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Super-wetting surfaces by plasma- and UV-based grafting of micro-rough acrylate coatings

Thomas Bahners[a,*], Lutz Prager[b], Alya Pender[b], Jochen S. Gutmann[a,c]

[a] Deutsches Textilforschungszentrum Nord-West gGmbH (DTNW), Adlerstr. 1, 47798 Krefeld, Germany
[b] Leibniz-Institut für Oberflächenmodifizierung e.V. (IOM), Permoserstr. 15, 04318 Leipzig, Germany
[c] Universität Duisburg-Essen, Physikalische Chemie and CENIDE, Universitätsstr. 2, 45141 Essen, Germany

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ABSTRACT

In Wenzel's model of the wetting behavior of rough surfaces, super-wetting can be achieved by micro-roughening a hydrophilic surface, but also by increasing the surface free energy of a micro-rough surface. Therefore, the objective of the present paper was to investigate the effect of grafting post-treatments of micro-rough surfaces having a good mechanical stability. The post-treatments were designed to increase the surface free energy and, accordingly, achieve pronounced surface wetting. Two potential designs of post-treatments were evaluated. A two-step plasma-based surface grafting and a UV-induced photo-chemical grafting.

The plasma-based post-treatment was performed in a two-step process. First, the micro-rough samples were activated in argon or oxygen plasma. The subsequent grafting modification was carried out by immersing the samples in aqueous solutions of p-toluenesulfonic acid, glycerin, and saccharose. For the photo-chemical post-treatment, the micro-rough samples were dipped in an aqueous solution of poly(ethylene glycol) methacrylate (PEG300MA) and irradiated using a UV broadband lamp.

Surface analysis showed that plasma-aided grafting resulted in the lowest water contact angles and extremely wetting surfaces. Following the photo-chemical grafting of PEG300MA, best results were of the order of 20°. In both cases, excellent stability of the layer and its wetting behavior was found.

1. Introduction

The wetting behavior of a surface is basically determined by the relation of the interfacial energies between the solid substrate and the liquid, γ_{sl}, between the substrate and the gaseous atmosphere, e.g. vapor, γ_{sv}, and between the liquid and the atmosphere, γ_{lv}. The relation between these quantities and the contact angle Θ_Y of a droplet on the surface is described by Young's equation. Besides affecting the wetting by an obvious change in substrate surface free energy (SFE) through the introduction of polar or non-polar groups, the wetting behavior can also be modified by increasing the surface roughness. In case that the droplet wets the liquid-substrate-interface completely, the apparent contact angle is often described by the rather simplified Wenzel model [1]. Wenzel's equation relates the apparent contact angle of the micro-rough surface Θ_W to the contact angle of the planar surface of the same material ('Young angle') Θ_Y by

$$\cos\Theta_W = r \cdot \cos\Theta_Y \quad (1)$$

where the roughness or Wenzel factor r is the ratio between the areas of rough and flat surfaces ($r \geq 1$).

Two potential cases have to be considered. Depending on the nature of the planar surface, the introduction of a micro-roughness *increases* the wettability of an intrinsically hydrophilic surface, but *decreases* the wettability on an already hydrophobic surface (cf. Fig. 1). While Eq. (1) suggests the transition from increased to decreased wettability at 90°, experimental measurements showed that this transition occurs at a 'critical contact angle' $\Theta_c < 90°$, which depends on the specific topography of the surface [2,3].

Given this background, it was proposed to create perfectly wetting surfaces by providing moderately hydrophilic surfaces with a suitable micro-roughness [4–6].

The authors of the present paper have applied the process of photo-induced micro-folding to produce micro-rough acrylate top-coats on planar substrates such as polymer films and coated fabrics and thus control the wettability of the formulations [7,8]. Photo-induced micro-folding is based on a two-step UV curing process of an acrylate layer applied to an arbitrary substrate [9–12]. First, the acrylate is treated by vacuum ultraviolet (VUV) radiation emitted from, e.g., xenon excimer lamps at 172 nm. Photons in this spectral range induce radical polymerization via the acrylic double bonds as well as C—C— and C—H-bond breakages resulting in radical formation and cross-linking with high quantum yield and

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[*] Corresponding author. Tel.: +49 02151 843 156; fax: +49 02151 843 143.
E-mail address: bahners@dtnw.de (T. Bahners).

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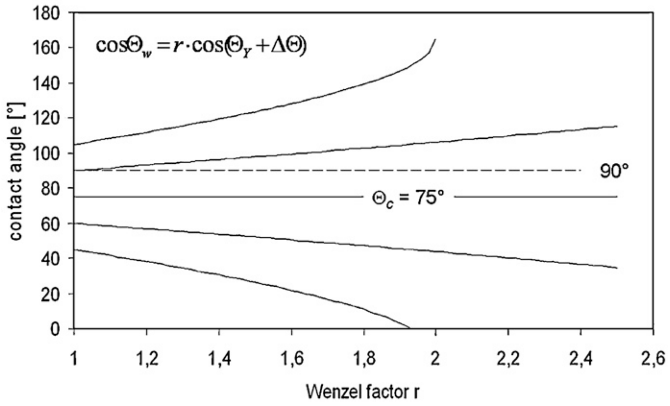

Fig. 1. The effect of surface roughness – described by the 'Wenzel factor' r – on contact angle of a rough surface. Θ_c denotes the 'critical contact angle', at which the transition from increasing wettability to decreasing wettability occurs. On real surfaces Θ_c differs from the theoretical 90° predicted by Wenzel's equation by $\Delta\Theta$, and was set to 75° in this simplified sketch.

are absorbed at a high rate [13]. Accordingly, penetration depths are extremely small. This results in a very fast curing of a thin surface layer of less than 100 nm thickness on top of the still liquid bulk. Due to shrinkage occurring during polymerization and cross-linking, a wavy surface topography with pronounced roughness and small peak-to-peak distances is generated ('micro-folding'). This structure is frozen-in through subsequent curing of the bulk volume in the second step. This is achieved by conventional broadband UV or electron beam (EB) irradiation. The chemistry, thickness, and viscosity of the acrylate layer on one hand, and the choice of the (V)UV sources (wavelength) and the respective irradiation doses on the other can be used to control the resulting surface topography.

