

THE INFLUENCE OF BIO-BASED CHAIN EXTENDER ON THE POLYURETHANE PROPERTIES

Vladan Mičić¹, Milojka Jokić^{1*}, Milovan Jotanović¹, Ivan Ristić², Suzana Cakić³,
Tamara Erceg², Jaroslava Budinski Simendić²

¹ Faculty of Technology, University of East Sarajevo, Karakaj 34a, 75400 Zvornik

² Faculty of Technology, University of Novi Sad, Bulevar Cara Lazara 1, 21000 Novi Sad

³ Faculty of Technology, University of Nis, Bulevar Oslobođenja 124, 16000 Leskovac

Abstract: The development of polymers obtained from renewable raw materials is important because it is known that the fossil sources will be depleted in the future. Due to this fact, the possibilities for the synthesis of polyurethanes based on renewable resources increases. This work analyzes the properties of polyurethane materials obtained from the renewable resources. Polyurethane elastomers were prepared by a two stage process in solution, which involved the synthesis of the pre-polymer and synthesis of the polyurethane elastomer. As a polyol component, poly (propylene glycol) was used. Toluendiisocyanate and hexamethylene diisocyanate were employed as isocyanate components. For some samples, petrochemically obtained chain extender, butanediol, was replaced by biobased product isosorbide. Characterization of polyurethane materials was carried out by infrared spectroscopy with Fourier transformation, thermogravimetric analysis and differential scanning calorimetry. The properties of synthesized polyurethane materials were improved by adding the nanoparticles in various proportions.

Keywords: renewable raw materials, polyurethane elastomers, silica nanoparticles.

1. INTRODUCTION

The development of polymers based on renewable resources have got more importance since the fuel reserves have been drastically reduced because of their widespread use, inter alia, as feedstock for polymer synthesis. Excessive exploitation of fossil fuels can result in their completely depletion in close future. The use of renewable resources as feedstock for monomers obtaining can help also in solving the environmental pollution and economical issues that appear as a consequence of high fossil fuels consumption. People only use about 6 billion tons of biomass, or 2-3% per total amount of biomass that are annually synthesized by plants [1]. The main reason for low use is the difference in price between the methods for obtaining raw materials from plants and from the fossil fuels on the other hand. Therefore, the main efforts in the science and technology of developed countries are aimed to reducing production costs and reducing the cost of obtaining polymer materials from renewable raw materials. As a part of the extraordinary progress made in the field of science and materials enginee-

ring, a huge number of questions are asked that require an analysis of the impact of the production and application of these materials on the living environment. Therefore, it is necessary to design new materials with exceptional properties that will be able to satisfy the needs of a modern society. Furthermore, there is a need for finding new, cost-effective energy sources as well as more efficient use of existing ones. In this field, materials will have significant role. Hereof, the aim of this paper was to investigate the possibilities of using the plant raw materials as feedstock for synthesis of polyurethanes, as very important polymer materials.

1.1. Bio-based polyurethane materials

Today, polymer materials are one of the most widely used materials. Polymers derived from biological sources are perceived as „greener“ than synthetic polymers, even if synthetic polymers are also biodegradable. The argument that justifies the use of renewable sources is the reduction the environmental pollution by carbon (IV) oxide using the bio-polymers.

* Corresponding author: micicvladan@yahoo.com

Currently, most polyols for the polyurethane industry (polyether and polyester polyols) are derived from petrochemical raw materials, which lead to the reduction in these resources, and the materials with a biological base gain importance with the rise of the oil crisis and the danger of global warming [2–5].

The synthesis of materials based on natural oils allows the development of alternative polymer synthesis pathways. Vegetable oils are suitable renewable raw materials for the production of polyurethane components, such as polyols. Transformations of the double bond in the molecule of triglyceride into hydroxyl groups and their application in the synthesis of polyurethane are the subject of many studies [6–10]. As polyol compound in technology of polyurethane, biodegradable polyesters, such as poly(lactide) and poly(ϵ -caprolacton), can be used, giving in that way degradable polyurethane material. That reduces the amount of waste polymer material, but also allows the production of new materials those are assessed as compatible with human tissue [11]. A biocompatible and biodegradable polyurethane elastomer can be obtained using the poly(ϵ -caprolactone) and polyethers as polyol components and L-lysine as a chain extender, wherein the different length of the used polyether polyol has an effect on the degree of phase separation and thermal stability of the polyurethane elastomers [12]. The properties of polyurethane elastomers can be significantly improved by the addition of a filler (micro or nano) which due to interactions with polymer chains contribute to the improvement of desired properties of polyurethane material. Polymer composites are used in various fields such as airline industry, medicine, construction, electronics, etc. The fillers used for the preparation of polyurethane composites are carbon nanotubes, graphite, glass fibers, nanoparticles (titanium (IV) oxide, for example), aromatic polyamide

