



Analysis of dynamic mechanical, thermal and surface properties of poly(urethane-ester-siloxane) networks based on hyperbranched polyester

Jasna V. Džunuzović^{a,*}, Marija V. Pergal^a, Rafał Poręba^b, Vesna V. Vodnik^c, Branislav R. Simonović^d, Milena Špírková^b, Slobodan Jovanović^e

^a Institute of Chemistry, Technology and Metallurgy (ICTM)—Center of Chemistry, University of Belgrade, Studentski trg 12-16, 11000 Belgrade, Serbia

^b Institute of Macromolecular Chemistry AS CR, v.v.i. (IMC), Nanostructured Polymers and Composites Department, Heyrovského nam. 2, 16206 Praha 6, Czech Republic

^c Institute of Nuclear Science “Vinča”, University of Belgrade, P.O. Box 522, 11001 Belgrade, Serbia

^d Institute of General and Physical Chemistry, University of Belgrade, Studentski trg 12-16, 11000 Belgrade, Serbia

^e Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia

ARTICLE INFO

Article history:

Received 20 July 2012

Received in revised form 4 September 2012

Available online 4 October 2012

Keywords:

Polyurethane network;

Hyperbranched polyester;

Poly(dimethylsiloxane);

Dynamic mechanical properties;

Thermal properties

ABSTRACT

Six polyurethane networks were synthesized from Boltorn® hyperbranched polyester of the second pseudo generation, α,ω -dihydroxy-(ethylene oxide-poly(dimethylsiloxane)-ethylene oxide) (EO-PDMS-EO) and 4,4'-methylenediphenyl diisocyanate. The effect of the EO-PDMS-EO content on the properties of prepared polyurethanes was investigated by dynamic mechanical thermal analysis (DMTA), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), swelling measurements, water contact angle and water absorption. Different techniques (FTIR peak deconvolution, DMTA and SEM) revealed that decrease of EO-PDMS-EO content promotes microphase separation in the synthesized polyurethanes. Samples synthesized with higher EO-PDMS-EO content have more hydrophobic surface and better waterproof performances, but lower crosslinking density. TGA results suggest that thermal stability of the synthesized polyurethane networks in nitrogen is significantly affected by the mutual influence of the crosslinking density and EO-PDMS-EO content. The results obtained in this work indicate that the synthesis of polyurethanes based on hyperbranched polyester and EO-PDMS-EO leads to the creation of networks with good thermal, thermomechanical and surface properties.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Polyurethane (PU) networks represent versatile materials because of their high performance characteristics, such as excellent adhesiveness, flexibility, toughness, hardness, high impact and abrasion resistance, low gas permeability, good electrical properties, high gloss, good water, solvent and weather resistance and broad application possibilities [1,2]. The crosslinked structure of these polymers is composed of physical and chemical network. Physical crosslinks are formed through the hydrogen bonding between the carbonyl and amine groups of adjacent chains, while three-dimensional chemical network can be produced in a controlled way using tri- or higher functional crosslinking agents [3]. Side reactions of isocyanates, such as formation of allophanate or biuret bonds, also lead to the chemical crosslinking and branching [4]. The properties of PU networks depend on the composition and chemical structure of all components, molecular weight of the soft segment and the nature of the used crosslinking agent [1].

According to the papers published over the past years, the use of aliphatic hydroxy-functional Boltorn® hyperbranched polyesters (HBPs) for the synthesis and modification of the PUs in a controlled manner attracted an increasing attention [3,5–10]. The reasons for that are globular, three-dimensional and compact structure of hyperbranched macromolecules, unique physical and chemical properties and presence of numerous end functional groups, which can be easily modified to adjust the final material for different application requirements [11–13]. Czech et al. have used Boltorn® HBP of the fourth pseudo generation as crosslinking agents for the synthesis of PU networks based on poly(tetramethylene oxide) [3]. The second pseudo generation of Boltorn® HBP (BH-20) was used by Cao and Liu for the preparation of hyperbranched PUs from polyethylene glycol and 4,4'-methylenediphenyl diisocyanate (MDI) [6]. Zhang and Hu have synthesized PU elastomers using BH-20, poly(neopentyl glycol adipate) diol, 1,4-butanediol and isophorone diisocyanate [7]. Boltorn® HBPs of various generation numbers were used by Asif et al. for the synthesis of PU acrylates [8] and by Bhowmick and Maji for the preparation of PUs based on isocyanate terminated polyurethane prepolymer [9]. Okrasa et al. have used Boltorn® HBP of the third pseudo generation and poly(tetramethylene oxide) for the synthesis of PU networks [10],

* Corresponding author. Tel.: +381 11 2635839; fax: +381 11 2636061.

