

Studying an Effect of Polyurethane Functionality Directed Stabilization of Silver Nanoparticles as a Pathway for Manufacturing Modern Antimicrobial Materials

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In the paper an activity of functional groups of polyurethanes, like urethane, urea and biuret, on in-matrix stabilization of silver nanoparticles formed in situ was discussed in details. Polyurethane and poly(urethane-urea) matrices in the nanocomposites are characterized by relatively high level of interaction between their functional groups and silver nanoparticles (AgNP) where as poly(urethane-biuret) matrix are characterized by lower stabilizing activity related to AgNP because of strong hydrogen bonding interactions between biuret groups and other functions of polymer chains. All nanocomposite systems have intermediate level of water and moisture sorption, and high bactericidal activity. Prepared composites could be successfully applied as modern antimicrobial polymer materials.

Keywords: Silver nanoparticles, Polyurethanes, Functionality, Interaction, Stabilization, Bactericidal materials.

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1. INTRODUCTION

Stabilization of silver nanoparticles (AgNP) in polymer matrices is a key factor of efficiency of polymer materials in their practical applications. Value of polymer-stabilized AgNP in different fields of application, namely medicine, optics, electronics was numerously proved by long-term studies of such nanomaterials [1]. One of the most practically valuable and applicable nanomaterials is silver-containing polyurethanes because of their active applying in medicine as effective antimicrobial materials [2]. Exploitation ability of AgNP containing polyurethanes is highly depend on stabilization of metal nanoparticles in the polymer matrices. Till the date it is known only few studies related to mutual influence of AgNP and polyurethane matrix in the composite materials however interaction between AgNP and functional groups of polyurethane is still poorly studied [3, 4].

Thus the aim of the work is studying the level of interaction between AgNP and functional groups of polyurethane matrix chains, like urethane, urea and biuret, in details. Additionally an antimicrobial activity of obtained AgNP-containing polymer materials was also evaluated.

2. EXPERIMENTAL

2.1 Materials

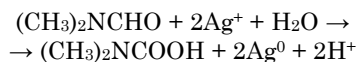
For synthetic purposes poly(propylene glycol) (PPG) of $M_w = 1000$, tolylene diisocyanate (mixture of 2,4-/2,6-isomers) (TDI), isophorone diisocyanate (IPDI), 1,4-butanediol, 4,4'-diaminodicyclohexylmethane, AgNO_3 , N,N-dimethylformamide (DMF) and dibutyltin dilaurate as a catalyst (all reagents are chemical grade) were used as received. Dimethylhexane-1,6-dicarbamate was synthesized from 1,6-hexamethylene diisocyanate in excess of methanol.

2.2 Synthesis of Polyurethanes

All polyurethanes with urethane, urethane/urea and urethane/biuret functionality have been synthesized by conventional polyaddition reaction. Briefly, the previously calculated quantity of PPG, TDI (or IPDI) and appropriate chain extender (1,4-butanediol, 4,4'-diaminodicyclohexylmethane or dimethylhexane-1,6-dicarbamate depend on the final functionality of polyurethane) were mixed at appropriate conditions in the presence of a catalyst (dibutyltin dilaurate). Reaction was continued under control of NCO groups content. Obtained polyurethane (PU), poly(urethane-urea) (PUU) and poly(urethane-biuret) (PUB) were used for producing composite polymer films and testing stabilizing activity of the polymer matrices to in-matrix formed AgNP.

2.3 Synthesis of Silver Nanoparticles

AgNP were synthesized by mixing of AgNO_3 in with PU (PUU) in DMF media followed by reduction of Ag^+ . In the case of PUB cross-linked polymer film has been immersed in AgNO_3 solution in DMF to achieve required load of silver precursor. Polymer-stabilized AgNP are formed via thermally induced reduction of Ag^+ by DMF according to reaction scheme:



Obtained by film casting and/or vacuum drying methods the composite polymer films were tested on interaction between AgNP and functional groups of synthesized polyurethanes as well as hydrophilicity and bactericidal activity of AgNP-containing polymer composites. Silver content for all composite samples was $1.5 \pm 0.2\%$ (relatively high silver load of the composites was selected for reliable confirmation of interactions between functional groups of the matrices and AgNP).

