Progress in Organic Coatings 88 (2015) 92–105

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Formation, structure and antibacterial activities of silazane networks grafted with poly(ethylene glycol) branches

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ARTICLE INFO

Article history:
Received 29 October 2014
Received in revised form 12 June 2015
Accepted 22 June 2015
Available online 17 July 2015

Keywords:
Silazane
Poly(ethylene glycol)
Anti-bacterial

ABSTRACT

The aim of this investigation was to develop coating materials based on poly(ethylene glycol) (PEG) covalently grafted onto silazane polymers for marine antifouling applications. The optimum conditions for grafting PEG were defined to have a high selectivity toward olefin hydrosilylation. Thick crack-free films were obtained by curing at room temperature of the PEG grafted silazane precursors. The solidification process has been investigated by FTIR spectroscopy, ^{29}Si NMR in the solid state, thermogravimetric analysis (TGA) as well as elemental analysis. The main reactions that occur during curing are hydrolysis-condensation reactions of alkoxysilane, Si—H and Si—N functionalities. The PEG-*graft*-PSZ coatings exhibit excellent repellency against gram-negative *Neisseria* sp. and gram-positive *Clostridium* sp. in comparison with the pristine polysilazane surface. The anti-adhesion performance of the coatings depends on the grafting density and the chain length of PEG. The shortest PEG(350 g/mol)-graft-PSZ with the highest graft density was found to have the best anti-adhesion performance. As the density of grafted PEG(750 g/mol) and PEG(2000 g/mol) chains onto the PSZ surface is approximately equal, the relative effectiveness of these two types of PEG is controlled by the length of the PEG chain. The PEG(2000 g/mol)-*graft*-PSZ coatings are more efficient than the PEG(750 g/mol)-*graft*-PSZ coatings for the bacterial anti-adhesion.

1. Introduction

Bacterial adhesion and marine biofouling on a surface may lead to increased operational and maintenance costs [1] or can be critical to the performance of a biomedical device [2]. Thus, a great attention has been paid to the development of protein resistant or non-fouling surfaces for a variety of biomedical devices [2] as well as for marine applications [3]. A coating of polyethylene glycol (PEG) is currently the most common approach to inhibit bioadhesion. The PEG grafted surface become difficult to be approached by incoming particles due to the high mobility, large exclusion volume and steric hindrance effect of the highly hydrophilic layer. For examples, glass [4], silicon [5,6], gold [7,8] or polymer [8–14] surfaces modified with PEG brushes and UV crosslinked PEG diacrylate solid membranes [6,15] are able to resist the adhesion of many proteins [5,9–11,16,17] and bacteria [4,6,8,14,18–21]. Furthermore, excellent fouling release properties relative to marine algal fouling were reported for surface active block copolymers with amphiphilic side chains [22,23]. Amphiphilicity was imparted by a hydrophobic aliphatic [22] or fluorinated [23] group combined with a hydrophilic PEG group. As a novel approach to functionalize oxide surfaces, PEG grafted on a titanium surface was used for its antiadhesive properties and for the covalent immobilization of an antimicrobial peptide [20]. Polysilazane polymers consist of backbones with alternating Si—N bonds and are widely used as precursors of silicon carbonitride ceramics [24–27]. The polymer-to-ceramic transformation is generally performed at high temperatures (above 1000 °C). On the other hand, alkoxy silyl substituted polysilazanes can be crosslinked by the reaction with atmospheric moisture to form a cured surface film on the substrate surface [28,29]. Motivated by cost, environmental concerns and regulations to limit the volatile organic compound (VOC) content, the paint and coating industries are increasingly shifting toward aqueous based systems, powder coatings or UV curable coatings. Moisture cured polysilazane coatings provide an interesting alternative to other standard technologies when they need low VOC and low energy consumption.

