1. Introduction

Metal-containing polymers represent a broad 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, textileizers, adhesives, additives, resins, catalysts and in the biomedlical 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 ligands 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 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 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-di-methyl-3-pyridinedicarboxylate with an excess of hydrazine hydrate as described 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 the 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 Co(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:Me₃Al=1:1:1. The molar ratio of benzene: DMF=10:1. The composition of the obtained polymers is shown in Table 1.
The poly(urethane-semicarbazide) synthesis:
1 – DH 2 – MDI-1 (R₁=–[–CH₂–CH=CH₂–CH₂–]ₙ–m); 3 – MDI-2 (R₂=–[–CH₂–CH₂–CH₂–CH₂–]ₙ–m);
4 – PU1 (DH, MDI-1); 5 – PU2 (DH, MDI-2)

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.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Macroglycol</th>
<th>Isocyanate (TDI)</th>
<th>Chain extender – DH</th>
<th>Metal Salts</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU1</td>
<td>HTPB – 1.0</td>
<td>2.0</td>
<td>1.0</td>
<td>–</td>
</tr>
<tr>
<td>PU1a</td>
<td>HTPB – 1.0</td>
<td>2.0</td>
<td>1.0</td>
<td>CuSO₄ – 1.0</td>
</tr>
<tr>
<td>PU1b</td>
<td>HTPB – 1.0</td>
<td>2.0</td>
<td>1.0</td>
<td>Co(NO₃)₂ – 1.0</td>
</tr>
<tr>
<td>PU2</td>
<td>PTMG – 1.0</td>
<td>2.0</td>
<td>1.0</td>
<td>–</td>
</tr>
<tr>
<td>PU2a</td>
<td>PTMG – 1.0</td>
<td>2.0</td>
<td>1.0</td>
<td>CuSO₄ – 1.0</td>
</tr>
<tr>
<td>PU2b</td>
<td>PTMG – 1.0</td>
<td>2.0</td>
<td>1.0</td>
<td>Co(NO₃)₂ – 1.0</td>
</tr>
</tbody>
</table>

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>
<thead>
<tr>
<th>Sample code</th>
<th>Temperature range 1, °C</th>
<th>ΔH2, J/g</th>
<th>Temperature range 2, °C</th>
<th>ΔH3, J/g</th>
<th>Temperature range 3, °C</th>
<th>ΔH4, J/g</th>
<th>Temperature range 4, °C</th>
<th>ΔH5, J/g</th>
<th>Melting temperature (Tm), °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU1</td>
<td>293.7–307.6</td>
<td>–33</td>
<td>448.9–458.5</td>
<td>–1924</td>
<td>549.4–558.2</td>
<td>–112</td>
<td>589.5–595.3</td>
<td>–55</td>
<td>195–198</td>
</tr>
<tr>
<td>PU1a</td>
<td>92.6–110.0</td>
<td>69</td>
<td>351.8–395.9</td>
<td>276</td>
<td>443.9–487.1</td>
<td>–5092</td>
<td>601.6–605.9</td>
<td>18</td>
<td>295–298</td>
</tr>
<tr>
<td>PU1b</td>
<td>428.8–440.9</td>
<td>–53</td>
<td>444.6–451.1</td>
<td>–609</td>
<td>462.7–481.0</td>
<td>–775</td>
<td>–</td>
<td>&lt;350</td>
<td>–</td>
</tr>
<tr>
<td>PU2</td>
<td>52.1–95.7</td>
<td>390</td>
<td>322.0–373.2</td>
<td>–2035</td>
<td>528.4–545.3</td>
<td>–378</td>
<td>–</td>
<td>–</td>
<td>262–265</td>
</tr>
<tr>
<td>PU2a</td>
<td>80.31–99.3</td>
<td>228</td>
<td>215.6–250.8</td>
<td>–280</td>
<td>421.9–443.1</td>
<td>–4591</td>
<td>459.9–501.1</td>
<td>–2256</td>
<td>224–227</td>
</tr>
<tr>
<td>PU2b</td>
<td>229.8–306.7</td>
<td>1895</td>
<td>311.1–339.0</td>
<td>–1575</td>
<td>405.4–430.4</td>
<td>–3109</td>
<td>457.2–467.8</td>
<td>–1004</td>
<td>210–213</td>
</tr>
</tbody>
</table>
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 SO₄²⁻, NO₃⁻ 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


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