Preparation and characterization of porous poly(urethane-urea) microparticles from poly(vinyl alcohol) and isophorone diisocyanate

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The porous poly(urethane-urea) (PUU) microparticles are synthesized from poly(vinyl alcohol) (PVA) and isophorone diisocyanate (IPDI) in the dimethyl sulfoxide/water (99/1 vol%) solution by a one-step method. Influences of the initial molar ratio of PVA and IPDI, the reaction time and temperature on the yield and the structure of PUU are studied. The highest yield of PUU microparticles is 70.1%. The PUU are thoroughly characterized by the chemical analytical methods, infrared spectrometry, thermal analysis, surface area and pore volume analysis. The largest surface area is $122 \ m^2 \cdot g^{-1}$ and the total pore volume is $0.62 \ cm^3 \cdot g^{-1}$. Mainly the mesopore structure of PUU microparticles with the presence of macropores is estimated. The size and morphology of the PUU microparticles are evaluated by the scanning electron microscopy. The size distribution of PUU microparticles, which are synthesized under different conditions, is in the range of 2–10 μm. Thermal decomposition of the PUU occurs in two stages according to TGA results.

Key words: poly(urethane-urea), poly(vinyl alcohol), porous polymers, thermogravimetric analysis (TGA), surface area

INTRODUCTION

Polyurethane (PU) and poly(urethane-urea) (PUU) as the polymer class have been already widely screened for coatings, adhesives, paints, powder moulding, optical area, biomedical and biotechnological applications [1, 2]. Urethane-based materials are of commercial interest in many applications because of their excellent properties such as abrasion resistance, high strength, chemical resistance, good biocompatibility and aging [3, 4]. Many PUU materials were obtained by using a diol, IPDI and diamine as a chain extender, or when the PU was cured with humidity [43]. Linear aliphatic polyester, tri-functional polyester [15], polycaprolactone diol [16–19], polypropylene glycol [18–20], poly(tetramethylene ether)glycol and 1,4-butane diol [15, 2], poly(tetramethylene adipate) [22], polyester polyol (commercial name is Desmophen 1019-55) [23], polyethylene glycol [20, 24], bisphenol A and hydroxyethyl acrylate [24] were used as diols for nonporous PUU particles.

Some studies have pointed out the importance of the porosity of the synthetic material, more specifically, a pore size distribution and structure, in promising biocompatibility and biodegradability [3]. Porous organic polymer networks could be used as gas storage, separation of materials, catalysts and supports for organic and biocatalysts, encapsulation agents for controlled release of drugs [25–27]. Only a few papers have been reported for the synthesis of porous PU particles [3, 28]. Wang and Ruckenstein reported the synthesis of PU particles in two steps [28]. In the first step, the PU prepolymer was made from poly[methylene(polyphenyl isocyanate)] and poly(propylene glycol). In the second step, the PU prepolymer was transferred into the flask which contained a catalyst, a mineral oil, a small amount of water and a calcium carbonate as a porogen. After reaction pores into the PU particles were produced when a mineral oil was extracted with benzene. PU particles were treated with a solution of hydrogen chloride in order to generate additional pores. Jabbari and Khakpour [3] reported the preparation of porous PU particles according to a two-step procedure in an aqueous medium. The PU particles were made from 4,4'-methylene bisphenyl isocyanate, polyethylene glycol and 1,4-butanediol which was used as a chain extender. Pores size in the PU particles depended on the amount of 1,4-butanediol in an initial reaction mixture. Porous PU or PUU materials were also synthesized

by the salt leaching technique [29–33]. Sodium chloride, sodium phosphate heptahydrate and ammonium chloride were used as salts. Guan et al. [34] reported the synthesis of porous polyurethane scaffolds by a freezing technique.

To summarize the current state of knowledge about synthesis of PU or PUU materials, the PVA was not used as the polyol in the reaction with IPDI in synthesis of porous PUU microparticles.

The aim of the present study was the one-step synthesis of the novel porous poly(urethane-urea) microparticles from poly(vinyl alcohol) and isophorone diisocyanate in dimethyl sulfoxide/water (99/1 vol%) solution. The effects of the reaction conditions, such as an initial molar ratio of poly(vinyl alcohol) and isophorone diisocyanate, the reaction time and temperature on the yield and the structure of the poly(urethane-urea) microparticles, the surface area, the total pore volume, the size distribution and thermal properties of microparticles were evaluated. The porous PUU microparticles with free isocyanate groups immediately after synthesis could be used in biotechnology as supports for bioactive compounds.

EXPERIMENTAL

Materials
Isophorone diisocyanate (IPDI) was purchased from Aldrich, Germany. Poly(vinyl alcohol) 100000 (PVA, degree of hydrolisation 86–89 mol%, viscosity (4% in water, 20 °C) is 34–45 mPa·s) was purchased from Fluka, Switzerland. Dimethyl sulfoxide (DMSO) was purchased from Sigma-Aldrich, France. Acetone was purchased from Reachem Slovakia, Slovakia. Diethyl ether was purchased from LACH-NER, Czech Republic. PVA was dried under vacuum at 60 °C for 24 hours and kept in a desiccator. All other reagents were used as received.

Synthesis of the PUU microparticles
The PUU microparticles from PVA and IPDI were synthesized by the one-step method in dimethyl sulfoxide/water (99/1 vol%) solution according to our previous work [35]. The initial concentration of PVA was 0.06 M (mole of repeating units of PVA). The initial molar ratio of PVA and IPDI was varied from 1:2.0 to 1:4.0. The obtained PUU microparticles were dried in vacuum at 60 °C. For determination of the microparticle size distribution, surface area, pore volume, pore size distribution of the PUU microparticles and elemental analysis, they were lyophilized by using a Christ Alpha 2–4 LSC lyophilizer.