The purpose of this work was to construct new antifouling coatings by covalent grafting of methoxy-terminated PEG chains onto polysilazane polymers through a highly stable silicon—carbon bond. Prime et al. [30] reported that replacing the terminal —OH of oligo(ethylene oxide) by —OCH_3 did not decrease the ability

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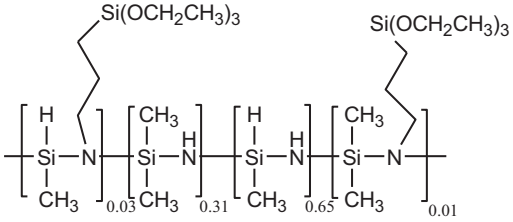
http://dx.doi.org/10.1016/j.porgcoat.2015.06.022
0300-9440/



Scheme 1. Molecular structure of PSZ.

of the surface to resist protein adsorption. Recently, preliminary results concerning the grafting of PEG chains onto oligosilazane were reported [31]. In this paper, a careful investigation of the network building from the PEG grafted silazane precursors is reported. Besides, the morphology of PEG chains in the cured material and the thermal stability of the surfaces are investigated. We have examined the effects of the length and grafting density of PEG chains upon bacteria adhesion. In addition to antibacterial activity, these coatings showed strong adherence to metal substrates (steel and aluminum) and the high crosslinked density of the moisture cured polymers confer high mechanical strength and good barrier properties. Altogether, these properties offer promising potential in terms of a one-coat system combining anticorrosive and antibacterial properties.

2. Experimental

2.1. Materials

Monomethoxy poly(ethylene glycol) (MPEG) with the average molecular weights of 350 g/mol, 750 g/mol and 2000 g/mol and Karstedt's catalyst were purchased from Sigma–Aldrich. All three types of MPEG were dried under vacuum before usage. The polysilazane precursor, polylmethyhydrosilazane containing triethoxysilanes was provided by the Clariant Company. The molecular structure of the polysilazane precursor is described on Scheme 1.

PSZ was used as received without any further purification. Allyl bromide (Allyl-Br) purchased from Acros was distilled under a nitrogen atmosphere in the dark and subsequently kept in darkness before usage. Allyl-Br is sensitive to light and may polymerize on exposure to light.

All synthetic procedures were performed under a dry argon atmosphere unless otherwise stated.

2.2. Synthesis

Allyl-terminated monomethyl polyethylene glycol (Allyl-PEG) were synthesized by the reaction of MPEG with an excess amount of allyl bromide. As a representative example, allyl bromide (60.5 g, 497 mmol), MPEG350 (25 g, 71 mmol) and sodium hydroxide (6 g, 150 mmol) were heated at 70 °C for 24 h. The purification protocol included the following steps: separation of sodium hydroxide by filtration, recovery of allyl-PEG trapped in sodium hydroxide by washing with chloroform, removal of allyl bromide and chloroform in a rotary evaporator, removal of unreacted MPEG traces by extraction in water/chloroform, removal of chloroform in a rotary evaporator and, finally vacuum drying of allyl-PEG for 12 h at 50 °C.

The yield of synthesis of allyl-PEGs is about 95%. Allyl-PEGs obtained were characterized by ^{1}H NMR and ^{13}C NMR to confirm their structure. ***Allyl-PEG350:*** ^{1}H NMR ($CDCl_3$): δ (ppm) 3.34 [s, 3H, C***H*****$_3$**—O], 3.4 ÷ 3.8 [m, 29H, —C***H*****$_2$**—C***H*****$_2$**—O], 3.99 [d, 2H, CH_2=CH—C***H*****$_2$**—O], 5.22 [m, 2H, C***H*****$_2$**=CH—], 5.87 [m, 1H, CH_2=C***H***—]. ^{13}C NMR ($CDCl_3$): δ (ppm) 58.41 [***C***H_3—O], 68.64 [—***C***H_2—CH_2—O—CH_3], 69.78 [—***C***H_2—***C***H_2—O—], 71.13 [—CH_2—***C***H_2—O—CH_3], 71.36 [CH_2=CH—***C***H_2—], 116.18 [***C***H_2=CH—CH_2—], 134.02 [CH_2=***C***H—CH_2—]. ***Allyl-PEG750:*** ^{1}H NMR ($CDCl_3$): δ (ppm) 3.36 [s, 3H, C***H*****$_3$**—O], 3.4 ÷ 3.8 [m, 67H, —C***H*****$_2$**—C***H*****$_2$**—O], 4.01 [d, 2H, CH_2=CH—C***H*****$_2$**—O], 5.23 [m, 2H, C***H*****$_2$**=CH—], 5.89 [m, 1H, CH_2=C***H***—]. ^{13}C NMR ($CDCl_3$): δ (ppm) 57.94 [***C***H_3—O], 68.53 [—***C***H_2—CH_2—O—CH_3], 69.63 [—***C***H_2—***C***H_2—O—], 70.99 [—CH_2—***C***H_2—O—CH_3], 71.10 [CH_2=CH—***C***H_2—], 115.78 [***C***H_2=CH—CH_2—], 133.99 [CH_2=***C***H—CH_2—]. ***Allyl-PEG2000:*** ^{1}H NMR ($CDCl_3$): δ (ppm) 3.37 [s, 3H, C***H*****$_3$**—O], 3.4 ÷ 3.8 [m, 194H, —C***H*****$_2$**—C***H*****$_2$**—O], 4.01 [d, 2H, CH_2=CH—C***H*****$_2$**—O], 5.24 [m, 2H, C***H*****$_2$**=CH—], 5.90 [m, 1H, CH_2=C***H***—]. ^{13}C NMR ($CDCl_3$): δ (ppm) 58.55 [***C***H_3—O], 68.98 [—***C***H_2—CH_2—O—CH_3], 70.12 [—***C***H_2—***C***H_2—O—], 71.48 [—CH_2—***C***H_2—O—CH_3], 71.72 [CH_2=CH—***C***H_2—], 116.54 [***C***H_2=CH—CH_2—], 134.36 [CH_2=***C***H—CH_2—].

