

1. Introduction

Metal-containing polymers represent a board classification of polymers with inorganic salt groups attached to the polymer chain. These polymers have been investigated for several decades, attracting scientific and commercial attention. These polymers have a wide variety of properties that lead to different application such as aqueous thickeners, textile sizers, adhesives, additives, resins, catalysts and in the biomedical field [1–6]. Among polymer materials, PU takes a leading position because of its outstanding mechanical properties. These include high elongation capacity, high resistance in aggressive environments, thermal stability, chemical resistance, versatility in their products and application. At present, PU is one of the largest polymer products in the plastic family. The PU is appreciated due to simple preparation, low cost and high surface area [7–10]. The heat stability and mechanical properties of the polyurethane can be improved by the addition of different fillers and additives. Modification of PUs by incorporating metal and functional groups are used extensively to improve various typically desired properties of materials, such as enhanced thermal stability, fire retardancy, flexibility and solubility. Complexation of a metal ion to functional polymeric ligand changes its activity due to polymeric effect, which has led to a variety of applications. [6, 11].

From the structural point of view, the organic ligands and central metals play crucial factors in the coordination self-assembly process and final properties.

Consequently, rational selection of metal ions and suitable organic ligands is still a challenge for construct expected architectures with unique properties [1–11]. It is known that hydrazides and derivatives are significant nitrogenous compounds that exhibit herbicidal, anticancer, anti-inflammatory, antiviral, antibacterial bioactivities. This class of compounds has the ability to readily coordinate to many transition metals and can be used as a chain extender in metal-containing PU [9, 12–14].

This study is focused on the synthesis of the new poly(urethane-semicarbazides) (PU) containing transition metal ions and the hydrazide moiety.

The objectives of research are as follows: to establish the structure of metal-containing PU; to establish the influence

NEW METAL-CONTAINING POLY(URETHANE-SEMICARBAZIDES) ON THE BASIS OF PYRIDINE DERIVATIVES

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Abstract: The growth of science and technology of polyurethanes leads to the development of new materials with more desirable properties. Modification of polyurethane (PU) by incorporating metal and functional groups are used extensively to improve various properties, such as enhanced thermal stability, fire retardancy, flexibility and solubility. In this investigation, a new metal-containing poly(urethane-semicarbazides) bearing a pyridine moiety have been synthesized and characterized by Fourier transform infrared spectroscopy (FTIR), differential thermal analysis (DTA/TG) and tensile strength measurements. The results showed that the incorporation of metal ions into the polymer chain greatly influenced their mechanical and thermal properties. The tensile strength measurements on the PU films showed a marked difference in the elongation and tensile strength for compositions with various metal salts. The nature of the anion of the salt also affects the properties of the polymers, since the anions are able to form complexes with hydrogen atoms of urethane-semicarbazide PU segments. According to the results of DTA, introduction of metal ions leads to the increase of the thermal stability of metal-containing PU, as compared to the original PU. FTIR spectra data confirmed that the metal ions Cu^{2+} , Co^{2+} are coordinated in the polymer metal chelates with hydrazide and urethane groups. The research results can be used to develop the new materials and methods for the preparation and designing of metal-containing polymers required in various areas, such as development of medical equipment, functional films and other related areas.

Keywords: poly(urethane-semicarbazides), metal-containing polymer, hydrazide derivatives, polyurethane, thermogravimetry, thermal stability, tensile strength.

of metal ions on the mechanical properties and the thermal degradation of metal-containing PU.

2. Materials and methods

All reagents and solvents used in this work were analytical grade and purchased locally. Hydroxyl terminated polybutadiene (HTPB, $M_n=3000$ g/mol) and polytetramethylene ether glycol (PTMEG, $M_n=1000$ g/mol) were dried by azeotropic distillation in benzene. Toluene-2,4-diisocyanate (TDI), benzene and dimethylformamide (DMF) were purified by vacuum distillation. Copper (II) sulfate, cobalt (II) nitrate were used after drying at 100 °C to constant weight.

FTIR spectra were conducted on KBr pellets from 500 to 4500 cm^{-1} on Bruker spectrometer. Thermogravimetric studies were carried out on a Diamond TG/DTA analyzer at heating rate of 10 °C/min from 25 to 700 °C. The tensile tests of polymers systems were performed on a tensile machine FU-1000 at a tensile rate of 100 mm/min and 25 °C.

