Role of textile substrate hydrophobicity on the adsorption of hydrosoluble nonionic block copolymers

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GRAPHICAL ABSTRACT
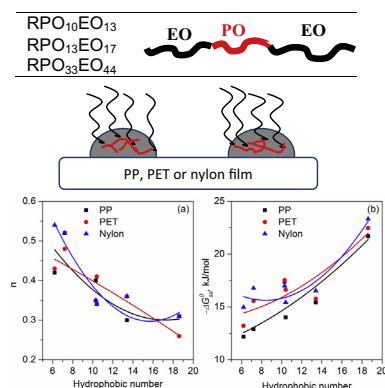
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ABSTRACT

The adsorption of polyalkylene glycols and co-polymers of ethylene oxide and propylene oxide on substrates relevant to textiles with varying surface energies (cellulose, polypropylene, nylon and polyester) was studied by using quartz crystal microgravimetry. Langmuirian-type isotherms were observed for the adsorption profiles of nonionic block polymers of different architectures. The affinity with the surfaces is discussed based on experimental observations, which highlights the role of hydrophobic effects. For a given type of block polymer, micellar and monomeric adsorption is governed by the balance of polymer structure (mainly, chain length of hydrophobic segments) and substrate's surface energy.

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1. Introduction

Polymer adsorption at the solid/liquid interface plays a critical role in technologies involving paintings, coatings, lubricant

formulations, ceramics additives, and adhesives [1]. Among these, surface modification with nonionic block copolymers is typical for lubrication and to facilitate the processing of synthetic and natural fibers in various textile operations. As such, research on interfacial and physicochemical behavior of finishes based on nonionic block copolymers has been a topic of great interest [2–19]. Because of their amphiphilic nature, nonionic block copolymers tend to form micelles in dilute aqueous solution and adsorb readily on a large variety of interfaces. The adsorption of nonionic block copolymers on highly hydrophobic [3,7,11,20,21] and highly hydrophilic [2,11,21] surfaces and the influence factors such as polymer architecture [5], temperature [4,22] and ionic strength [23] have been the subject of extensive investigation.

Brandani and Stroeve [24] used Surface Plasmon Resonance to study the adsorption–desorption behavior of block copolymers of poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) on hydrophobic surfaces (from alkanethiol self-assembled monolayers); their results indicate non-Langmuirian, irreversible adsorption of the copolymers and an adsorption maximum around the critical micelle concentration (CMC). The results also indicate higher mass adsorbed for the block copolymers containing higher molar number of the PPO blocks. Further studies showed that the kinetics of adsorption of the same block copolymers is affected by the relative size of PPO and PEO blocks comprising the copolymer [24].

Prior research in our group included elucidation of the influence of the nature of nonionic block copolymer, such as molecular size and the length of hydrophobic chain on their adsorption behavior on polyethylene terephthalate (PET) surfaces [10]. It was found that the adsorption isotherms of the nonionic polymers on PET surfaces followed a Langmuirian-type behavior (S- or LS-types) and was heavily influenced by the chain length of the hydrophobic group, i.e. the hydrophobic number strongly correlated with their affinity with the surface. In this communication, we report on the influence of the hydrophobicity of different substrates on the adsorption of nonionic block copolymers. This is of special relevance in textile applications, which involve fibers produced from synthetic polymers (polyester fiber, nylon/aramid fiber, olefins, acrylic/modacrylic fibers), regenerated cellulose and other natural sources (cotton, wool, and silk), all displaying remarkably different surface energy and hydrophobicity. Here, we used thin films of cellulose, polypropylene (PP), nylon and PET [25] and a quartz crystal microbalance with dissipation monitoring (QCM-D) to evaluate the adsorption of nonionics block copolymers of different architectures.

2. Materials and methods

All experiments were performed with deionized water from an ion-exchange system (Pureflow, Inc.) which was further processed in a Milli-Q® Gradient unit to ensure ultrapure water with resistivity greater than18 MΩ.