Grafting of allyl-PEG molecules onto the polysilazane (PSZ) chain was performed by using a hydrosilylation reaction between the Si—H group of PSZ and the terminal C=C bond of the allyl-PEG with an excess amount of PSZ in presence of Karstedt's catalyst. The catalyst Pt (dvs) was added into a three-necked flask containing an amount of allyl-PEG ([Pt]/[allyl-PEG] molar ratios of 1×10^{-3} or 3×10^{-3}). After stirring for 15 min, PSZ was added ([Si—H]/[allyl-PEG] molar ratios of 7, 10, 16.5 or 26.5). The reaction occurred under argon or dry air (in this case, the reaction flask was equipped with a long glass fitting containing anhydrous calcium chloride). The reaction proceeded with stirring at a temperature of 70, 80 or 85 °C. The taking of samples was regularly carried out for tracking the kinetics of reaction. We define that a, b, c are the different protons and carbon atoms on the allyl branch of the PEG molecule, whereas a′, b′, c′ are the different protons and carbon atoms of the same branch after being grafted onto the PSZ chain. Different Si—H/allyl molar ratios of 10, 16.5 and 26.5 were investigated for all three types of allyl-PEG. The grafted products are symbolized as PSZ–PEG**X**–**Y** with **X** being the molecular weight of MPEG and **Y** being the Si—H/allyl molar ratio. The products obtained were colorless or slightly yellow viscous oils (from PEG350), pastes (from PEG750) or solids (from PEG2000) which are soluble in aromatic solvents.

Thin films (ca. 1 μm thick) were prepared by dip-coating technique from 10% ethyl acetate (for PSZ and PSZ–PEG350) or chloroform (for PSZ–PEG750 and PSZ–PEG2000) solutions using a substrate dipping speed of 240 mm/min and withdrawal speed of 120 mm/min. The substrates used were degreased aluminum plates (2.5 cm × 5 cm × 0.1 cm). The films used to track the crosslinking reaction course were dried at 21–22 °C and 50% humidity. Free and supported 60 μm thick films were obtained from PSZ, PSZ–PEG350 or a chloroform:toluene (50:50, v:v) solution of PSZ–PEG750 and PSZ–PEG2000 using an automatic film applicator Sheen 1137. Thick films were cured for 7 days at 25 °C and 84% humidity, which is the optimum cure time as determined from hardness measurements according to the Persoz method (Fig. S1 in supporting information). The methanol extraction of the isomers of allyl-PEG and/or unreacted allyl-PEG was followed by FTIR spectrometry in transmission mode on free films. It took about 10 min, 20 min and 3 h to extract ungrafted PEG from PSZ–PEG350, PSZ–PEG750 and PSZ–PEG2000, respectively. As-prepared PEG grafted PSZ films are translucent while they are transparent in the naked eye after extraction of free PEG chains (Fig. S2 in supporting information).

The conversions of Si—H, NH and C=C were calculated using the following equations:

$$\%C_{Si-H} = \frac{\frac{A_{Si-H(o)}}{A_{Si-CH_{3(o)}}} - \frac{A_{Si-H(t)}}{A_{Si-CH_{3(t)}}}}{\frac{A_{Si-H(o)}}{A_{Si-CH_{3(o)}}}} \times 100$$