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OPEN Analysis of time-dependent hydrophobic recovery on plasma-treated superhydrophobic polypropylene using XPS and wettability measurements

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In specific applications like ice-repellent coatings or membrane separation technology, wettability is a key parameter affecting the applicability of commodity polymers. This study presents a technique to fine-control the wetting properties of a hierarchically structured polypropylene surface, enabling the transition between superhydrophobic and superhydrophilic states. To demonstrate the tunability of the wetting properties of polypropylene (PP) substrate, we prepared in a consecutive way superhydrophobic (advancing contact angle (CA_{adv}) of 152°) and superhydrophilic (CA_{adv} of 0°) material by solvent-treatment and mild air plasma treatment. The optimal plasma treatment parameters to achieve superhydrophilic wetting behaviour, which is stable for at least one week of storage in air was also explored. Water contact angle measurement and X-ray photoelectron spectroscopy were used to monitor the time dependency of hydrophobic recovery on a hierarchically structured PP surface. With a simple model considering structural and wetting parameters, we characterized the droplet spreading behaviour of plasma-treated roughened surfaces, which exhibited superhydrophilic wetting behaviour with equilibrium CA_{adv} of nearly 0°. The proposed model, which aligns well with experimental data, can be used to compare the droplet spreading behaviour of plasma-treated roughened surfaces.

Keywords Superhydrophobicity, Superhydrophilicity, Polypropylene, Plasma surface modification, Hierarchically structured surface, Hydrophobic recovery

Polypropylene (PP) is frequently used in diverse applications because of its reasonably good mechanical properties, low density, relatively low cost, and easy recyclability^{1,2}. With the growing need for a circular economy and thus mono-material products with better recyclability, the diversity of requirements that must be met for the same material also increases. The surface property is one of the critical properties that must be customizable for successful mono-material products for advanced applications. The modification of the wetting properties of the surface is necessary towards the extremes of either superhydrophobic (water contact angles (WCAs) higher than 150° and contact angle hysteresis (CAH) below than 10°) or superhydrophilic (WCA < 10°) behaviour^{3,4}.

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It is well known, that surface energy and microstructure are the two main contributors to the adhesion and wetting properties of any material. It has also been shown that processes resulting in micro-roughness make PP superhydrophobic even without specific surface chemistry modification^{5,6}.

Predicated on its wettability characteristics, polypropylene exhibits a diverse range of potential applications in scientific and industrial contexts^{7–9}. PP can be used to produce a superhydrophobic coating with high added value, which can be used in building waterproofing and self-cleaning and ice-repellent coatings^{10–12}. On the other hand, highly hydrophilic surfaces can also be beneficial for some applications^{13,14}. For example, hydrophilic porous PP is often used as material for separators in electrochemical cells, such as lithium batteries and membranes, for efficient oil/water emulsion separation. In the case of oil/water emulsion separation, hydrophilic PP membrane can efficiently separate micron-sized oil droplets from surfactant-stabilized emulsions with more than 99.5% separation efficiency¹⁵. Among various methods, oxygen plasma treatment has been studied for several years as an eco-friendly technique for hydrophilic surface modification¹⁶. Plasma treatment can increase surface roughness¹⁷ and/or modify surface energy^{18,19} depending on the treatment parameters. It can alter the outermost layers of the substrates and can reduce thermal degradation. Plasma treatment can also serve as an activation step, which is further combined with chemical functionalization²⁰.

Due to the phenomenon of ageing in plasma-treated surfaces, their properties can be time-dependent, which severely influence the practical applications of these materials^{21,22}. Because of thermodynamic preference, the surface free energy of the plasma-treated polymer can decrease via reorientation of polar chemical groups from the top layer of the polymer into the bulk and the adsorption of airborne contaminations from the atmosphere on the chemically active sites of the surface^{23–26}. Several studies suggested that the main ageing mechanism is the reorientation of the hydrophilic groups formed by plasma treatment, however adsorption of airborne contaminations from the atmosphere could also contribute to the hydrophobic recovery^{27–29}.

