



The effect of epoxyurethane modification on surface and thermal properties of fluorinated epoxyfunctional siloxane high—solid coatings



Łukasz Byczyński^{a,*}, Michał Dutkiewicz^{b,c}, Hieronim Maciejewski^{c,d}

^a Faculty of Chemistry, Rzeszow University of Technology, Al. Powstańców Warszawy 6, 35-959 Rzeszow, Poland

^b Centre for Advanced Technologies, Adam Mickiewicz University, Umultowska 89b, 61-614 Poznan, Poland

^c Poznań Science and Technology Park, A. Mickiewicz University Foundation, Rubież 46, 61-612 Poznan, Poland

^d Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89b, 61-614 Poznan, Poland

ARTICLE INFO

Keywords:

Polyurethane
Siloxane
Fluorine
Thermal degradation
High solids
Cross-linking

ABSTRACT

In this work series of high-solids crosslinked hybrid networks based on the comb-like structure fluorinated epoxyfunctional siloxane modified with the epoxy-terminated urethane oligomer and cured with diethylenetriamine, were obtained. The structure of the obtained poly(urethane-siloxane) thermosets was confirmed by FTIR spectroscopy. The thermal properties of the samples were investigated by DSC and TG analyses. The coupled TG-FTIR-MS technique for analysis of gases evolved during thermal decomposition of hybrid materials, was employed. The water contact angles, water absorption and some performance properties of the obtained hybrid coatings were also investigated. The synthesized poly(urethane-siloxane) networks are basically hydrophobic materials. An increased amount of epoxyurethane resulted in a decrease of glass transition temperature, Persoz hardness, and thermal stability as well as in increase of water absorption.

1. Introduction

Polysiloxanes due to their specific structure are characterized with low glass transition temperature $T_g < -120$ °C, relatively low free surface energy values and high thermal stability even up to 300 °C, as well as high gas permeability, but their mechanical properties are rather poor [1]. They are employed in various unique purposes in such areas as: electronics, automotive as well as paint and varnish industries. Polysiloxane coatings, which are resistant to weather conditions, are useful for antiques restoration, hydrophobization of construction materials or protecting walls against graffiti, which nowadays is a frequently encountered problem. Additionally, due to their neutral physiological effect, siloxanes are also used in cosmetology and pharmacy [2].

Recently the interest of synthesis of new class of siloxanes containing fluorocarbofunctional groups has been the subject of studies of many researches due to their hydrophobic nature [3,4]. Fluorine-containing organosilicon derivatives were used as surfactants, for surface modification of lenses and optical fibers, as components of many cosmetic preparations as well as modifiers of fluorine and silicon rubbers [5,6]. Polysiloxanes containing mixed functional groups in the side chain can be easily obtained by hydrosilylation process of selected olefins [7]. The coatings formed from this kind of siloxanes, which are

characterized by comb-like structure, and containing fluorine moieties show water contact angle as high as 114°, after proper preparation of the surface [3].

One of the method of improving of some mechanical properties of siloxanes is their modification with polyurethanes (PU) and formation of hybrid organic-inorganic poly(urethane-siloxane) materials (PU-Si). These materials combine properties of both homopolymers, which is reflected in the latest research reports [8–14]. PU-Si have been widely used as protective coatings, selective membranes, medical implants and surface modifiers for various polymers and fibers [15–18]. The hybrid poly(urethane-siloxane) copolymers are mostly obtained by incorporation of usually linear polydimethylsiloxane into PU backbone as a part of soft segments [19,20]. Recently, the investigations on polyurethanes with other siloxane structures have been developed including semi-interpenetrating polymer networks (semi-IPNs) [21], and networks based on comb-like structure co-poly(dimethyl)(methyl, hydroxypolyoxyethylenepropyl)siloxane cured with aliphatic diisocyanates [22], as well as based on epoxy-terminated urethane oligomer and co-poly(dimethyl)(methyl, 3-glycidoxypropyl)siloxane, cured with aliphatic diethylenetriamine [23,24].

Technologies designed for manufacturing any kinds of products should nowadays be analyzed in terms of broadly understood ecological aspects, at the stage of synthesis, safe application and final waste

* Corresponding author.

E-mail address: lbyczynski@prz.edu.pl (Ł. Byczyński).

management of the specific product. Thus, in this study a new approach to obtaining hybrid poly(urethane-siloxanes) based on reactive epoxy and amino groups were developed. A beneficial pro-environmental effect involving reduction of volatile organic compounds (VOC) in the final product was obtained by formation of a low viscosity system composed functionalized polysiloxane and epoxy-functional urethane oligomer which were cured by means of an amine. This approach so far has rarely been employed in obtaining of hybrid poly(urethane-siloxanes) [25,26]. However, from our preliminary studies it results that this kind of materials shows high thermal stability and hydrophobicity and their performance properties strongly depend on the kind of employed urethane oligomer [23,24]. So far, the comb-like structure siloxane containing mixed functional groups i.e. fluorocarbofunctional and oxirane has not been employed in synthesis of hybrid poly(urethane-siloxane) coatings.

Thus, the aim of this work is to investigate the effect of modification of co-poly(dimethyl)(methyl, 3-glycidxypropyl)(methyl, 1,1,2,2,3,3,4,4-octafluoropenthyloxypropyl)siloxane by epoxy-functional urethane oligomer on their surface and thermal properties, including evolved gases analyses and some coatings performance properties.

