compositions with carboxyl-free PUA matrix, whereas functionalized PUAs demonstrate remarkably smaller silver particle aggregates. Note, that determined sizes of silver structures are non-typical for functionalized PUA matrices, however moderate reducing activity of polymer macrochains activates a formation of silver nanoparticles and their partial aggregation at a surface layer of PUA film samples to submicron metal structures. A conventional size of silver nanoparticles synthesized within the polyurethane matrices is in the range of 20–70 nm with a primary crystallites size of 10–15 nm [12].

Contact angle measurements.

Processes of diffusion, sorption and coordination of Ag$^+$ ions by the PUA matrices improve a hydro-philicity of the composites due to additional sorption of by-products mainly of ionic nature (counter-ions). As a result, contact angle values of metal based compositions decrease from 71–84 to 52–66° (Table 2). Enhanced hydrophilicity of composite samples may provide fast elimination of active components (ionic or nanoparticulate silver) to external aqueous media (including biological ones) during its practical uses and broaden the application areas for nanosilver based composites.

DMA.

Sorption of Ag$^+$ ions by the PUA matrices affect on molecular mobility of polymer macrochains as it clearly seen from the results of dynamic mechanical spectroscopy (Table 2). The PUA matrices (except of non-carboxylated lPUA-1) are characterized by three glass transitions at a temperature range of –78...–70 °C (T_{g1}; relaxation of PPO segments), –30...–20 °C (T_{g2}) and –16...–4 °C (T_{g3}) – both correspond to relaxation transitions of mixed phases consist of urethane and acrylic constituents.

When the ionic silver absorb by polymer matrix and metal-containing composites form the T_g values undergo an appropriate changes. As it was observed a shift of T_{g1} of lPUAs matrices to higher temperatures by 2–3 °C is observed because of coordination of Ag+ ions by helix structures of PPO chains as well as interactions between polar oxyethylene units of PPO with a surface of silver nanostructures. Oppositely, T_{g1} of bPUA-4 shifts to lower temperature region by 2 °C due to low coordination ability of branched PPO macrochains as a result of partially disordered structure of oligoether. Irregular changes in T_{g2} and T_{g3} behavior demonstrate a a substantial differences in interaction energy between silver moieties (ions, nanoparticles) and electron donor functional groups (carboxylate, urethane, ester) of PUAs matrices.

UV-vis

A character of interaction between silver moieties and PUAs matrices was studied by UV-vis spectral analysis of metal-containing systems (Table 2). The Ag-containing composite systems are characterized by two maxima of surface plasmonic resonance (SPR) of silver nanostructures. The first one at the spectral region of 380–400 nm corresponds to SPR of silver nanostructures interacted with COOH functionalities of PUA macrochains [13]. The second SPR maximum positioned above 420 nm is typically due to dipole-dipole interactions between (nano)silver and electron donor groups of PUAs macrochains having lower (compared to COOH

functionality) stabilizing activity against metal nanoparticles (hydroxyls, urethanes, esters, amides etc).

Conclusions

The new silver-containing polymer materials were manufactured by diffusion/sorption approach. Diffusion of Ag⁺ ions into poly(urethane-acrylate) matrix contained 40 wt% of acrylics results in coordination of inorganic ionic constituent by highly reactive electron donor functionalities (mainly oxyethylene and carboxylate) of the polymer chains followed by partial reducing of Ag+ ions to the nanoparticles. A presence of COOH groups in PUA structure enhances coordination and stabilization activity of the matrices and reduces a size of silver nanostructures. Molecular architecture and functionality of PUAs have a great impact on its Ag+ sorption ability. The facts of interactions between silver moieties and the macrochains of the matrices were observed by FTIR studies. The shifts of maxima and redistribution of intensities of few characteristic bands, mainly C=O and –C–O–C–, for Ag-containing PUAs were identified. In accordance with DMA studies a shift of relaxation transition temperature of PPO fragments in the composites evidences of coordination of Ag⁺ ions by oligoether fragments or interaction between PPO segments and a surface of silver nanostructures. Substantial ratio of silver immobilizes within a surface layer of PUAs film samples as submicro-sized aggregates. The aggregation of silver nanoparticles do not suppress plasmonic properties of Ag based polymer systems and optical as well as bactericidal activity of silver-polymer nanomaterials produced may be used in different fields of application.