Characterization of the PUU microparticles
Determination of functional groups and elemental analysis
The amounts of isocyanate and hydroxyl groups were determined by chemical methods [36]. Determination of the amount of isocyanate groups was performed immediately after synthesis of the PUU microparticles and it was recalculated with respect to weight loss in the drying process. The elemental analysis was performed by using a Thermo Scientific Flash 2000 series CHNS-O analyzer.

FT-IR analysis
The functional groups in PUU were characterized by using a Perkin Elmer FRONTIER FT-IR spectrometer.

Thermal analysis
The TGA investigations were carried out by using a Perkin Elmer Simultaneous Thermal Analyzer STA 6000 in the temperature range between 30–600 °C in the 20 cm³·min⁻¹ flow of nitrogen and the heating rate of 10 °C·min⁻¹. The DSC investigations were carried out by using a Perkin Elmer DSC 8500 in the temperature range between 0–250 °C in the 40 cm³·min⁻¹ flow of nitrogen and the heating rate of 10 °C·min⁻¹.

Determination of size and morphology of the PUU microparticles
The size and morphology of the PUU microparticles were investigated by using the scanning electron microscope Hitachi SU 70.

Determination of the surface area, the total pore volume and the pore size distribution of PUU microparticles
The surface area, the total pore volume and the pore size distribution of the PUU microparticles were determined by using a Micromeritics Tristar II instrument. The samples were degassed at 140 °C for 2 hours prior to experiments to eliminate any volatile compounds from the lyophilized PUU microparticles. The Brunauer–Emmett–Teller (BET) surface area was evaluated from the isotherm analysis in the relative pressure range of 0.05–0.22. The total pore volume was determined from the adsorption isotherm at the relative pressure of 0.98. The pore size distributions were derived from desorption branch by using a Barret–Joyner–Halenda (BJH) model.

RESULTS AND DISCUSSION

Synthesis and characterization of PUU microparticles
The PUU microparticles were synthesized from PVA and IPDI in the DMSO/H_2O (99/1 vol%) solution by the one-step method. The chemical structure of the PUU microparticles depends on many factors, such as the initial molar ratio of components, their reactivities, the reaction time and temperature. Changing the initial molar ratio of PVA and IPDI from 1:2.0 to 1:4.0 resulted in increasing the yield of PUU microparticles from 48.5 to 67.4%, increasing the quantity of isocyanate groups from 0.6 to 1.7% and decreasing the quantity of hydroxyl groups from 11.6 to 6.8% (Table 1). A gel was formed immediately when the initial molar ratio of PVA and IPDI was 1:5.0 or when the concentration of PVA was higher than 0.06 M.

No.	PVA:IPDI initial molar ratio	Yield of PUU, %	Quantity of NCO groups, %	Quantity of OH groups, %
1.	1:2.0	48.5	0.6	11.6
2.	1:2.5	52.5	1.3	10.5
3.	1:3.0	61.5	1.5	8.1
4.	1:3.5	66.6	1.6	7.3
5.	1:4.0	67.4	1.7	6.8

Changing the synthesis time from 60 to 90 min, when the initial molar ratio of PVA and IPDI was 1:4 and the reaction temperature was 90 °C, resulted in increasing the yield of the PUU microparticles from 47.2 to 67.4%. Prolongation of the reaction time to 180 min resulted in increasing the yield of the PUU microparticles to 70.1% (Fig. 3a). It was observed that the yield of the synthesized PUU microparticles was largely dependent on the reaction temperature (Fig. 1b) than on reaction time.

Increasing the reaction temperature of synthesis of the PUU microparticles from 70 to 90 °C, when the initial molar ratio of PVA and IPDI was 1:4.0 and the reaction time was 90 min, resulted in increasing the yield of the PUU microparticles from 61.0 to 67.4%. Further increasing the reaction temperature to 150 °C resulted in the decreased yield of the PUU microparticles to 51.4%. The steric hindrance and the re-

action temperature play a major role in the reaction between secondary alcohol groups of PVA and primary or secondary isocyanate groups of IPDI. According to literature [37, 38], relative reactivities of the primary and secondary isocyanate groups in urethane formation depend on the catalyst, the reaction temperature and the reactivity of alcohol. IPDI reacts mainly with the secondary isocyanate group without an added catalyst [37, 38]. At higher temperatures, the difference in reactivity between the secondary and primary isocyanate group is reduced [37, 38]. On the other hand, with increasing steric hindrance of the alcohol, the urethane reaction proceeds more selectively towards to formation of primary than secondary urethanes [37, 38]. It is supposed that the reaction will proceed mainly between the hydroxyl group of PVA and the secondary isocyanate group of IPDI. Water plays an important role in the reaction mixture. Firstly, water behaves as a blowing agent and, secondly, helps to form urea linkages. It can be summarized as follows: the reaction between the isocyanate group of IPDI and water leads to emission of the gaseous carbon dioxide and production of the amino group, which can form urea linkage with the isocyanate group. Reactivity between the amino group and isocyanate group is higher than reactivity between the hydroxyl group and isocyanate group [2, 37, 38]. At higher temperatures (near 100 °C and higher), it is proposed that water starts to evaporate from the DMSO/water solution and the formation of urea linkages is reduced. The carbon and nitrogen contents from the elemental analysis confirmed the formation of urea linkages and the increasing amount of IPDI in the reaction mixture resulted in increasing their content in the PUU (Table 2). Increasing the reaction time and temperature of synthesis of the PUU microparticles, when the initial molar ratio of PVA and IPDI was 1:4.0, resulted in decreasing the quantities of isocyanate and hydroxyl groups in the PUU (Fig. 2).
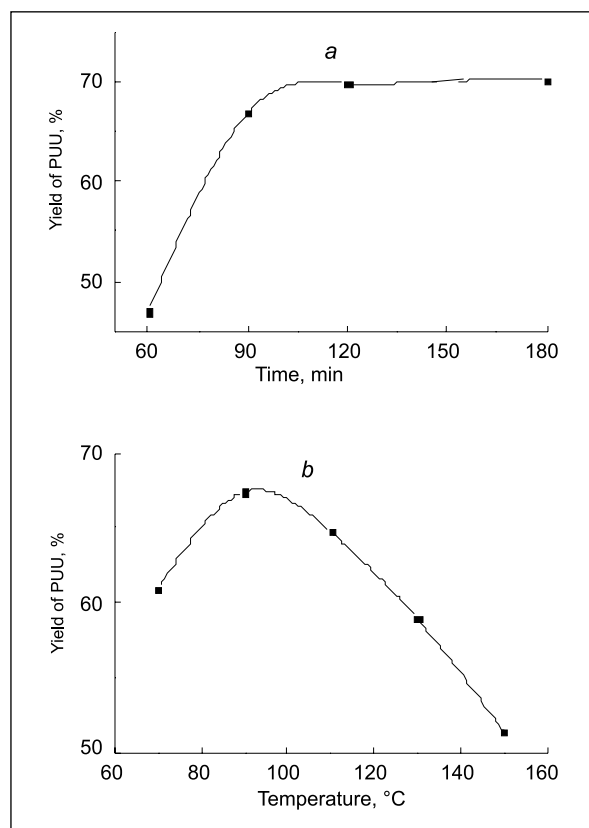
Table 2. **Elemental analysis of PUU microparticles**

