



Synthesis and properties of high-solids hybrid materials obtained from epoxy functional urethanes and siloxanes



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ARTICLE INFO

Article history:

Received 29 July 2014

Received in revised form 11 February 2015

Accepted 21 February 2015

Keywords:

Polyurethane

Siloxane

Epoxide

Free surface energy

High solids

Crosslinking

ABSTRACT

In this work series of novel high-solids crosslinked hybrid networks based on the epoxy-terminated polyurethane prepolymer and the comb-like structure co-poly(dimethyl)(methyl, 3-glycidoxypropyl)siloxane cured with diethylenetriamine, were obtained. The viscosity lowering of epoxy-terminated polyurethane prepolymer with temperature allowed for the preparation of the hybrid systems without using of any solvent. The structure of the obtained poly(urethane-siloxane) thermosets was confirmed by FT-IR spectroscopy. The DSC studies reveal, that the addition of siloxane resulted in the decrease of the glass transition temperature of the hybrid materials. The synthesized poly(urethane-siloxane) networks are hydrophobic, with the free surface energy of 17–31 mJ/m². An increased amount of siloxane resulted in an increase of water contact angle and decrease of degree of water absorption as well as of FSE, which confirms a hydrophobic nature of the employed siloxane. Some properties of obtained hybrid materials based coatings were also studied.

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1. Introduction

While analyzing the dynamic progress recently occurring in materials science, one cannot fail to notice the outstanding accomplishments related to synthesizing and application methods combining organic and inorganic polymer materials produced in response to the increasingly specialized requirements imposed by such contemporary disciplines as e.g. transplantology, electronics, or defense and space industries. Examples of such materials include copolymers synthesized with the use of polyurethanes and polysiloxanes [1,2]. In order to understand the reasons for the growing interest in poly(urethane-siloxane) copolymers it is necessary to investigate the properties of each homopolymer separately.

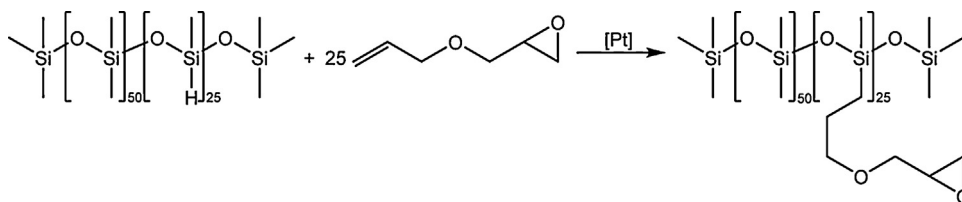
Polyurethanes (PU) are polymers built of alternating flexible polyol segments and rigid urethane-urea segments originating from diisocyanates and chain extenders. Adequately selected diisocyanates, as well as polyols with known molecular weights, and low molecular weight chain extenders make it possible to obtain polyurethanes with a wide range of physical properties which are important for a variety of applications. Because of

their good mechanical properties, particularly high abrasion resistance, polyurethanes have been used in manufacturing various products, such as e.g.: foam materials, elastomeric coatings, and anti-corrosive varnishes, widely applied in construction, furniture and automotive industries. These materials have been produced for over 70 years, the period which has witnessed rapid development of polyurethane technologies. Nevertheless, ongoing advancements in technology, medicine, electronics and economy constitute a growing challenge for these materials, connected for instance with environmental requirements or the necessity to increase thermal resistance [3].

Polymer chain of polysiloxane consists of alternating atoms of silicon and oxygen, and a typical representative of this group of polymers is polydimethylsiloxane (PDMS). Weak interactions mainly resulting from the activity of dispersion forces between chains of these polymers are the reason why siloxanes are characterized with low glass transition temperature $T_g < -120^\circ\text{C}$. These polymers also demonstrate stable dielectric properties, which do not change in a wide spectrum of temperatures and humidity, as well as relatively low free surface energy values. Moreover, polysiloxanes are known for high thermal stability even up to 300 °C. This is the effect of the aforementioned groups of Si–O, which are characterized by higher bonding energy (ca. 460 kJ/mol) in comparison with e.g. C–O bonds (ca. 350 kJ/mol) or C–C

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Scheme 1. Synthesis of co-poly(dimethyl)(methyl, 3-glycidoxypropyl)siloxane (EPS).

bonds (ca. 340 kJ/mol) occurring in typical organic compounds [4]. Because of all these properties, polysiloxanes are used for various unique purposes in such areas as: electronics, automotive as well as paint and varnish industries. Furthermore, polysiloxane coatings, which are resistant to water and weather conditions, are useful for purposes connected with antiques restoration, hydrophobization of construction materials and in protecting external walls against graffiti, which in our times is a frequently encountered problem. Additionally, due to their neutral physiological effect, siloxanes are also used in cosmetology and pharmacy [5].