fibers. In the last few years, the production of polymer composites based on vegetable oils has become interesting in many areas. Polyurethane resins prepared from castor oil were used as a material for the production of composite graphite electrodes [13]. Structuring of nanocomposite is one of the greatest challenges in polymer science in the last two decades. The primary goal is to combine properties of inorganic phases with the best properties of the polymer matrix. The properties of new materials have shown, in many cases, remarkable improvements. For example, inorganic-organic hybrid materials provide better durability, mechanical and chemical resistance and adhesiveness [14,15].

2. EXPERIMENTAL

2.1. Materials

For the polyurethane elastomers synthesis, two types of isocyanates were employed: 2,4-Diisocyanato-1-methylbenzene (TDI) (density 1.214 g cm⁻³ at 25 °C) and 1,6-diisocyanatohexane (HDI) (density 1.047 gcm⁻³ at 20 °C).

Polypropylene glycol (PPG) with a molecular weight of 400 g mol⁻¹ was used as the polyol component (density 1.01 gcm⁻³ at 20 °C). As the chain extender, 1,4,3,6-dianhydro-D-glucitol (isosorbide) is employed (density 1.30 gcm⁻³ at 25 °C). TDI, HDI, PPG and isosorbide were procured from Sigma-Aldrich. The solvent was tetrahydrofuran (density 0.899 gcm⁻³ at 25 °C), purchased from Fisher Scientific. Dibutyltin dilaurate was used as catalyst (density 1.066 gcm⁻³ at 25 °C, supplied by Sigma Aldrich). Silicon (IV) oxide or silica nanoparticles were used as filler (type R812, manufacturer Evonik, Germany) whose properties are shown in Table 1.

Table 1. Properties of silicon (IV) oxide type R812

Properties	Units	Characteristic value
Behaviour toward water		Hydrophobic
Specific surface area (BET)	m ² g ⁻¹	260±30
The average size of primary particles	nm	7
Bulk density	g l ⁻¹	50
Loss on drying (2h / 100 °C)	wt %	≤0.5
Loss of ignition (2h / 1000 °C)	wt %	1.0-2.5
pH value		5.5-7.5
Content SiO ₂	wt %	≥ 99.8

2.2. Synthesis of thermoplastic polyurethane materials

The polyurethane elastomers were synthesized by a two-step procedure in solution, which includes the prepolymer synthesis (reaction of diisocyanate and polyol) in the first step and the synthesis of polyurethane elastomers by the addition of a chain extender in the second step. Certain amounts of diisocyanate and polyol component were measured in vial, depending on the desired amount of the soft segment in polyurethane composition. After addition of 5 ml of tetrahydrofuran solvent and 5 drops of the DBTDL catalyst, the reaction mixture was stirred for two hours at 60 °C. After two hours of stirring, the chain extender was added in reaction mixture, as

well as 5 drops of catalyst, and the synthesis continued for one hour at the same temperature. The feed amount of chain extender was determined based on the desired amount of soft segments in polyurethane composition. For the synthesis of composite material, composition of 50 wt% of soft segment was chosen and in the second stage the required quantity of filler, silicon (IV) oxide was added. After the polymerization has completed, the obtained samples were removed to the Petri plates because of easier evaporation of solvent and formation of film. Composition of polyurethane elastomers with different amounts of soft segments is given in Table 2, and composition of hybrid materials with different amounts of nanofiller silicon (IV) oxides is given in Table 3.

Table 2. Composition of polyurethane materials with different amount of soft segments (SSC)

Sample	Ratio NCO/OH, r	TDI, g	HDI, g	PPG, g	IS, g	SSC, %
PU-HDI-IS-30 %	1.15/1	-	0.3501	0.2448	0.2591	30
PU-HDI-IS-50 %	1.15/1	-	0.2260	0.3543	0.1430	50
PU-HDI-IS-70 %	1.15/1	-	0.1264	0.4359	0.0654	70
PU-TDI-IS-30 %	1.15/1	0-4255	-	0.2750	0.2219	30
PU-TDI-IS-50 %	1.15/1	0-2711	-	0.3724	0.1250	50
PU-TDI-IS-70 %	1.15/1	0-2045	-	0.4130	0.0880	70

Table 3. Composition of hybrid polyurethane materials with different amounts of nanofiller silicon (IV) oxide with content of soft SSC segments of 50%