No.	PVA:IPDI initial molar ratio	Carbon content, %	Nitrogen content, %	Hydrogen content, %
1.	1:2.0	62.7	11.4	9.7
2.	1:2.5	63.1	11.7	9.8
3.	1:3.0	63.7	12.2	9.9
4.	1:3.5	63.8	12.4	9.9
5.	1:4.0	63.9	12.7	10.0

The structure of PUU has been proven by the chemical analysis (Tables 1 and 2) and attenuated total reflectance FT-IR spectra (Fig. 3). The FT-IR spectra of PUU microparticles, which were synthesized using various molar ratios of PVA and IPDI, show almost the same band with a slight peak shift with the increasing amount of IPDI in the initial mixture at 3 338–3 332 cm^{-1} related to N-H, peaks at 2 950 cm^{-1} and 2 904 cm^{-1} related to C-H from alkyl groups, the peak at 1 637 cm^{-1} related to C=O of the urea group, the peak at 1 550 cm^{-1} related to amide II (d N-H, n C=N), the peak at 1 237 cm^{-1} related to amide III (another type of d N-H, n C=N) and the peak with a slight shift at 1 056–1 052 cm^{-1}
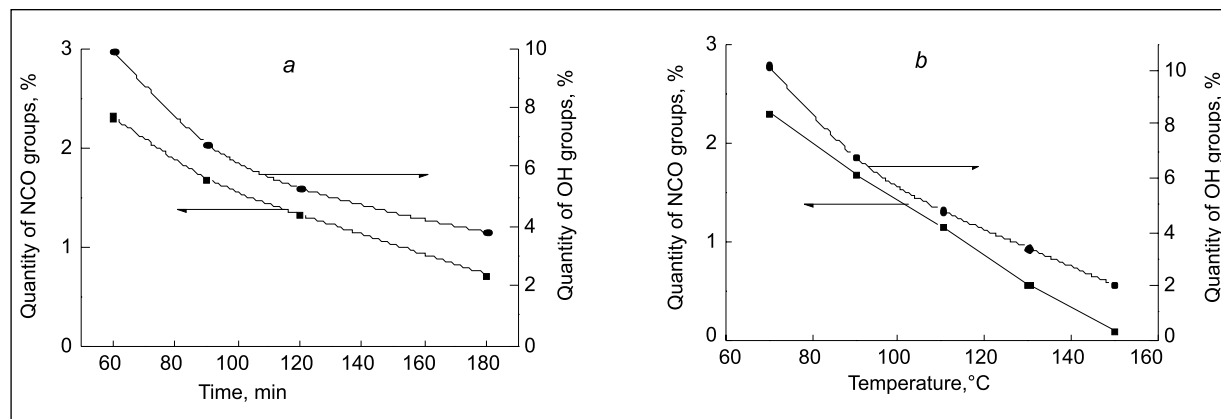

Fig. 1. Yield of PUU microparticles as a function of reaction time (*a*: $T = 90$ °C) and temperature (*b*: $t = 90$ min) ([PVA]:[IPDI] = 1:4.0)

Fig. 2. Quantity of isocyanate and hydroxyl groups of PUU as a function of reaction time (*a*: *T* = 90 °C, [PVA]:[IPDI] = 1:4.0) and temperature (*b*: *t* = 90 min, [PVA]:[IPDI] = 1:4.0)
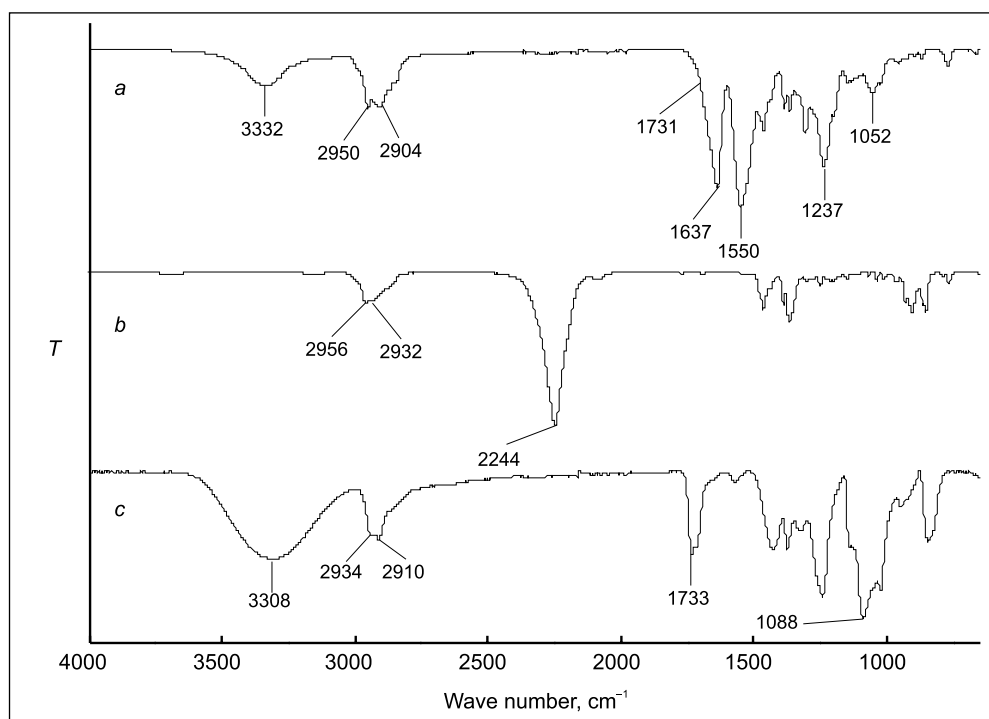
Fig. 3. FT-IR spectra of PUU ([PVA]:[IPDI] = 1:4, *t* = 90 min, *T* = 90 °C) (*a*), IPDI (*b*) and PVA (*c*)

