SYNTHESIS, SPECTROSCOPIC AND THERMAL CHARACTERIZATION OF NEW METAL-CONTAINING ISOCYANATE BASED POLYMERS

Berta Barta Holló[1], Ivan Ristić[2]*, Jaroslava Budinski-Simendić[2], Suzana Cakić[3], Imre Miklós Szilágyi, Katalin Mészáros Szécsényi[1]

[1] Faculty of Sciences, University of Novi Sad, Novi Sad, Serbia

[2] Faculty of Technology, University of Novi Sad, Novi Sad, Serbia

[3] Faculty of Technology, University of Niš, Leskovac, Serbia

* E-mail:

Abstract

To overcome the polyurethanes low heat resistance and obtain new PU based materials, in continuation of our research in the synthesis of hybrid polymers we report here the synthesis of metal-containing polyurethanes formed in the reaction of pyrazole based coordination compounds [Cu$ampf$(NO$_3$)$_2$MeOH]·MeOH and [Cu$ampf$Cl$_2$] where $ampf$ denotes N,N'-bis(4-acetyl-5-methylpyrazol-3-yl)formamidine ligand, and two isocyanates, 1,6-diisocyanatohexane (**HDI**) and Bayhydur 3100 (**Bay**, a hydrophilic linear polymer based on 1,6-diisocyanatohexane) using dibuthyltin-dilaurate catalyst. The formed materials where characterized by FT-IR spectrometry and thermal methods. The formation of the new polymers, beside the corresponding FT-IR spectra, was proved by differential scanning calorimetry (DSC) determining their glass transition temperatures. The thermal decomposition of the materials was examined by simultaneous thermogravimetric (TG) and DSC measurement. For the evaluation of the decomposition mechanism the data obtained by coupled TG − mass spectrometric (MS) measurements were used.

Keywords: hybrid materials, polyurethanes, Cu(II) coordination compounds, DSC, TG–DSC, TG–MS

Introduction

Polyurethanes (PU) are widely used in products such as high performance elastomers, electrical and electronic equipment, coatings, thermal insulation foams, etc thanks to the wide range of possibilities to design PU materials with desired properties. The main drawback of polyurethanes is their poor heat resistance. The acceptable mechanical properties of PU (strength, modules, etc.) diminish at about 80-90 °C, while the thermal degradation occurs above 250 °C [1]. The thermal stability of polyurethanes can be increased by introducing heterocyclic groups such as the imide group, into the main polymer chain, since heterocyclic polymers are high temperature materials that have good mechanical and electrical properties. It has recently been reported that the introduction of a heterocyclic group into polyurethane increases the total thermal stability of polyurethane [2].

Inorganic-organic hybrid materials provide improved endurance, mechanical and chemical resistance and thermal properties of composites. Organic-inorganic materials become the subject of increasing interest in scientific and professional fluidity from the development of a soft inorganic chemical approach, where the mild synthetic routs provide a diverse approach to chemically-adjusted hybrid organo-inorganic networks. Later research was shifted towards more sophisticated metal containing composites with higher added value.

The incorporation of the metal into the polymer is a promising way of modifying the polymer. One of the known techniques for synthesis of metal-coordinated polymers is the polymerization of a chosen monomer with the appropriate metal complexes. When the monomer participates in the coordination with the metal salt, this facilitates its chemical structure, and then influences the formation of the polymer matrix and the properties of the ultimate polymer [3]. The metal containing polymers, in the main chain or side chain, is one of the most active achievements of ongoing research. These polymers possess properties of both organic and inorganic components [4]. Several monographs [5,6], reviews [7-9] and papers [10] have been published describing the syntheses, properties and applications [11] of various polymeric materials with metals. Metal polyurethanes and polymers are subject to extensive research, since these polymers show low viscosity, liquid crystalline properties and unusual thermal properties. Metals are usually incorporated into a polyurethane chain using an ionic bond [12,13] or through coordination [14]. Sandwich metal with a polyurethane structure is most often encountered. Among the available methods, the incorporation of metals by coordinating is often used, as this method leads to the formation of fused heterocyclic ring structures that improve the thermal stability of polyurethane. Since the synthesis of metal containing isocyanates can be difficult, metal-containing diols are commonly used for the synthesis of polyurethanes with metal ion. Matsuda et al. [15] reported the use of bivalent metal salts of mono (hydroxyethyl) phthalate in the synthesis of metallopolyurethanes.

In this report we describe the synthesis and property evaluation of metal-containing polyurethanes formed in the reaction of pyrazole based coordination compounds of Cu(II) with functional groups appropriate for polyurethane formation with isocyanates.

Experimental

Synthesis of hybrid materials

Synthesis of the coordination complex [Cu*ampf* $(NO_3)_2$MeOH]·MeOH (**1**) and [Cu*ampf*Cl$_2$] (**2**) (*ampf* = *N,N'*-bis(4-acetyl-5-methylpyrazol-3-yl)formamidine) is described earlier [16].