Numerous studies have focused on the wettability recovery of plasma-treated polymer surfaces. According to these works, the process of hydrophobic recovery can be influenced by many factors, such as the plasma parameters³⁰, the relative humidity³¹, the crystallinity of the polymer³², and the temperature of the environment³³, among other things. Polymers with lower crystallinity have also been reported to be more reactive with plasma³⁴. While studies have revealed the parameters greatly affecting hydrophobic recovery on plasma-treated (PP) surfaces and provided valuable applications for plasma treatments, comparing different surface topographies remains challenging as most research focuses on PP with a flat surface. Only a few studies have examined the ageing behaviour of plasma-treated, roughened, superhydrophilic PP surfaces^{35–37}. However, the ageing of hierarchically structured polymer surfaces could hinder practical applications. Additionally, the long-term stability of plasma-induced superhydrophilic, roughened PP surfaces under normal conditions has been rarely investigated. Since the applicability of these surfaces is determined by the rate of wettability recovery under ambient conditions, studying the stability of plasma-treated superhydrophilic PP surfaces is essential³⁸.

In our previous study^{39,40}, we introduced a new method based on phase separation to prepare a hierarchically structured (micro- and nanoscale patterned) layer on an extruded PP sheet, achieving a WCA of more than 160°. The main steps of the method are solvent treatment in hot xylene for a certain time followed by drying and then peeling the outer skin layers that formed.

The goal of this paper is to provide a detailed study of the hydrophobic recovery of plasma-treated, roughened, superhydrophobic PP surfaces. As a model material, we used roughened PP surfaces prepared with our novel method^{39,40}, which differ from the well-studied smooth surfaces.

We introduce the time dependency of hydrophobic recovery on a hierarchically structured PP surface, which is based on the study of the changes in WCAs and surface composition over time. We examine the changes in wettability of extruded PP sheets with a hierarchical surface structure, ranging from superhydrophobic to superhydrophilic behaviour, using air plasma treatment.

Surface morphology was examined by scanning electron microscopy (SEM), optical profilometry and atomic force microscopy (AFM). The physicochemical properties of the surfaces after the plasma treatment were investigated by X-ray photoelectron spectroscopy (XPS) and WCA analysis. We describe the droplet spreading behaviour of plasma-treated roughened surfaces, which showed superhydrophilic characteristics. The applied model illustrates the influence of structural and wetting parameters on ageing time. The better understanding the effect of micro- and nanoscale roughness combined with the changes of surface functional groups might help in the development of PP products with tailored surface properties for the diverse of requirements and thus extending its application for new areas.

Experimental

Materials

Extrusion grade PP homopolymer (Tipplen H681F, MOL Petrochemicals Co. Ltd., Hungary) was used with a melt flow rate (MFR, 230 °C, 2.16 kg) of 1.7 g/10 min.

Preparation of plasma treated samples

Cold plasma treatment was carried out on PP samples having smooth surface and also on samples having hierarchically structured surface. Samples having hierarchical surface structure were made out of the same extruded sheets as samples with smooth surface. During the surface modification process³⁹, when a hierarchical surface structure is created, the extruded samples were solvent-treated with xylene (mixture of isomers, purity 98%, VWR Chemicals, Germany) at 125 °C for 60 s. After the solvent immersion step, the samples were dried at 30 °C for 24 h in an air-ventilated oven (UT6120, Thermo Fischer Scientific, USA), then 24 h in a vacuum oven (FCD-3000, Faithful, China) at 30 °C. The surface modification process to obtain a hierarchical surface structure

has been discussed previously in detail³⁹. All samples comprised sheet dimensions of 1 mm in thickness, 50 mm in width, and 20 mm in length.

Surface treatment was conducted in an air atmosphere, using a cold plasma apparatus (Smartplasma 10, Plasma Technology GmbH, Germany) operating in the radiofrequency range.

The pressure inside the vacuum chamber (0.15 and 0.30 mbar), treatment time (60 to 600 s), and power (24 to 64 W) were varied during the plasma treatment, to explore its effect on the sample. Plasma-treated samples were stored at room temperature in a dust-free container afterward for ageing in normal conditions.

Heat treatment of plasma treated samples

To investigate the thermal stability of the introduced hydrophilic surface , we carried out thermal ageing tests on plasma treated samples (0.15 mbar, 40 W and 600 s) in a furnace at 70 $^{\circ}$ C or 150 $^{\circ}$ C for 60 min.