REFERENCES

1. *Maitz M.F.* Applications of synthetic polymers in clinical medicine. Biosurf. Biotribol. 2015, **1**: 161-176. https://doi.org/10.1016/j.bsbt.2015.08.002.

2. *Akindoyo J.O., Beg M.D.H., Ghazali S., Islam M.R., Jeyaratnam N., Yuvaraj A.R.* Polyurethane types, synthesis and applications. RSC Adv. 2016, 6: 114453-114482. https://doi.org/10.1039/C6RA14525F.

3. *Velankar S., Pazos J., Cooper S.L.* High-performance UV-curable urethane acrylates via deblocking chemistry. J. Appl. Polym. Sci. 1996, **62**: 1361-1376. https://doi.org/10.1002/(SICI)1097-4628(19961128)62:9<1361::AID-APP6>3.0.CO;2-F.

4. *Zuccheri T., Colonna M., Stefanini I., Santini C., Di Gioia D.* Bactericidal activity of aqueous acrylic paint dispersion for wooden substrates based on TiO₂ nanoparticles activated by fluorescent light. Materials. 2013, **6**: 3270-3283. https://doi.org/10.3390/ma6083270.

5. *Lawson M.C., Shoemaker R., Hoth K.B., Bowman C.N., Anseth K.S.* Polymerizable vancomycin derivatives for bactericidal biomaterial surface modification: structure-function evaluation. Biomacromol. 2009, **10**: 2221-2234. https://doi.org/10.1021/bm900410a.

6. *Kim J.-Y., Suh K.-D.* Microphase separation of PEG-modified urethane acrylate and the swelling behavior of its gels. Colloid Polym. Sci. 1996, **274**: 1025-1032. https://doi.org/10.1007/BF00658367.

7. *Kim Y., Kim J.-W.* Silver nanowire networks embedded in urethane acrylate for flexible capacitive touch sensor. Appl. Surface Sci. 2016, **363**: 1-6. https://doi.org/10.1016/j.apsusc.2015.11.052.

8. *Barrera N., Guerrero L., Debut A., Santa-Cruz P.* Printable nanocomposites of polymers and silver nanoparticles for antibacterial devices produced by DoD technology. PLOS ONE. 2018, **13**: e0200918. https://doi.org/10.1371/journal.pone.0200918.

9. *Soto-Quintero A., Guarrotxena N., García O., Quijada-Garrido I.* Curcumin to Promote the Synthesis of Silver NPs and their Self-Assembly with a Thermoresponsive Polymer in Core-Shell Nanohybrids. Sci. Rep. 2019, **9**: 18187. https://doi.org/10.1038/s41598-019-54752-4.

10. *Pallavi S.G., Vishnumurthy K.A., Natarajan K.* Effect of silver nanoparticles on the ammonia gas sensing behavior in diphenylamine based conjugated polymer. Adv. Mater. Lett. 2019, **10**: 215-221. https://doi.org/10.5185/amlett.2019.2122.

11. *Naylor S., Bras W., Derbyshire G., Mant G.R., Bogg D., Ryan A.J.* Simultaneous time-resolved synchrotron X-ray scattering studies on block copoly(ether-urethane) phase behavior. Nucl. Instrum. Methods. Phys. Res. B. 1995, **97**: 253-256. https://doi.org/10.1016/0168-583X(94)00373-4.

12. *Tolstov A.L.* Production and physicochemical characteristics of silver-containing polyurethane systems. Theoret. Experim. Chem. 2013, **49**: 347-370. https://doi.org/10.1007/s11237-014-9336-z.

13. *Tolstov A.L., Matyushov V.F.* Nanocomposites based on aerosil, vinyl polymers, and silver particles. Theoret. Experim. Chem. 2014, **50**: 127-131. https://doi.org/10.1007/s11237-014-9357-7.