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2.4 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 Shimadzu UV-2400 PC spectrometer in spectral region of 300-700 nm. Water sorption experiments were performed according to ASTM D570-standard. Moisture sorption testing was carried out in isothermal condition at 20 °C and 100 % humidity. Bactericidal activity was evaluated using *Escherichia coli* (*E. coli*) *DH5a* strain grown on LB-agar at 37 °C for 16 hrs. Relative bactericidal efficiency of AgNP-containing composite polymer films was determined by measuring a zone of bacteria lysis.

3. RESULTS AND DISCUSSION

3.1 FTIR Spectral Analysis

Manufacturing traditional AgNP-containing polyurethane based bactericidal materials requires knowledge on interaction of nano-sized silver particles with polyurethane functionalities because technical and exploitation characteristics of the materials are depend on stabilization of nanodispersed metal in the polymer matrix. It is known that polyurethanes consist of different functional

groups. But only few ones affect on reactivity of polyurethanes toward to AgNP [2]. There are ether (oxyethylene and much lesser, oxypropylene), urethane, urea and other (biuret, allophanate, ester) functional groups. To the date an interaction of nanosized metallic silver with ether groups studied well, whereas interaction between AgNP and urethane and, especially, urea and biuret functional fragments is poorly studied yet. To solve this problem FTIR analysis of neat polymers and their AgNP-containing nanocomposites (Fig. 1) was applied. Selected data on FTIR characteristic absorption bands of corresponding functional groups of neat polymers and polymer matrices in the AgNP-containing composites are summarized in Table 1.

As it could be seen introducing AgNP into PU matrix shifts maxima of stretching vibration bands of urethane groups (νNH_b , $\nu\text{C} = \text{O}_{\text{ureth-b1}}$, $\nu\text{C} = \text{O}_{\text{ureth-b2}}$, $\nu\text{C}-\text{N}$, where b, b1 and b2 subscript indices show different modes of hydrogen bonding in urethane groups) by 3-6 cm^{-1} to low frequency region. Some shift ($\Delta\nu = 2-3 \text{ cm}^{-1}$) was also identified for deformation vibration bands of N-H and O-C-N fragments of urethane groups. These indicative changes are evidenced of partial destruction of intra- and intermolecular hydrogen bonding network because of partial participation of urethane groups of PU matrix in interaction with surface atoms of AgNP.

