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# MECHANICAL & THERMAL ASPECTS OF METALLCOORDINATION POLYURETHANES

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**Abstract**

*The physical, mechanical and thermal properties of polyurethane produced by the reaction of urethane prepolymers with coordination compounds of copper were studied. The peculiarity of the used metal complexes is catalytic activity in the low-temperature dissociation of urethane groups and the ability to interact with the isocyanate groups with the subsequent formation of azoaromatic derivatives. It was found that when urethane prepolymers interacted with the bulky coordination compounds of copper the rigid blocks of coordination-related azo groups were formed which had a significant influence on the supramolecular organization of polyurethanes, and the complex of their physical and mechanical properties. It was shown that the metal complex structuring did not lead to a deterioration of the thermal stability of polyurethanes.*

**Key words:** *Polyurethanes, modification, copper coordination compounds, physical-and-mechanical properties, thermal resistance*

## 1. INTRODUCTION

Polyurethanes are the polymers for creating a material with a wide range of operational parameters - high hardness, high elastic modulus, high elasticity, resistance to abrasion, solvents, oils and high strength. Changing the chemical nature of the initial components it is possible to vary these parameters within a wide range to get both high-impact plastics, and elastomers (Hepburn 1991). One of the ways to influence the chemical composition and morphology of polyurethane (PU) is to use coordination compounds of transition metals (CCTM) for their synthesis (Arun Prasath 1999; Jayakumar 2003; Kosyanchuk 2003; Kozak; 2012; Shen 1998; Wang 2010). It was found that CCTM can interact with sterically unhindered isocyanate groups and lead to the formation of coordination-related stack azo aromatic structures. Due to the formation of such structures it is possible to implement the electrons transfer through the stacks (Davletbaeva 1996, 2001, 2006). In industry, molded polyurethanes are mainly based on urethane prepolymers (UP). As the use of 2,4-toluene diisocyanate (TDI) is most preferable for UP synthesis, the terminal groups in UP are the hindered isocyanate groups at ortho-position. The reduction of isocyanate groups at para-position and their subsequent transformation into the azo groups is only possible in case of the catalytic dissociation of urethane groups. Worked out bulky coordination compounds of copper (BCCC) exhibit catalytic activity during the low-temperature dissociating of urethane groups and the ability to interact with the isocyanate groups with the subsequent formation of aromatic azo derivatives. In the process of catalytic dissociation of urethane groups it was possible to reduce the isocyanate groups at para-position and their subsequent conversion into azo groups (Davletbaev 2012). It was found that the dissociation of urethane groups was accompanied by preferential formation of coordination-related azo-derivatives; part of the isocyanate groups went to carbodiimides formation.

The aim of this work was to investigate the effect of chemical reactions taking place during the interaction of the urethane prepolymer with BCCC on physical, mechanical and thermal properties of polyurethanes.

## 2. EXPERIMENTAL

Urethane prepolymers were synthesized on the basis of reaction systems 1 mol of polyoxytetramethyleneglycol (Mn = 1379) - 2 moles of TDI (UP1), and 1 mol polyethylenebutylene glycol adipate (Mn = 2000) - 2 moles of TDI (UP2). It was used 4,4'-methylene-bis-(o-chloroaniline) (MOCA) to cure the UP1 and UP2. Considering that a large amount of isocyanate groups goes for the interaction with the metal complex, the mole fraction of MOCA was lower than necessary stoichiometrically.

For the preparation of coordination compounds of copper there were used: copper chloride (II), N,N'-diethylhydroxylamine (DEHA), γ-aminopropyltriethoxysilane (AGM).

UP was evacuated for 0.5 hours at a residual pressure of 0.7 kPa until the bubbles were disappeared. Then the calculated amount of metal complex compounds was injected into the reaction mixture and was stirred for 1 hour till formation of homogenous mass. Further MOCA was added in molten form. After the end of the synthesis reaction the mixture was poured into a pre-heated mold. The molds were kept in an oven for 24 hours at T=100°C. Polyurethane samples were then held at normal temperature for 2 weeks.