(n C-O-C) related to ether. The scheme outlines the synthetic route used to prepare the PUU microparticles using PVA and IPDI in the presence of water in the reaction mixture. Immediately after the synthesis the PUU microparticles consist of macromolecules with three types of constitutional units: a constitutional unit with one urethane group which was formed by the reaction between the hydroxyl group of the hydroxyethylene monomeric unit on PVA and one isocyanate group of IPDI and a free isocyanate group at the end of branch, from which the amino group could be formed by the reaction with humidity in the drying process of the PUU (type I); an unreacted hydroxyethylene constitutional unit of PVA (type II) and a constitutional unit with two urethane groups after the crosslinking reaction of two isocyanate groups and two hydroxyl groups of PVA chains

(type III). The poly(urea) segments could present in constitutional units of type I and III.

The non-isothermal stabilities of PVA and PUU microparticles were studied using TGA measurements (Table 3, Fig. 4). According to the DSC results, the melting point of PVA is 189.3 °C. A melting point of the PUU was not detected because of its crosslinked structure. Decomposition of PVA proceeds in the two stages according to the TGA and DTGA results. The first stage with the maximum of decomposition temperature at 309.4 °C mainly involves dehydration accompanied by the formation of some volatile products. In the second stage, the polyene residues are further degraded at 433.8 °C to yield carbon and hydrocarbons [42]. In the case of PVA-based PUU microparticles, which were obtained when the initial molar ratios of PVA and IPDI were changed from 1:2.0 to 1:4.0, TGA and
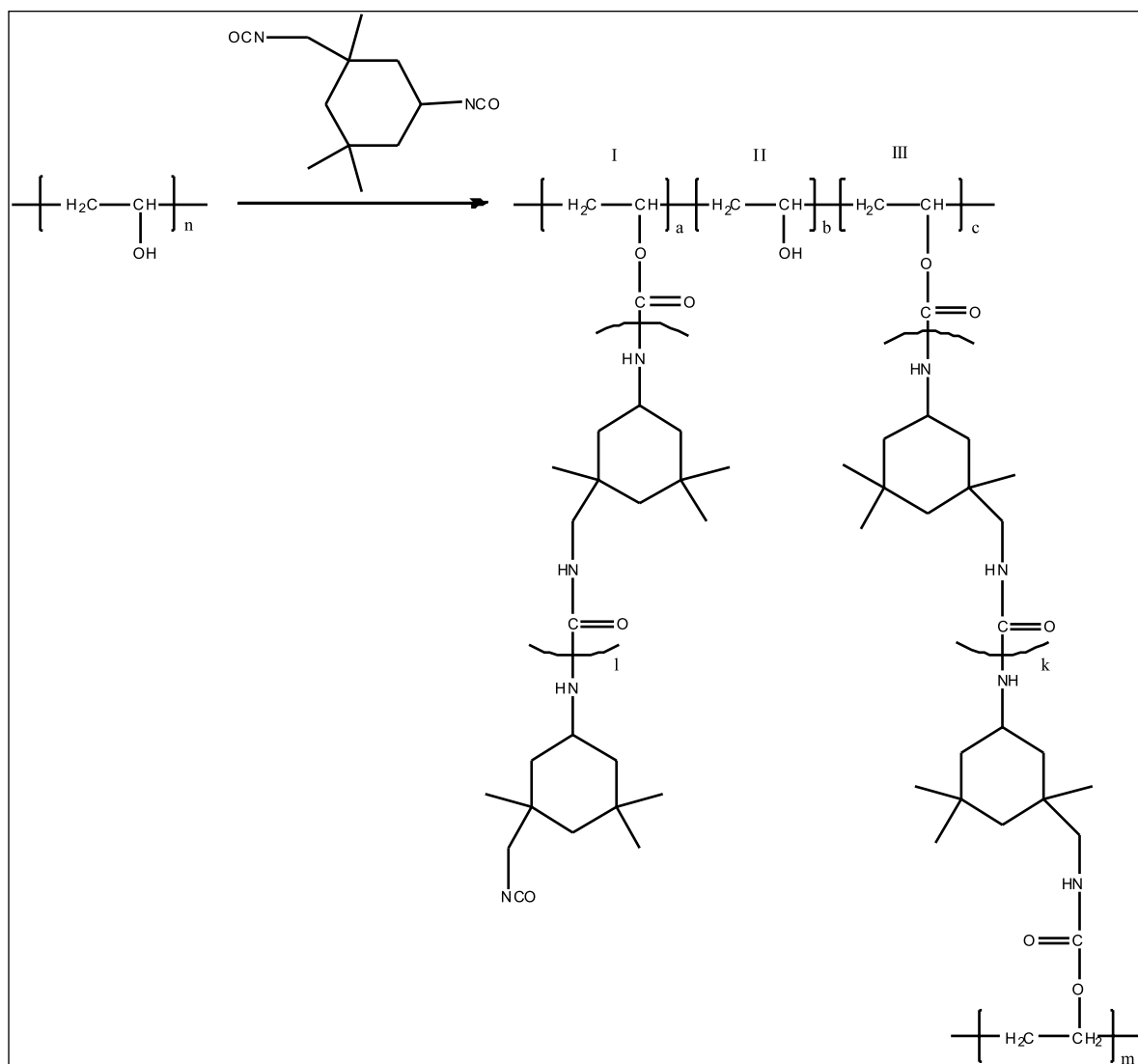
Scheme. Structure of synthesized PUU (*l* and $k \geq 0$)

DTGA curves also show the two-step decomposition profile (Fig. 4, Table 3).