E-mail address: jasnav2002@yahoo.com (J.V. Džunuzović).

etc. According to these and other published papers, most PUs based on HBP's were synthesized using polyether or polyester macrodiols.

The incorporation of poly(dimethylsiloxane) (PDMS) macrodiols into PUs, using appropriate synthetic procedure, has been frequently used to improve and modify thermal, oxidative and hydrolytic stability and surface properties of PUs, since poly(dimethylsiloxane)s have good thermal and oxidative stability, low glass transition temperature, high flexibility, good biocompatibility, low surface tension, low moisture and good gas permeability and UV stability [14–17].

Polyurethane networks based on PDMS macrodiols and Boltorn® HBP's appear to be promising candidates for different applications, especially in coatings, since such multicomponent system can link and combine various properties of all its constituents [18–20]. Large number of end hydroxyl groups in HBP is responsible for the fast curing and creation of the highly crosslinked system with good chemical resistance and mechanical properties, while PDMS provides good thermal and surface properties and elasticity in such highly crosslinked material, because of its low glass transition temperature. Therefore, the aim of this work is the synthesis of a series of PU networks based on BH-20, α,ω -ethylene oxide-poly(dimethylsiloxane)-ethylene oxide (EO-PDMS-EO) and MDI by a two-step polymerization in solution. Besides applied synthetic procedure, ethylene oxide end groups present in macrodiol provide better compatibility between reactants. The influence of the EO-PDMS-EO content on the hydrogen bonding, water resistance, swelling behavior, morphology, dynamic mechanical and thermal properties of the synthesized PUs was investigated.

2. Experimental

2.1. Materials

Boltorn® hydroxy-functional aliphatic hyperbranched polyester of the second pseudo generation (BH-20; Perstorp Specialty Chemicals AB (Sweden)), synthesized from the 2,2-bis(hydroxymethyl)propionic acid and a tetrafunctional ethoxylated pentaerythritol, was dried at 50 °C under vacuum for two days prior to use. From the number average molecular weight, determined by vapor pressure osmometry ($M_n = 1340$ g/mol), and hydroxyl number, determined by titration method (501.1 mg KOH/g), functionality of BH-20 was calculated ($f = 12$) [12]. α,ω -Dihydroxy-(ethylene oxide-poly(dimethylsiloxane)-ethylene oxide) (EO-PDMS-EO; ABCR) was dried over molecular sieves (0.4 nm) before use. M_n of the EO-PDMS-EO was calculated from the ^1H NMR ($M_n = 1200$ g/mol) [21]. 4,4'-Methylenediphenyl diisocyanate (MDI; Aldrich, purity >98%) was used as received. The content of the –NCO groups in MDI was determined using titration method (33.6 wt.%) [22]. The catalyst stannous octanoate ($\text{Sn}(\text{Oct})_2$; Aldrich), was used as solution in anhydrous *N*-methyl-2-pyrrolidone (NMP; Across). NMP was distilled before use and kept over molecular sieves (0.4 nm). Tetrahydrofuran (THF; J. T. Baker) was dried over lithium aluminum hydride and distilled before use. Toluene (Lach-ner) was used as received.