In a recently published study, the authors applied photonic micro-folding to inherently hydrophilic lacquers prepared from hydroxypropylacrylate and polyethylenglycol monoacrylate [8]. They produced surfaces with two-scale surface topographies with areas of shallow aspect ratio separated by high "walls" up to 40 μm high. The ratio of actual to projected surface area (Wenzel factor) depended on the curing conditions and varied, according to white light interferometry, from 1.2 to 2.5. The water contact angle on these surfaces (advancing contact angle) basically followed the prediction of Wenzel's equation and, with an increase in the roughness factor r to 1.3, decreased from 37° to below 10°. On surfaces with Wenzel factors in excess of approximately 1.3, a transition in wetting behavior occurred in a way that a water droplet more or less spontaneously covered a large area of the rough surface. The analyses by the authors indicated that further or full wetting was prohibited by high features of the surface profile, which acted as geometric barriers. It has to be noted at this point, that subsequent studies of the behavior of these surfaces under real-life conditions in an urban/industrial environment showed insufficient stability of these super-hydrophilic layers. Minute surface defects combined with the extreme wetting properties led to water sorption underneath the layers and subsequent delamination.

Based on the assumption that, according to Wenzel's equation, super-wetting could basically be achieved by micro-roughening a hydrophilic surface, but also by increasing the surface free energy of a micro-rough surface, the objective of the presented paper was to investigate the effect of grafting post-treatments of micro-rough surfaces of good mechanical stability in order to increase the surface free energy and to achieve pronounced surface wetting. Two potential designs of post-treatments were evaluated; a two-step plasma-based surface grafting and a UV-induced photo-chemical grafting. Although both concepts are well documented, some specific aspects shall be summarized in the following paragraphs.

It is well-known that a plasma treatment in "simple" process gases such as oxygen, nitrogen or argon leads to an increase in surface free energy and wettability. However, these processes can be regarded as unselective, since the electron energy is high compared to prevailing bond energies, and species in the gas phase are manifold. Accordingly, a broad range of surface groups are generated [14]. On the other hand, the effects of plasma treatments of such simple design are not stable, but recover within days as was reported among many other researchers by, e.g., Wavhal and Fisher [15]. Their paper is of great interest in the given context, as Wavhal and Fisher compared the effect of a simple argon plasma treatment with the effect of plasma-based grafting of poly(acrylic acid) (PAA) on the wettability of polyethersulfone (PES) membranes and found a durable and well-defined surface modification following the grafting process. Similar treatments of polymers as varied as PES, polyacrylonitrile [16], polysulfone [16,17], or poly(tetrafluoroethylene) [18] are reported in the literature. Plasma-grafting has the obvious advantage of selective surface functionalization through the specific choice of the graft monomer, its concentration and duration of the grafting step [19]. In general, plasma-based grafting can be performed as a one-step process, i.e. by using the vaporized graft monomer or a mixture of the monomer with a carrier gas as process gas. Often, a two-step process is more feasible with plasma-activation, e.g. in argon, as the first step and followed by graft-polymerization (as mentioned in the literature by, e.g., [15,17,18]). For this study, it is interesting to note that Gancarz et al. [17] report significant differences in the properties of membranes that were functionalized by grafting of acrylic acid from vapor as compared to grafting from solution. Indeed, grafting from solution did affect the pore size distribution, which effectively produced more hydrophobic samples in contrast to the envisaged increase in wettability.

Photo-chemical processes have proven their potential for an effective and durable functionalization of polymers, if treatments are conducted in reactive media, which can be a gaseous atmosphere or a liquid agent [20–26]. The absorption of UV photons either at the surface of the substrate – i.e. at the interface between substrate and reactive medium – or in the bulk of the reactive medium, leads to radical generation and subsequent reactions. Besides the recombination of radicals and cross-linking of polymer chains at the substrate surface, the addition of radicals from the reactive medium, and the addition of bi-functional molecules with ensuing cross-linking between the functional groups result in photo-induced grafting or cross-linking of functional groups.

In view of increasing surface free energy and wettability, polyethylene glycol methacrylate (PEGMA) was considered in this study. The photo-induced immobilization of various PEGMAs and the effect on the wettability of textile fabrics have been studied earlier by Bahners et al. [27,28]. In view of the conservation of the micro-rough surface topography, which is crucial in the context of the underlying concept of this work, it is finally important to consider the effect of cross-linking or homo-polymerization of the PEGMAs. As can be expected, the irradiation/activation of dimethacrylated PEGs such as PEG400DMA and PEG600DMA studied in [27,28] results in the deposition of a significant layer, which effectively masks the texture of the substrate. The photo-induced cross-linking of the monomethacrylated PEGs leads to significantly smaller deposition.

2. Materials and methods

2.1. Acrylate design

Two acrylate formulations designated by A and B were employed in this study, and are presented in Table 1. While a hydrophilic nature was basically favored, the acrylates were