Methods of analysis

Surface and cross-section morphology were analysed with a scanning electron microscope (SEM, Jeol JSM-IT 200, Jeol, Japan). The investigated samples were previously sputter-coated with gold for increased electrical conductivity.

For checking the wettability of PP surfaces, WCAs were measured in a drop shape analyser (Krüss DSA 30, Germany) with the sessile drop method. To measure the advancing contact angle (CA_{adv}), 20 µl droplets of MilliQ water were deposited on the surfaces by a drop-build up technique with the use of a microsyringe in a chamber with controlled temperature (25 ± 2 °C) and relative humidity (>80%). The receding contact angle (CA_{rec}) was measured while the volume of a sessile drop was slowly decreased by 10 µl. Contact angle hysteresis (CAH) was calculated from the difference between the CA_{adv} and CA_{rec} . CA_{adv} of plasma-treated samples monitored as a function of time. The sessile drops were analyzed with the Advance image analysis software to calculate contact angles based on the tangent of the drop profile at the apparent intersection of the three phase contact line where the liquid–gas interface meets the solid–liquid interface. The micro-scale morphology of the sample surfaces was examined with Dektak8 Advanced Development Profile* (Veeco Instruments Inc, USA). The data were collected in an area of 1 mm × 1 mm. The nanoscale morphology of the sample surfaces was analysed with a PSIA XE-100 atomic force microscope (AFM, Park Systems Corp., South Korea) in tapping mode. The data were collected in an area of 5 μ m × 5 μ m.

Changes in the chemical composition of surfaces were detected by XPS. The samples were examined by XPS with a twin anode X-ray source (XR4, Thermo Fisher Scientific, USA) and a hemispherical energy analyser with a 9-channel multi-channeltron detector (Phoibos 150 MCD, SPECS). The base pressure of the analysis chamber was approximately $2 \cdot 10^{-9}$ mbar. Samples were analysed with a Mg K_a (1253.6 eV) anode without monochromatization. Peak fitting was carried out with the CasaXPS software. Wide-range scans and high-resolution narrow scans of the C1s and O1s photoelectron peaks were recorded.

The crystallinity of the samples was determined by differential scanning calorimetry (DSC 12E, Mettler-Toledo, Switzerland). Two subsequent heating cycles were used in the DSC tests. In the first cycle, the sample was heated from 30 °C to 220 °C at a rate of 10 °C/min, where it was held for 5 min, then cooled back to 30 °C at a cooling rate of 10 °C/min, and finally re-heated to 220 °C at a rate of 10 °C/min. The degree of crystallinity (X_c) was calculated with the Eq. (1):

$$X_c = \left(\frac{\Delta H_m}{\Delta H_0}\right) \times 100\tag{1}$$

where ΔH_m and ΔH_0 are melting enthalpy of the first run and melting enthalpy of a 100% crystalline sample; for PP it is 207 J/g⁴¹.

Results and discussion

Surface morphology and wettability before plasma treatment

The drastic change in PP surface morphology upon solvent treatment according to our method described in our previous study³⁹ is showcased in Fig. 1.

It can be seen that after the treatment the initially smooth extruded surface (Fig. 1a) became rough on microand nanoscales (Figs. 1b). Microscale structure is a consequence of the presence of spherulites on the outmost surface, and nanoscale roughness is the consequence of the roughened surface of the spherulites³⁹. The structure found with the optical profilometer (Fig. 1c) correlates well with the SEM images in Fig. 1b. The root mean square (RMS) of microscale surface roughness is around 10 μ m and the RMS of nanoscale roughness is around 52 nm. The role of this described roughness on wetting behaviour is clearly visible in water contact shapes (Fig. 1a,b inset), with high CA_{adv} (152 ± 1°) and low CAH (4 ± 2°) values showing a significant increase in hydrophobicity compared to that of the untreated PP (CA_{adv}: 100 ± 1° and CAH: 7 ± 1°).