For the preparation of new metal containing polymers, 1,6-diisocyanatohexane (**HDI**) or Bayhydur 3100 (**Bay**), were mixed with the complexes **1** or **2** and dissolved in 15 cm^3 of tetrahydrofurane. To the reaction mixture dibuthyltin-dilaurate catalyst is added (mass fraction 0.1 %). To increase the incorporation of the copper(II)-complexes into the polymer **HDI** or **Bay** was added in excess (see Table 1). The excess of isocyanates was later removed by washing with tetrahydrofurane. The reaction mixture is stirred at room temperature, whereby the polymer is separated.

Table 1 Composition of the reaction mixtures for the preparation of hybrid polyurethane materials

Sample	1	2	HDI	Bay
HDI-1	26.5 mg (0.05 mmol)		82 mg (5 mmol)	
HDI-2		22.1 mg (0.05 mmol)	22.5 mg (0.27 mmol)	
Bay-1	26.4 mg (0.05 mmol)			23.6 mg (0.1 mmol)
Bay-2		22.4 mg (0.05 mmol)		25.9 mg (0.1 mmol)

Measurements

Scanning electron microscopy – energy dispersive X-ray analysis (SEM-EDX) data were obtained by a JEOL JSM-5500LV scanning electron microscope after sputtering an Au/Pd layer on the samples.

IR data were collected on a Thermo Nicolet Nexus 670 FT-IR spectrometer at room temperature in the range of 4000–400 cm^{-1} with resolution of 4 cm^{-1} by ATR method using ZnSe crystal.

Simultaneous thermogravimetric and differential scanning calorimetric analysis, TG–DSC measurements were performed by SDT Q600 (TA Instruments, USA) thermal analyzer. Sample (< 3 mg) was placed in an open alumina pan. The measurements were carried out in nitrogen and air atmosphere (flow rate: 100 cm^3 min^{-1}) to 600 °C with a heating rate of 10 and 20 °C min^{-1}. Sample holder/reference: alumina crucible/empty alumina crucible.

TG–DSC–MS data were collected using the same instrument coupled online with Hiden Analytical HPR-20/QIC mass spectrometer. The experimental conditions: < 3 mg sample mass, nitrogen atmosphere (flow rate 50 cm^3 min^{-1}) from room temperature to 600 °C, heating rate 10 °C min^{-1}.
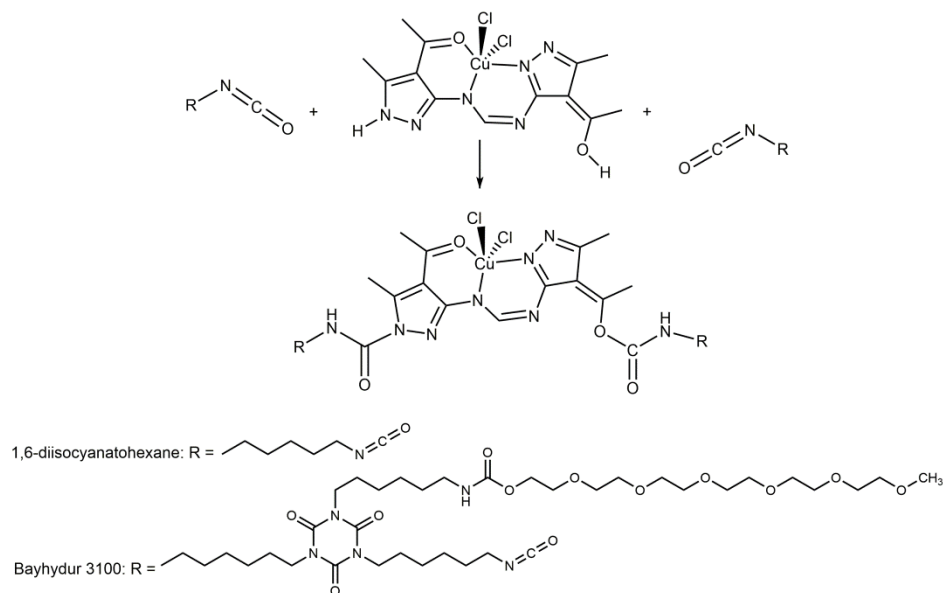
Thermal effects of the polymerization of isocyanates with copper(II)-compounds and the glass transition temperatures (Tg) of the new materials were measured using a Q20 DSC (TA Instruments, USA) calibrated against indium. Standard aluminum pans with lid containing 3–5 mg of the reaction mixture were scanned at a heating rate of 2 °C min^{-1} in temperature range from 20 to 230 °C.