Sample	TDI, g	HDI, g	PPG, g	IS, g	(SiO ₂), mass%
PU-TDI-IS-50%-1 %	0.2743	-	0.3714	0.1256	1
PU-TDI-IS-50%-5%	0.2706	-	0.3734	0.1266	5
PU-TDI-IS-50%-10%	0.2735	-	0.3751	0.1280	10
PU-TDI-IS-50%-15%	0.2690	-	0.3725	0.1281	15
PU-HDI-IS-50%-1%	-	0.2282	0.3548	0.1450	1
PU-HDI-IS-50%-5%	-	0.2260	0.3542	0.1433	5
PU-HDI-IS-50%-10%	-	0.2270	0.3537	0.1422	10
PU-HDI-IS-50%-15%	-	0.2305	0.3536	0.1489	15

2.3. Fourier Transform Infrared Spectroscopy analysis

The FT-IR spectra of obtained polyurethane samples were recorded by spectrophotometer Bomem Hartmann & Braun, MB-series in solid state, using the KBr pellet.

2.4. Thermogravimetric analysis

Thermogravimetric analyses (TGA) were performed on Setaram Setsys Evolution-1750 instrument. Samples of approximately 10 mg were heated from 25 °C to 700 °C at the heating rate of

20 °C min⁻¹ in nitrogen atmosphere with the gas flow rate of 20 cm³ min⁻¹.

2.5. Differential scanning calorimetry (DSC)

Thermal properties of synthesized samples were analyzed by differential scanning calorimeter (TA Instruments Q20) in nitrogen atmosphere. The gas flow during the investigation was 50 cm³ min⁻¹. In order to investigate the characteristic shifts in thermoplastic polyurethane elastomers and its hybrids, the thermal properties were tested in a temperature range from -90 °C to 180 °C. The heating rate was 10 °C min⁻¹. The weight of the samples was

about 6 mg. The instrument sensitivity is 10 mV cm⁻¹.

3. RESULTS

FTIR spectrums of polyurethane elastomers based on HDI, PPG and isosorbide as chain extender, exhibit a characteristic stretching of amino linkages (NH) at 3336 cm⁻¹, a combination of urethane (NH-CO-O) and ester bond (CO-O) at 1718

cm⁻¹, combination of NH out of plane of bending and CN at 1540 cm⁻¹, which is characteristic for all types of polyurethane materials. The peak corresponding to OH groups (3401 cm⁻¹) is disappeared in the spectra of the synthesized material for all samples. That confirms a high degree of reaction (greater than 98%). The presence of free isocyanate (NCO) group, at about 2250 cm⁻¹, has not been recorded for the synthesized samples (Figure 1).

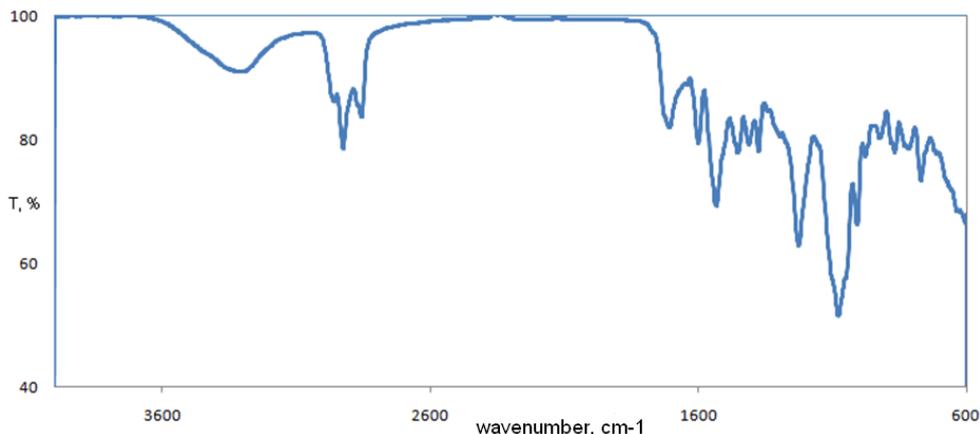


Figure 1. FTIR spectrum of polyurethane based on HDI and poly(propylene glycole) and isosorbide as a chain extender (with an amount of soft segments of 50%)

Thermal properties of thermoplastic polyurethane elastomers with and without the addition of SiO₂ nanofillers are given in Tables 4 and 5.

In pure polyurethane, two glass transition temperatures are present that correspond to the T_g values of soft and hard segments. Except for the sample PU-HDI-30% where T_g was not detected, probably due to the phases non-homogeneity of the

soft and hard segment. Increasing the hard segment content leads to a decrease in the T_g of soft segments and an increase in T_g of hard segments. The values of the glass transition temperature are higher in the TDI based polyurethane, compared to the HDI based samples, as the isocyanate component, Figure 2. This is also expected since TDI is aromatic and HDI is an aliphatic isocyanate.

