# Photoreactive composite coating with composition dependent wetting properties

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**Abstract.** Photoreactive composite thin layers with tunable wetting properties from superhydrophilic to superhydrophobic nature were prepared. To achieve extreme wetting properties, the adequate surface roughness is a crucial factor, which was achieved by the incorporation of plasmonic Ag-TiO$_2$ particles, as polymer filler, into the smooth polymer film with adjusted hydrophilicity. The initial copolymer films were synthesized from hydrophilic 2-hydroxyethyl-acrylate (HEA) and hydrophobic perfluorodecyl-acrylate (PFDAc) monomers. In the case of hydrophobic PFDAc, the photocatalyst- roughened thin films displayed superhydrophobic behavior ($\gamma_s^{tot} \sim 2.3\pm1.7$ mJ/m$^2$, $\Theta > 150°$), while the roughened hydrophilic pHEA layers possessed superhydrophilicity ($\gamma_s^{tot} \sim 72.1\pm0.2$ mJ/m$^2$, $\Theta \sim 0°$). The photoactivity of the composites was presented both in solid/ gas (S/G) and solid/ liquid (S/L) interfaces. According to the light-emitting diode (LED) light photodegradation tests on ethanol (EtOH) as volatile organic compound (VOC) model- molecules at the S/L interface, the superhydrophobic hybrid layer was photooxidized 88.3% of the initial EtOH (0.36 mM). At S/L interface the photocatalytic efficiency was depended on the polarity of the model pollutant molecules: the photooxidation of hydrophobic SUDAN IV ($c_0 = 0.25$ mg/mL) dye reached 80%, while in the case of the hydrophilic Methylene Blue dye ($c_0 = 0.002$ mg/mL) it was only 17.3% after 90 min blue LED light ($\lambda = 405$ nm) illumination.

*Keywords: coatings, nanomaterials, polymer composites, surface roughness, adjustable wetting*

## 1. Introduction

The superhydrophobic and superhydrophilic behaviors of different surfaces have attracted much attention in industrial fields as well as scientific research [1, 2]. The superhydrophilic coating material leads to a water contact angle ($\Theta$) lower than 5° on solid surface. These materials are already commercially used for antifogging glasses, mirrors and outward walls of buildings. [1, 2]. After the discovery of the photo- induced superhydrophilicity of photocatalyst (TiO$_2$) layers in 1997 [3], commercially applicable photofunctional materials that have self-cleaning properties were synthetized with the use of pure TiO$_2$ particles and composite thin films [4]. The ultraviolet (UV) light – excitable TiO$_2$ is also well-known as an effective photocatalyst material in the field of environmental remediation or different energy related topics [5, 6]. It is possible to extend the absorption spectrum of the semiconductor photocatalysts by, for example, modifying the catalyst particles with different metallic or non-metallic elements. The synthetized functionalized catalysts can be excited by

the near-UV or visible (VIS) light due to the absorption of metal nanoparticles at lower energy wavelengths [5, 6].

The incorporation of semiconductor photocatalystic particles in an appropriate polymer-based support or binder material is expected to create antimicrobial and self- cleaning properties, which would extend its field of application. The state-of-the-art materials in the area of photocatalyst/ polymer composite layers are the functional surfaces, which are gaining attention for different practical applications, such as self-cleaning superhydrophobic coating [7] and food packing materials with antibacterial behaviors [8]. Polymers are often used as photocatalyst binders due to their low weight, flexibility, low cost and impact resistance. Moreover, the adjustable properties and easy modification of different polymers are also well known from literature [9]. For example, the wetting properties of a polymer surface can be easily adjusted with the monomer composition using hydrophilic and hydrophobic monomers in an adequate ratio [10]. So, if we use polymeric material for the photocatalyst immobilization, a very useful composite surface can be obtained with adjustable properties.

Surfaces with $\Theta$ values higher than 150° (superhydrophobicity) can exhibit water repellent self-cleaning effects, as found in lotus leaves in nature [11]. For preparing superhydrophobic coating materials, hydrophobic surface functionality as well as surface roughness on two different scales are required: similarly to the surface of the lotus leaf, microstructure is superimposed by nanostructures, and this unique structure, referred to as dual-roughness, can reduce the contact area of water droplets with a surface, resulting in the emergence of water repellent behaviors. The dependence of the $\Theta$ on the surface roughness has been described by Wenzel's or Cassie-Baxter's models [11]. These models can be applied under the assumption that the water droplet is sufficiently larger than the surface roughness. In the past, much effort has been made for preparing superhydrophobic surfaces with high stability [12].

The aforementioned adequate surface roughness necessary for the superhydrophobic nature can be also achieved by the incorporation of photocatalyst particles into a low energy polymer matrix and thus, the study of superhydrophobic photocatalyst/polymer nanocomposite surface is not novel, because many authors reported similar results [13–18]. Nevertheless, these layers were synthetized with difficult

preparation techniques such as radio frequency-magnetron sputtering [13], electron beam treatment [14], spin- coating in an inert atmosphere (argon gas) [15], deposition technic in closed chamber and elevated (300 °C) temperature [16, 18] or dip- coating process [17] and the obtained coating provides only superhydrophobic properties beside the photoactivity. In our previous work we successfully prepared inorganic/ organic photoreactive composite layers that have also superhydrophobic properties [7]. However, to the best of my knowledge, no studies have been performed yet concerning the adjustable wetting of a photoreactive hybrid layer from superhydrophobic to superhydrophilic properties. In this paper, we present a simple, inexpensive and large scale thin film forming technique for fabricating VIS-light active Ag-TiO$_2$ plasmonic photocatalyst containing composite surfaces that exhibit adjustable wetting features.

## 2. Materials and methods
### 2.1. Preparation of the Ag-TiO$_2$/polyacrylate hybrid layers

The Ag-TiO$_2$ plasmonic photocatalyst as polymer filler with 0.5 wt% silver nanoparticles content was synthesized through the direct functionalization of TiO$_2$ particles. The process is detailed in our previous publications [5, 6].