2. Experimental

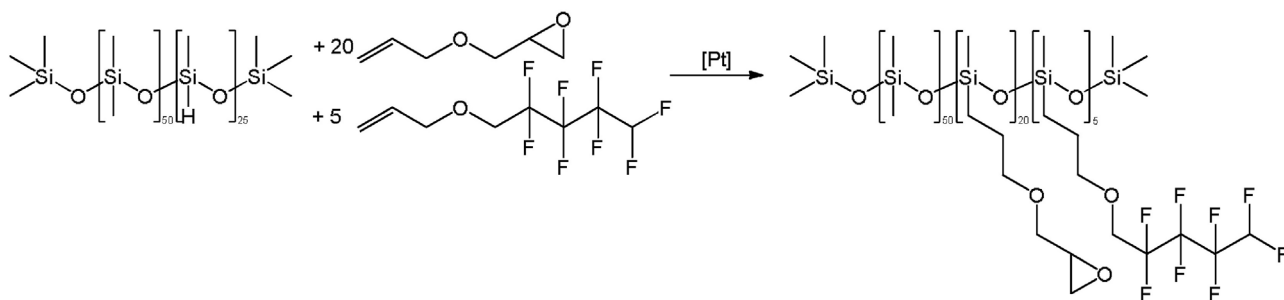
2.1. Materials

Poly(dimethyl-co-hydromethyl)siloxane containing 50 dimethylsiloxy and 25 methylhydridesiloxy units (PDMS, $M_n = 5500$), was purchased from Gelest (Arlington, VA, USA). Allyl glycidyl ether and Karstedt catalyst were supplied by Aldrich. 1,1,2,2,3,3,4,4-Octafluoropentyl allyl ether was synthesized according to the well-known Williamson reaction and detailed procedure given by Maciejewski et al. [27,28]. All chemicals used for its synthesis including 2,2,3,3,4,4,5,5-octafluoropentanol and allyl chloride were purchased for Sigma-Aldrich. Isophorone diisocyanate (IPDI), glycidol, diethylene-triamine (DETA) and dibutyltin dilaurate (DBTDL) from Aldrich 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-glycidxypropyl)(methyl, 1,1,2,2,3,3,4,4-octafluoropenthyloxypropyl)siloxane (EPFS)

Co-poly(dimethyl)(methyl, 3-glycidxypropyl)(methyl, 1,1,2,2,3,3,4,4-octafluoropenthyloxypropyl)siloxane was synthesized by the hydrosilylation of allyl glycidyl ether and 1,1,2,2,3,3,4,4-octafluoropentyl allyl ether with poly(dimethyl-co-hydromethyl)siloxane in the presence of Karstedt complex $[Pt_2\{(CH_2 = CHSiMe_2)_2O\}_3]$ as catalysts according to Scheme 1.

In the first step, poly(dimethyl-co-hydromethyl)siloxane (100 g) and 1,1,2,2,3,3,4,4-octafluoropentyl allyl ether (24.8 g, 0.091 mol)



Scheme 1. General route of EPFS.

Table 1
Structure of compounds employed for the synthesis of poly(urethane-siloxane) hybrid materials (SDP).

Compound	Structure
EPFS	
EPU	
DETA	

were placed in a three-neck round-bottom flask equipped with a thermometer, reflux condenser and magnetic bar. A Karstedt catalyst (2% in xylene) 220 μ L (5×10^{-5} mol Pt per mol Si-H) was then added at room temperature. After the introduction of the catalyst, the solution was heated to 110 °C. When complete conversion of fluorinated olefin occurred (as monitored by FT-IR analysis), allyl glycidyl ether (46 g, 0.37 mol) was added in excess of 10%. After introducing the entire amount of reagents, the solution was maintained for 1 h at the same temperature as before. Then, the reaction mixture was cooled, and the excess olefin was evaporated under vacuum to yield the product as a viscous oil. The structure of synthesized EPFS is presented in Table 1. The formation of the desired product was verified by NMR and FTIR analysis:

$^1\text{H NMR}$ (CDCl_3 , 298 K, 500 MHz) δ (ppm): 0.07–0.20 (SiCH_3); 0.54 (SiCH_2); 1.60 (CH_2); 2.61 (OCH_2); 2.81 (CH); 3.42 (OCH_2); 3.69 (OCH_2); 5.29 (CF_2H).

$^{13}\text{C NMR}$ (CDCl_3 , 298 K, 125 MHz) δ (ppm): 1.05 (SiCH_3); 13.40 (CH_2); 23.18 (SiCH_2); 44.35 (OCH_2); 50.82 (CH); 67.49 (OCH_2); 75.58 (OCH_2); 99.59 (CF_2); 101.96 (CF_2); 117.37 (CF_2H); 134.41 (CF_2).

FT-IR (cm^{-1}): 2961 and 2873 (ν_{sym} and ν_{asym} of C–H); 1074 and 1012 ($\nu_{\text{C-O-C}}$ and $\nu_{\text{Si-O-Si}}$); 1259 and 793 cm^{-1} ($\delta_{\text{C-H}}$ in SiCH_3); 1171 cm^{-1} ($\nu_{\text{C-F}}$); 911 cm^{-1} (oxirane ring).

2.3. Synthesis of epoxy-terminated polyurethane prepolymer (EPU)

The epoxy-terminated urethane oligomer (EPU) was synthesized in a two – stage polyaddition reaction with the use of isophorone diisocyanate, poly(oxytetramethylene)diol ($M_n = 1000$) and glycidol. The molar ratio of IPDI:PTMO:Gly was 2:1:2. The synthesis and detailed characteristic of EPU were described in Ref. [23]. The structure of synthesized EPU is presented in Table 1.

Download English Version:

<https://daneshyari.com/en/article/4999132>

Download Persian Version:

<https://daneshyari.com/article/4999132>

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