2.2. Synthesis of polyurethane networks

A series of six polyurethane networks (PU2-60, PU2-50, PU2-40, PU2-30, PU2-20 and PU2-15) was synthesized by a two-step polymerization in solution, using BH-20 as crosslinker. The weight percent of the EO-PDMS-EO is indicated by the last two numbers in the name of the synthesized PUs. The total molar ratio of –NCO and –OH groups (from BH-20 and EO-PDMS-EO) was kept at constant value of 1.05 [22]. Samples were synthesized in a four-neck round-bottom flask, placed in a silicone oil bath, equipped with an inlet for dry argon, a mechanical stirrer, a dropping funnel and a reflux condenser. The synthesis of PU2-30 is described. After dissolving EO-PDMS-EO (3.50 g, 2.9 mmol) in the mixture NMP/THF (24.2 mL/3.8 mL), MDI (4.76 g, 19.0 mmol) was added into the flask, mixed with stirring and heated

to 40 °C under an argon atmosphere. Then, catalyst solution in NMP (0.28 mL; 0.15 mol% based on the EO-PDMS-EO) was added [22]. NCO-terminated prepolymer was obtained after 30 min, by keeping the reaction mixture at 40 °C under continuous stirring [22]. The –NCO content was controlled by dibutylamine back-titration method [23]. Subsequently, BH-20 (3.41 g, 2.5 mmol) dissolved in NMP (30.3 mL) was added drop-wise and the reaction mixture was stirred at 40 °C for 10 min. Then, reaction mixture was cast on a Petri dish, previously lubricated with silicone oil. The reaction proceeded in a force-draft oven at 80 °C for 45 h, at 110 °C for 1 h, and in a vacuum oven at 50 °C for 10 h. The thickness of the synthesized PUs was about 1 mm. Before performing any characterization, samples were kept for 14 days in desiccator at room temperature.

2.3. Characterization

FTIR spectra of the synthesized PUs were recorded using attenuated total reflection (ATR) mode on NICOLET 380 FTIR spectrometer. Based on the device characteristics, the uncertainty on each IR data is 4 cm^{-1} . The deconvolution errors were ± 0.5 –1.0% for all PUs.

Equilibrium swelling measurements were performed at room temperature by immersion of the samples in toluene for 48 h and in THF for 24 h. The equilibrium swelling time was determined by separate periodical measurements of the samples' weight until constant value. All weight measurements were performed using a digital balance having an accuracy of ± 0.0001 g. Test samples were squares ($10.0\text{ mm} \times 10.0\text{ mm} \times 1.0\text{ mm} \pm 0.2\text{ mm}$), weighing approximately 0.2 g. After swelling, specimens were taken out and their weight, w , was measured. Then, swollen PUs were dried in vacuum oven at 50 °C and then, the weight of the deswollen PUs, w_g , was measured. Results from three measurements of each network were averaged. The equilibrium swelling degree, q_e , was calculated using conventional gravimetric method:

$$q_e = \frac{w - w_0}{w_0} \quad (1)$$

where, w_0 is the sample weight before swelling. The errors associated with the calculation of the q_e values were obtained using standard deviation method and Origin Pro-8 software and are reported as error bars in the figure (Fig. 4).

Density of the PUs was measured at 20.1 °C, using pycnometer and distilled water as medium. The average of four measurements was used. The standard deviation method (Origin Pro-8 software) was used for the calculation of the errors in density measurements.

Water absorption of the PU samples ($10.0\text{ mm} \times 10.0\text{ mm} \times 1.0\text{ mm} \pm 0.2\text{ mm}$) was investigated at room temperature by their immersion in distilled water for 48 h. After two days, weight of the specimens, w_w , was measured. The average value of three measurements for each sample was used. The weight percent of the water absorption was calculated as follows:

$$\text{Water absorption} = \frac{w_w - w_{w0}}{w_{w0}} \times 100 \quad (2)$$

where, w_{w0} is the weight of dry sample. The errors obtained in water absorption measurements were calculated using standard deviation method (Origin Pro-8 software). The weight percent of the water uptake was checked after 30 days.

The water contact angles of the PUs were determined on Krüss DSA100 using the sessile drop method. Measurements were performed at 22 °C, 30 s after deposition of the single drops (20 μL) on the sample surface. The average of five measurements was used as a final result, while the standard deviations (Origin Pro-8 software) associated with this measurement are reported for each sample.

Dynamic mechanical thermal analysis (DMTA) of the synthesized PUs was performed on ARES G2 rheometer (TA Instruments) at a

Download English Version:

<https://daneshyari.com/en/article/10631000>

Download Persian Version:

<https://daneshyari.com/article/10631000>

[Daneshyari.com](https://daneshyari.com)