Physical and mechanical tests of polyurethanes were performed on a tensile testing machine Testometric M500-50 CT at strain rate of samples 50 mm/min.

Thermograms of samples were taken at derivatograph of Paulik-Paulik-Erdey system considering the nature of the relaxation at a heating rate 5°C/min up to 500°C. The weight of samples was 0.1 g. The initial oxidation temperature, oxidation temperature and the temperature of 5 and 50% weight loss were selected as the thermal stability criteria (Berg 1969).

## 3. RESULTS AND DISCUSSION

### *3.1. Mechanical properties*

It turned out that the metal complex structuring has the most beneficial effect on the polyurethanes which were cured at low molar content of MOCA ([NCO]:[$NH_2$] = 1:0,7 and 1:0.5). In this case, the critical tensile stress increases at two or more times (Fig. 1-3), elongation at break increases more than twice as well. Tear resistance of CCTM samples increases significantly (50-70%) (Fig. 5). The improvement of CCTM properties is in a certain concentration range of the structuring metal complex. In CCTM based on UP-2, this interval is in the range of 0.05% - 0.25%, while the using of UP-1 shifts it to higher concentrations of the metal complex - 0.25-0.5%. Within the above-noted concentration range the elongation set does not change. It should be noted that the elongation set is determined by plastic deformation in elastomers and its absence indicates perfect network of the polymer. The tensile stress of all samples decreases at 100, 200 and 300% strain. It was also found that the metal complex structuring has a negligible impact on such factors as the hardness and rebound resilience of the samples.

Figure 4 shows the stress - strain curves for CCTM obtained on the basis of urethane prepolymer at [NCO]:[$NH_2$] = 1:0,9. It was found that at nearly stoichiometric molar ratio of isocyanate and amine groups, the samples strength increases slightly.

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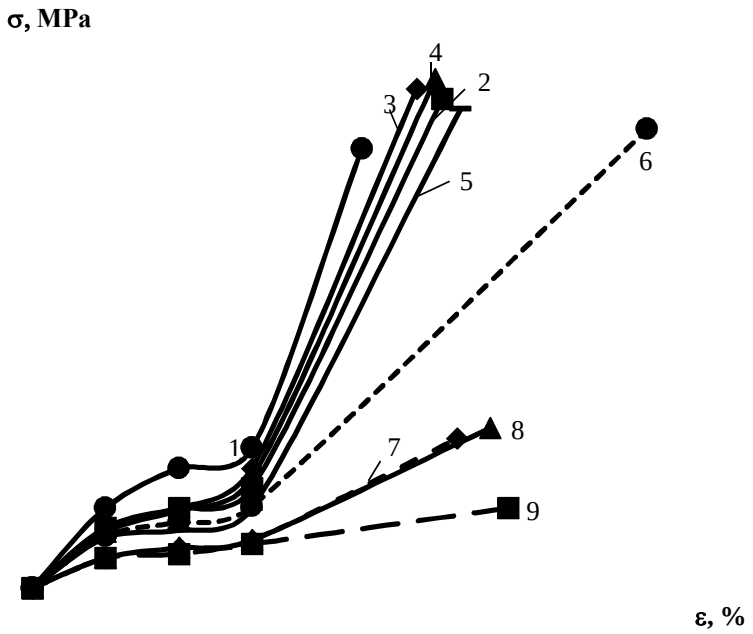



Fig. 1. Stress – strain curve of polyurethanes, based on the 1 mol of UP2, 0.7 mol of MOCA and metal complex system (% mass.): 1 - 0; 2 - 0,05; 3 - 0,1; 4 - 0,125; 5 - 0,25; 6 - 0,3; 7 - 0,4; 8 - 0,5; 9 - 0,75