The maximum decomposition temperature of PUU microparticles in the first stage occurs at 348.9 °C and it was 39.5–45.1 °C higher than the decomposition temperature of PVA. The second stage maximum decomposition temperature was close to the second step decomposition temperature of PVA. The first peak indicated the thermal decomposition of ure-thane and urea linkages. The strength of the hydrogen bonds between urea groups is stronger than that between urethane groups because the polarity of urea groups is stronger than that of urethane groups [41]. The hydrogen bonds in PUU increased the stability and the decomposition temperature. Increasing the amount of IPDI in the initial reaction mixture resulted in increasing the amount of urea segments, crosslinked units and increasing the decomposition temperature.

Table 3. **TGA results of PVA and PUU (*t* = 90 min, *T* = 90 °C)**

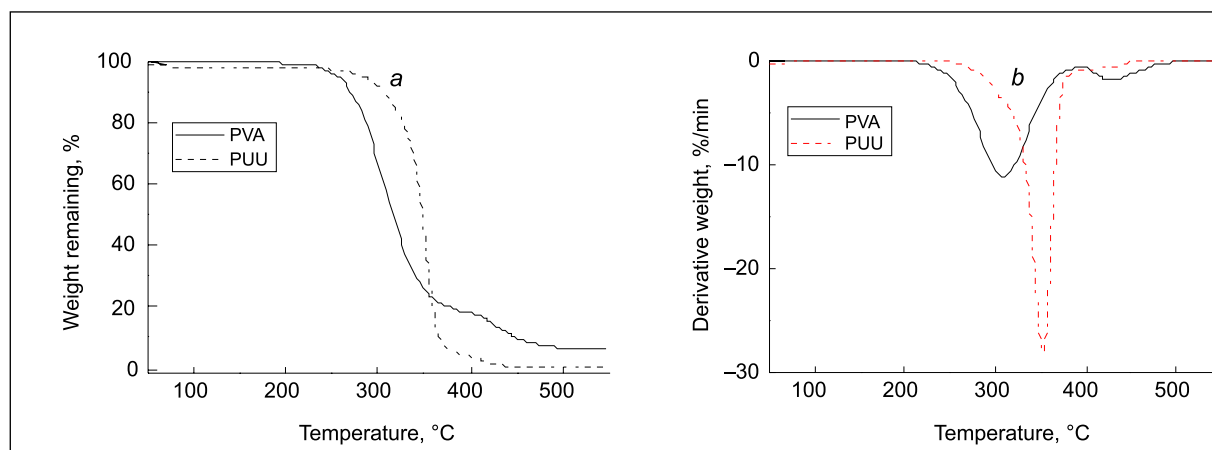| No.	PVA:IPDI initial molar ratio	First decomposition step			Second decomposition step		
		T_{init}, °C	T_{max}, °C	Δm, %	T_{max}, °C	T_{end}, °C	Δm, %
1.	PVA	249.2	309.4	78.1	433.8	481.6	11.2
2.	1:2.0	246.6	348.9	89.5	428.4	452.8	7.2
3.	1:2.5	246.8	352.1	89.9	427.9	453.1	6.5
4.	1:3.0	246.6	353.3	89.2	426.9	452.7	6.3
5.	1:3.5	246.9	354.5	89.7	429.6	453.9	6.7
6.	1:4.0	246.8	352.6	89.8	430.4	453.3	6.2

Fig. 4. TGA (*a*) and DTGA (*b*) curves of PVA and PUU microparticles ([PVA]:[IPDI] = 1:4.0, *t* = 90 min and *T* = 90 °C)

As was shown in Scheme, the PUU chains are crosslinked. When the solvent is removed from the system, the space that it had previously occupied becomes the pore volume and network of intercommunicating pores left behind. The nitrogen adsorption and desorption isotherms at –196 °C and the slit-shaped pore size distribution analysis of PUU microparticles were calculated using BET and BJH methods, respectively (Fig. 5).

PUU microparticles display the type IV gas sorption isotherm with the H3 hysteresis loops which provided aggregates of plate-like particles with distribution of slit-shaped pores width (Fig. 5a) [43]. The information about the surface area and the total pore volume is summarized in Table 4. The nitrogen adsorption and desorption isotherms show the clear hysteresis loop, which indicates the mesoporous structure. The remarkable rise to the medium and high pressure region (p/p_o = 0.8–1) of the nitrogen adsorption and desorption isotherms implies the presence of macropores in PUU microparticles. According to the results of Table 1, changing the initial molar ratio of PVA and IPDI from 1:2.0 to 1:4.0, when the reaction time was 90 min and the temperature was 90 °C in the synthesis of PUU microparticles, resulted in increasing the urea segments and cross-links

Table 4. Porous properties of PUU microparticles (*t* = 90 min, *T* = 90 °C)

No.	PVA:IPDI initial molar ratio	Surface area, $m^2 g^{-1}$	Total pore volume, $cm^3 g^{-1}$
1.	1:2.0	83.1	0.36
2.	1:2.5	87.6	0.45
3.	1:3.0	94.1	0.45
4.	1:3.5	104.3	0.45
5.	1:4.0	112.7	0.46

