Microstructure and properties of poly(urethane-siloxane)s based on hyperbranched polyester of the fourth pseudo generation

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ABSTRACT

Poly(urethane-siloxane) networks based on hydroxyethoxy propyl terminated poly(dimethylsiloxane) (PDMS) as the soft segment and 4,4′-methylenediphenyl diisocyanate (MDI) and two hyperbranched polyesters with different core as the hard segments were characterized by swelling experiments, thermal analyses (DSC and TG), thermomechanical analysis (DMTA), X-ray scattering studies, SEM and AFM analyses, water contact angle and water absorption measurements, as well as surface free energy determination. From these studies, structure–property relationships were elucidated. Hyperbranched polyesters based on 2,2-bis(hydroxymethyl)propionic acid and ethoxylated pentaerythritol or di-trimethylolpropane as core (BH-40 and HBP-4) were used as crosslinkers for the samples of different series. Both series are composed of samples having different PDMS (i.e., soft segment) content. The crosslinking density and extent of hydrogen bonding showed an influence on the polyurethane (PU) properties. It was found that higher crosslinking density and better thermal stability of PUs based on BH-40 compared to HBP-4 based PUs are due to the less dense structure of BH-40. DMTA experiments revealed that the networks exhibit two glass transition temperatures, of the soft and hard segments, and one secondary relaxation process. The crosslinking density and extent of the microphase separation increased and thermomechanical properties were improved with decreasing content of PDMS. With increasing PDMS content, the surface of the polyurethane networks became more hydrophobic, the surface free energy decreased and thermal stability was improved. The obtained results revealed that synthesized PUs have good thermal and thermomechanical properties, which can be tailored for the potential use in the coating technology by changing the type of hyperbranched polyester or PDMS content.

1. Introduction

Polyurethanes (PUs) are considered as one of the most useful class of polymers in coating applications. Contrary to the other polymers, PUs have superior elastomeric properties and can be prepared using many available reactants. The careful design of PU structure is crucial to obtain good mechanical properties and adhesive strength of the coatings [1,2]. Macrodiol can play an important role to improve these properties. PUs based on polyester macrodiol have better mechanical properties and adhesive strength, whereas PUs based on polyether macrodiol show higher hydrolysis resistance, water-vapor permeability and softness of the coatings [3].

Poly(dimethylsiloxane) (PDMS) is being recognized due to low surface tension, unique flexibility, low glass transition temperature,

high thermal stability and good water resistivity [4]. To attain better and specific physical properties, a mixed or special type of macrodiol is used in PU coatings. However, pure PDMSs have weak mechanical properties, which limit their application, except in the case when PDMS is crosslinked and reinforced with adequate fillers [5]. Another very effective and important way to improve the mechanical properties of a weak, rubbery polymer such as PDMS, without chemical crosslinking, is the controlled synthesis of segmented copolymers, mainly polyurethanes and polyureas. In numerous subsequent papers of Yilgör et al., the preparation and properties of thermoplastic polyurethane and polyurea copolymers based on end-functionalized PDMS prepolymers, such as hydroxy-hexyl, aminopropyl, methylaminopropyl PDMS as the soft segment, are reported [6–12]. In the last few years, PDMS has been used in PUs synthesis to improve the properties such as thermal stability, adhesive strength, shape memory properties and water resistance without substantial damaging PU mechanical properties [13,14]. Recently, PU with PDMS has been tested as a component of marine

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coating due to its smooth surface, to protect the coating from the fouler attachment. Due to the low surface energy of the PDMS, the PU coating is enriched by Si and makes the surface very smooth [13]. The incorporation of PDMS segments into a PU backbone results in improved clarity and non-sticking properties, as well as good film and hydrophobic properties of the resulting polymers. However, the compatibility between PU and PDMS prepolymer is poor due to the great difference between their solubility parameters, which makes it difficult to prepare this modified PUs.

In our previous work it has been shown that the combination of PDMS macrodiol and hydroxy-functional hyperbranched polyesters (HBPs) can be successfully used for the synthesis of PU networks [15–18]. Namely, hyperbranched polyesters are dendritic, multibranched polymers and due to that they have obtained great attention as crosslinking agents for the synthesis of PU networks [19–27]. PU networks based on PDMS and HBP are good candidates for coating applications, because numerous end functional groups in HBP provide fast curing and formation of highly crosslinked system with good mechanical properties, while the presence of PDMS improves surface and thermal properties and introduces elasticity in such materials, due to its low glass transition temperature. We have shown that during the synthesis of PU networks based on PDMS macrodiol and commercially available Boltorn® hyperbranched polyester of the second pseudo generation (BH-20) in the melt, the heterogeneous network was formed due to the appearance of macroscopic phase separation [15]. After that, PU networks based on BH-20 and hyperbranched polyester of the third pseudo generation (BH-30) were synthesized using two-step polymerization in solution, in order to improve the compatibility between reactants [16–18]. However, PU networks based on BH-20 still had high percent of sol fractions, relatively low crosslinking density and relatively good thermal stability. The present work represents continuation of our efforts to prepare poly(urethane-siloxane) networks with good thermal, mechanical and surface properties.