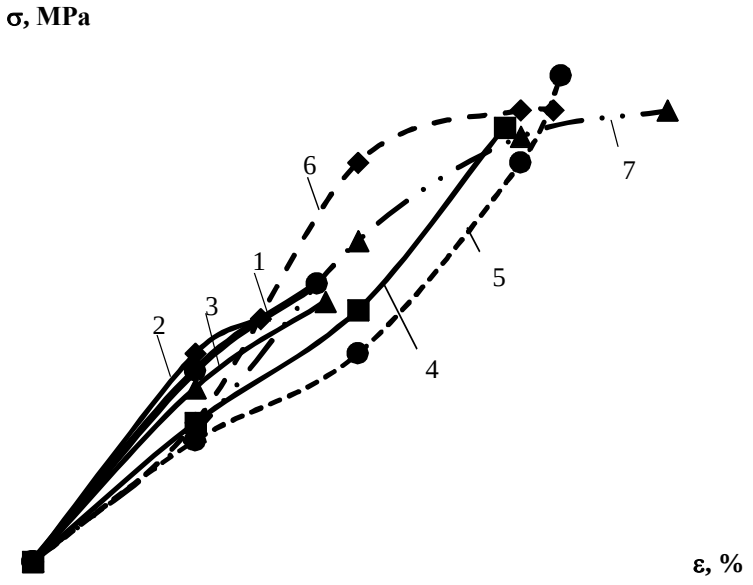



Fig. 2. Stress – strain curve of polyurethanes, based on the 1 mol of UP1, 0.7 mol of MOCA and metal complex system (% mass.): 1 - 0; 2 - 0,05; 3 - 0,175; 4 - 0,25; 5 - 0,3; 6 - 0,5; 7 – 1

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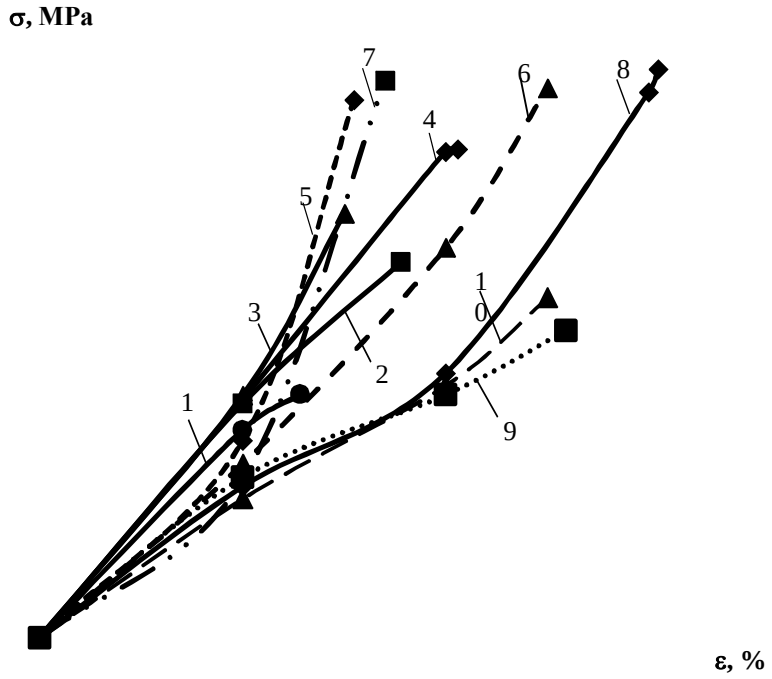



Fig. 3. Stress – strain curve of polyurethanes, based on the 1 mol of UP1, 0.5 mol of MOCA and metal complex system (% mass.): 1 - 0; 2 - 0,01; 3 - 0,05; 4 - 0,1; 5 - 0,175; 6 - 0,25; 7 - 0,3; 8 - 0,5; 9 - 0,75; 10 - 1