(Scheme, Types I and III) and increasing the surface area from 83.1 to 112.7 $m^2 \cdot g^{-1}$, and the total pore volume from 0.36 to 0.46 $cm^3 \cdot g^{-1}$. The reaction time was varied from 60 to 180 min and had minor influence on the surface area and the total pore volume of PUU microparticles (which were synthesized when the initial molar ratio of PVA and IPDI was 1:4.0 and the reaction temperature was 90 °C). On the other hand, the surface area and the total pore volume depend more on the reaction temperature (Fig. 6). Increasing the reaction temperature from 70 to 150 °C, when the initial molar ratio of PVA and IPDI was 1:4.0 and the reaction time was 90 min, resulted in decreasing the surface area from 122.0 to 71.2 $m^2 \cdot g^{-1}$ and the total pore volume from 0.62 to
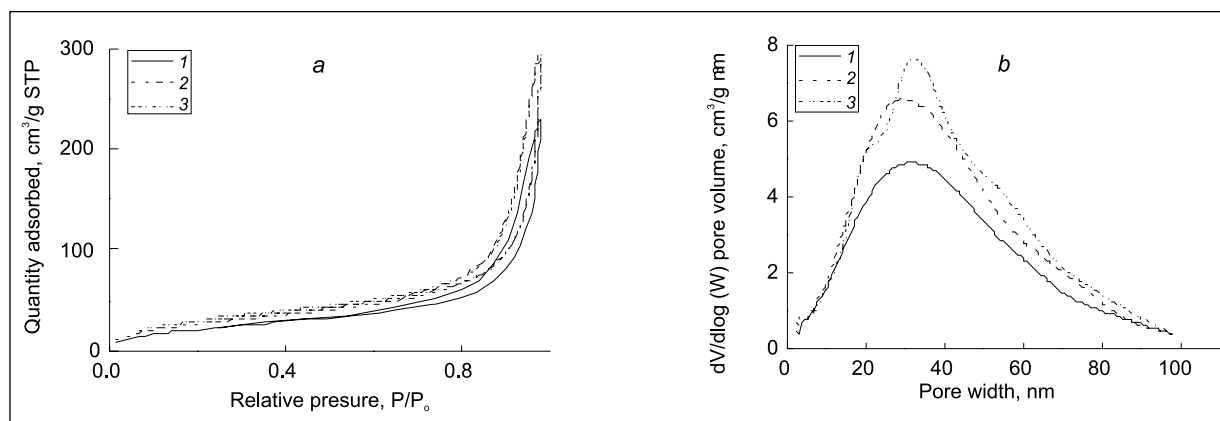

Fig. 5. Nitrogen adsorption/desorption isotherms (*a*) and the BJH slit-shaped pore size distribution (*b*) of PUU microparticles (1: [PVA]:[IPDI] = 1:2.0; 2: [PVA]:[IPDI] = 1:3.0; 3: [PVA]:[IPDI] = 1:4.0 (*t* = 90 min, *T* = 90 °C))
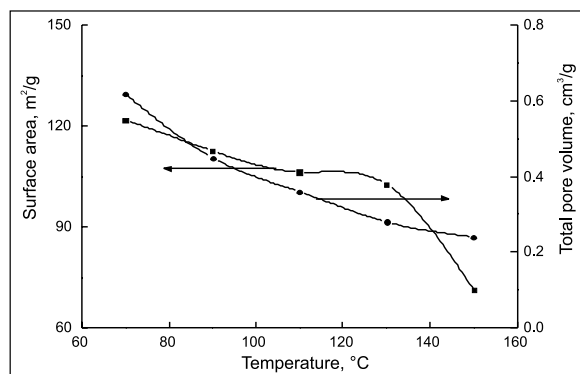
Fig. 6. Surface area and total pore volume of PUU microparticles as a function of reaction temperature ([PVA]:[IPDI] = 1:4.0, *t* = 90 min)

0.24 cm$^3 \cdot$g^{-1}. Increasing the reaction temperature resulted in evaporation of water from the DMSO/water solution and decreasing formation of urea linkages, and crosslinks in PUU.