Discussion of the results

In order to obtain new hybrid metal containing polymers, two isocyanates, 1,6-diisocyanatohexane (**HDI**) and Bayhydur 3100 (**Bay**, a hydrophilic linear polymer based on 1,6-diisocyanatohexane) [17], and two coordination complexes of the formula [Cu*ampf*(NO$_3$)$_2$MeOH]·MeOH (**1**) and [Cu*ampf*Cl$_2$] (**2**) containing reactive NH and carbonyl functional groups were used.

The isocyanates are very reactive. Therefore they are often used for cross linking of various monomers or prepolymers. Due to the high reactivity of isocyanates, they are chosen for the reaction with the functional groups of copper(II) complexes **1** and **2**. During the reaction the acidic hydrogen of the –NH group in the formamidine moiety moves to the oxygen of the acetyl substituent, reducing this way the steric hindrance

as is described earlier [10]. The formed –OH function and the –NH group of the pyrazole ring easily react with the isocyanate groups leading to carbamate formation [18]. The course of the reaction is presented in Scheme 1 by the reaction of the isocyanates and the coordination compound **2**.

Scheme 1 Reaction of the isocyanates with [Cu*ampf*Cl$_2$] (**2**).

The new hybrid polymers were analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) to prove the presence of copper in the structures. Unfortunately the results could not afford a semi-quantitative elemental analysis of the new materials. The qualitative analysis showed that all the hybrid polymers contained copper.

The DSC analysis confirmed the existence of a glass transition temprature in the obtained hybrid polymers, which is undoubtedly a proof that the synthesis of the hybrid polymer has occurred. Considering that these compounds have both urethane and urea bonds (see Scheme 1) which readily take part in hydrogen bonds formation, Tg values are expected to be high. Indeed, the DSC results show high Tg values in the hybrid polymer samples (see Fig 1. For the sake of the clarity, the curves are shifted vertically in all the following figures). A large number of hydrogen bonds, that are established between the polymer chains, certainly lead to a decrease in the segments mobility that is reflected on the Tg values. The Tg values are higher in the polymers based on HDI as isocyanate component. Given that the HDI chain is shorter than Bay, and therefore the density and the number of hydrogen bonds are proportionally higher in HDI polymers, the stiffness of the chains and the Tg values are also higher.
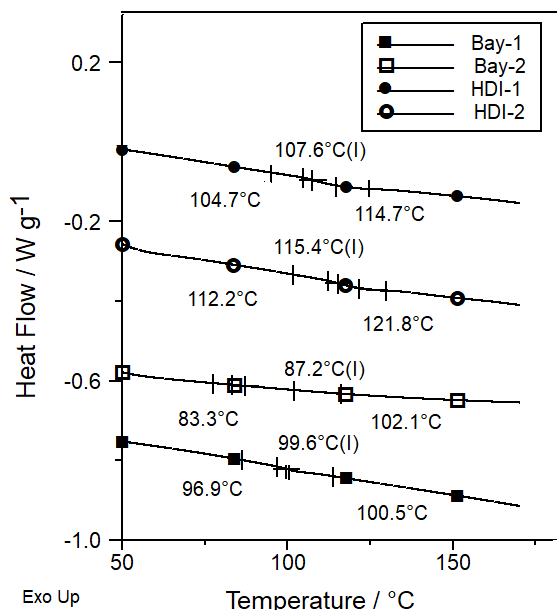
Figure 1 The glass transition temperatures (*T*g) of the hybrid polymers.

IR spectroscopy

In the spectra of the hybrid polymers **HDI-1** and **HDI-2** νOH bands around 3300 cm^{-1} appear as a result of the urethane bond formation in the reaction of the isocyanate groups of the **HDI** and the –NH and –OH groups of the coordination compounds **1** and **2** (see scheme 1). A more convincing proof for the reaction between the copper(II) complexes with **HDI** is that in the spectra of the hybrids the vibration of the νNCO group at 2260 cm^{-1} is missing. The skeleton vibrations in the spectrum of **HDI** appear in the region from 1500 to 700 cm^{-1}. In addition, in the spectra of the **HDI-1** and **HDI-2** above 1500 cm^{-1} bands for νC=O and νC=N stretching, characteristic for the urethane bond, appear. Similar differences are observed in the FTIR spectra of the hybrid polymers **Bay-1** and **Bay-2** and Bayhydur 3100 (**Bay**). The vibration for νNCO is also missing from the spectra of **Bay-1** and **Bay-2**. Due to its polymeric structure and different functional groups, the IR region of **Bay** from ~1700 to ~700 cm^{-1} is rich in bands compared to the same region of **HDI**. It contains intensive and sharp bands of νC=O (1680 cm^{-1}) and νC=N (1458 cm^{-1}) which are split into bands of lower intensity in its hybrid polymers. This observation refers to the formation of new bonds between the –NCO group of the polyisocyanate crosslinker and the –OH or/and –NH group of the pyrazole ring.

Thermal properties

The thermal properties of the crosslinkers and the formed hybrid polymers were determined by simultaneous TG–DSC measurements in dynamic nitrogen and air atmospheres.