Aqueous fluorochemical cationic dispersion (pPF-DAc) fluropolymer – produced by DuPont – (Capstone ST-110, active solid content: 25 wt%, pH = 4–6) was used as the hydrophobic binder. The hydrophilic polyacrylate was synthesized by the free-radical UV polymerization of 2-hydroxyethyl acrylate (HEA, purchased from Fluka) in aqueous medium. During the synthesis, 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651, purchased from Aldrich Chemicals) photoinitiator was added in the amount of 0.57 wt% of the monomer. The mixture was exposed to UV light (light source: Q81 type lamp, Heraeus Gmbh, Hanau, Germany; power: 70 W; $\lambda_{max}$ = 265 nm) for 30 minutes. After the polymerization process, the resulting aqueous poly-2-hydroxyethyl acrylate (pHEA) solution (nominal polymer content: 50.0 mg/mL) was used in further synthetic steps.

The 5×5 cm$^2$ photoreactive hybrid layers consist of Ag-TiO$_2$ photocatalysts and polyacrylate binder and 2×2 cm$^2$ smooth polyacrylate layers were prepared by applying the spray-coating technique on glass plate sample holders. The gravimetrically measured

amounts of material deposited on the glass plates were 5.3±0.5 mg/cm². The contents of the photocatalyst in the polyacrylate-based hybrid layers was systematically set to 80.00± 0.11 wt% to achieve the desired surface roughness, indicated in a previous publication [7]. During the preparation process, aqueous suspensions were prepared with varied pHEA/pPFDAc content (the pHEA/pPFDAc weight-to-weight ratios were 1:0, 8:2, 6:4, 4:6, 2:8 and 0:1, respectively) and evenly sprayed on 4 and 25 cm² glass substrates from a distance of 15 cm using a type R180 Airbrush spray gun at an operating pressure of 3 bar.

## 2.2. Methods of characterization

The surface structure, morphology and roughness of the prepared hybrid thin layers with different pHEA/pPFDAc contents were examined applying a SEM–Hitachi S-4700 field emission scanning electron microscope (secondary electron detector, acceleration voltage: 10 or 20 kV), and a Form Talysurf Series 2 mechanical profilometer (TaylorHobson Ltd., Leicester, Great Britain) at resolutions of 0.25, 1 μm and 3 nm in *x*, *y* and *z* directions, respectively. The thickness of the thin composite layers was measured using an Elcometer 224 type digital profile gauge. For optical characterization, diffuse reflectance UV–VIS spectra were recorded via CHEM2000 UV–VIS (USB2000+UV-VIS, Ocean Optics Inc., Dunedin, FL) spectrophotometer, equipped with an integrating sphere [6].

The initial contact angles (Θ) on Ag-TiO₂/polymer layers were measured according to the sessile drop technique [7] at 25.0±0.5 °C under atmospheric pressure, applying an EasyDrop drop shape analysis system (Krüss GmbH, Hamburg, Germany) equipped with DSA100 software, a Peltier temperature chamber and a steel syringe needle of 0.5 mm diameter and using distilled water as a test liquid. The initial Θ were measured after 15 min contact time. During these measurements only the initial Θ after deposition of water droplet was determined in each case [19]. In the case of the smooth and photocatalyst particles roughened superhydrophobic (r-pPFDAc) and superhydrophilic (r-pHEA) photoreactive thin films the advancing ($\Theta_{adv}$) and receding ($\Theta_{rec}$) contact angles were also measured according to the protocol of Drelich [20]. According to the theory of Drelich and Chibowski [21] the obtained $\Theta_{adv}$ and receding $\Theta_{rec}$ are also suitable for the estimation of the total apparent surface free energy ($\gamma_s^{tot}$) of the layer, knowing the surface tension of the probe liquid, ($\gamma_l$, 72.1 mN/m in the case of distilled water at 25 °C) and its contact angle hysteresis, which is defined as the difference between the $\Theta_{adv}$ and $\Theta_{rec}$, as shown by Equation (1):

$$\gamma_s^{tot} = \frac{\gamma_1 (1 + \cos\Theta_{adv})^2}{2 + \cos\Theta_{rec} + \cos\Theta_{adv}} \tag{1}$$

The apparent dynamic Θ of the hybrid layers were also determined by the Wilhelmy plate method. A digital surface tensiometer was applied (Force tensiometer – K100, Krüss GmbH, Hamburg, Germany). The 19.5×12.8×0.3 cm³ steel plates coated with hybrid layers (5.3±0.5 mg/cm² on both sides) were immersed into distilled water with a rate of 6 mm/min, while the changes in apparent $\Theta_{adv}$ and $\Theta_{rec}$ were calculated online by LabDesk 3.2 Software. The measurements were run at 25.0±0.5 °C.

The photocatalytic properties of the Ag-TiO₂/polyacrylate hybrid layers were studied during ethanol degradation tests under blue LED light (General Electric's, Hungary, λ = 405 nm) illumination at S/G interface. To quantify the degradation of EtOH test molecules, gas chromatographic (GC) measurements were carried out (Shimadzu GC-14B, Kyoto, Japan). During the measurements, 5 μL of EtOH (abs., Molar Chemicals, Hungary) was injected into the reaction chamber containing 25 cm² (25.0±0.5 °C) hybrid layers, fixed at 5 cm distance from the light source. The $c/c_0$ values calculated from peak areas were determined as the function of illumination time, where *c* is the concentration of EtOH at time (*t*) and $c_0$ is the initial concentration ($c_0$ = 0.36 mM). The apparent reaction rate constants ($k'$ [min⁻¹]) were calculated for first-order decay as shown by Equation (2) [7]:

$$\ln\frac{c}{c_0} = -k't \tag{2}$$

The photocatalytic activity of the hybrid layers was also measured at S/L interface. During these measurements hydrophilic Methylene Blue (Reanal, Hungary) in aqueous medium (distilled water) and hydrophobic SUDAN IV (Reanal, Hungary) dye in organic medium (ethanol with 5 v/v% water content) were chosen as model pollutants to evaluate the photocatalytic activity of the hybrid layers. The photocatalytic activity, i.e. the decreasing concentration of the dyes were measured with a spectrophotometer and the tests were carried out directly in a quartz cuvette

containing the superhydrophobic photoreactive thin film ($3 \times 0.9$ cm$^2$) and the dye solutions (3 mL). The absorbance spectra were taken after 0, 10, 20, 30, 40, 50, 60, 75 and 90 min of LED light illumination. The concentration of the dyes were 0.25 mg/mL and 0.002 mg/mL in the case of hydrophobic SUDAN IV and hydrophilic Methylene Blue, respectively.

## 3. Results and discussion

In our previous work, UV- excitable ZnO containing photocatalyst particles with primer mean particle diameter of 20 µm were immobilized in a low energy fluoropolymer binder to obtain bifunctional thin layers: besides the photocatalytic activity, lotus leaf-like wettability was achieved due to the incorporated photocatalyst particles enhanced surface roughness [7]. To achieve such wetting properties, the amount of the immobilized photocatalyst was proven to be at least 80 wt.%. At this composition the measured surface roughness value of the hybrid layer was 15.2 µm and this rough, thin film exhibits water repellent superhydropobic properties. In this work, the wetting properties of layers with adequate surface roughness were modified via the systematic adjustment of hydrophilic pHEA and hydrophobic pPFDAc besides keeping the previously determined photocatalyst-to-polymer ratio (8:2) to achieve a wide range of wettability, from superhidrophylicity to superhydrophobicity.

### 3.1. Wetting properties of thin films and the determined surface energy values

The wetting properties of the smooth polymer thin films with varied composition and the corresponding roughened hybrid layers was determined by static/ initial $\Theta$ measurements. The $\Theta$ values were measured after 15 min of contact time. Figure 1 shows the measured initial $\Theta$ as a function of polymer composition. The increasing hydrophobic fluoropolymer content (from left to right) was increased the measured $\Theta$ values, i.e. decreased the wettability of the polymer layer. The initial pHEA layer has a relative low $\Theta$ value (27.4°) indicating the hydrophilic nature of the polymer. However, at 20 wt% of fluoropolymer-content in the binder the measured $\Theta$ value was achieved the 60° and gradually increased to 105° with the increasing pPFDAc content. Results of static contact angle measurements were also confirmed, that the composite films roughened by Ag-TiO$_2$ photocatalyst particles showed highlighted wetting properties
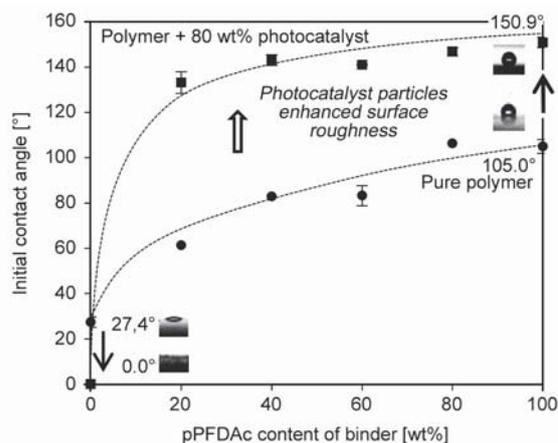


**Figure 1.** Measured apparent static initial water contact angles on pure polyacrylate thin films and Ag-TiO$_2$ photocatalyst particle roughened polyacrylate hybrid layers as a function of the hydrophobic pPFDAc content of the copolymer binder ($T = 25\pm0.5$ °C).

compared to the pure polymer thin layers, and even superhydrophilic characteristic ($\Theta = 0°$) could be achieved at 100 wt% pHEA content in the copolymer. The results showed that the measured $\Theta$ values of polymer films with flat surfaces were varied between 27.4 and 105.0°, however, the wetting properties of the photocatalyst- roughened surfaces can be adjusted from superhydrophilic (pHEA; $\Theta = \sim 0°$) to superhydrophobic (pPFDAc; $\Theta = 150.9°$). So, the initial wetting character of smooth thin layers was highlighted by the increased surface roughness caused by the photocatalyst incorporation into the polymer matrix.