As a result, the yield, surface area and total pore volume of PUU microparticles were decreased. The morphology and size distribution of PUU microparticles were investigated by using the electron microscope Hitachi SU 70 (Fig. 7) and it confirmed our proposal that the PUU microparticles are of plate forms and have slit-shaped pores. Size distribution of the PUU microparticles, which were synthesized using various initial molar ratios of PVA and IPDI at different reaction time and temperature, is in the range of 2–10 μm and the size of agglomerates is from 10 to 30 μm.
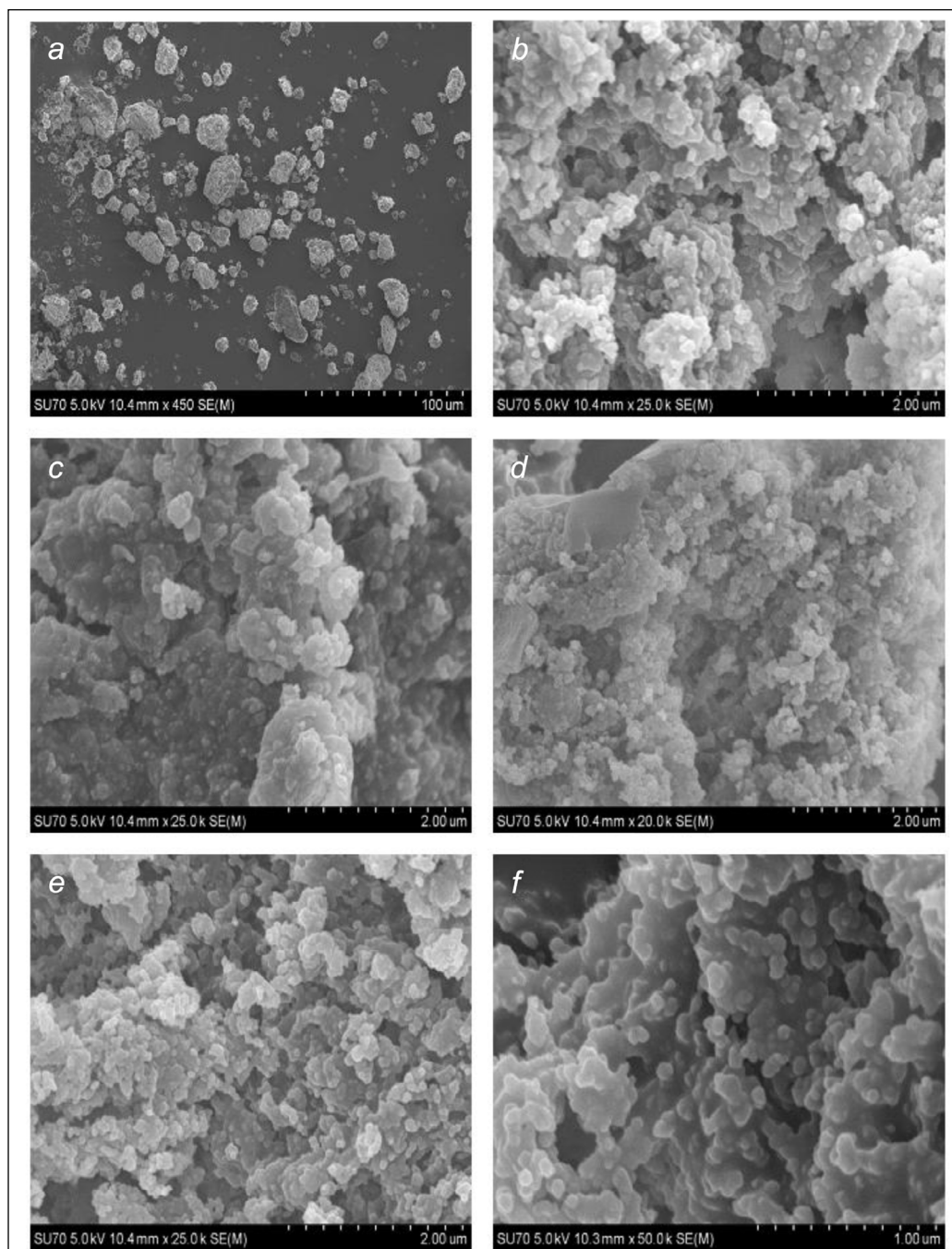

Fig. 7. SEM photos of the PUU microparticles size distribution (*a*: [PVA]:[IPDI] = 1:4) and surface morphology (*b*: [PVA]:[IPDI] = 1:2.0, *c*: [PVA]:[IPDI] = 1:2.5, *d*: [PVA]:[IPDI] = 1:3.0, *e*: [PVA]:[IPDI] = 1:3.5, *f*: [PVA]:[IPDI] = 1:4)

CONCLUSIONS

Porous PUU microparticles in the size range of 2–10 μm were synthesized from PVA and IPDI by a one-step method in DMSO/water (99/1 vol.%) solution for the first time. Structure of PUU microparticles has been proposed by chemical analysis and FT-IR spectra. The morphology of PUU microparticles was studied by optical and scanning electron microscopy. The highest yield of PUU microparticles (70.1%) was obtained when the initial molar ratio of PVA and IPDI was 1:4.0, reaction time was 180 min and temperature was 90 °C. The first stage of the maximum decomposition temperature of PUU microparticles was started at 348.9 °C and it was 39.5–45.1 °C higher than the decomposition temperature of PVA. It is proposed that the first peak indicated the decomposition of urethane and urea linkages. The second stage of the maximum decomposition temperature was close to the second step decomposition temperature of PVA. Mainly the mesopore structure of PUU microparticles with the presence of macropores was estimated. The largest surface area (122 m^2·g^{-1}) and pore volume (0.62 cm^3·g^{-1}) of the PUU microparticles were obtained when the initial molar ratio of PVA and IPDI was 1:4.0, reaction temperature was 70 °C and time was 90 min.