О.Л. Толстов,
Інститут хімії високомолекулярних сполук НАН України, 48, Харківське шосе, Київ, 02160, Україна,
E-mail: a.tolstov@ukr.net
В.Ф. Матюшов,
Інститут хімії високомолекулярних сполук НАН України, 48, Харківське шосе, Київ, 02160, Україна,
Є.В. Лебедєв,
Інститут хімії високомолекулярних сполук НАН України, 48, Харківське шосе, Київ, 02160, Україна,
Д.О. Климчук,
Інститут ботаніки імені М.Г. Холодного НАН України, 2, вул. Терещенківська, Київ, 01004, Україна

ФОРМУВАННЯ ТА ДОСЛІДЖЕННЯ СРІБЛОВМІСНИХ КОМПОЗИТІВ НА ОСНОВІ ІОНОМЕРНИХ ПОЛІ(УРЕТАН-АКРИЛАТ)ІВ, ОТРИМАНИХ МЕТОДОМ ДИФУЗІЇ/СОРБЦІЇ

Срібловмісні полімерні композити були отримані методом дифузії/сорбції іонів срібла в попередньо синтезовані функціоналізовані полі(уретан-акрилат)ні матриці. Особливості процесу координації іонів Ag^+ карбоксильними групами полімерних ланцюгів з подальшим їх відновленням визначено за допомогою методів ІЧ- та УФ-вид спектроскопії, СЕМ та ін. За допомогою спектральних досліджень встановлена взаємодія між срібловмісною складовою та функціональними групами полімерної матриці. Зсув температур релаксаційних переходів фрагментів ППО в складі срібловмісних полімерних систем у високотемпературну область, згідно з даними ДМА, є додатковим свідченням взаємодії різних форм срібла (іонів, кластерів або наночастинок) з олігоетерними фрагментами матриці. Умови сорбційного процесу, хімічна будова полімерних матриць і висока реакційна здатність іонів Ag^+ забезпечують трансформацію іонного срібла у відновлену високодисперсну металеву форму та її подальшу іммобілізацію в поверхневому шарі полімерних матриць у вигляді наночастинок або агрегатів субмікронного розміру. Нанодисперсне срібло навіть в агрегованій формі демонструє наявність інтенсивного поверхневого плазмонного резонансу в діапазоні 400–500 нм, положення максимуму якого залежить від функціональності полімерної матриці.

Ключові слова: поліуретан, акрилати, іономери, срібло, взаємодія, структура, властивості.

А.Л. Толстов,
Институт химии высокомолекулярных соединений НАН Украины, 48, Харьковское шоссе, Киев, 02160, Украина,
E-mail: a.tolstov@ukr.net

В.Ф. Матюшов,
Институт химии высокомолекулярных соединений НАН Украины, 48, Харьковское шоссе, Киев, 02160, Украина,

Е.В. Лебедев,
Институт химии высокомолекулярных соединений НАН Украины, 48, Харьковское шоссе, Киев, 02160, Украина,

Д.А. Климчук,
Институт ботаники имени Н.Г. Холодного НАН Украины, 2, ул. Терещенковская, Киев, 01601, Украина

ФОРМИРОВАНИЕ И ИССЛЕДОВАНИЕ СЕРЕБРОСОДЕРЖАЩИХ КОМПОЗИТОВ НА ОСНОВЕ ИОНОМЕРНЫХ ПОЛИ(УРЕТАН-АКРИЛАТ)ОВ, ПОЛУЧЕННЫХ С ПОМОЩЬЮ МЕТОДА ДИФФУЗИИ/СОРБЦИИ

Серебросодержащие полимерные композиты были получены методом диффузии/сорбции ионов серебра в предварительно синтезированные функционализированные поли(уретан-акрилат)ные матрицы. Особенности процесса координации ионов Ag^+ карбоксильными группами полимерных цепей с последующим их восстановлением установлены с помощью методов ИК- и УФ-вид спектроскопии, СЭМ и др. Использование спектральных методом позволило установить факт взаимодействия между серебросодержащим компонентом и функциональными группами полимерных матриц. Сдвиг температур релаксационных переходов фрагментов ППО в составе серебросодержащих полимерных систем, по данным ДМА, является дополнительным свидетельством взаимодействия различных форм серебра (ионов, кластеров или наночастиц) с олигоэфирными фрагментами матрицы. Условия протекания процесса сорбции ионов серебра, химическая структура матриц и высокая реакционная способность ионов Ag^+ способствуют трансформации ионного серебра в восстановленную высокодисперсную форму и ее иммобилизации в поверхностном слое полимерных матриц в виде частиц и их агрегатов нано- и субмикронного размера. Нанодисперсное серебро даже в агрегированной форме демонстрирует наличие интенсивного поверхностного плазмонного резонанса, спектральное положение максимума которого лежит в области 400–500 нм и зависит от функциональности полимерной матрицы.

Ключевые слова: полиуретан, акрилаты, иономеры, серебро, композиты, взаимодействие, структура, свойства.