The wetting properties of the smooth and Ag-TiO$_2$ particles roughened (r-pPFDAc) and (r-pHEA) composite layers were also studied by dynamic advancing ($\Theta_{adv}$) and receding ($\Theta_{rec}$) contact angles measurements (Figure 2a). These were carried out according to the protocol of Drelich [20]. In the case of superhydrophobic r-pPFDAc layer, increasing the volume of the water drop leads to reduction of the $\Theta_{adv}$ from $\Theta_{7.5 \mu L} = 165.2°$ to $\Theta_{23.0 \mu L} = 150.6°$. Note, that this latter value is very close to the initial $\Theta$ value (150.9°), which was measured after 15 min contact time, indicating the steady state condition of the initial/ static water contact angle (Figure 1.). The $\Theta_{rec}$ were gradually decreasing as the volume of the drop was decreasing and the final value was much lower (125.0°) than the static contact angle (150.9°). This is maybe due to the presence of surface hydrophilic photocatalyst particles, which caused that it is difficult to remove liquid from surfaces during the measurements
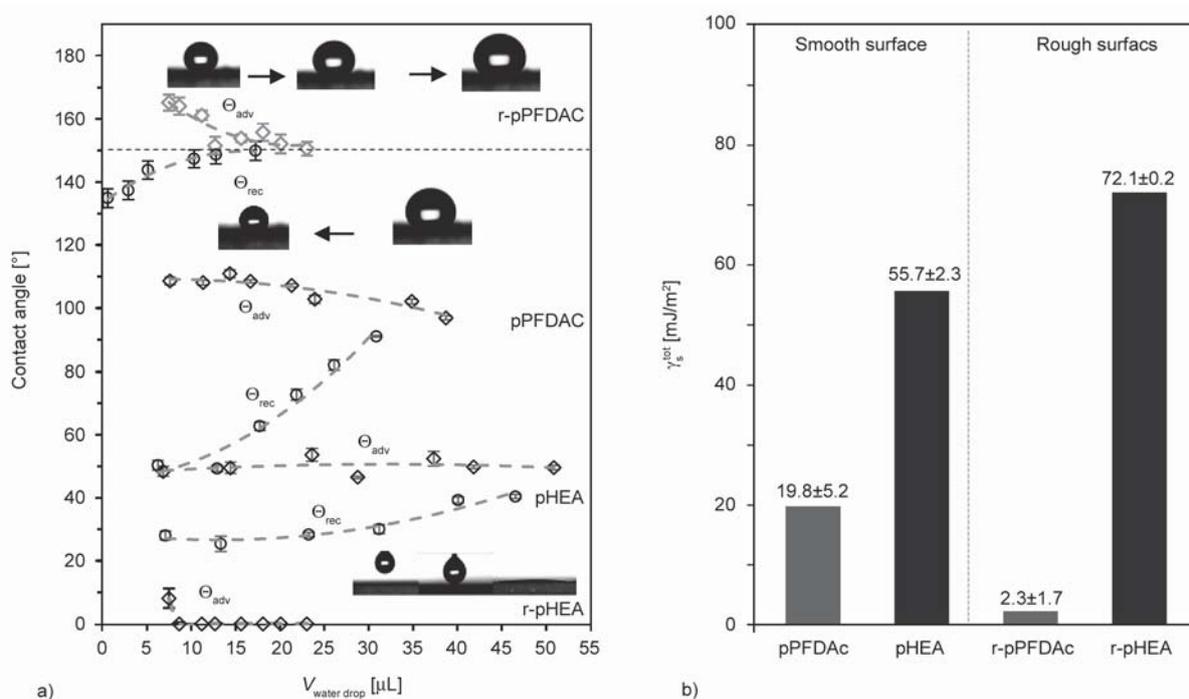
**Figure 2.** Evolution of advancing and receding contact angles on smooth and roughened (r-) pPFDAc and pHEA hybrid layers (a), as well as the determined total apparent surface free energy ($\gamma_s^{tot}$) values of initial (smooth) and roughened polyacrylate thin layers (b).

of $\Theta_{rec}$. In the case of the smooth hydrophobic pPF-DAc polymer layer the obtained $\Theta_{adv}$ and $\Theta_{rec}$ values were ~110 and ~45°, respectively, while in the case of hydrophilic smoot pHEA film these values were ~35 and ~24°, respectively. As regards the superhydrophilic r-pHEA hybrid layer, it was impossible to adequately measure the dynamic contact angle because even the smallest drop tended to spread very rapidly. A gradual increase of the drop volume led to further spreading and the contact angles were far too small to be measured accurately. This is also indicating the very well wetting, superhydrophilic nature of the film.

According to the theory of Chibowski and coworkers [21, 22] the obtained $\Theta_{adv}$ and $\Theta_{rec}$ are also suitable for the estimation of the total apparent surface free energy (γstot) of the layer (see Equation (1)). The determined γstot values of the pure hydrophobic pPFDAc and hydrophilic pHEA thin layers were 19.8±5.2 and 55.7±2.3 mJ/m² respectively. This result agrees with our previous measurements and the previously-reported surface energy values of the low-energy flat Teflon-like surfaces [7]. The roughening-induced changes in $\gamma_s^{tot}$ values are represented in Figure 2b. The enhanced surface roughness of a hybrid layer containing 80 wt% Ag-TiO$_2$ caused a drastic change in the measured γstot value: in the

case of high energy (hydrophilic) pHEA polymer binder the measured value of roughened surface was increased up to 72.1±0.2 mJ/m², while in the case of low energy pPFDAc polymer the value was decreased to 2.3±1.7 mJ/m². In other words, the hydrophilic/hydrophobic nature of the initial smooth surface was enhanced with the surface roughness, the hydrophilic surface becomes more hydrophilic or superhydrophilic, while the low energy hydrophobic hybrid layer showed superhydrophobic properties after the roughening process.

