Applied Surface Science 387 (2016) 28–35

Contents lists available at ScienceDirect

Applied Surface Science

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

Post-functionalization of plasma treated polycarbonate substrates: An efficient way to hydrophobic, oleophobic plastics

Guilhem Godeau, Sonia Amigoni, Thierry Darmanin, Frédéric Guittard*

Univ. Nice Sophia Antipolis, CNRS, LPMC, UMR 7336, 06100 Nice, France

ARTICLE INFO

Article history:
Received 26 March 2016
Received in revised form 15 May 2016
Accepted 8 June 2016
Available online 14 June 2016

Keywords:
Plasma treatment
Post-functionalization
Huisgen reaction
Hydrophobic
Wetting properties

ABSTRACT

This work presents a new strategy of plasma treatment and post-functionalization of polycarbonate substrates in order to enhance their hydrophobic properties. While the plasma treatment is used to change the morphology and increase the roughness, the Huisgen reaction is used to decrease the surface energy or to add specific properties. Surface post-functionalization allows the covalent grafting of alkyl, aryl or perfluoroalkyl chains. The modified surfaces are investigated for their morphology, the observations performed show significant changes. The studies, made on the wettability, show important change in wettability with highly hydrophobic features (water apparent contact angle $\theta > 140^\circ$). Starting on a single polycarbonate surface, this multistep approach allows for the preparation of various polycarbonate surfaces with hydrophilic, oleophilic, highly hydrophobic, highly oleophobic or even fluorescent features to polycarbonate plastic surfaces.

1. Introduction

Highly hydrophobic and highly oleophobic surfaces present a wide range of interest for both the industrial and the scientific communities. These applications can be found in various fields including water proof textiles, self-cleaning windows, anti-fog or anti-icing glass, biomedical applications (anti-bioadhesion surfaces) or in the environmental domain to develop oil/water separation membranes [1–4]. Due to this wide field of applications, obtaining these properties became a challenge for researchers, and the solution to this challenge was found in nature [5]. Observations in nature revealed a wide range of hydrophobic surfaces with high water adhesion like rose petals [6–9] or with low water adhesion like lotus leaves [10,11]. Some insects also display highly oleophobic properties due to specific surface textures [12,13]. Different models are proposed to describe these phenomena. One of the first reported model was the Young Dupré model that describes the water static or apparent contact angle θ of a smooth surface as a consequence of the surface tension between the vapor, the liquid and the solid [14]. The proposed model is:

$$\cos\theta^{Y} = (\gamma_{sv} - \gamma_{sl})/\gamma_{lv} \tag{1}$$

where θ^Y is the apparent or static contact angle, γ_{sv} the solid/vapor surface tension, γ_{sl} the solid/liquid surface tension and γ_{lv} the liquid/vapor surface tension. Other models are reported to describe the wettability of rough substrates. The Wenzel and the Cassie-Baxter equations include surface roughness as an important parameter [15,16]. The Wenzel equationis:

$$\cos\theta = r\cos\ \theta^{Y} \tag{2}$$

where r is the roughness parameter (r = actual surface/planar surface)) assumes that the liquid enters into all the surface asperities, which dramatically increases the solid/liquid contact area, this model is used to describe both high θ and highly adherent surfaces only if $\theta^Y > 90^\circ$ (otherwise the roughness parameter increases the surface hydrophilicity). The Cassie-Baxter equation assumes that vapor cannot escape and hence forms vapor bubbles beneath the droplet and thus the droplet retains its general spherical shape and rests upon the surface asperities [17]. As a result, the contact area between the surface is dramatically reduced. The Cassie-Baxter equation is used to describe low adhesion surfaces with self-cleaning properties. This equation is:

$$\cos\theta = f r_f \cos\ \theta^{Y} + (f-1) \tag{3}$$

where r_f is the roughness ratio of the substrate wetted by the liquid, f the solid fraction and $(1 - f)$ the air fraction. The Cassie-Baxter equation explains that superhydrophobic properties with low hysteresis can be obtained if the air fraction is important and even if the materials are intrinsically hydrophilic ($\theta^Y < 90^\circ$) [18]. The Cassie-

---

* Corresponding author.
E-mail addresses: guittard@unice.fr, thierry.darmanin@unice.fr (F. Guittard).

http://dx.doi.org/10.1016/j.apsusc.2016.06.053

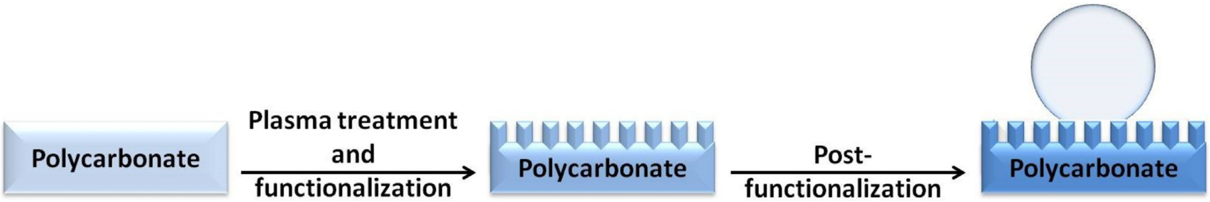

Fig. 1. Schematic representation of the surface modifications.

