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Visualization of the distribution of surface-active block copolymers in PDMS-based coatings

A. Camós Noguer[a,b], R. Latipov[b], F.B. Madsen[a], A.E. Daugaard[a], S. Hvilsted[a], S.M. Olsen[b], S. Kiil[a,*]

[a] Department of Chemical and Biochemical Engineering, Technical University of Denmark (DTU), Building 229, 2800 Kgs. Lyngby, Denmark
[b] Department of Fouling Release Systems, Hempel A/S, Lundtoftegårdsvej 91, 2800 Kgs. Lyngby, Denmark

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ABSTRACT

Poly(dimethylsiloxane) (PDMS) has been widely employed in the area of fouling-release coatings and other fields due to its unique combination of properties including low elastic modulus and low glass transition temperature. The drawback of PDMS in some applications is its hydrophobic surface, which results in non-specific protein adsorption and wettability issues. Poly(ethylene glycol)-based surface-active block copolymers and surfactants have been added to PDMS coatings and films to impart biofouling resistance and hydrophilicity to the PDMS surface with successful results. Information regarding the distribution and release of these block copolymers from PDMS-based coatings has been previously reported. However, the distribution and behaviour of these compounds in the bulk of the PDMS coating are not fully understood.

A novel fluorescent-labelled triblock PEG-b-PDMS-b-PEG copolymer was synthesized and added to a PDMS coating for visualization purposes. The surface-activity and biofouling resistance of the synthesized copolymer was confirmed by water contact angle measurements and seawater immersion experiments. Confocal laser scanning microscopy (CLSM) images showed that the triblock copolymer aggregates in spherical domains within the PDMS coating film. The size of these domains vary between 1 and 7 μm, with larger domains being present on the bulk of the film and smaller closer to the surface. The diffusion of the copolymer could be observed over time, with copolymer molecules diffusing from the bulk to the surfaces of the PDMS film. Finally, an overview of the possibilities provided by the presented methodology in the field of fouling-release coatings is discussed.

1. Introduction

Polydimethylsiloxane (PDMS) is an extensively used polymer in a range of areas such as dielectric elastomers, microfluidic systems, microreactors, membranes, adhesives, coatings and biomedical devices [1–3]. In the field of marine biofouling, PDMS is the most widely employed binder for fouling-release coatings (FRC), which have become a solid alternative to biocidal antifouling coatings after the ban of tributyltin (TBT) in the early 2000s [4]. The widespread use of PDMS in such different areas is due to its unique combination of properties, including thermal and chemical stability, low elastic modulus, low glass transition temperature, smooth surface and low cost, among others [2,5–8]. However, the hydrophobic nature of PDMS has been a drawback in areas such as microfluidics, biomedicine and marine coatings due to adsorption of proteins and cells on its surface, as well as wettability issues [2,3,9,10].

1.1. Functionalization of PDMS surfaces

To change the surface properties of PDMS and make it hydrophilic, different methods have been employed such as oxygen plasma exposure, surface adsorption of surfactants and chemical modification (grafting) [2,9,10]. These methods are generally too expensive and/or complicated and therefore not suitable for some of the aforementioned applications. In addition, the PDMS surface tends to recover its hydrophobicity over time [11].

A different method to modify the surface properties of PDMS coatings and films is gaining popularity, namely the addition of small amounts of surface-active copolymers and amphiphiles to uncured PDMS mixtures [2,9,12,13]. The idea of adding small amounts of copolymers to change the surface properties of polymeric materials was first introduced by Zisman and co-workers in 1964 [14]. Upon curing, copolymer molecules migrate to the PDMS surface and impart hydrophilicity to the surface [12]. Several patents [15–21] and articles [22–26] have been published in the field of fouling-release coatings describing the addition of various amphiphilic copolymers (usually

* Corresponding author.
E-mail address: sk@kt.dtu.dk (S. Kiil).

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known as “silicone oils”) with the objective of modifying the hydrophobic surface properties of PDMS coatings. Poly(ethylene glycol) (PEG) has been one of the most widely employed polymers for that purpose. For example, PDMS-PEG block copolymers have been used to reduce the amount of biofouling and barnacle adhesion strength on PDMS-based fouling-release coatings [27]. Likewise, these have been used for other purposes such as to improve the wettability of PDMS surfaces for microelectromechanical systems [28] and for capillary-driven systems in the biomedical field [29]. Similarly, other PEG-based block copolymers have been added to modify the surface properties of PDMS to improve its wettability [2,10] or to supress non-specific protein adsorption [9,30].