Dynamic contact angles were also determined applying the Wilhelmy plate method [23]. The plots in Figure 3 represent online contact angle data calculated during the measurements. It should be noted, however, that dynamic contact angle measurements have been made for a wide variety of different liquids and surfaces [24, 25], the dynamic wetting characterization of superhydrophobic surfaces is difficult and can easily misinterpreted, because a reliable dynamic measurement requires homogenous sample, relative smooth surface and symmetric shape [26]. In this case a good run will show the slope of the advancing and receding portions of the plot, which is constant in the mean and equal for both stages of the measurement: the two lines must be parallel, a very
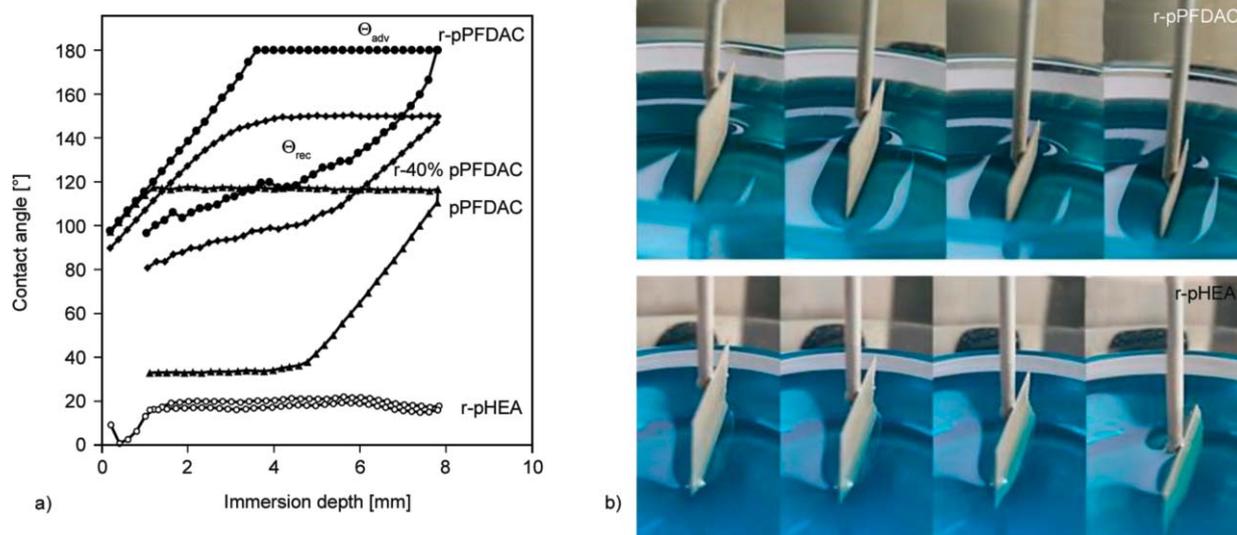
**Figure 3.** Directly measured apparent dynamic water contact angles on polyacrylate-based thin films (the r-stands for roughened) as a function of the immersion depth of the coated Wilhelmy-plate ($T = 25\pm0.5\,°C$) (a), as well as the photos of the r-pPFDAc and r-pHEA coated plates during the immersion process in distilled water (coloured with methylene blue for better imagine) determined average dynamic contact angles on polyacrylate-based thin films as a function of the binder composition (b).

simple trick which may also work as an internal quality check of the run [29].

In the case of flat fluoropolymer (pPFDAc) coating this tendency can be observed ($\Theta_{adv} = \sim118°$; $\Theta_{rec} = \sim33°$), however, the roughened composite layer (r-pPFDAc) has shown disturbed and non-parallel lines. This is obviously due to the rough and heterogeneous surface and the obtained 180° advancing contact angle is also should be handle with care because there is no justification for experimental contact angle of 180° unless liquid if floating above the surface like in the case water droplet placed on a hot plate. However, the non-wetting nature of the r-pPFDAc layer is clearly indicated the inserted photo in Figure 3. The immersion of plate with superhydrophobic coating resulted in dented water surface during the measurement, while in the case of superhydrophilic coating (r-pHEA) the meniscus climbed up due to the capillary forces ($\Theta_{adv} = \sim20°$; $\Theta_{rec} = \sim17°$).

The results of the dynamic contact angle measurements also prove the expanded wetting range of the polyacrylate-based layers and it can be seen that the wetting properties of the composite layers could be tailored by the hydrophilicity of the polymer matrix.

## 3.2. Surface morphology and porosity of the composites

The dependence of surface roughness on the wetting properties (i.e. the measured liquid contact angle) has been described by Wenzel's or Cassie-Baxter's

models [11]. A low surface free energy flat surface must be roughened to get superhydrophobic surfaces with high ($\Theta > 150°$) water contact angle [7]. The captured SEM images (Figure 4a–4c) show the relative smooth surface of the initial, Ag-TiO$_2$ photocatalyst-free pure fluoropolymer layer. The prospected flat surface was also evidenced by mechanical profilometric measurements (Figure 5). The measured $R_q$ values of the initial pHEA and pPFDAc polymer surfaces were $2.1\pm0.8$ and $3.7\pm0.9$ μm, respectively. However, in the case of the photocatalyst nanoparticles roughened hybrid layers quasi-spherical microscale-aggregates of the primer photocatalyst particles can be observed on the composite surface with diameters ranging from 5 to 40 μm (Figure 4d–4f). Accordingly, the determined $R_q$ values of the roughened r-pHEA and r-pPFDAc hybrid surfaces were $11.7\pm2.2$ and $15.2\pm1.2$ μm, respectively. Moreover, according to the SEM pictures, at increased magnifications, nanostructures could be identified superposed on the microscale structure.