Air-plasma treatment induced superhydrophilicity on superhydrophobic surfaces

We investigated the effect of plasma treatment parameters on wettability with a focus on the influence of pressure, power and treatment time. The wettability results of the roughened samples show that the lower pressure (0.15 mbar compared to 0.30 mbar) is advantageous for the creation of a more hydrophilic surface (see Table S1 in Supporting information). This finding is consistent with those of Yun et al., who found that lowering vacuum pressure is optimal for the plasma treatment of PP to achieve maximum hydrophilicity³⁴. Subsequently, we focused on only 0.15 mbar and varied the other plasma treatment parameters.

Table 1 shows the combined effect of power and plasma treatment duration on the degree of hydrophilicity.



Fig.1. SEM images of (**a**) the surface of the extruded sheet, (**b**) the surface of the solvent-treated sheet, (**c**) surface 3D profile of the solvent-treated sheet shown with an optical profilometer, (**d**) SEM image of an individual particle in (**b**) and (**e**) AFM image of the surface of the solvent-treated sheet. During the surface modification according to our method³⁹ the solvent temperature was 125 °C and the immersion time was 60 s.

Designation	Power (W)	Treatment time (s)	CA _{adv} (°)
PP	-	-	100 ± 1
PP_LP300	24	300	20±2
PP_LP600	24	600	24±2
PP_MP300	40	300	21±1
PP_MP600	40	600	19±1
PP_HP300	64	300	18±1
PP_HP600	64	600	12±2
SHPP	-	-	152 ± 1
SHPP_LP60	24	60	40±3
SHPP_LP300	24	300	~ 0
SHPP_LP600	24	600	~ 0
SHPP_MP60	40	60	~ 0
SHPP_MP300	40	300	~ 0
SHPP_MP600	40	600	~ 0
SHPP_HP60	64	60	~ 0
SHPP_HP300	64	300	~ 0
SHPP_HP600	64	600	~ 0

Table 1. Plasma-treated samples wettability results with the use of 0.15 mbar. The SHPP_LP_60 suffix refers to the surface morphology of PP (PP: samples with smooth surface, SHPP: samples with roughened surface), the applied power (low power (LP): 24 W; medium power (MP): 40 W; high power (HP): 64 W), and the plasma treatment time (60 s, 300 s, 600 s).

 CA_{adv} measurements were performed immediately after the plasma treatment. According to the surface analysis (not published here), one can conclude that in these cases the plasma treatment has little or no influence on the surface morphology of both PP and SHPP samples. Thus, changes in wettability are due to changes in the chemical composition of the surface due to the introduced hydrophilic functional groups. As expected, increasing power and treatment time leads to more hydrophilic surfaces. For samples with the original smooth PP surface, the treatment reduced the CA_{adv} from ~ 100° to ~ 20°, making the samples hydrophilic. At the same treatment conditions, the previously roughened sample showed CA_{adv} of 152° and ~ 0° before and after plasma treatment, respectively. This impressive reduction in CA_{adv} is due to the morphology of the sample, which affects the apparent contact angle measured on the surface⁴². The sample with microscale and nanoscale roughness exhibits higher hydrophobicity before plasma treatment and also exhibiting higher hydrophilicity after plasma treatment. The surface wettability – based on the high CA_{adv} and low CAH values (see section "Surface morphology and wettability before plasma treatment") of the SHPP sample –can presumably be interpreted in terms of the Cassie-Baxter's wetting model⁴³. We further note that extensively long, high-power plasma treatment (64 W for 10 min) led to the discoloration (yellowing) of the samples, due to degradation.

Wetting kinetics and ageing of plasma-treated superhydrophilic surfaces

As mentioned before, plasma treatment can produce surfaces that are not in a state of thermodynamical equilibrium, giving way to ageing kinetics and changes in wettability. Studying these changes is crucial from a practical point of view, because it determines how long the surfaces retain their properties after treatment. The thermodynamical value of the cosine contact angle is defined by an equilibrium of three interfacial tension values, however in practical circumstances, the measured contact angle is not equivalent to the thermodynamical contact angle. Slight deviations (i.e. evaporation of the liquid) can result in the measured contact angle being time-dependent or undergo spreading due to surface roughness, heterogeneity or porous structure⁴⁴⁻⁴⁶.