The thermal stability of **HDI** is practically the same in both the atmospheres (see DTG curves in Fig 2) with a slightly different decomposition mechanism. The decomposition is faster in air than in the inert atmosphere. In air it ends around 160 °C, while in nitrogen is completed near 200 °C. The thermal stability of Bayhydur (**Bay**) is significantly higher than that of **HDI** in accordance with its polymeric

structure (see Fig 2). The decomposition mechanism of **Bay** is seemingly independent of the atmosphere. The decomposition of **HDI** is accompanied by endothermic effects in both the atmospheres while the decomposition of **Bay** starts with exothermic effects. In air its decomposition is exothermic in the full temperature range, whereas the decomposition in nitrogen above 400 ^{o}C turns into endothermic processes despite the practically identical DTG curves in these two atmospheres.
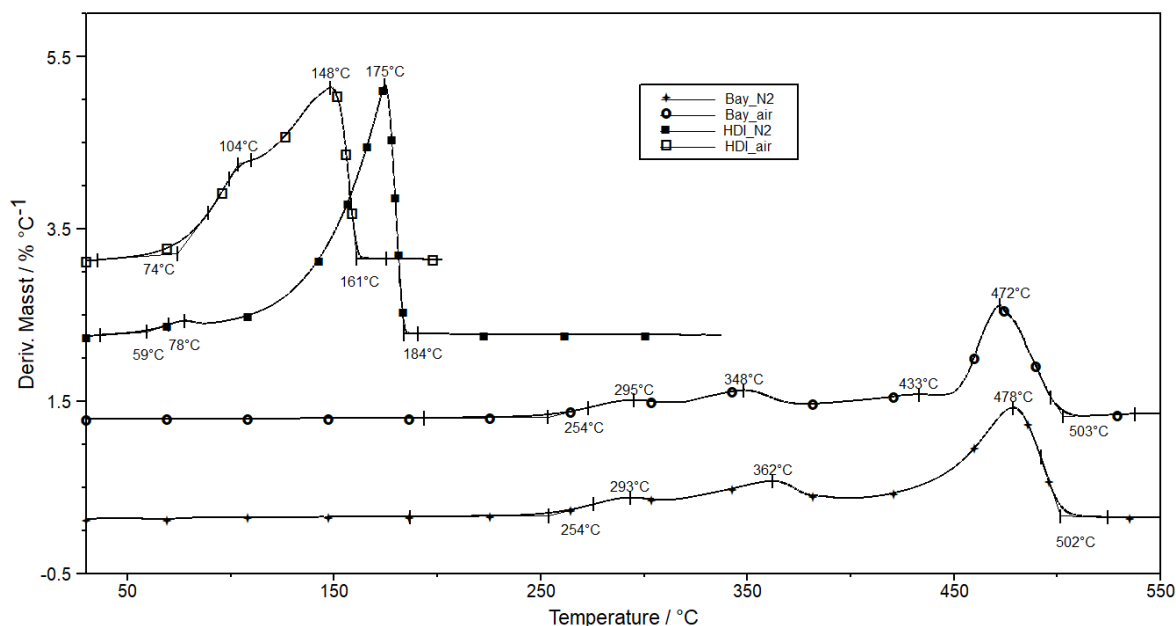

Figure 2 DTG curves of **HDI** and **Bay** in N$_2$ and air at a heating rate of 20 ^{o}C min^{-1}.