This is due to the nanoparticles aggregation during the composite film forming process: the initial Ag-TiO$_2$ photocatalyst particles with ~50 nm primary (nominal) particle size were aggregated into 5–40 μm microparticles. This structure ensures high porosity and accessibility which is advantageous for photocatalytic process. However, it is also worth to note, that the reported penetration depth of UV light (254 nm) into porous TiO$_2$ film is just a few micrometer [27],
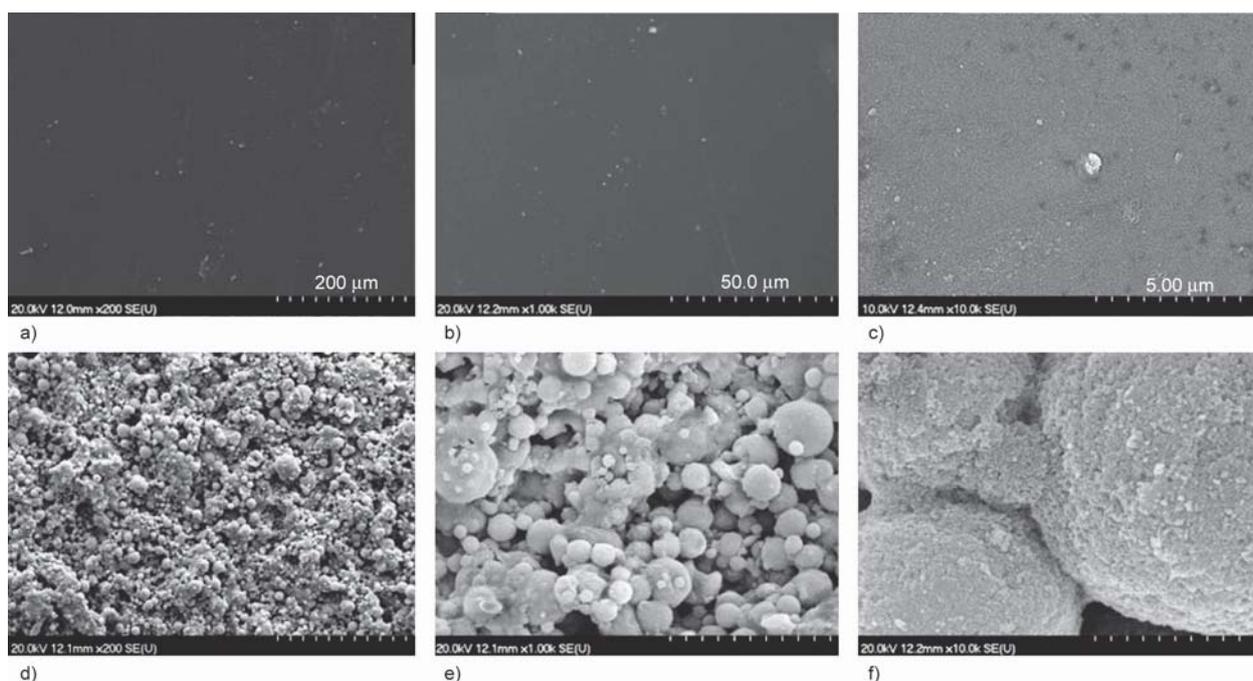
**Figure 4.** SEM images of the prepared smooth pPFDAc polymer layer (a–c) and the 80 wt% Ag-TiO$_2$ containing pPFDAc (d–f) thin layers with different magnifications: 200× (a, d), 1000× (b, e), 10000× (c, f).

thus photooxidation actually take place only at surface of the 100 μm porous film. Due to this phenomenon the photoreactive hybrid layers were shown rough surface both in micro- and nanoscale. The average thickness of the composite layers was measured by Elcometer 224 type digital profile gauge and found to be 91.3±10.4 μm. Beside this measured layer thickness value, the calculated film thickness was also determined from the specific surface amount of hybrid layers (5.3 ±0.5 mg/cm$^2$) and the previously determined density of the components ($\rho_{Ag-TiO_2}$: 4.32 g/cm$^3$; polymer: 1.10 g/cm$^3$). According to the calculation, the average layer thickness of the hybrid

layers was 19.3±3.2 μm. The difference between the measured and calculated values are referred to the film porosity [7]. The results revealed that the calculated average porosity value was 78.1%.

### 3.3. Characterization of optical and photocatalytic properties of thin films

The optical parameters of polyacrylate binder and polyarcrylate/Ag-TiO$_2$ hybrid layers were studied and compared applying UV-VIS diffuse reflectance spectroscopy (Figure 6). The absorption spectrum of the initial plasmonic Ag-TiO$_2$ photocatalyst sample was also presented for reference. As demonstrated in our previous papers, the presence of silver nanodots on the surface of semiconductor TiO$_2$ photocatalysts, resulted in a plasmonic peak in the visible-light region with a wavelength maximum of 450 nm [5, 6]. It was also proven that these plasmonic photocatalysts presented increased photocatalytic activity under blue (405 nm) LED light illumination compared to the initial P25 TiO$_2$ [5, 6]. In this noble metal–semiconductor composite photocatalyst, visible light is harvested due to the surface plasmon resonance of the AgNPs, while the metal–semiconductor interface separates the generated electrons and holes. The emission spectra of the used LED were also presented in Figure 6 (grey dashed line). The plasmonic peak and the well- known UV- light absorbance edge of TiO$_2$ were also presented in the
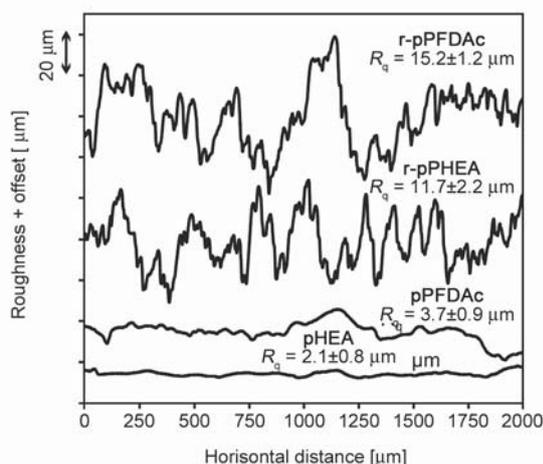


**Figure 5.** Measured profilometer data for the prepared pure polymer thin layers and the corresponding photocatalyst roughened photoreactive hybrid films.
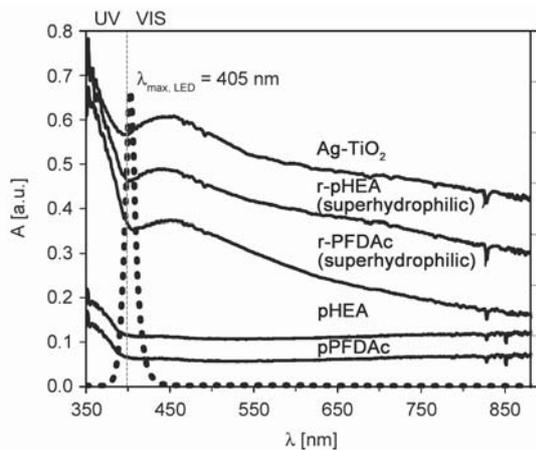
**Figure 6.** Diffuse reflectance spectra of the prepared hybrid thin layers and the initial plasmonic Ag-TiO₂ photocatalyst, as well as the emission spectrum of the LED lamp used in photodegradation tests (dashed line).

case of the roughened hybrid films containing 80 wt% plasmonic photocatalyst particles.