The chain extender (DH) was synthesized by refluxing an alcohol solution of diethyl 2,6-dimethyl-3,5-pyridinedicarboxylate with an excess of hydrazine hydrate as describe in [15]. Polyurethanes were prepared by a two-step procedure under an argon atmosphere. In the first step, the synthesis was carried out in a 3-necked flask by a mixture of polyol (HTPB or PTMG) and TDI in order to form an NCO-terminated prepolymer (MDI) (2,3). In

second step, the MDI was dissolved in benzene, DH – in DMF; and into the solution of MDI – with stirring and in small portions – the solution of DH was added. After the whole solution of DH was added, the stirring process continued for 40 minutes, and the resulting mass was poured – in a thin layer – into a mold and dried to constant weight. The synthesis was carried out under constant stirring in the environment of anhydrous benzene and dimethylformamide (DMF) (10:1) at a molar ratio MDI:DH=1:1. **Fig. 1** presents the steps involved in the PU preparation.

Metal-containing polymers were obtained by the same method. The corresponding metal salt (CuSO_4 (a) and $\text{Co}(\text{NO}_3)_2$ (b)) were each separately dissolved in anhydrous DMF and added directly into the reaction mixture after adding of the DH solution. The molar ratio of MDI:DH: Me^{2+} =1:1:1, the molar ratio of benzene:DMF=10:1. The composition of the obtained polymers is shown in **Table 1**.

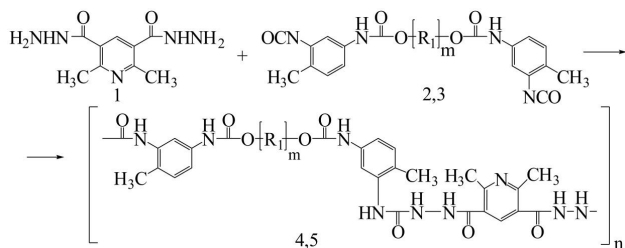


Fig. 1. The poly(urethane-semicarbazide) synthesis:
 1 - DH; 2 - MDI-1 ($R_1 = -[CH_2-CH=CH-CH_2-]_m-$);
 3 - MDI-2 ($R_1 = [-CH_2-CH_2-CH_2-CH_2O-]_m-$);
 4 - PU1 (DH, MDI-1); 5 - PU2 (DH, MDI-2)

Table 1
 Sample Codes and Contents of PU composition

Sample code	Molar ratio			Metal Salts
	Macroglycol	Isocyanate (TDI)	Chain extender - DH	
PU1	HTPB - 1.0	2.0	1.0	-
PU1a	HTPB - 1.0	2.0	1.0	CuSO ₄ - 1.0
PU1b	HTPB - 1.0	2.0	1.0	Co(NO ₃) ₂ -1.0
PU2	PTMG - 1.0	2.0	1.0	-
PU2a	PTMG - 1.0	2.0	1.0	CuSO ₄ - 1.0
PU2b	PTMG - 1.0	2.0	1.0	Co(NO ₃) ₂ -1.0

3. Results

The static mechanical properties of pure PU and metal-containing PU were analyzed at room temperature to estimate their tensile characteristics (Fig. 2, 3). It should be noted that the introduction of metal salts into the macromolecule PU1, PU2 leads to an increase of the mechanical characteristics of polymers; the highest values of elongation and tensile strength were found for the sample PU1a (supposedly due to the stronger bond of Copper (II) salts with active polyurethane groups).

The greatest tensile strength has the sample PU1b*, which differs from PU1b, because after drying, it was held for another 1 hour at 100°C. The high tensile strength can be explained by the fact that the heat treatment of polymer systems can increase the structural homogeneity and stabilize their size.

For the group of PU2 samples when the metal salts are introduced, on the contrary, the tensile strength decreases (for Co²⁺ the strength is greater than for Cu²⁺, as in the first case), but the elongation increases and especially significantly for PU2b samples.

In order to determine more accurate interrelation between the properties and the structure, the polymers were investigated by FTIR spectroscopy. It has been discovered that in the spectrum of the sample PU1b, the characteristic absorption bands of the (NH), (C=O) groups are displaced to the low-frequency region in comparison with the spectrum of the original PU1. For PU2b, on the contrary, there is a displacement of the absorption bands of the

groups -NH, -C=O to the high-frequency region. FTIR spectra data confirmed that the metal ions Cu²⁺, Co²⁺ are coordinated in the polymer metal chelates with hydrazide and urethane groups.