Despite the wide use of this approach, there is a lack of knowledge regarding the distribution, mobility, behaviour and interaction of block copolymer additives in polymeric hosts. Most of the work has been focused on the final properties of the surface of these materials, studied either by direct (e.g. X-ray photoelectron spectroscopy (XPS)) or indirect methods (e.g. contact angle measurements and atomic force microscopy (AFM)) [9,12]. Nonetheless, there is a lack of understanding of the processes occurring in the bulk of the film. Due to the importance of these copolymers on the final properties of the PDMS-based films, new methods are aimed at better understanding the distribution and behaviour of the copolymers hosted in the bulk of these materials. To that purpose, different methods have been presented in our previous work, regarding the diffusion [31], release [32] and degradation [33] of PDMS-PEG-based amphiphilic copolymers in PDMS fouling-release coatings. However, none of the methodologies developed allowed visualization of the distribution of the amphiphilic copolymer in the bulk of the PDMS coating.

1.2. Fluorescent-based visualization techniques

The development of fluorescence-based techniques has proven to be a powerful tool to study and visualize some of the abovementioned phenomena. For example, Kósa et al. [34] used fluorescent probes to study the morphology and the diffusion processes taking place within interpenetrating polymer networks. Martin and Webber [35] studied the behaviour and micellization of amphiphilic block copolymers labelled with different probes in solution, while Konash et al. [36] studied the distribution and interaction of enzymes incorporated into a polymer matrix. Finally, Cui et al. [37] recently used perylenediimide to label a silicone oil added to a supramolecular gel matrix, where the secretion of the silicone oil was exploited for self-healing purposes.

1.3. Aim and scope

This paper presents a method for visualizing the distribution of surface-active amphiphilic copolymers added to PDMS films and coatings, inspired by the work of Madsen et al. [38,39], where 4-methylumbelliferone, a fluorescent moiety, was used to label a crosslinker for PDMS. The synthetic pathway was chosen because it allowed the coupling of three different techniques (i.e. Piers-Rubinsztajn reaction, hydrosilylation and click chemistry) in mild conditions, which produced a relatively high yield of the desired product with an acceptable dispersity (D).

Here, a novel copolymer is synthesized for analytical purposes. A PEG-b-PDMS-b-PEG triblock copolymer is labelled with 4-methylumbelliferone, added to an uncured PDMS mixture and applied as a free film. Upon curing, the properties of the coating films are analysed and compared to a coating where the labelled copolymer was substituted by a commercial copolymer of similar characteristics. The similarities and divergences between the commercial and synthesized copolymer are discussed and compared to the properties of the coatings. Finally, the distribution and migration of the labelled triblock copolymer within the coating film are studied by confocal laser scanning microscopy (CLSM), allowing the visualization of the fluorescent-labelled molecules at different depths inside the bulk of the film over time.

2. Experimental

2.1. Materials

3-choloropropylmethyldimethoxysilane, hydride-terminated dimethylsiloxane (DMS-H11, M_w ~ 1500 g/mol determined by ^{1}H NMR) and platinum-divinyl tetramethyldisiloxane (Karstedt’s catalyst), with 2.1–2.4% Pt in xylene, were purchased from Gelest Inc. Mono-allyl-terminated poly(ethylene glycol), (PolyglykolA500, M_w ~ 500 g/mol), was purchased from Clariant. All other chemicals were acquired from Sigma-Aldrich and used as received unless otherwise stated.

Silanol-terminated polydimethylsiloxane (4000 cSt) was obtained from Dow Corning and a 16-functional pre-polymerized alkoxysilane crosslinker (Dynasylan 40) was received from Evonik Industries. Dibutyltin dilaurate was received from TIB chemicals.

4-methyl-7-(prop-2-yn-1-yloxy)-2H-chromen-2-one, an alkyne-terminated coumarin molecule, was produced using the method described by Madsen et al. [40] and will not be covered here.

All the glassware used was flame-dried prior to usage, and all the reactions were carried out under a nitrogen atmosphere.