Baxter equation can also explain the parahydrophobic properties with extremely high hysteresis if the air fraction is lower and/or by reducing θ^Y [19]. Considering all these models, two parameters seem to be preponderant to control surface interactions: θ^Y, which depends on γ_{sv} and γ_{lv}, and the surface roughness. Oils present a high capacity to spread on surfaces due to their typically low γ_{lv}. Therefore, the control of oleophobic properties needs additional parameters to impede their spreading [1,19–23]. In particular, surface structures with reentrant curvatures can lead to strongly oleophobic properties [22,23].

The key point for hydrophobic/oleophobic surface elaboration is the answer to the question: "how to control surface energy and surface morphology?" Diverse solutions have been found in order to give answers to this question. Globally, two main strategies are often used [1,2]. The first starts with small molecules, which are self-assembled or polymerized in order to form a structured surface. Hydrophobic/oleophobic treatments can be employed at different moments during fabrication to enhance the surface properties. This approach can be classified as a bottom-up approach [24]. An example of a bottom-up approach is the electrodeposition of conducting polymers [25–28]. This strategy has been widely studied and allows for the preparation of highly structured surfaces with hydrophobic/oleophobic properties in one step. This strategy is clearly efficient but is limited to conductive substrates and is not suitable for other non-conductive surfaces like plastics. The second strategy starts with smooth hydrophobic/oleophobic substrates, to which structure is often removed then added using physical or chemical treatments. This type of strategy can be described as a top-down approach [29]. An example is plasma etching where structure is added on to surface by plasma treatment [30–36]. This strategy has been reported as efficient in the literature and can be used on various materials including polymers, nanotubes or particles [37–39]. After plasma treatment, it is also possible to add functionality using chemical treatments. For example, surface polymerization on plasma-treated surfaces has successfully been used for the grafting of polyacrylic acid, polythiophene, or polypyrrole on substrates [40,41]. For example, surface plasma polymerization has also been reported on nanoparticle surfaces using thiophene as a monomer [42,43]. Indeed, thiophene and their derivatives such as 3,4-ethylenedioxythiophene and 3,4-propylenedioxythiophene are very often used to develop conducting polymers [44,45]. But, they have also been cited for plasma polymerization [46–48]. After surface structuration, it is possible to add additional functionality by performing post-polymerization modifications. Diverse strategies are reported for surface post-functionalization, among them the chemical reactions known as click chemistry are particularly studied [49]. Reactions like the Diels-Alder reaction, Staudinger-Vilarassa reaction or the thiol-Michael reaction have been successfully used for surface post-functionalization [50–53]. The Huisgen reaction modified by Sharpless has been used for modification on macromolecules, biomolecules, nanoparticles or surfaces [54–59]. This reaction is of particular interest for post-functionalization. Due to the soft conditions of the Huisgen reaction, low temperature and reaction in water/alcohol mixture, this reaction is particularly well adapted for plastic post-modifications and for combination with plasma treatment [60–62]. Due to the number of modification steps, this approach can be considered complex when compared to other methods described in the literature for hydrophobic surface elaboration [34,63–69]. But the use of the Huisgen reaction allows for different functionalizations (hydrophobic, oleophobic or fluorescent) on only one prepared surface.

In this work, using 3,4-propylenedioxythiophene derivatives with two azide groups, we report for the first time the combination of surface etching, plasma polymerization and click post-functionalization for hydrophobic surface elaboration. Different conditions for plasma treatment are investigated in order to get structured surfaces. Plasma polymerizations were performed on surfaces followed by post-functionalization (Fig. 1), all the functionalizations were followed using FT-IR. The substrates were modified using alkyl, aryl or perfluoroalkyl chains. The modified substrates were investigated for their roughness, morphology and wettability.

2. Materials and methods

2.1. Synthesis

3,3-bis(bromomethyl)-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine, **ProDOT-2Br**: 2.5 g of 2,3-dimethoxythiophene (17.5 mmol) was dissolved in 100 mL of toluene. 9.1 g of 2,2-dibromomethylpropan-1,3-diol (35 mmol) and 665 mg of *para*-toluenesulfonic acid monohydrate (3.5 mmol) was added. The mixture was warmed at 110 °C for 36 h. The mixture was then cooled at room temperature. The toluene phase was extracted with $NaHCO_3$ 5% in water (2 × 30 mL) and brine (30 mL), and dried (Na_2SO_4). The solvents were removed under reduced pressure. The compound was finally purified on column (8/2, cyclohexane/DCM).

Yield: 3.9 g of white solid (66%). All spectroscopic data agreed with the literature [70].

3,3-bis(azidomethyl)-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine, **ProDOT-2N$_3$**: 1.35 g (3.95 mmol) of **ProDOT-2Br** was dissolved in 100 mL of DMF and 2.57 g (10 eq, 39.5 mmol) of NaN_3 was added. The mixture was stirred overnight at 110 °C. The reaction was then allowed to cool at room temperature. 200 mL of

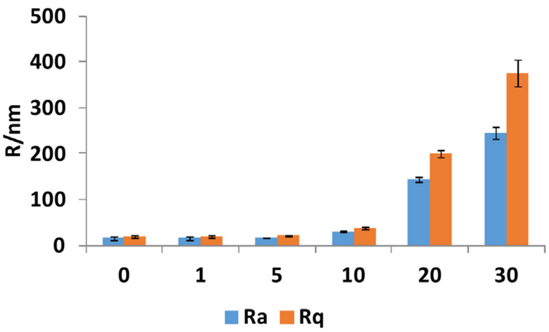

Fig. 2. Surface roughness measurements for different plasma irradiation times (error bars show the standard error of each measurment).