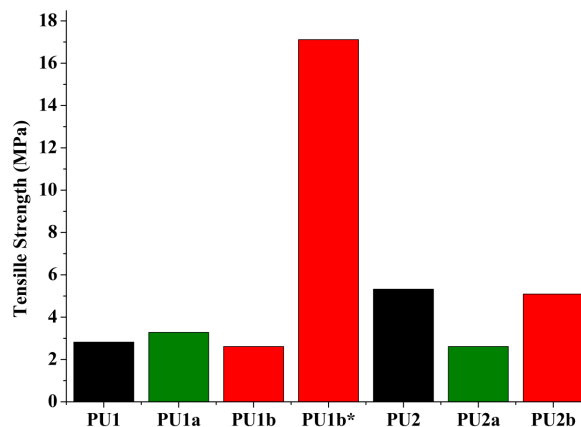


Fig. 2. Tensile strength of pure and metal-containing PU samples

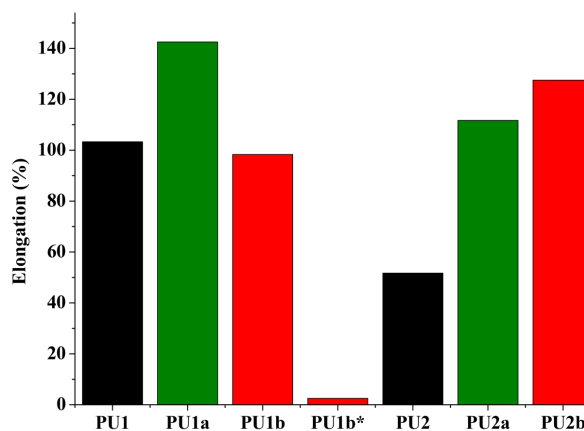


Fig. 3. Elongation at break of pure and metal-containing PU samples

According to the results of DTA (Table 2), introduction of metal ions leads to the increase of the thermal stability of metal-containing PU, as compared to the original PU.

An intensive decomposition of the sample PU1 is observed at 450 °C, and when heated above 299 °C this polymer loses 5 % of its weight. Introduction of metal ions into the polymer matrix leads to an increase of the thermal stability of the polymers, which is expressed in a narrower interval of thermodestruction.

Table 2
 Results of differential thermal analysis of the PU samples

PU sample	Temperature range 1, °C	ΔH_1 , J/g	Temperature range 2, °C	ΔH_2 , J/g	Temperature range 3, °C	ΔH_3 , J/g	Temperature range 4, °C	ΔH_4 , J/g	Melting temperature (T _m), °C
PU1	293.7-307.6	-33	448.9-458.5	-1924	549.4-558.2	-112	589.5-595.3	-55	195-198
PU1a	92.6-110.0	69	351.8-395.9	276	443.9-487.1	-5092	601.6-605.9	18	295-298
PU1b	428.8-440.9	-53	444.6-451.1	-609	462.7-481.0	-775	-	-	<350
PU2	52.1-95.7	390	322.0-373.2	-2035	528.4-545.3	-378	-	-	262-265
PU2a	80.31-99.3	228	215.6-250.8	-280	421.9-443.1	-4591	459.9-501.1	-2256	224-227
PU2b	229.8-306.7	1895	311.1-339.0	-1575	405.4-430.4	-3109	457.2-467.8	-1004	210-213

So, when PU1a is heated above 444 °C, it loses 5 % of its weight, and the intensive decomposition takes place at 470–480 °C, which is significantly higher than for non-metal polymers. PU1b is even more heat resistant; its thermal destruction occurs at 490 °C. It should be noted that for similar polyurethanes based on isophthalic acid dihydrazide, 5 % weight loss is observed at 270 °C, and intensive thermal destruction – at 300 °C.

4. Discussion and conclusions

Due to the increase of the inter-chain interactions caused by the complexation of the metal with the macroligand, the flexibility of the polymer chain is reduced, which makes the metal-containing polymers more durable. It is shown that the tensile strength of metal-containing polyurethane-semicarbazides is higher than the strength of free-metal polymers. The

increase in strength is influenced by the nature of the salt. So, among the salts Co(II), Cu(II), the most active are the salts of cuprum. The greater the electronegativity of the cation is, the stronger the bond is with the active PU groups and the higher the tensile strength is. The nature of the anion of the salt also affects the properties of the polymers, since the anions are able to form complexes with hydrogen atoms of urethane-semicarbazide segments PU. The most active among SO_4^{2-} , NO_3^- is the nitro group. The research results can be used to develop the new materials and methods for the preparation and designing of metal-containing polymers required in various areas, such as development of medical equipment, functional films and other related areas. Further work is necessary to determine more accurate interrelation between the structure and the properties of metal-containing PU.