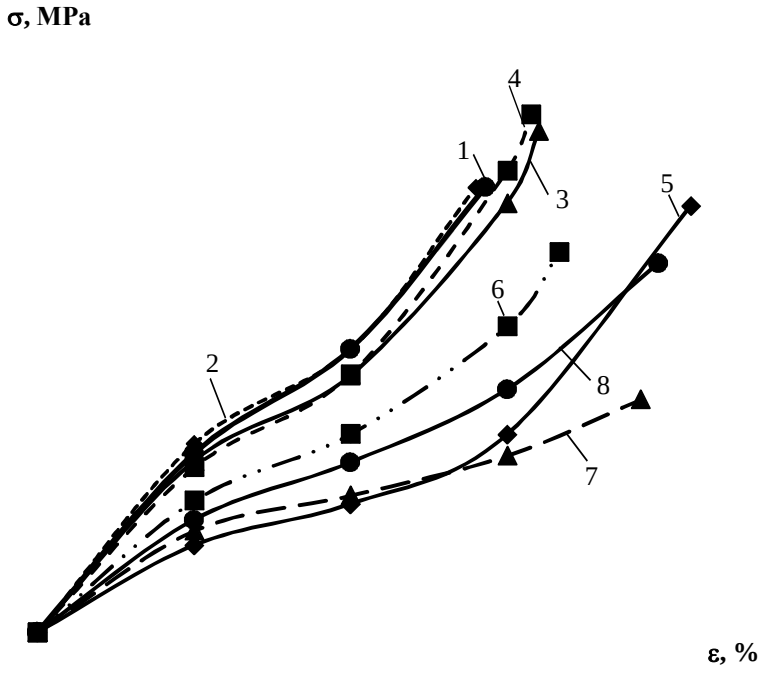



Fig. 4. Stress – strain curve of polyurethanes, based on the 1 mol of UP1, 0.9 mol of MOCA and metal complex system (% mass.): 1 - 0; 2 - 0,05; 3 - 0,1; 4 - 0,25; 5 - 0,3; 6 - 0,5; 7 - 0,75; 8 - 1

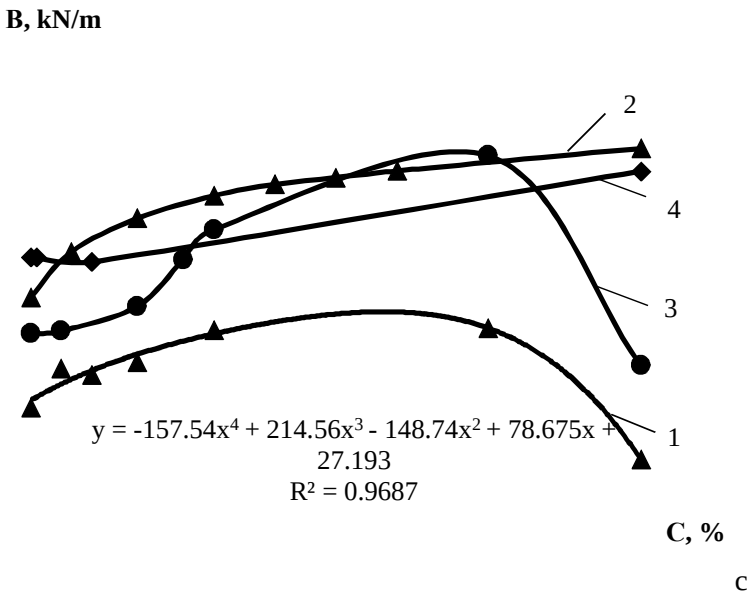



Fig. 5. Tear resistance – metal complex concentration curve of polyurethanes, based on UP1: 1 - 1:1,48:0,25 0,5 MOCA; 2 - 1:1,48:0,25 0,7 MOCA; 3 - 1:1,48:0,25 0,9 MOCA; 4 - 1:0:4 0,9 MOCA