However, the absorbance spectra of the initial hydrophilic pHEA and hydrophobic pPFDAc binders indicate the transparent nature of the polymer thin films. So, the transparent polymer binder material with adjustable wetting properties serve as support material for the attached plasmonic photocatalyst nanoparticles and ensure high photocatalyst dispersibility and mechanical stability. The improved mechanical stability of the polymer binder based

photoreactive hybrid thin films was reported elsewhere using the adhesive tape test method [5].

After the wetting, morphological and optical properties of the hybrid layers the photocatalytic behavior was also measured. The photocatalytic properties of the composite thin films were studied both at S/G and S/L interface, as well. As a result of 90 min of blue LED light (Figure 6) illumination of the samples ($\lambda_{max}$ = 405 nm), the layers consist of pure photocatalyst decomposed approximately the whole amount of the model compound at the solid-gas interface (the initial EtOH concentration was 0.36 mM), while the immobilized catalyst showed moderate reaction rates (Figure 7a), furthermore, an unambiguous growth-tendency was observed considering the decomposition rate constants ($k'$) as the fluoropolymer content increased (Figure 7b). The data points labelled as 'control' in Figure 7a represent the photodegradation of EtOH in the absence of photoreactive thin layers (glass slide sample holder). It can be seen, that the degree of photolysis was ca. 12%, however, in the presence of photocatalysts, the films exhibited much higher photooxidation rate. In the case of the r-pPFDAc layer the amount of decomposed EtOH (88.3% decrease in the 0.36 mM initial concentration) was comparable with the efficiency experienced in the case of pure Ag-TiO₂ films (99.4%). So the photocatalytic activity of this layers were
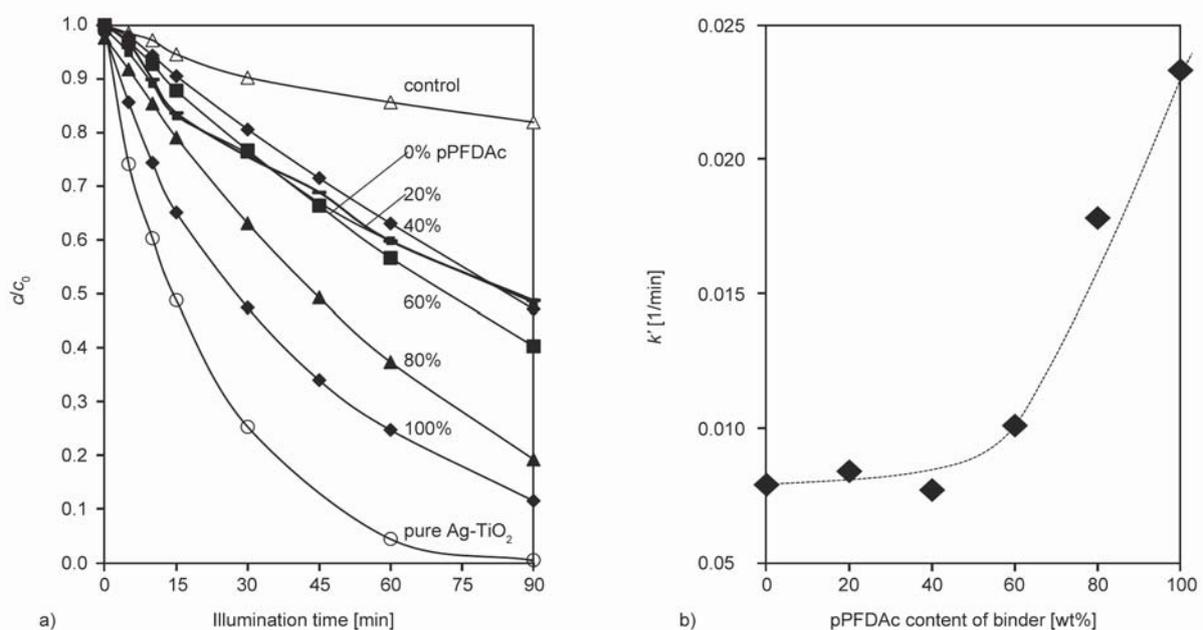


**Figure 7.** Characterization of EtOH decomposition on Ag-TiO₂/polyarcylate hybrid layers under LED light illumination ($\lambda$ = 405 nm) as the function of illumination time (the legends refer to the composition of the polymer binder) (a) and the determined apparent photocatalytic oxidation rate constants for first-order decay as a function of pPDAc content of the binder ($\ln(c/c_0) = -k't$) (b).

evidenced at S/G interface using ethanol test molecules as model VOC.

Next the photoactivity of the hybrid layers was also presented at the S/L interface. The superhydrophilic nature of an irradiated semiconductor surface is not unusual, because under UV- irradiation $TiO_2$ acquires superhydrophilic properties [1]. However, the photocatalytic activity of a photoreactive and even superhydrophobic coating is not yet reported in the literature. Thus, the photocatalytic behavior of the superhydrophobic layer was also demonstrated and studied in the case of hydrophilic and hydrophobic model pollutants (Figure 8). According to the results the hydrophilic aqueous Methylene Blue solution did not wet the surface of the hybrid film (see inserted photo inFigure 8b with blue aqueous liquid drop) and therefor the ratio of the photodegraded Methylene Blue dye ($c_0 = 0.002$ mg/mL) was only 17.3% after 90 min blue LED light ($\lambda = 405$ nm) irradiation. However, the photooxidation of hydrophobic SUDAN IV solutions ($c_0 = 0.25$ mg/mL) almost reached the 80%. This is because the adequate wetting of the superhydrophobic film surface by hydrophobic medium (see the red dye stain in Figure 8b), which means high contact area between the surface photocatalyst particles and the model pollutants molecules. When

the hydrophobic surface, contacted earlier with air, is immersed into water then air can stay attached to the surface [28]. This air film also can be seen on the surface of the film in aqueous medium at $t = 0$ min irradiation (Figure 8a).