References

- Zhang, X.-L., Tang, G.-M., Wang, Y.-T. (2018). Tunable luminescent behaviors of Ag-containing metal coordination polymers with N-heterocyclic and sulfonate group. *Polyhedron*, 147, 26–35. doi: <https://doi.org/10.1016/j.poly.2018.03.006>
- Zhang, J., Wang, C.-C. (2017). Three two-dimensional coordination polymers constructed from transition metals and 2,3-norbornanedicarboxylic acid: Hydrothermal synthesis, crystal structures and photocatalytic properties. *Journal of Molecular Structure*, 1130, 223–230. doi: <https://doi.org/10.1016/j.molstruc.2016.10.033>
- Yuan, N., Zhang, M., Cai, H., Liu, Z., Zhao, R. (2019). Two new coordination polymers constructed from s-block alkaline earth metals and 2-hydroxynicotinic acid. *Inorganic Chemistry Communications*, 101, 130–134. doi: <https://doi.org/10.1016/j.inoche.2019.01.030>
- Ho, C.-L., Wong, W.-Y. (2011). Metal-containing polymers: Facile tuning of photophysical traits and emerging applications in organic electronics and photonics. *Coordination Chemistry Reviews*, 255 (21–22), 2469–2502. doi: <https://doi.org/10.1016/j.ccr.2011.01.052>
- Gil, M., Kim, H., Bae, J., Cha, S.-H., Lee, K. J. (2015). Preparation of metal-ion containing polymers: Synthesis and characterization of methacrylic copolymers containing copper ion. *Polymer*, 77, 297–304. doi: <https://doi.org/10.1016/j.polymer.2015.09.049>
- Jayakumar, R., Nanjundan, S., Prabakaran, M. (2006). Metal-containing polyurethanes, poly(urethane-urea)s and poly(urethane-ether)s: A review. *Reactive and Functional Polymers*, 66 (3), 299–314. doi: <https://doi.org/10.1016/j.reactfunctpolym.2004.12.008>
- Somarathna, H. M. C. C., Raman, S. N., Mohotti, D., Mutalib, A. A., Badri, K. H. (2018). The use of polyurethane for structural and infrastructural engineering applications: A state-of-the-art review. *Construction and Building Materials*, 190, 995–1014. doi: <https://doi.org/10.1016/j.conbuildmat.2018.09.166>
- Sultan, M., Javeed, A., Uroos, M., Imran, M., Jubeen, F., Nouren, S. et. al. (2018). Linear and crosslinked Polyurethanes based catalysts for reduction of methylene blue. *Journal of Hazardous Materials*, 344, 210–219. doi: <https://doi.org/10.1016/j.jhazmat.2017.10.019>
- Aruna, P., Kumar, D. B. R. (2008). Anionomeric waterborne poly(urethane semicarbazide) dispersions and their adhesive properties. *Journal of Applied Polymer Science*, 110 (5), 2833–2840. doi: <https://doi.org/10.1002/app.28834>
- Khatoun, H., Ahmad, S. (2017). A review on conducting polymer reinforced polyurethane composites. *Journal of Industrial and Engineering Chemistry*, 53, 1–22. doi: <https://doi.org/10.1016/j.jiec.2017.03.036>
- Hasnain, S., Nishat, N. (2012). Synthesis, characterization and biocidal activities of Schiff base polychelates containing polyurethane links in the main chain. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 95, 452–457. doi: <https://doi.org/10.1016/j.saa.2012.04.018>
- Paixão, D. A., Marzano, I. M., Jaimes, E. H. L., Pivatto, M., Campos, D. L., Pavan, F. R. et. al. (2017). Novel copper(II) complexes with hydrazides and heterocyclic bases: Synthesis, structure and biological studies. *Journal of Inorganic Biochemistry*, 172, 138–146. doi: <https://doi.org/10.1016/j.jinorgbio.2017.04.024>
- Wang, X., Fu, X., Chen, M., Wang, A., Yan, J., Mei, Y. et. al. (2019). Novel 1,3,5-thiadiazine-2-thione derivatives containing a hydrazide moiety: Design, synthesis and bioactive evaluation against phytopathogenic fungi in vitro and in vivo. *Chinese Chemical Letters*, 30 (7), 1419–1422. doi: <https://doi.org/10.1016/j.ccl.2019.03.038>
- Garin, A. B., Rakarić, D., Andrić, E. K., Kosanović, M. M., Balić, T., Perdih, F. (2019). Synthesis of monosubstituted dipicolinic acid hydrazide derivative and structural characterization of novel Co(III) and Cr(III) complexes. *Polyhedron*, 166, 226–232. doi: <https://doi.org/10.1016/j.poly.2019.03.059>
- Nesterova, E. Y., Kositsyna, E. S., Tsyganok, L. P., Vishnikin, A. B. (2012). Copper(II) and cobalt(II) salt complexes with 2,6-dimethyl-3,5-pyridinedicarboxylic acid dihydrazide. *Russian Journal of Inorganic Chemistry*, 57 (3), 350–357. doi: <https://doi.org/10.1134/s0036023612030217>

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