2.2. Synthetic procedure

The PEG-b-PDMS-b-PEG block copolymer labelled with 4-methyl-7-(prop-2-yn-1-yloxy)-2H-chromen-2-one was synthesized in a 4-step reaction, which can be seen in Fig. 1 and is described below.

2.2.1. Synthesis of PDMS(Cl) (1)

3-choloropropylmethyldimethoxysilane (1.00 g, 5.47 mmol) was dissolved in dry toluene (16 mL) in a three neck round-bottom flask. Hydride-terminated dimethylsiloxane (17.24 g, 16.4 mmol) was added to the mixture and stirred for 10 min. Tris(pentafluorophenyl) borane in dry toluene (0.7 mL, 0.002 M, 0.03 mol%) was added to the mixture. Methane gas immediately developed, and the reaction was kept under stirring for 5 min at RT, until no more methane formation could be observed. The product obtained was used without further purification.

IR (cm^{-1}): 2962 (C—H stretch); 1258 (Si—CH_3 deformation); 1008 (Si—O—Si stretch); 785 (Si—C stretch).

^{1}H NMR ($CDCl_3$, δ_H, ppm): −0.04 to 0.09 (m, 3H, Si-C*H*$_3$); 0.61 (m, 2H, Si-C*H*$_2$-CH$_2$-CH$_2$-Cl); 1.81 (m, Si-CH$_2$-C*H*$_2$-CH$_2$-Cl); 3.49 (t, J^3 = 7.0 Hz, Si–CH$_2$-CH$_2$-C*H*$_2$-Cl), 4.68 (m, Si-*H*).

^{13}C NMR ($CDCl_3$, δ_C, ppm): 0.4–1.6 (Si-*C*H$_3$); 15.0 (Si-*C*H$_2$-CH$_2$-CH$_2$-Cl); 26.7 (Si-CH$_2$-*C*H$_2$-CH$_2$-Cl); 47.6 (Si-CH$_2$-CH$_2$-*C*H$_2$-Cl).

2.2.2. Synthesis of PEG-b-PDMS(Cl)-b-PEG (2)

Mono-allyl-terminated PEG (14.24 g, 28.4 mmol) was added to the round-bottom flask containing the PDMS(Cl) (**1**). Platinum-divinyl tetramethyldisiloxane was dissolved in dry toluene and added to the mixture (0.5 mL, 0.01 mM, 150 ppm). The reaction mixture was heated to 65 °C and allowed to react for 4 h. At the end of the reaction, the excess of allyl-PEG (insoluble in toluene) was removed by decantation. The toluene was removed by rotatory evaporation under vacuum to obtain the product in the form of a clear brown oil (**2**).

IR (cm^{-1}): 3470 (—OH stretch); 2962 (C—H stretch); 2870 (aliphatic C—H stretch); 1258 (Si—CH_3 deformation); 1070 (CH$_2$—O—CH$_2$ stretch); 1008 (Si—O—Si stretch); 785 (Si—C stretch).

^{1}H NMR ($CDCl_3$, δ_H, ppm): −0.02 to 0.05 (m, Si-C*H*$_3$); 0.51 (m, Si-C*H*$_2$-CH$_2$-CH$_2$-O); 0.62 (m, 2H, Si-C*H*$_2$-CH$_2$-CH$_2$-Cl); 1.61 (m, Si-CH$_2$-C*H*$_2$-CH$_2$-O); 1.81 (m, Si-CH$_2$-C*H*$_2$-CH$_2$-Cl); 2.66 (s, C-O*H*); 3.41 (t, J^3 = 7.1 Hz. Si-CH$_2$-CH$_2$-C*H*$_2$-O); 3.49 (t, J^3 = 7 Hz, Si-CH$_2$-CH$_2$-C*H*$_2$-Cl); 3.48–3.69 (m, O-C*H*$_2$-C*H*$_2$-O).

^{13}C NMR ($CDCl_3$, δ_C, ppm): 0.4–1.6 (Si-*C*H$_3$); 14.0 (Si-*C*H$_2$-CH$_2$-CH$_2$-O); 15.0 (Si-*C*H$_2$-CH$_2$-CH$_2$-Cl); 23.1 (Si-CH$_2$-*C*H$_2$-CH$_2$-O); 26.7 (Si-CH$_2$-