Therefore, the aim of this paper is the synthesis of a series of PU networks based on Boltorn® HBP of the fourth pseudo generation (BH-40), hydroxyethoxy propyl terminated PDMS and 4,4′-methylenediphenyl diisocyanate, in order to investigate their structure-properties relationship. Several PU networks with a content of soft PDMS segment between 15 and 40 wt.% were prepared. Crosslinking agent for the samples in a series was commercial Boltorn® hydroxy-functional, fourth pseudo generation aliphatic hyperbranched polyester based on 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) as AB_2 monomer and ethoxylated pentaerythritol as tetrafunctional core. For the comparison, another hydroxy-functional aliphatic hyperbranched polyester of the fourth pseudo generation (HBP-4) based on bis-MPA and di-trimethylolpropane as core was synthesized and used as crosslinker. According to our knowledge, there is no study available so far in the open literature on the investigation of the influence of soft PDMS content and the type of HBP on the swelling, thermal, mechanical and surface properties of this particular polyurethane networks prepared in the form of films.

2. Experimental

2.1. Materials

Hydroxyethoxy propyl terminated poly(dimethylsiloxane) (PDMS, from ABCR) was dried over molecular sieves (0.4 nm) before use. The number-average molecular weight (M_n) determined by ^{1}H NMR spectroscopy, was 1200 g/mol and this value was used in the calculations of the reaction mixtures composition for the synthesis of polyurethanes. The molecular weight of the central PDMS-block

Table 1
Properties of the hydroxy-functional aliphatic hyperbranched polyesters of the fourth pseudo generation.

Sample	M_n (g/mol)	M_w/M_n	HN (mg KOH/g)	f	f_{theor}
BH-40	2720	2.8	470.5	23	64
HBP-4	2820	1.9	492.5	25	64

is M_n = 1090 g/mol [28]. 4,4′-Methylenediphenyl diisocyanate (MDI) (Aldrich) with an isocyanate content of 33.6 wt.%, was used as received. Boltorn® hydroxy-functional aliphatic hyperbranched polyester of the fourth (BH-40) pseudo generation was kindly provided by Perstorp (Specialty Chemicals AB, Sweden). Commercial BH-40 was synthesized from 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) and ethoxylated pentaerythrytol using pseudo one-step procedure [29]. Hydroxy-terminated fourth pseudo generation hyperbranched polyester (HBP-4) was synthesized from bis-MPA (Aldrich) and di-trimethylolpropane (DiTMP, Fluka Chemika) as a core, using pseudo one-step polymerization described below and methanesulphonic acid (Aldrich) as catalyst. Hyperbranched polyesters were dried overnight at 50 °C under vacuum before use. Polydispersity index, M_w/M_n, of the HBPs was determined by GPC and listed in Table 1. Number average molecular weight of HBPs was determined using vapor pressure osmometry, while values of the hydroxyl numbers, HN, were determined by titration method [30]. From the obtained M_n and HN values, average functionalities, f, of HBPs were calculated (Table 1). Stannous octanoate ($Sn(Oct)_2$, from Aldrich) was used as diluted solution in anhydrous N-methyl-2-pyrrolidone (NMP). The solvent NMP, supplied from Acros, was dried over calcium-hydride and distilled before use. Tetrahydrofuran (THF) supplied from J.T. Baker was refluxed with lithium-aluminum hydride and distilled before use. Toluene (from Lach-Ner) was used as received.

2.2. Synthesis of hyperbranched polyester of the fourth pseudo generation (HBP-4)

Aliphatic hyperbranched polyester of the fourth pseudo generation was synthesized from bis-MPA as AB_2 monomer and DiTMP as a B_4 core by acid-catalyzed polyesterification in melt. HBP-4 was synthesized in a four-necked round bottom flask equipped with a nitrogen inlet, drying tube, contact thermometer and mechanical stirrer. Di-trimethylolpropane (10.0 g; 0.04 mol), bis-MPA (321.6 g; 2.4 mol) and catalyst methanesulphonic acid (1.608 g) were loaded in the flask. The used molar core/monomer ratio was applied to prepare perfect HBP of the fourth pseudo generation. The reaction was led for 2 h at 140 °C under stream of nitrogen. After that, reduced pressure was applied to the flask until completion of reaction. The reaction was followed by measuring acid number. When the acid number reached value of 10.82, the reaction was stopped.

2.3. Synthesis of the polyurethane films

The PU networks were synthesized by catalyzed two-step polymerization in solution using hydroxyethoxy propyl terminated poly(dimethylsiloxane) and 4,4′-methylenediphenyl diisocyanate as reactants and hyperbranched aliphatic polyester as crosslinking agent. The molar ratio of reactive groups NCO/OH was 1.05 [31,32]. The mixture of solvents NMP/THF (9/1, v/v) was employed as reaction medium. The concentration of all reactants in the reaction mixture was about 20 wt.%. PU networks based on BH-40 and HBP-4 as crosslinkers were synthesized in the same manner. As an example, the synthesis of a PU network based on BH-40 with 30 wt.% of soft segment (PU4-30) is described. The number in the name of samples shows the PDMS weight content. A four necked