Finally, it is also should be noted that self-photodegradation of the polymer binder could cause problem during long term irradiation time as reported in our previous paper [5]. The reason for this is that the light induced reactive oxygen species also can destroy the organic polymer matrix. However, we have reported that this undesired photodedradation can be avoided by the application of appropriate composite catalyst [29]. Hydroxyapatite (HAp)/$TiO_2$ composite catalyst was synthetized by *co*-precipitation method, where the HAp microlamellae serve as support material for the surface attached $TiO_2$ particles. Thus, HAp serves as a spacer to prevent direct contact polymer and $TiO_2$, so the photodegradation of polymer was significantly reduced [29].

## 4. Conclusions

Photoreactive hybrid layers with adjustable wetting properties were prepared with micro- and nanosized dual-scale surface roughness. The films with composition- dependent wetting properties consist of
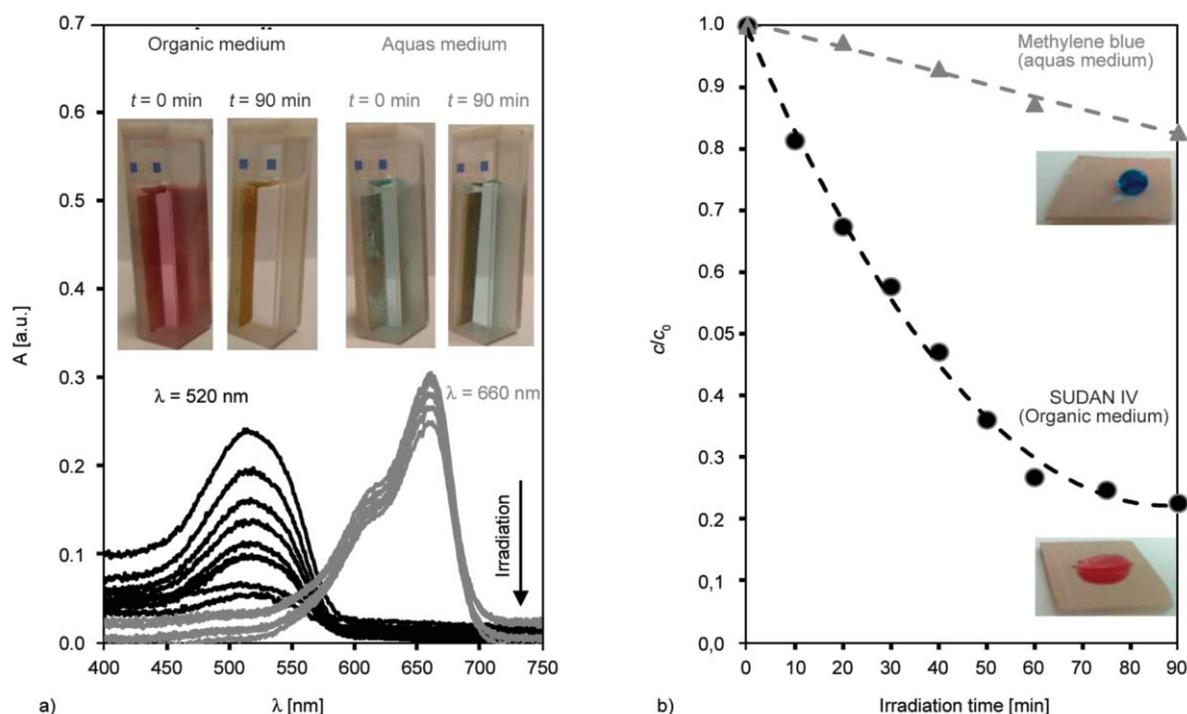


**Figure 8.** The effect of LED light ($\lambda = 405$ nm) irradiation on the absorbance spectra of the hydrophobic SUDAN IV and aqueous Methylene Blue solutions (a) and the corresponding normalized concentration changes (b) of dyes. The inserted images show the photos of dye solutions before and after irradiation (a) and the aqueous and hydrophobic liquid drops on the surface of the superhydrophobic hybrid film (b).

plasmonic Ag-TiO$_2$ photocatalyst particles (80 wt%) and transparent copolymer binder (20 wt%) with tailored hydrophilicity. Thus, the initial wetting properties of high energy pHEA ($\Theta = 27.4°$, $\gamma_s^{tot} = 55.7\pm2.3$ mJ/m$^2$) and low energy pPFDAc ($\Theta = 105.0°$, $\gamma = \gamma_s^{tot} = 19.\pm5.2$ mJ/m$^2$) flat polymer films were increased with the photocatalyst enhanced surface roughness. In the case of roughened pHEA and pPFDAc layers superhydrophilic ($\Theta = 0°$, $\gamma \geq \gamma_s^{tot} = 72.1\pm02$ mJ/m$^2$) and superhydrophobic ($\Theta = 150.9°$, $\gamma_s^{tot} = 2.3\pm1.7$ mJ/m$^2$) characters were experienced, respectively. The photocatalytic properties of the thin layers were first measured at S/G interface using ethanol as model VOC test molecules and the photodegraded percentage amount of the initial 0.36 mM EtOH varied between 51.3 and 88.3%. This is due to the porous structure of the thin films with high inner surfaces. However, at S/L interface the photocatalytic efficiency was depend on the polarity of the used model pollutants: the superhydrophobic rough thin film was photodegraded only the hydrophobic SUDAN IV dye solution. The advantage of this current surface compared to previous photoreactive composite coatings is the monomer composition dependent wetting properties. These dual photocatalytic and adjustable wetting properties of the prepared composite layers could be interesting at the area of water treatment, where the polarity of the pollutants varies on a wide scale.

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