2.1. Materials

The nonionic surfactants used included polyalkylene glycols (PAG) from Dow Chemical Co. (Midland, MI), and triblock copolymers based on ethylene oxide and propylene oxide (Pluronics®) from BASF Corporation, Florham Park, NJ. The generic chemical structures of PAGs and Pluronics with different structural parameters m and n are shown in Fig. 1 and more details are provided in Table 1. It is worth noting that the supplied samples not only have different monomer composition but also different molecular weights. Nevertheless, these polymers are comparatively purer and better defined than the complex commercial formulations typically used.

Fig. 1. Chemical structure of polyalkylene glycols (PAGs) (left) and co-polymer of polyethylene oxide and polypropylene oxide (Pluronics) (right).

Table 1
Structural information of polyalkylene glycols (PAGs) and Pluronics®.

Symbol[1]	Commercial name[2]	MW	n (PO)	m (EO)	HLB[3]
R-PO$_{10}$EO$_{13}$	UCON 50-HB-400	1230	10	13	11.9
R-PO$_{13}$EO$_{17}$	UCON 50-HB-660	1590	13	17	12.0
R-PO$_{33}$EO$_{44}$	UCON 50-HB-5100	3930	33	44	8.5
EO$_{19}$PO$_{29}$EO$_{19}$	Pluronic P65	3400	29	19	21.7
EO$_{76}$PO$_{29}$EO$_{76}$	Pluronic F68	8400	29	76	27.7
EO$_{37}$PO$_{56}$EO$_{37}$	Pluronic P105	6500	56	37	17.3

[1] R, P and E stand for butyl, propylene oxide and ethylene oxide groups, respectively.
[2] UCON polymers are from Dow Co. and Pluronic polymers are from BASF Co.
[3] HLB values were calculated by the method described by Guo et al. [26].

Micro-crystalline cellulose was obtained from Avicel® PH-101 (Fluka Chemical Corporation). Medium density polyethylene (PE, received as a powder), polypropylene (PP, syndiotactic, with Mn and Mw of 54,000 and 127,000, respectively) and nylon 6 (with a Tg of 62.5 °C and particle size of 3 mm) were purchased from Sigma–Aldrich. Poly (ethylene terephthalate) (PET) was provided by Goulston Inc. (Monroe, NC). Polyvinylamine (PVAm) was donated by BASF Corporation. Xylene (HPLC grade), hexafluoroisopropanol (HFIP, 99.5+ %), 50% N-methylmorpholine-N-Oxide (NMMO) and Dimethyl Sulfoxide (DMSO) were purchased from Fisher Scientific.

2.2. Film substrates

The solid supports used in this investigation were gold sensors (Q-Sense Co, diameter is 12 mm). Prior to use the sensors were cleaned with Piranha solution (H$_2$SO$_4$ (98%): H$_2$O$_2$ (30%) = 70:30 v/v) for one hour and then subjected to UV-ozone radiation for 10 min immediately before spin-coating with the substrate polymer solutions. Fiber precursor materials were dissolved in diluted solution and then employed in the spin coater to cast a uniform ultrathin film onto the QCM sensors. Details on the development of cellulose and synthetic films can be found elsewhere [25,27,28]. The thickness of spin-coated organic film on QCM sensors were controlled in the range of 10–50 nm.

2.3. QCM-D technique

A QCM-D E4 model (Q-Sense Inc.) was used to evaluate the adsorption of the nonionic polymers on the polymeric ultrathin films. The principle of the QCM technique involves the monitoring of the shift of resonant frequency (Δf) of a gold-coated piezoelectric material (quartz crystal), which depends on the total oscillating mass. If the film is thin and rigid, the decrease in frequency is proportional to the mass of the film, as stated by Sauerbrey equation [29]:

$$\Delta m = -\frac{c\Delta f}{n} \tag{1}$$

where C = 17.7 ng Hz^{-1} cm^{-2} for a 5 MHz quartz crystal and n = 1,3,5,7 is the overtone number.

Because the frequency can be detected very accurately, the QCM operates as a very sensitive balance with ng/cm^2 resolution. Besides frequency, QCM-D can simultaneously monitor the changes in energy dissipation ΔD of the adsorbed films. Energy dissipation relates to the conformation of adsorbed layer. Therefore, one of the advantages of QCM-D is that it can indicate changes