The thermal stability of the hybrid polymer samples **HDI-1** and **HDI-2** containing coordination compounds [Cu*ampf*(NO$_3$)$_2$MeOH]·MeOH (**1**) and [Cu*ampf*Cl$_2$] (**2**), *ampf* = *N,N'*-bis(4-acethyl-5-methylpyrazol-3-yl)formamidine, is significantly higher than that of the pure **HDI** (see DTG curves in Fig 3). The onset temperatures are a little higher in nitrogen (245 ^{o}C *vs*. 237 ^{o}C for **HDI-1** and 216 ^{o}C *vs*. 205 ^{o}C for **HDI-2**). The polymer containing the nitrato complex is more stable than that with the chlorido complex. **HDI-1** and **HDI-2** in air decompose without residue to 500 ^{o}C and 600 ^{o}C, respectively, whereas in nitrogen the decomposition above 500 ^{o}C slows down. In air the decomposition is highly exothermic in the whole temperature range, while in nitrogen it stars with two small endothermic effects. Above 400 ^{o}C in nitrogen the decomposition becomes exothermic and above 550 ^{o}C it is again endothermic (see Fig 4). Around 100 ^{o}C a small glass transition step is observed while ~180 ^{o}C a second-order phase transition is taking place in both gases.
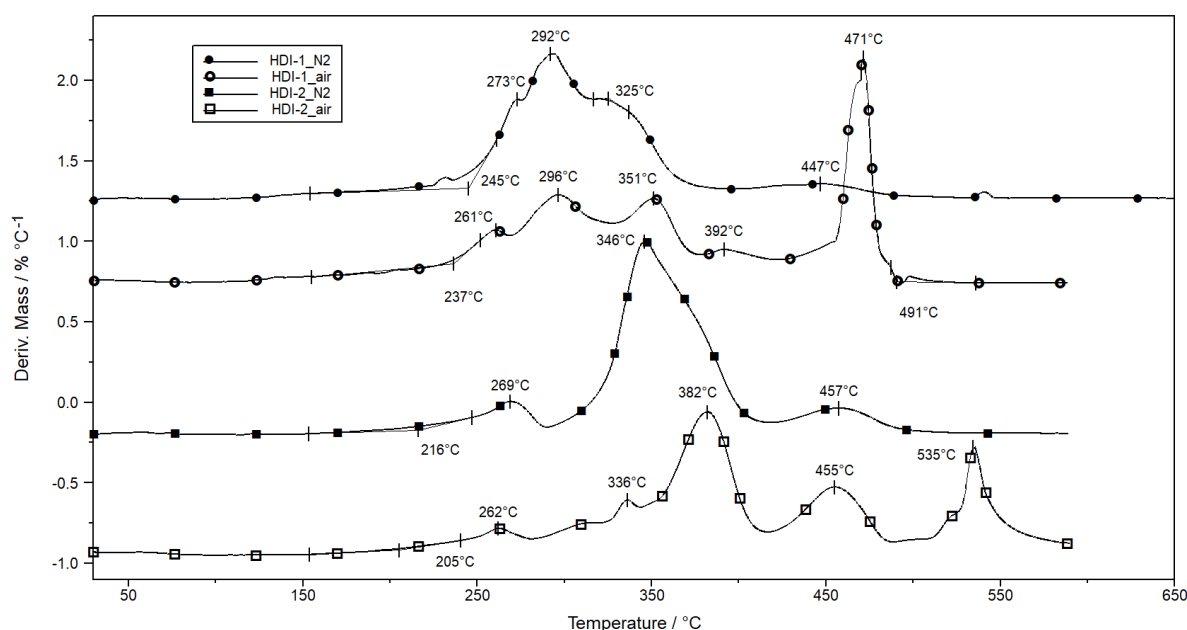
Figure 3 DTG curves of **HDI-1** and **HDI-2** in nitrogen and air at a heating rate of 20 ^{o}C min^{-1}.

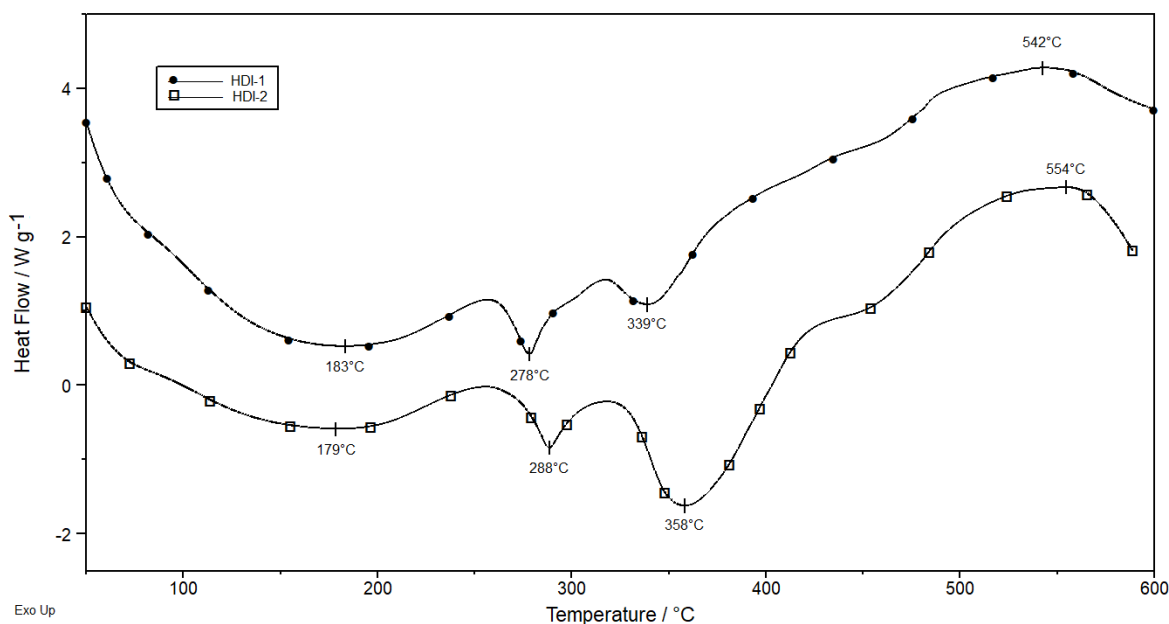**Figure 4** DSC curves of **HDI-1** and **HDI-2** in nitrogen at a heating rate of 20 ^{o}C min^{-1}.