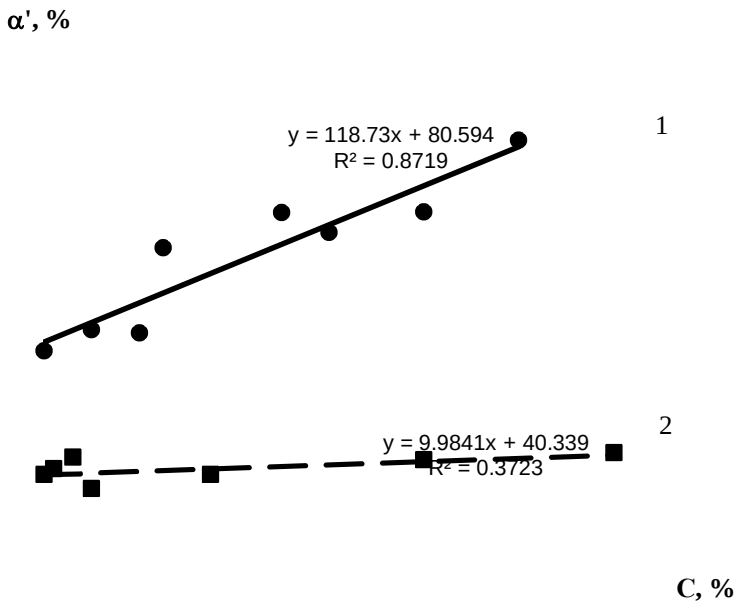



Fig. 6. Dependence of equilibrium swelling of polyurethanes based on 0.7 mol MOCA in acetone on metal complex concentration (% mass.): 1 - UP2, 2 - UP1

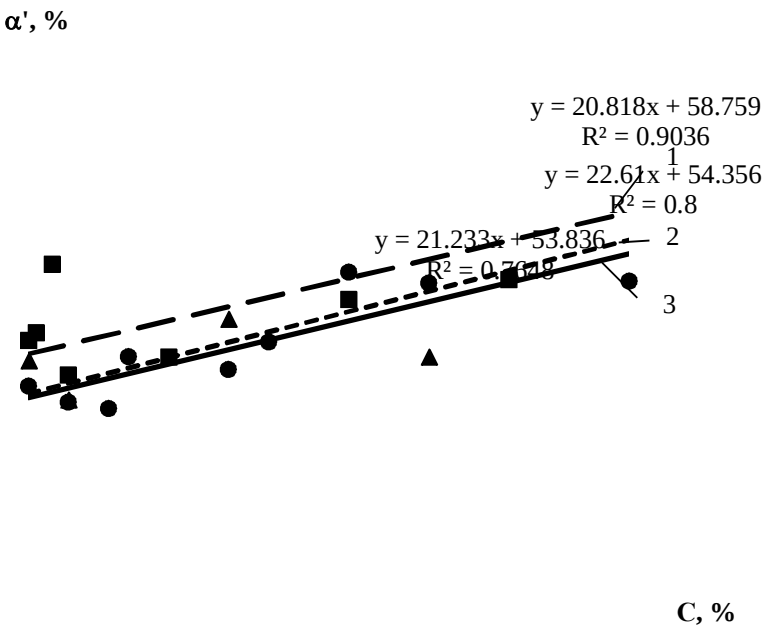



Fig. 7. Dependence of equilibrium swelling of polyurethanes based urethane prepolymer in toluene on metal complex concentration (% mass.):

