PROCEEDINGS OF THE INTERNATIONAL CONFERENCE
NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. **4** No 2, 02NNSA09(3pp) (2015)

Ag$^+$ Adsorption/Complexation Behavior of Polyurethanes of Fifferent Structure and Functionality

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(Received 31 May 2015; published online 27 August 2015)

Nanostructurized polyurethanes of different structure and functionality were obtained and used for studying silver ions adsorption from aqueous medium. Formation of (Ag$^+$)$_n$-polymer complexes was confirmed by combination of UV-vis/FTIR spectroscopy. Silver ions capacity of polyurethanes obtained reaches 1.1-1.4 • 10^{-5} mol/g for polymers based on polyester (polyether), aromatic diisocyanate and amine-functionalized chain extender (cross-linker). Presence of urea fragments in polymer macrochains increase Ag$^+$ adsorption capacity of polyurethanes as well.

Keywords: Polyurethanes, Silver, Composites, Thin Films, Chemical Structure, Complex.

PACS numbers: 81.05.Qk, 82.35.Np, 87.85.Rs

1. INTRODUCTION

Metal-containing polymer composite materials attract a great attention in science and industry. The main fields of their application are electronics, optics, medicine etc [1]. Using polyurethanes for preparation of metal-containing polymer materials is very popular because of their excellent technical and exploitation properties, high stability, biocompatibility [2]. Among variety of approaches for producing of such materials the most applicable are introducing fine metal particles into polymer matrix or *in situ* formation of highly-dispersed metals in polymers [3]. According to the literature adsorption of metals in ionic form mainly uses for metals concentration or decontamination of waste water [4-5]. The very few researches report an application of adsorption technique for producing metal-containing polymer systems, mainly for medical uses [6]. At the same time the studies of structure-dependent Ag$^+$ adsorption behavior of polyurethanes and its effect on lyophilic properties of the metal-filled polymers were not conducted yet.

The aim of this work is determination of the features of Ag$^+$ ions adsorption by polyurethane matrices of different structure and functionality as well as an effect of Ag$^+$ ions bonded by the matrix on lyophilic properties of metal-containing polyurethane.

2. EXPERIMENTAL SECTION

2.1 Materials

For preparation of polyurethanes as oligomeric diols poly(butylenes glycol adipate) (PBGA) of M_w = 800 and poly(propylene glycol) (PPG) of M_w = 1000 were used. As diisocyanate constituent the tolylene diisocyanate (TDI) (mixture of 2,4/2,6-isomers with weight ratio of 80/20) and isophorone diisocyanate (IPDI) were taken. 1,1,1-trimethylol propane (TMP), tris-(2-hydroxyethyl)amine (TEA) and 4,4'-diaminodicyclohexylmethane (DDM) were used ans cross-lonkers/chain extenders. As catalyst a dibutyltin dilaurate (DTD) was used as received. Ethyl acetate, N,N-dimethylformamide, 1,4-dioxane and distilled water were used as solvents. For preparation of metal-containing polyurethanes silver nitrate of chemical grade has been used as silver source.

2.2 Sample Preparation

Polyurethanes (PU) have been prepared via convenient polyaddition process between polyether and diisocyanate components followed by addition of chain extender (cross-linker) at appropriate conditions. Solutions of PU were casted onto Teflon plate and film-forming and curing processes were continued under moisture-free conditions. Polymer films obtained have a thickness of 100-150 µm. After elimination of solvent the polymers were used for silver ion adsorption experiments.