ACKNOWLEDGEMENTS

References

1. D. Randall, S. Lee, *The Polyurethane Book*, John Wiley & Sons, New York (2002).
2. M. Lonescu, *Chemistry and Technology of Polyols for Polyurethanes*, Rapra Technology, Shropshire (2005).
3. E. Jabbari, M. Khakpour, *Biomaterials*, **21**, 2073 (2000).
4. E. Baruch-Teblum, Y. Mastai, K. Landfester, *Eur. Polym. J.*, **46**, 1671 (2010).
5. S. N. Jaisankar, D. J. Nelson, C. N. Brammer, *Polymer*, **50**, 4775 (2009).
6. J. Liu, F. Qiu, G. Cao, Y. Guan, Q. Shen, D. Yang, Q. Guo, *J. Polym. Sci., Part B: Polym. Phys.*, **49**, 939 (2011).
7. L. Zhuang, Z. Cao, G. Cao, Z. Wang, F. Qiu, Q. Shen, *Optik*, **124**, 2551 (2013).
8. F. Qiu, Z. Cao, G. Cao, Y. Guan, Q. Shen, Q. Wang, D. Yang, *Mater. Chem. Phys.*, **135**, 518 (2012).
9. D. K. Chattopadhyay, B. Sreedhar, K. V. S. N. Raju, *J. Polym. Sci., Part B: Polym. Phys.*, **44**, 102 (2006).
10. H. S. Kim, J. H. Yeum, S. W. Choi, J. Y. Lee, I. W. Cheong, *Prog. Org. Coat*, **65**, 341 (2009).
11. P. Florian, K. K. Jena, S. Allauddin, R. Narayan, K. V. S. N. Raju, *Ind. Eng. Chem. Res.*, **49**, 4517 (2010).
12. Z. Wang, Z. Hou, Y. Wang, *J. Appl. Polym. Sci.*, **127**, 710 (2013).
13. K. K. Jena, D. K. Chattopadhyay, K. V. S. N. Raju, *Eur. Polym. J.*, **43**, 1825 (2007).
14. K. B. Gireesh, K. K. Jena, S. Allauddin, K. R. Radhika, R. Narayan, K. V. S. N. Raju, *Prog. Org. Coat*, **68**, 165 (2010).
15. F. Najafi, F. Manouchehri, M. Shaabanzadeh, *J. Chem. Health Risks*, **2**, 23 (2011).
16. M. Lahtinen, C. Price, *Polym. Int.*, **51**, 353 (2002).
17. J.-E. Yang, Y.-H. Lee, Y.-S. Koo, Y.-J. Jung, H.-D. Kim, *Fibers Polym.*, **3**, 97 (2002).
18. M. Lahtinen, R. K. Pinfield, C. Price, *Polym. Int.*, **52**, 1027 (2003).
19. V. Durrieu, A. Gandini, M. N. Belgacem, A. Blayo, G. Eisele, J.-L. Putaux, *J. Appl. Polym. Sci.*, **94**, 700 (2004).
20. C. Herrmann, D. Crespy, K. Landfester, *Colloid Polym. Sci.*, **289**, 1111 (2011).
21. Y.-S. Kwak, S.-W. Park, H.-D. Kim, *Colloid Polym. Sci.*, **281**, 957 (2003).
22. I. W. Cheong, H. C. Kong, J. H. An, J. H. Kim, *J. Polym Sci., Part A: Polym. Chem.*, **42**, 4353 (2004).
23. S. A. Madbouly, J. U. Otaigbe, A. K. Nanda, D. A. Wicks, *Macromolecules*, **38**, 4014 (2005).
24. Z. H. Fang, J. J. Shang, Y. X. Huang, J. Wang, D. Q. Li, Z. Y. Liu, *Express Polym. Lett.*, **4**, 704 (2010).
25. R. Dawson, A. I. Cooper, D. J. Adams, *Prog. Polym. Sci.*, **37**, 530 (2012).
26. D. Wu, F. Xu, B. Sun, R. Fu, H. He, K. Matyjaszewski, *Chem. Rev.*, **112**, 3959 (2012).
27. M. T. Gokmen, F. E. Du Prez, *Prog. Polym. Sci.*, **37**, 365 (2012).
28. X. Wang, E. Ruckenstein, *Biotechnol. Prog.*, **9**, 661 (1993).
29. H. Haugen, V. Ried, M. Brunner, J. Will, E. Wintermantel, *J. Mater. Sci. Mater. Med.*, **15**, 343 (2004).
30. H. Haugen, J. Will, W. Fuchs, E. Wintermantel, *J. Biomed. Mater. Res., Part B*, **77**, 65 (2006).
31. D. Eglin, S. Grad, S. Gogolewski, M. Alini, *J. Biomed. Mater. Res., Part A*, **92**, 393 (2010).
32. D. Jovanovic, G. E. Engels, J. A. Plantinga, et al., *J Biomed. Mater. Res., Part A*, **95**, 198 (2010).
33. G. Dubey, K. Mequanint, *Acta Biomater.*, **7**, 1114 (2011).
34. J. Guan, K. L. Fujimoto, M. S. Sacks, W. R. Wagner, *Biomaterials*, **26**, 3961 (2005).
35. S. Budriene, T. Romaskevic, K. Pielichowski, J. Pielichowski, *Polym. Adv. Technol.*, **18**, 67 (2007).
36. R. Makuska (ed.), *Synthesis and Characterization of Polymers* (In Lithuanian), University Press, Vilnius (2006).
37. H. Gotz, U. Beginn, C. F. Bartelink, H. J. M. Grunbauer, M. Moller, *Macromol. Mater. Eng.*, **287**, 223 (2002).
38. R. Lomolder, F. Plogmann, P. Speier, *J. Coat. Technol.*, **69**, 51 (1997).
39. S. Zhang, Z. Ren, S. He, Y. Zhu, C. Zhu, *Spectrochim. Acta, Part A*, **66**, 188 (2007).
40. H. S. Mansur, C. M. Sadahira, A. N. Souza, A. A. P. Mansur, *Mater. Sci. Eng., C.*, **28**, 539 (2008).
41. L. Ning, W. De-Ning, Y. Sheng-Kang, *Macromolecules*, **30**, 4405 (1997).
42. K. Lewandowska, *Thermochim. Acta*, **493**, 42 (2009).
43. K. S. W. Sing, *Pure Appl. Chem.*, **54**, 2201 (1982).

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AKYTŲ POLI(URETANKARBAMIDINIŲ) MIKRODALELIŲ IŠ POLI(VINILALKOHOLIO) IR IZOFORONDIIZOCIANATO SINTEZĖ IR TYRIMAS

Santrauka

Akytos poli(uretankarbamidinės) (PUK) mikrodalelės susintetintos iš poli(vinilalkoholio) (PVA) ir izoforondiizocianato (IPDI) dimetilsulfoksido / vandens tirpale (99/1 tūrio %) vienstadijiniu metodu. Ištirta PVA ir IPDI molinio santykio, reakcijos trukmės bei temperatūros įtaka PUK išeigai ir sandarai. Didžiausia PUK mikrodalelių išeiga yra 70,1 %. PUK sandara nustatyta iš IR spektrų ir patvirtinta cheminės analizės duomenimis. Iš terminės analizės duomenų nustatytas terminis polimerų stabilumas. PUK destrukcija vyksta dviem stadijomis: I stadijoje skyla uretaniniai ir karbamidiniai ryšiai, o II – pagrindinė grandinė. Iš PUK mikrodalelių paviršiaus ploto ir akučių tūrio nustatymo duomenų gauta, kad PUK mikrodalelės yra akytos: didžiąją dalį sudaro mezoakutės, tačiau yra ir makroakučių. Didžiausias PUK mikrodalelių paviršiaus plotas – 122 m²g⁻¹, bendras akučių tūris – 0,62 cm³g⁻¹. Elektroniniu ir optiniu mikroskopais įvertinta mikrodalelių morfologija. Mikrodalelių dydis priklauso nuo sintezės sąlygų ir yra 2–10 μm.