1 – UP1 and 0,7 MOCA, 2 - UP1 and 0,9 MOCA, 3 - UP2 and 0,7 MOCA

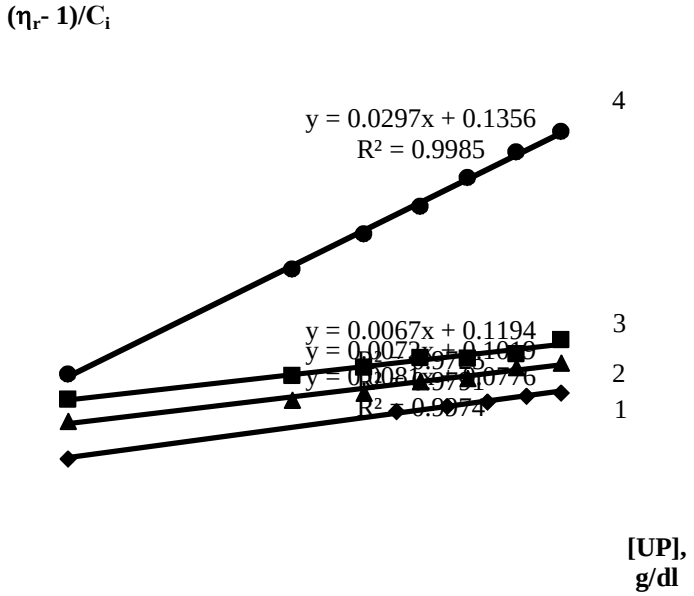



Fig. 8. Concentration curves of the reduced viscosity of the reaction products of UP1 and metal complex system: 1 – 0%, 2 – 0,5%, 3 – 0,75%, 4 – 1% (acetone, T=20°C).

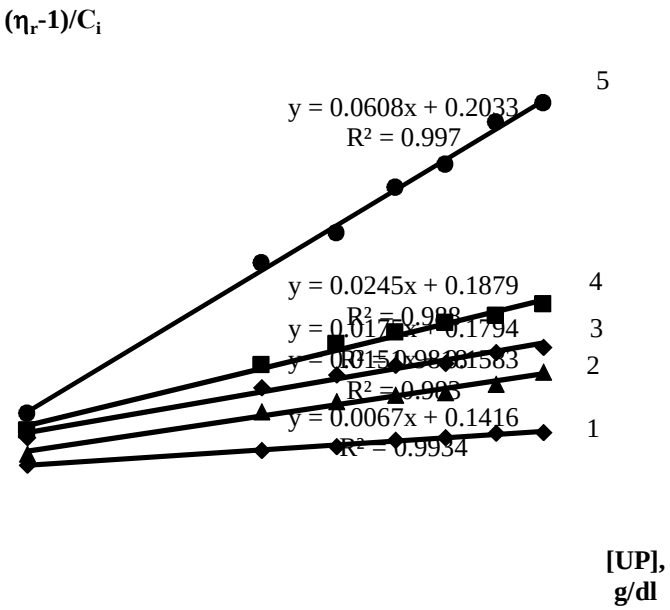



Fig. 9. Concentration curves of the reduced viscosity of the reaction products of UP2 and metal complex system: 1 – 0%, 2 – 0,1%, 3 – 0,25%, 4 – 0,3%, 5 – 0,5% (acetone, T=20°C).

Formation of labile sites of polymer network due to the formation of intermacromolecular coordination bonds naturally leads to a slight increase of CCTM swelling in acetone and toluene (Fig. 6 - 7).

The results of viscometric studies of reaction products of the metal complex system with UP1 and UP2 are shown in Figures 8-9.

According to Fig. 8 and 9, the angle of the concentration curves of the reduced viscosity depends on both the dosage of the metal complex system and the nature of oligodiol. The most prominent are the changes in the case of the prepolymer based on oligoesterdiol. Remarkable increase in the slope angle and the reduced viscosity $\eta_c$ values designate the appearance of intermolecular interactions, which are the most likely to be caused due to the coordination binding of electron-donor groups by copper ions. Azo groups have the highest ability for coordination binding in the studied polymer system. An important fact for the results analysis is that the isocyanate groups and carbodiimides are not able to coordination binding with the copper ions. The linear dependence of the intrinsic viscosity [η] of reaction products of the urethane prepolymer and the metal complex system on its content is observed. Considering that only the azo reaction is based on direct interaction of the isocyanate groups with the metal complex system, it can be concluded that the formation of azoaromatic compounds makes main contribution to the reaction process. The results of physical and mechanical tests are generally agree with the results of viscometric studies. Thus, the most likely reason for the reduction of tensile stress at 100, 200 and 300% strain may be the formation of coordination-related azo groups and the occurrence of labile coordinating intermolecular interactions (Fig. 10).