Table 1 – Composition and Ag$^+$ adsorption behavior of PU of different structure

Code	Polymer Composition	Chain Extender (Cross-linker)	Catalyst	Ag$^+$ capacity (10^{-6} mol/g)	Silver content, wt%
PU-1	PBGA/TDI	TMP	+	7.9	0.085
PU-1a	PBGA/TDI	TEA	-	13.8	0.150
PU-2	PPG/TDI	TMP	+	6.8	0.073
PU-2a	PPG/TDI	TEA	-	10.7	0.116
PU-3	PPG/IPDI	TMP	+	3.6	0.039
PU-3a	PPG/IPDI	TEA	+	8.5	0.092
PU-4	PPG/IPDI	DDM	-	6.1	0.066

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Adsorption of Ag^+ ions by polyurethane films was performed by immersing the polymer film into 0.01 M aqueous solution of $AgNO_3$ until the equilibrium state (controlled by electrochemical potential measurements) reaches. Swelled polymer films were washed by distilled water followed by drying in the dark to prevent photochemical reduction of ionic silver into metallic form.

2.3 Characterization

FTIR spectral analysis was performed using Bruker Tensor 37 spectrometer in the spectral range of 4000-600 cm^{-1} and a resolution of 0.5 cm^{-1}. UV-vis spectra were recorded using ULAB UV-108 spectrometer in spectral region of 250-500 nm. Silver content during adsorption experiments were determined by electrochemical potential measurements using Ionomer EL-74 equipped with both Ag^+-specified and comparative electrodes. Moisture sorption testing was carried out in isothermal condition at 20 ^{o}C and 100 % humidity.

3. RESULTS AND DISCUSSION

Fig.1 shows FTIUR spectra of typical polyurethane before and after adsorption of Ag^+ ions. PU-4 polymer could be characterized by few typical absorption bands. There are stretching vibration bands of hydrogen-bonded (H-bonded) NH groups (vNH) centered at 3325 cm^{-1}, stretching vibrations of free and H-bonded C=O of urethane groups (vC=O_{ureth}) with maxima at 1749 and 1716 cm^{-1}, vibration band of H-bonded C=O of urea groups (vC=O_{urea}) at 1635 cm^{-1}, deformation vibration bands of NH groups (γNH) at 1552, 1536 and 1274 cm^{-1}, stretching vibration band of C-N (vC-N) with maxima at 1461 and 1151 cm^{-1}, absorption band of conjugated O–C–N bonds (vO–C–N) at 1373 cm^{-1}, vibration band of C–O–C bonds of ether fragments with maxima at 1099 and 1089 cm^{-1}, complex vibration band vC–O/vC–N centered at 931 cm^{-1}, deformation vibration band of C=O groups at 786 and 771 cm^{-1}.

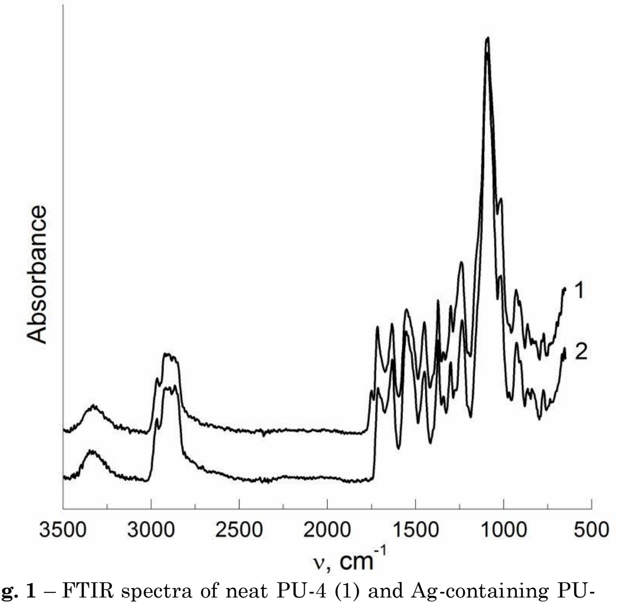

Fig. 1 – FTIR spectra of neat PU-4 (1) and Ag-containing PU-4 (2).

Complexation of Ag^+ ions by electron donor groups of polymer matrix initiates corresponding changes of spectral positions and integral intensity of vNH, vC=O_{ureth}, vC=O_{urea} δNH vC–O–C bands and appearance of new vibration modes of C=O groups. At the same time redistribution of H-bonding network of polymer matrix was determined as well.