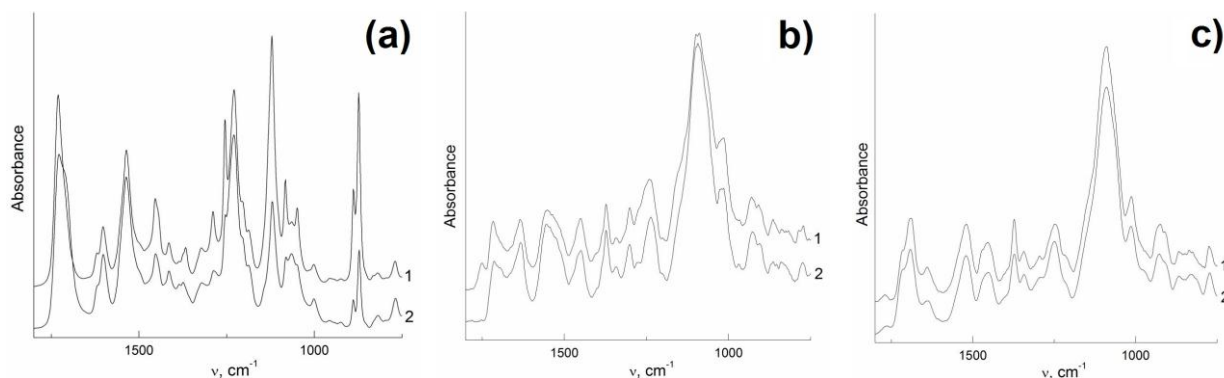


Fig. 1 – FTIR spectra in wavenumber range of 1750-750 cm^{-1} for PU- (a), PUU- (b) and PUB-based (c) samples: (1) neat polymer, (2) AgNP containing polymer composite

Table 1 – Selected characteristic FTIR absorption bands of PU, PUU and PUB and their AgNP-containing systems

Wavenumber, cm^{-1}		$\Delta\nu$, cm^{-1}	Wavenumber, cm^{-1}		$\Delta\nu$, cm^{-1}	Wavenumber, cm^{-1}		$\Delta\nu$, cm^{-1}	Note
PU	PU-AgNP		PUU	PUU-AgNP		PUB	PUB-AgNP		
3306	3301	5	3339	3331	8	3347	3335	12	νNH
			1750	-	-	1769	1767	2	$\nu\text{C} = \text{O}_{\text{ureth-f}}$
1726	1720	6							$\nu\text{C} = \text{O}_{\text{ureth-b1}}$
1712	1709	3	1714	1711	3	1716	1714	2	$\nu\text{C} = \text{O}_{\text{ureth-b2}}$
			-	1695	-	1689	1692	3	$\nu\text{C} = \text{O}_{\text{ureth-b3}}$
						1640	1639	1	$\nu\text{C} = \text{O}_{\text{biur-b}}$
			1635	1632	3				$\nu\text{C} = \text{O}_{\text{urea-b}}$
			1550	1555	5	1544	1551	7	γNH
1535	1533	2	1533	1526	7	1520	1521	1	γNH
1375	1372	3	1373	1372	1	1372	1372	-	$\gamma\text{O}-\text{C}-\text{N}$
1283	1288	5	1274	1278	4	1295	1290	5	δNH
1122	1119	3	1151	1145	6	1144	1147	3	$\nu\text{C}-\text{N}$
1088	1088	-	1092	1092	-	1090	1090	-	$\nu\text{C}-\text{O}-\text{C}$
959	957	2	931	926	5	969	976	7	$\nu\text{C}-\text{O}/\nu\text{C}-\text{N}$
769	768	1	773	769	4	774	771	3	$\delta\text{C} = \text{O}$

Table 2 – Basic characteristics of obtained polyurethanes and polyurethane-based nanosystems

Sample	Visual observations	UV-vis	Water absorption	Moisture absorption	Zone of lysis
		λ , nm	%	%	mm
PU	colorless, transparent	-	3.1	2.7	0
PU-AgNP	yellow, transparent	424	4.3	3.4	2.0-2.5
PUU	colorless, transparent	-	4.0	2.9	0
PUU-AgNP	yellow, transparent	438	6.1	3.8	~ 2.5
PUB	colorless, opaque	-	4.7	4.2	0
PUB-AgNP	dark brown, non-transparent	441	7.5	6.7	2.5-3.0

Similar effects were observed for PUU-based nanosystem, in which additional influence renders urea functional groups (disappearing $\nu C = O_{ureth-f}$ at 1750 cm^{-1} and shift of $\nu C = O_{urea-b}$ by 3 cm^{-1} to low frequencies). Other spectral changes in PUU-AgNP system were practically the same with PU-based composite.

However, for PUB-based composite the specific features of biuret functionality decreases stabilizing activity of the matrix. Strong hydrogen bonding formed by biuret groups (each biuret group forms at least three hydrogen bonds [5]) do not undergo a destruction while metal nanoparticles appear in the matrix. The main reason of such behavior is, probably, due to higher bonding energy of H-bonds of biuret groups with biuret/urethane functions of PUB macrochains compared to dipole-dipole interaction between biuret functionality and AgNP. This is resulted in lower number of the bonds participated in stabilization of AgNP.