The thermal behavior of the hybrid polymers of Bayhydur, **Bay-1** and **Bay-2** is very similar to that described for the hybrids with **HDI**: their thermal stability is somewhat higher in nitrogen than in air (onset 235 ^{o}C and 207 ^{o}C for **Bay-1** and 230 ^{o}C and 221 ^{o}C for **Bay-2** in nitrogen and air in Fig 5, respectively). The polymer **Bay-1** with the nitrato complex is more stable than that the corresponding chlorido complex, **Bay-2**. The highly exothermic decomposition in air is complete to 550 ^{o}C for both

hybrids, while in nitrogen the endothermic decomposition turns into exothermic one only above 500 °C. The decomposition is not completed to 600 °C. Below the decomposition temperature an endothermic second order phase transition is observed, too.

It is interesting to note that the thermal stability of the hybrid polymers with **Bay** is lower than that of the crosslinker (254 °C onset in Fig 2) in contrast to the stability of the **HDI** hybrids which have a significantly higher thermal stability than the **HDI**. However, taking into account that the proton of the –NH group of **Bay** may be involved in H-bond formation with the oxygen atoms of the side chain of another molecule, by the introduction of the coordination compound the compactness of the crosslinker is disturbed which leads to a lower thermal stability of the hybrid polymer. The mechanism of degradation of **Bay-1** and **Bay-2** is very similar to the decomposition of **Bay**. This is most probably the consequence of the small amount of the coordination compound in the polymers compared to the amount of Bayhydur, which is the main component of the hybrids and therefore determines its thermal properties.
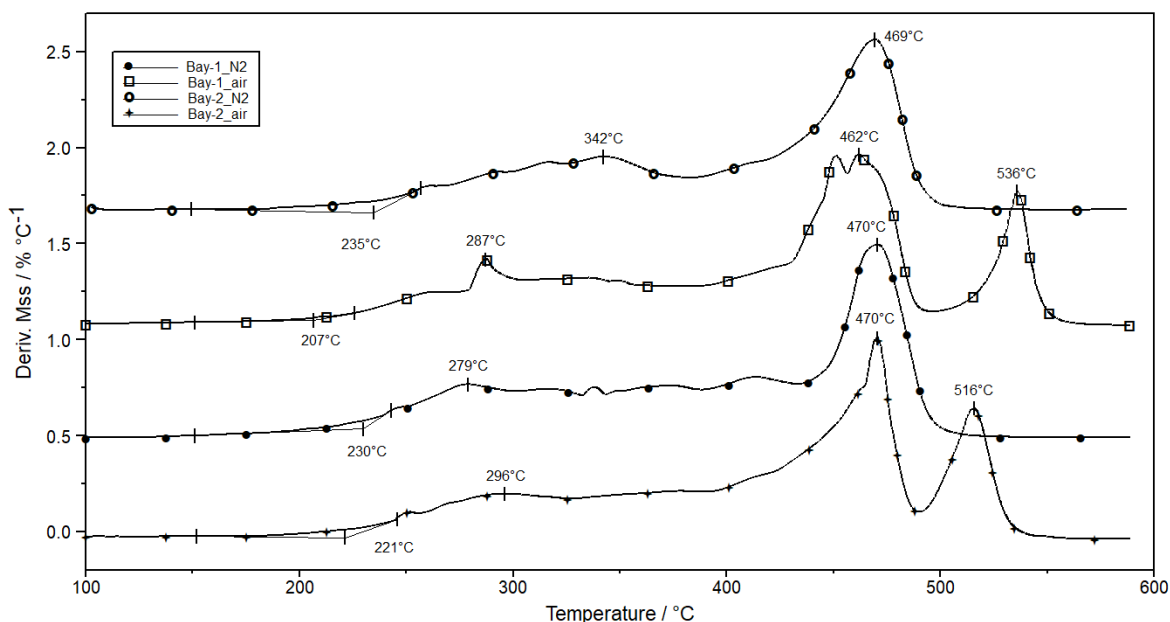

Figure 5 DTG curves of **Bay-1** and **Bay-2** in nitrogen at a heating rate of 20 °C min^{-1}

In order to understand the decomposition mechanism of the new materials coupled TG–MS measurements were carried out. In Fig 6 the relative signal intensities of the fragments giving the most intensive signals in the mass spectrum of the 1,6-hexamethylene diisocyanate [19] are presented with the corresponding DTG curve. The relative signal intensity in the mass spectrum of **HDI** from the NIST data base is decreasing in the order of $41 > 53 > 43 > 85 > 99 > 69$. In the evolved gases this order changes to $41 > 43 > 53 > 69$ in all of the samples[*]. In the high temperature region fragments with m/z ratio of 85 and 99 were detected with very low intensities. As Bayhydur may be regarded as a hexamethylene diisocyanate derivative, all these fragments are expected in the hybrids of **Bay**, too.