We observed that the water droplet wetting kinetics differed on various plasma-treated surfaces, all exhibiting superhydrophilic wetting behavior with a similar equilibrium CA_{adv} of nearly 0°, this phenomenon exclusive to plasma-treated surfaces that were previously roughened. To find the cause of this unique droplet spreading behaviour, we investigated the kinetics of wetting on differently plasma-treated samples, while also exploring ageing effects on the wetting behaviour of plasma-treated surfaces (Table 2).

In Table 2, the spreading times for each sample indicate the time required for complete wetting after different ageing days. In Table 2, "not reached" refers to when the complete wetting could not be achieved within the frame of the investigation time, which was 60 min, for example, in the case of SHPP_MP60 and SHPP_HP60 samples. "No data" means that the spreading time was not measured, for example, in the case of SHPP HP600. The importance of plasma treatment time is clearly shown by the fact that at a given pressure, as the plasma treatment time increases, film wetting develops faster. The samples plasma-treated for the shortest time (SHPP_LP60, SHPP_MP60, SHPP_HP60) either did not reach or required the longest time to develop film wetting.

Up to a certain point (SHPP_MP600: 0.15 mbar, 40 W, 600 s), the time needed to reach film wetting continuously decreases with higher power and longer treatment time. Due to the more intense treatment parameters, the concentration of hydrophilic groups forming on the surface increases, which allows faster spreading on the surface⁴⁷. In the case of SHPP_MP600, the drop immediately reaches near-zero equilibrium contact angle even after seven days of ageing. Applying more intense parameters than in the case of SHPP_MP600, the time needed for the drop to achieve film wetting increases, which effect we attribute to possible degradation.

The effect of hydrophobic recovery can be observed in wetting kinetics data (droplet spreading) measured after various ageing times. These data allow us to compare the hydrophilicity of samples on which water droplets exhibit identical, near-zero equilibrium contact angles.

To determine the changes in surface functional groups as a function of ageing time, XPS studies for the plasma-treated roughened and smooth samples were performed.

Table 3 shows the calculated atomic compositions of the plasma-treated roughened samples (SHPP_LP300) and smooth samples (PP_LP300) as determined by XPS at different ageing times. SHPP_LP300 was selected for XPS analysis due to its pronounced change in its wetting kinetic.

Spreading time for complete wetting (s)									
	Immediately after treatment	1 day after treatment	2 days after treatment	3 days after treatment	7 days after treatment				
SHPP_LP60	not reached	not reached	not reached	not reached	not reached				
SHPP_LP300	4	24	33	44	180				
SHPP_LP600	0	4	5	9	12				
SHPP_MP60	40	not reached	not reached	not reached	not reached				
SHPP_MP300	1	4	20	20	20				
SHPP_MP600	0	0	0	0	0				
SHPP_HP60	10	150	180	not reached	not reached				
SHPP_HP300	0	0	9	9	10				
SHPP_HP600	0	0	no data	no data	10				

Table 2. Wetting kinetics: spreading time (s) needed for water droplets to reach complete wetting $(\sim 0^{\circ})$ after droplet deposition measured on different ageing days.

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		SHPP_LP300				PP_LP300				
		elemental composition (%)		O/C atomic ratio	CA _{adv} (°)	elemental composition (%)		O/C atomic ratio	CA _{adv} (°)	
		С	0			С	0			
	Before plasma treatment	97.8	2.1	2.1	152	97.9	2.0	2.0	100	
Ageing time (day)	0	71.0	20.5	28.9	0	71.0	19.8	27.9	20	
	1	73.6	18.8	25.5	0	73.8	17.6	23.8	29	
	2	75.7	17.1	22.6	0	75.4	16.1	21.4	41	
	3	77.7	16.1	20.7	0	77.3	14.6	18.9	47	
	7	79.6	14.6	18.3	0	79.5	12.9	16.2	52	

Table 3. Surface composition of roughened (SHPP_LP300) and smooth (PP_LP300) samples measured by XPS in comparison with CA_{adv} measurements. *O/C atomic ratio: the relative amount of oxygen atom compared to carbon atom on the surface.