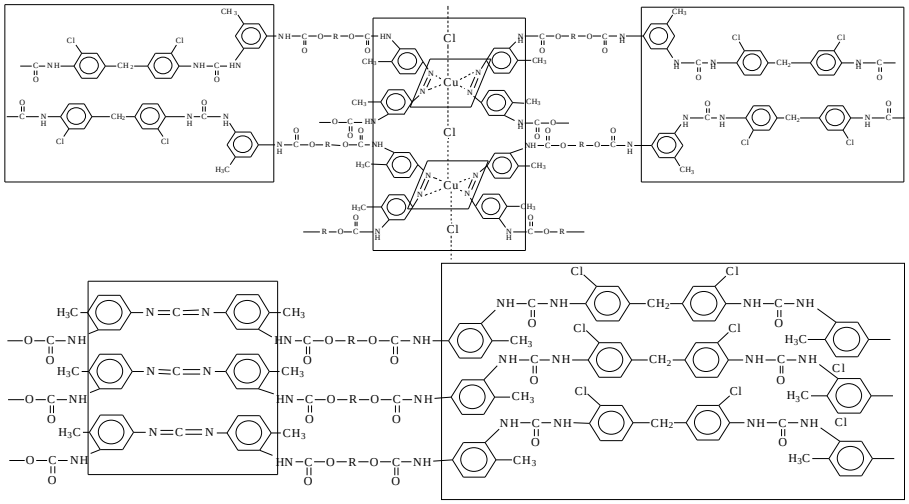


Fig. 10. The structure of metal coordinated polyurethanes

At the same time, intermolecular coordination interactions lead to double increase in elongation at break, the tensile and tear strength of the samples. The formation of the azo groups was possible at a significant lack of amines [NCO]:[$NH_2$] = 1:0,5-1:0,7. From a practical and economic point of view, is it important that the strength of samples is not affected by a decrease in the content of MOCA. That is CCTM obtained at [NCO]: [$NH_2$] = 1:0,5-1:0,7 are inferior to the strength of the samples obtained at [NCO]: [$NH_2$] = 1:0,9. Meanwhile the elongation at break of the samples increases, and they turn low modulus. Highly toxic and expensive MOCA consumption is reduced as well, and the pot-life of the urethane forming system significantly increases. An additional benefit is a reduction in volume resistivity of samples in the range of 10,000 to 100,000 times at the optimal content of the metal complex.

The use of the MOCA in a molar ratio [UP]:[MOCA] = 1: (0.9-0.95) gives highly crosslinked polyurethane. Because of sufficient high cross-link density of the polymer at such molar ratio the formation of domains due to the hard segments segregation is not possible. However, the use of metal complex structuring at high degree of crosslinking is not able to influence significantly the supramolecular organization of polyurethanes. At low molar content of MOCA the rigid blocks formed by the interaction of urethane prepolymer' terminal isocyanate groups with MOCA, are combined into domains. This fact is favored by the virtual absence of chemical cross-linking sites. When the urethane prepolymer containing terminal isocyanate groups interacts with the bulky copper coordination compounds, the rigid blocks are formed which are inherently different from the hard urethane-urea blocks.

*3.2. The study of the thermal stability of metal coordinated polyurethanes*

It is known that transition metals due to their ability to interact with the double bonds lead to the formation of free radicals in polymers. This fact was the reason that the unsaturated polymers containing transition metals, have low thermal stability. Despite the fact that polyurethanes do not contain unsaturated (double) bonds the study of heat resistance of polyurethanes, structured by coordination compounds of copper, was an important problem of this work.