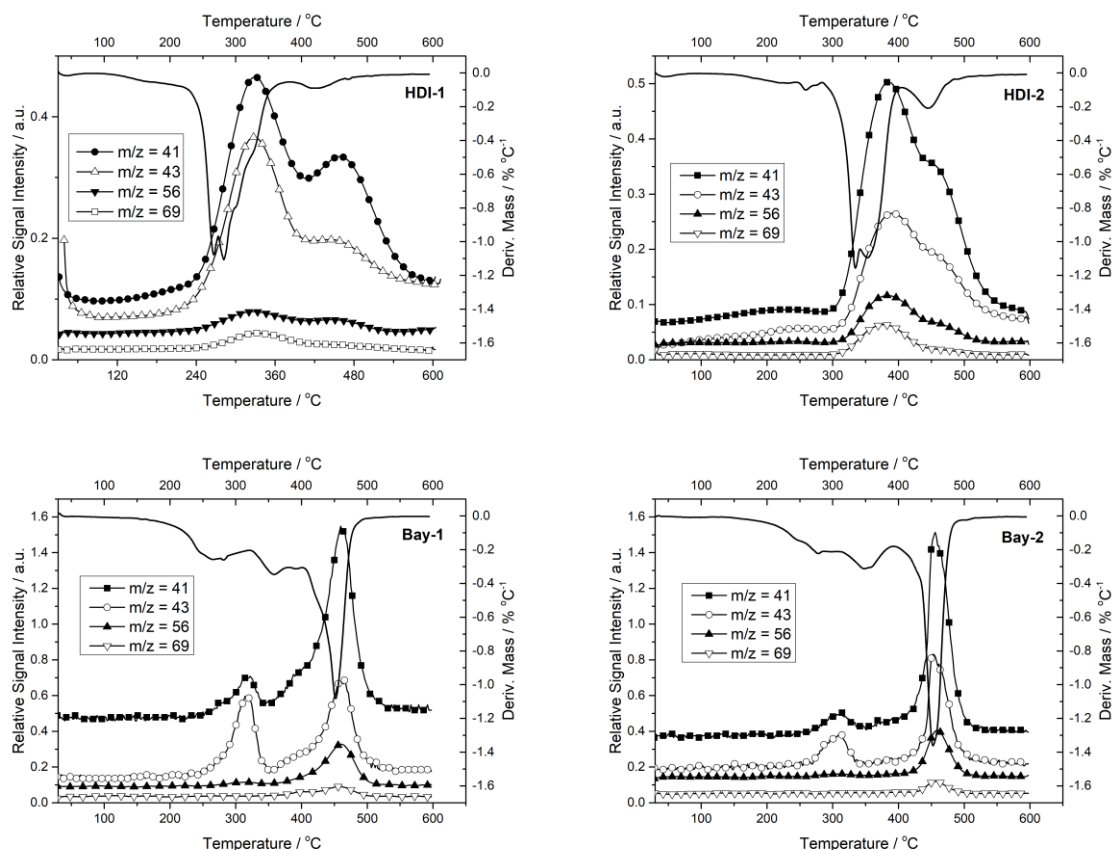[*] The order of magnitude is the same in all the MS spectra.

Figure 6 The characteristic MS curves for hexamethylene diisocyanate in the evolved gases formed during the thermal decomposition of **HDI-1**, **HDI-2**, **Bay-1** and **Bay-2** in nitrogen at 10 ^{o}C min^{-1} heating rate