As given above, a study focusing on the synthesis of hybrid materials combining the properties of both polymers seems to be justified, which is additionally reflected by the latest research reports [1,5–14] confirming that polyurethanes modified with siloxanes are characterized by lower glass transition temperature and enhanced thermal stability with simultaneously decreased hydrophilicity. Because of this they have been used as protective coatings, selective membranes, medical implants and surface modifiers for various polymers and fibers [6,9,10,15–17].

In our opinion, the modification of polyurethanes by means of siloxane compounds has not taken full advantage of all structural options possible to achieve in these copolymers and mainly involved production of poly(urethane–siloxane) copolymers (PU–PDMS) in which some flexible segments were replaced with polydimethylsiloxane. Polysiloxanes, which were used to synthesize this type of copolymers, in vast majority had linear structure on both sides terminated with reactive hydroxyl or amino groups and were capable of polyaddition reaction with isocyanate groups [1,7,18–21]. Significantly less frequent modification of polyurethanes was conducted by employing polysiloxanes in which hydroxyl groups were present on one side of the chain [22–25]. Because of the easier migration of PDMS chain to the surface, copolymers of this type are found with lower free surface energy in comparison with similar PU–PDMS copolymers modified with conventional α,ω -dihydroxypolydimethylsiloxane.

In recent years there has been growing focus on obtaining PU modified by means of difunctional siloxane polymers of a different type, i.e. with more complex structure, in addition to dimethylsiloxane mers ($-\text{Si}(\text{CH}_3)_2\text{O}-$) $_n$ containing various organic, e.g. acetoxy or alkyl-fluorine substituents which contribute to other beneficial properties in the obtained copolymers [10,26]. On the other hand, there have been very few reports concerning poly(urethane–siloxane) synthesis based on multifunctional polysiloxane containing alkoxyhydroxyl groups in the side chain which enabled production of cross-linked poly(urethane–siloxane) duroplastics [9,27].

In the 21st century, technologies designed for manufacturing any kinds of products must also be analyzed in terms of broadly understood ecological aspects, at the stage of synthesis, safe application and final waste management of the specific product. The previously reported modification of polyurethanes in order to obtain hybrid polymer materials occurred mainly via polyaddition reaction of reactive isocyanate groups originating from diisocyanates with hydroxyl or amino groups of respective polysiloxanes. Due to the high viscosity of the obtained copolymers,

synthesis reactions usually required organic solvent to be used in significant amounts, exceeding even 70% of the total weight of the basic raw materials. Significantly less frequently water, which is definitely nontoxic, was the reaction medium [1,9].

In our study we employed a new approach to obtain hybrid poly(urethane–siloxanes) based on reactive epoxy and amino groups. Obtaining of a lower viscosity system by employing epoxy-functional urethane oligomer which at later stages is crosslinked by means of an amine at the presence of functionalized polysiloxane has a beneficial pro-environmental effect involving reduction of volatile organic compounds (VOC) in the final product. While synthesis of polyurethane thermosets from urethane derivatives containing epoxy groups has been reported [28–30], this approach has never been employed in obtaining of hybrid poly(urethane–siloxanes). Additionally, we employed a novel type of functionalized polysiloxane with a comb-like chain structure, which has not been used for polyurethane modification.

The aim of our investigations is to develop new way of synthesis of ecological, high solids materials based on epoxyfunctional urethane, and co-poly(dimethyl)(methyl, 3-glycidoxypropyl)siloxane, which are cured with diethylenetriamine and to study the effect of their composition on surface and thermal properties.

2. Experimental

2.1. Materials

Isophorone diisocyanate (IPDI), glycidol, allyl-glycidyl ether, diethylenetriamine (DETA), dibutyltin dilaurate (DBTDL) and Karstedt catalyst solution in xylene (2% Pt) from Aldrich as well as co-poly(dimethyl)(methyl, hydrogen)siloxane of 4.3 mmol/g SiH content from Evonik were used without further purification. Poly(oxytetramethylene)diol (PTMO, $M_n = 1000$), was purchased from Aldrich and dried in a vacuum oven at 105 °C before use. Toluene from Honeywell was distilled and dried over 4 Å molecular sieves.

2.2. Synthesis of co-poly(dimethyl)(methyl, 3-glycidoxypropyl)siloxane (EPS)

EPS was synthesized in the hydrosilylation reaction of allyl-glycidyl ether with co-poly(dimethyl)(methyl, hydrogen)siloxane (Scheme 1). Process was carried out in the presence of Karstedt catalyst with no solvent. Co-poly(dimethyl)(methyl, hydrogen)siloxane (50 g, 9.1 mmol), allyl-glycidyl ether (26 g, 227.3 mmol) were placed together in three neck, round bottom flask equipped with thermometer, condenser and magnetic bar and above mixture was heated up to 60 °C. Next Karstedt catalyst in xylene (105 mg, 1.14×10^{-5} mol Pt) was added and a solution was allowed to heat up to 110 °C. Reaction progress was controlled with FT-IR spectroscopy and reaction mixture was kept in 110 °C for 8 h to the complete disappearance of Si–H bond band at 2100 cm^{-1} . Obtained product was characterized by ^1H , ^{13}C NMR and FT-IR spectroscopy.

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