3.2 UV-vis Spectrometry

The results of UV-vis spectroscopy of prepared nanosystems (see Table 2) show clear plasmon resonance (PR) adsorption band of AgNP with maxima at 424 nm for PU-AgNP and at 430 nm for PUU-AgNP sample. For PUB-AgNP composite a position of maximum of PR band was detected at 441 nm.

It is well-known fact that a position of PR band is highly depend upon combination of two basic factors of AgNP-containing systems: (1) size of AgNP and (2) interaction of surface atoms of AgNP with functional groups of capping agent. Summarizing FTIR analysis, UV-vis and visual observation it can be concluded that strong interaction of AgNP with urea groups of PUU affect a spectral position of PR band of PUU-AgNP nanosystem. In opposite, stabilization activity of PUB matrix in PUB-AgNP sample is lower and do not allowed to prevent aggregation of formed AgNP that finally leads to formation of bigger particles, losing transparency of the nanosystem and shift a maximum of PR band to longer wavelength. As it was supposed a presence of Ag^+ and AgNP is not enough condition for destruction of strong intermolecular hydrogen bonding network between biuret groups and other functions of PUB matrix that, in combination of relatively low urethane groups content, reduces stabilizing activity of PUB.

3.3 Water and Moisture Sorption

Experimental results of water and moisture sorption (see Table 2), which are carried out using standard techniques, shown that a presence of highly polar urea and biuret groups in polyurethanes increases level of H_2O absorption by the matrices from 2.7 (3.1) to 4.2 (4.7) %. Introducing AgNP into polymers drastically increases water/moisture absorption by 1.3-1.6 times. Nevertheless, absolute values of water/moisture absorption level have not critical influence on mechanical characteristics of prepared samples that is allowed to use all AgNP-containing composites as practically valuable materials for bactericidal application.

3.4 Antimicrobial Testing

Bactericidal testing experiments (see Table 2) had shown an absence of any antimicrobial activity of pure polymers. Otherwise, obtained polymer nanocomposites are characterized by strong antimicrobial activity (a size of zone of *E. coli* lysis reaches 3.0 mm). An enhanced bactericidal efficiency of PUB-AgNP compared to PU-AgNP and PUU-AgNP nanosystems could be explained by increased hydrophilicity of PUU-based composite.

4. CONCLUSION

Detailed studies of nanosystems based on polyurethanes of different functionality and in-matrix synthesized silver nanoparticles shown a great influence of intra- and intermolecular as well as intercomponent interactions on characteristics of obtained polymer composite systems. It was found that a presence of urethane and urea functional groups in polyurethane polymer matrices allowed to stabilize nanosized silver particles and to prepare composite nanosystems. Introducing biuret groups into polyurethane structure decreases stabilizing activity of polymer matrix because of strong hydrogen bonding between biuret groups and other functionality of the matrix. Obtained nanocomposites are characterized by appropriate hydrophilicity and high bactericidal efficiency for practical application.

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REFERENCES

1. *Metal Nanoparticles: Synthesis, Characterization and Applications* (Eds. by D.L. Feldheim, C.A. Foss, Jr) (New York: Marcel Dekker Inc.: 2002).
2. A.L. Tolstov, *Theoret. Experim. Chem* **49**, 347 (2013).
3. C.-W. Chou, S.-H. Hsu, H. Chang, et al., *Polym. Degrad. Stabil.* **91**, 1017 (2006).
4. H.-L. Liu, S. A. Dai, K.-Y. Fu, et al., *Int. J. Nanomed.* **5**, 1017 (2010).
5. E.W. Hughes, H.L. Yakel, H.C. Freeman, *Acta Cryst.* **14**, 345 (1961).