The other characteristic fragments of the decomposition are presented in Fig 7. Opposite to the fragmentation of **HDI** from the data base and in the accordance with the expectation, during the thermal decomposition of the new materials, the most abundant fragments in the evolved gases are those with lower *m/z* ratio. As can be seen, the shapes of the MS curves follow the shape of the DTG curve. The order of magnitude and the intensity order of the fragments are identical in all the samples. The decomposition starts with the fragment of *m/z* = 14 which belongs to a CH_2^+ ion. In **Bay-2** despite the very small mass loss to the onset temperature (< 1 %) around 150 ^{o}C peaks with *m/z* = 18 and 17 appear which relative intensity ratio agrees with that for water. However, at the higher temperatures this ratio changes significantly referring most probable to NH_3 and NH_4^+ formation, too. The fragment with *m/z* = 50 which was related to the 4-acetyl-5-methylpyrazole moiety from the coordination compound with the *ampf* ligand [10], was found among the fragments in all the samples. However, its intensity was so low that could not be used as a straightforward proof for the presence of the coordination compound in the structure characterization of the hybrids.
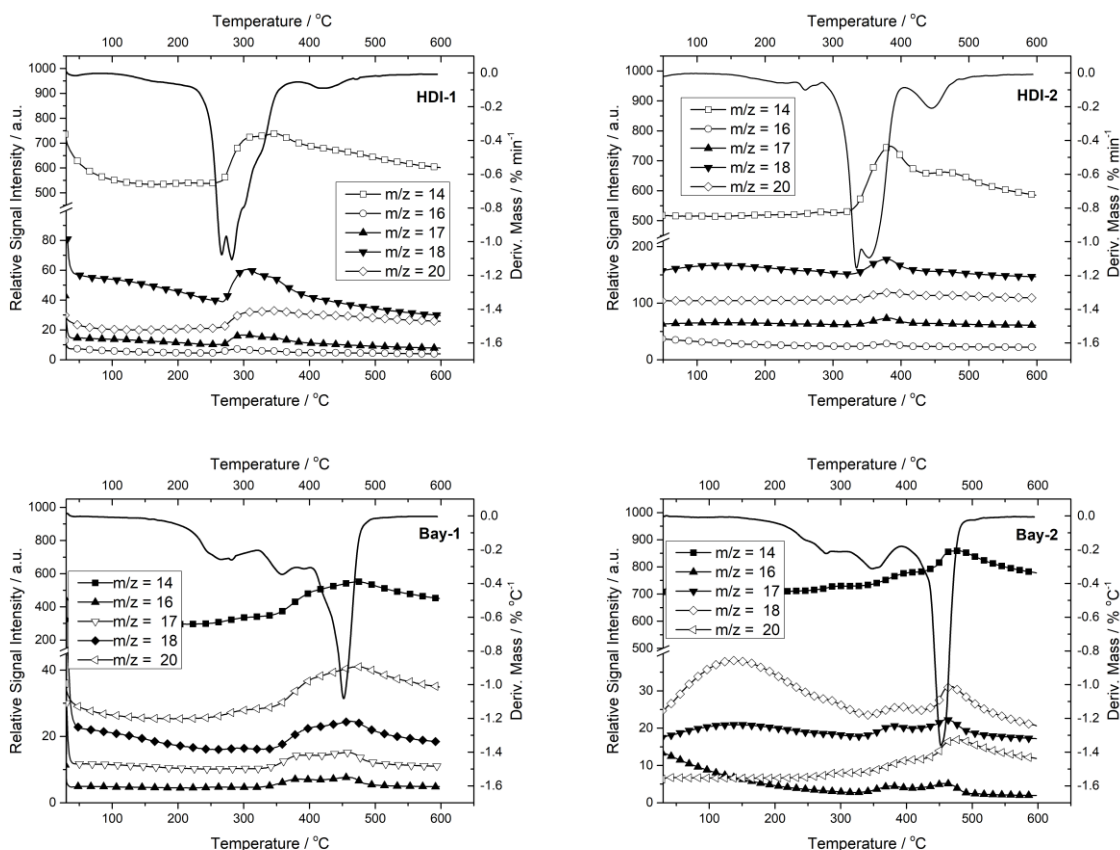
Figure 7 The most intensive MS curves of the hybrid polymers **HDI-1**, **HDI-2**, **Bay-1** and **Bay-2** evolved during their thermal decomposition in nitrogen at 10 ^{o}C min^{-1} heating rate

Conclusions

In the reaction between the isocyanate groups of 1,6-diisocyanatohexane (**HDI**) or Bayhydur 3100 (**Bay**) and the reactive –NH and –C=O groups of the coordination compounds [Cu*ampf*(NO$_3$)$_2$MeOH]·MeOH or [Cu*ampf*Cl$_2$] [*ampf* = *N,N*'-bis(4-acetyl-5-methylpyrazol-3-yl)formamidine], in the presence of dibuthyltin-dilaurate catalyst four new copper(II) containing hybrid materials were formed and characterized by FT–IR spectrometry and glass transition temperatures. *T*g for **HDI** hybrids appear in the temperature range of 100 ^{o}C – 125 ^{o}C, while for hybrids with **Bay** in 80 ^{o}C – 105 ^{o}C. The thermal decomposition of **HDI** hybrid polymers **HDI–1** and **HDI–2** is significantly higher than that of **HDI** and starts above 200 ^{o}C, while hybrid polymers **Bay–1** (DTG onset 207 ^{o}C, air) and **Bay–2** (DTG onset 221 ^{o}C, air) start to decompose below the decomposition temperature of **Bay** (DTG onset 254 ^{o}C, air). There is no significant difference in the decomposition temperatures measured in flowing air or nitrogen. Among the decomposition fragments all the most intensive peaks of **HDI** 41 > 53 > 43 > 85 > 99 > 69 from the NIST database can be found in all the hybrid polymers and regardless of the compound, their relative intensity ratio follows the order 41 > 43 > 53 > 69. The intensity of the fragments with higher *m/z* ratio is significantly lower. The fragment which was related to the ligand of the coordination compounds in our earlier work (*m/z* = 50) is also detected in all the hybrids but with much lower intensity than before.

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