Figures 11-12 show the curves of thermogravimetric analysis for polyurethanes derived from urethane prepolymer cured with different molar content of MOCA and structured by different amounts of metal complex. It turned out that the metal complex structuring does not change both the initial weight loss

temperature and the thermal oxidative decomposition rate of polyurethanes. These results are in agreement with published data (Davletbaeva 2002; Kozak 2002), confirming the fact that the transition metal ions, coordinately related to the polymer matrix, have no effect on the heat resistance of polyurethanes, and may even lead to its rise.

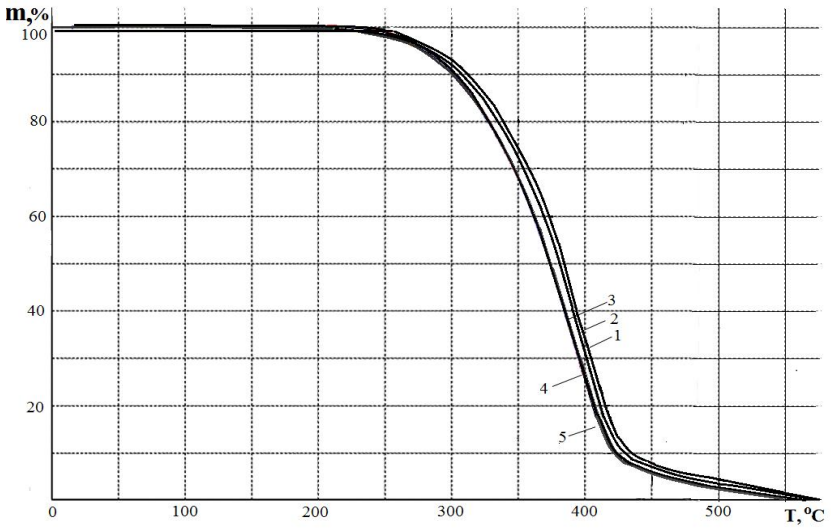



Fig. 17. Thermogravimetric curves of polyurethanes, based on 1 mol UP1 and 0.7 mol MOCA, modified by metal complex system (% mass.):

1 – 0; 2 - 0,1; 3 - 0,25; 4 - 0,5; 5 - 0,75

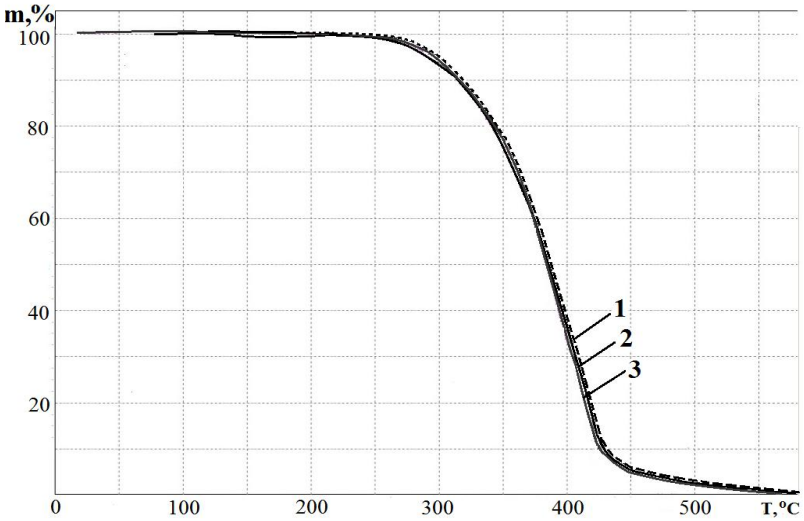



Fig. 18. Thermogravimetric curves of polyurethanes, based on 1 mol UP1 and 0.9 mol MOCA, modified by metal complex system (% mass.):

**1 - 0; 2 - 0,25; 3 – 0,5**

## 4. CONCLUSIONS

It was found that when the urethane prepolymer interacting with coordination compounds of copper the rigid blocks of coordinately related azo groups were formed which have a significant influence on the supramolecular organization of polyurethanes, and the complex of their physical and mechanical properties alike.

## ACKNOWLEDGEMENTS

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