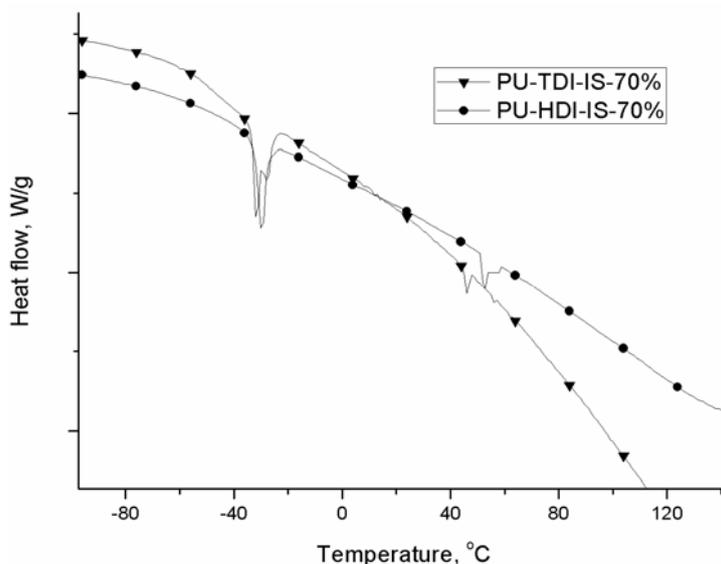


Figure 2. T_g values for polyurethane samples based on different isocyanate components (PU-TDI-IS-70% and PU-HDI-IS-70%)

The PU-HDI-IS-30% sample shows the lowest thermal stability, due to the lowest amount of the soft segment. Increasing of soft segment content increased the thermal stability of all samples. According to this results can concluded that increasing of soft segment contents leads to ordered polymer with higher concentration of hydrogen bonds which caused higher thermal stability.

Analyzing the results shown in Table 5, it is noticed that the addition of nanofillers to PU-TDI-IS-50% material contributes to the increase of ther-

mal stability. The highest thermal stability is observed for the samples with 15% of SiO₂ nanoparticles in TDI based PU matrix, figure 3. Comparison the results obtained by TG analysis for the sample of pure PU-HDI-IS-50% and the sample containing nanoparticles, it can be noticed that addition of nanoparticles improves thermal stability of the samples. It is very important to have information about thermal properties of polyurethane materials, because they determine their application.

Table 4. Thermal properties of polyurethane elastomers derived from the DSC and TGA measurements

Sample	T _g of soft segment (°C)	T _g of hard segment (°C)	T _{dec} (°C)	T _{5%} (°C)	T _{10%} (°C)
PU-TDI-IS-30%	/	67	227	231	274
PU-TDI-IS-50%	-22	58	224	226	272
PU-TDI-IS-70%	-35	45	234	247	280
PU-HDI-IS-30%	/	/	66	67	238
PU-HDI-IS-50%	-17	58	220	223	259
PU-HDI-IS-70%	-25	52	222	225	265

Table 5. Thermal properties of polyurethane elastomers with the addition of SiO₂ nanoparticles derived from the DSC and TGA measurements

Sample	T _g of soft segment (°C)	T _g of hard segment (°C)	T _{dec} (°C)	T _{5%} (°C)	T _{10%} (°C)
PU-TDI-IS-50%-1%	-21	62	245	248	290
PU-TDI-IS-50%-5%	-20	60	249	250	292
PU-TDI-IS-50%-10%	-22	/	250	253	294
PU-TDI-IS-50%-15%	-19	71	254	256	295
PU-HDI-IS-50%-1%	-17	51	232	233	272
PU-HDI-IS-50%-5%	-15	/	235	239	274
PU-HDI-IS-50%-10%	-19	/	236	238	277
PU-HDI-IS-50%-15%	-10	52	232	233	275