Fig. 2 demonstrates UV-vis spectrum of poly(urethane-urea) (PU-4) after Ag^+ adsorption. Earlier studies have shown complex ionic structure of ionic silver in aqueous solution [7-8]. For such systems a presence of complex ionic aggregates with adsorption in UV region (Ag_4^{2+} with $\lambda_{1\text{-max}}$ at ~280 nm, Ag_3^+ with $\lambda_{2\text{-max}}$ at 302 nm and Ag_2^+ with $\lambda_{3\text{-max}}$ at 313 nm) [8]. When the adsorption process is carried out an intensity of $\lambda_{1\text{-max}}$ drops down followed by an appearance of new multimodal band at about 350 nm. The spectral position of this band and their asymmetric structure evidences of overlapping few band attributed to metal-polymer complex with Ag^+ coordinated by C=O groups of PU-4 (favorably by urea due to its high coordination activity) ($\lambda_{4\text{-max}}$ ~310 nm), ionic aggregates and clusters with atoms having different electronic state ($\lambda_{5\text{-max}}$ and $\lambda_{6\text{-max}}$ at 337 and 342 nm, correspondingly). The band of surface-initiated plasmonic resonance of larger silver nanostructures at $\lambda > 380$ nm was not observed during experiments.

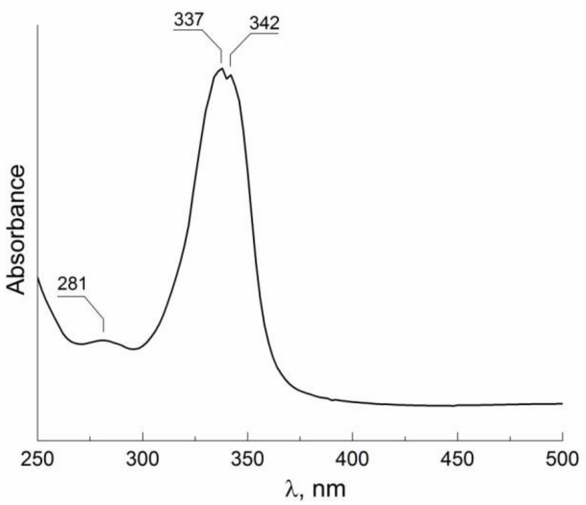

Fig. 2 – UV-vis spectrum of Ag^+-filled PU-4.

Analysis of complexation behavior of polyurethanes (Table 1) shown high dependence of adsorption capacity and final silver content of the polymers from their chemical structure. Introducing amine constituent into polyurethane structure increases Ag^+ capacity up to 2.5 times. Moreover aromatic structure of hard domains of polyurethanes increases adsorption capacity as well. Otherwise a presence of urea fragments with high coordination ability to Ag^+ ions in the polymer chains increases silver adsorption compared to polymer with pure urethane functionality.

4. CONCLUSION

Polyurethanes of different chemical structure (amine-/urea functionalized, linear/cross-linked) have been synthesized and applied for studying an adsorption of silver ions from aqueous medium. It was shown that urea functional fragments in a structure of polyurethane could bond Ag$^+$ ions into metal-polymer complex that was confirmed by UV-vis and FTIR spectral data. The results of Ag$^+$ adsorption experiments evidence of great effect of polymer functionality on silver ions capacity of polyurethane films studied. Maximum of Ag$^+$ capacity is peculiar to polyurethanes obtained from prepolymer based on polyester (polyether) and aromatic diisocyanate, and extended (cross-linked) by amine-containing polyol. Thus, structurization of polymers, namely polyurethanes at nanolevel allows to substantially increase their metal adsorption properties.

AKNOWLEDGEMENTS

The authors kindly thank colleagues of the Center for Collective Use of Instruments at the Institute of Macromolecular Chemistry of the National Academy of Sciences of Ukraine for their assistance in research.

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