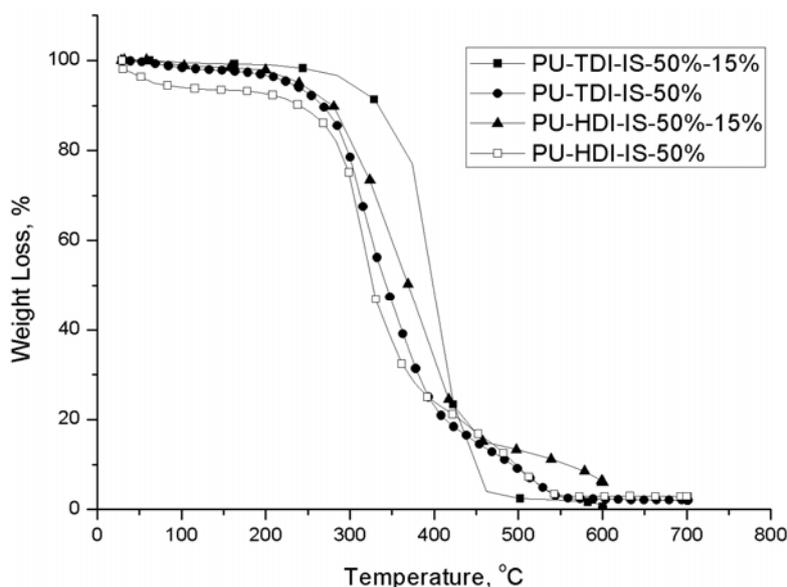


Figure 3. TG weight loss curves of pure polyurethane (PU-TDI-IS-50%, PU-HDI-IS-50%) and nanocomposites (PU-TDI-IS-50%-15%, PU-HDI-IS-50%-15%)

4. CONCLUSION

In this work, the synthesis of polyurethane was carried out using two types of diisocyanate: 2,4-Diisocyanato-1-methylbenzene (TDI) and 1,6-hexamethylene diisocyanate (HDI). Polypropylene glycol (PPG) was used as polyol component and 1,4,3,6-Dianhydro-D-sorbitol (isosorbide) was employed as chain extender. Tetrahydrofuran was used as solvent and dibutyltin dilaurate was used as catalyst. Silica, type R812, was used as nanofiller for preparation of polyurethane nanocomposites. The structure of polyurethane samples was confirmed by FT-IR method. Characteristic stretches of urethane and ester bonds are recorded in the range from 4000 to 400 cm^{-1} . The peak corresponding to OH groups disappeared in the FTIR spectrums of polyurethane elastomers for all samples and that confirms a high degree of reaction. Also the presence of free isocyanate group has not been recorded. Thermal properties of polyurethane elastomers and composites were determined by TG and DSC methods. In pure polyurethanes, two glass transition temperatures occur, which is the consequence of separating the phases of soft and hard segments. Exceptions are samples PU-TDI-IS-30%, where Tg of soft segments was not recorded, and PU-HDI-IS-30%, where no Tg of soft or hard segments were recorded. Looking at the thermal stability of pure polyurethane elastomers, it can be seen that the lowest heat stability has a sample PU-HDI-IS-30%, and the highest PU-TDI-IS-70% due to the share of soft segment that is more stable in comparison to urethane groups, so the degradation begins with the destruction of urethane bonds in the hard segment. It is established that addition of silica nanoparticles in showed range improves thermal properties of polyurethane materials. The highest thermal stability had a PU-TDI-IS-50%-15% sample. The use of polyurethane based on renewable resources and other biopolymers is a positive step towards reduction of CO₂ emission. Biopolymers have a potential to solve the problem with disposal of plastic waste due to its biodegradability as well as the future problems related to the lack of fossil fuels originated from raw materials. Continuous work on further improvements of the properties of polyurethanes produced from renewable sources can expand their application, which is very important from the aspect of their industrial production.

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УТИЦАЈ БИООБНОВЉИВОГ ПРОДУЖИВАЧА ЛАНЦА НА СВОЈСТВА ПОЛИУРЕТАНСКИХ МАТЕРИЈАЛА

Сажетак: Развој полимера добијених из обновљивих сировина добија све више на значају јер је познато да ће фосилни извори сировина бити истрошени. Због ових разлога у свету се све више испитују могућности синтезе веома битних полимерних материјала – полиуретана на основу обновљивих сировина. У овом раду извршена је анализа својстава полиуретана добијених на основу обновљивих сировина. Полиуретански еластомери су добијени двостепеним поступком у раствору, који обухвата најпре синтезу преполимера а затим полиуретанског еластомера. Као полиолна компонента коришћен је поли(пропилен гликол), а изоцијанати су били изофлорондиизоцијанат и хексамедилен диизоцијанат. Ради могућности замене петрохемијски добијеног продуживача ланца коришћен је изосорбид уместо бутандиола. Карактеризација полиуретанских материјала извршена је инфрацрвеном спектроскопијом са Фуријеовом трансформацијом, термогравиметријском анализом и диференцијалном скенирајућом калориметријом. Побољшање својстава синтетисаних полиуретана остварено је додавањем наночестица у различитим односима.

Кључне речи: синтеза, обновљиве сировине, полимери, наноматеријали.

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