Table 3 shows that after the plasma treatment, the concentration of oxygen increased significantly due to the introduction of polar functional groups. The introduced oxygen functional groups resulted in samples with a hydrophilic surface. Immediately after the plasma treatment (day 0), the oxygen concentration on the surface of sample SHPP_LP300 was slightly higher compared to sample PP_LP300. During ageing, both samples showed a similar decrease in oxygen concentration but the CA_{adv} measured on their surfaces significantly differed.

The roughened sample with higher crystallinity ($X_C \approx 41\%$) had a higher concentration of atomic oxygen compared to samples with a smooth surface and lower crystallinity ($X_C \approx 37.9\%$). This result can be controversial since lower crystallinity was previously found to have greater chemical reactivity with plasma^{32,34}. However, the increase in the specific surface area of the roughened samples provides a larger surface area for the formation of functional groups, which could counterbalance its greater crystallinity. As shown, 7 days of ageing resulted in a 28.8% decrease in oxygen concentration with SHPP_LP300, and 34.8% with PP_LP300 samples. All this clearly shows that the increase in crystallinity hinders hydrophobic recovery due to higher structural regularity in the polymer matrix. Despite the decreasing oxygen concentration, the hierarchical surface structure enables film wetting, even after multiple days of ageing.

For the characterization of the functional groups formed on the samples and their changes as a function of ageing time, the best-fitted high resolution C1s spectra were investigated. Figure 2 and Fig. 3 show the comparison of C1s spectra of the SHPP_LP300, and PP_LP300.

As can be seen in Fig. 2 and Fig. 3, before plasma treatment there is only a slight difference in the surface composition of SHPP_LP300 and PP_LP300 samples. In addition to the C–C/C–H peak at 284.7 eV, which presents in the highest concentration, other peaks also appeared at higher binding energies for the C-O peak at 286.7 eV, C=O peak at 287.9 eV, O-C=O peak at 289.1 eV and C–O–C peak at 286 eV. The presence of oxygen-containing groups on the surface of samples might be the result of either thermo-oxidative degradation during the extrusion of the sheets, oxidation of the samples in the air, or intrinsically contained oxygen in the samples. For both samples, due to the plasma treatment, the concentration of the polar functional groups containing oxygen increased significantly. The ageing behaviour of SHPP_LP300 and PP_LP300 was periodically analysed to follow the effect of hydrophobic recovery in the first 7 days of ageing. The hydrophobic recovery occurred predominantly in the first two days after the plasma treatment. After that, we did not experience significant changes in the concentration of functional groups. Table 4 shows the relative concentrations of the functional groups of SHPP_LP300 and PP_LP300 after the plasma treatment calculated from C1s high-resolution spectra.

Table 4 shows the decrement of the C–C/C–H bond relative concentration from 96.1 to 71.8% (SHPP_LP300) and from 91.6 to 76.3% (PP_LP300) after the plasma treatment and then a gradual increase during ageing time (days). In the first two days of ageing, the concentration of oxygen functional groups decreased drastically, which shows that the rate of hydrophobic recovery is faster at the beginning of ageing and, after two days, slows down gradually.

Hydrophobic recovery is known to be highly dependent on ageing temperature³³. To investigate the stability of the plasma-induced hydrophilicity of SHPP_MP600 samples with roughened surfaces, we stored them at 70 °C and 150 °C for one hour before measuring their CA_{adv} (see supporting information Table S4). We found that heat treatment caused the surfaces to become highly hydrophobic. A one-hour heat treatment at 70 °C increased the CA_{adv} on the polymer surface to 140 ± 1° and a one-hour heat treatment at 150 °C caused an even greater hydrophobic recovery to 145 ± 1°.

Approach to characterize droplet spreading behaviour of superhydrophilic, roughened PP surfaces

As stated above, the wetting behaviour of aged superhydrophilic surfaces cannot be expressed with one contact angle parameter, because during droplet spreading, the apparent contact angle shows a monotonous decline after water droplet deposition. The characterization of recovery requires a dynamic approach, since wettability changes over time. To overcome this difficulty, we aimed to find models that can properly describe the measurement data, and the parameters which can be used to compare these surfaces.



Fig.2. High resolution XPS spectra for PP samples, C1s spectra of SHPP_LP300 with ageing time, (**a**) before plasma treatment, (**b**) immediately after plasma treatment, (**c**) 2 days and (**d**) 7 days after plasma treatment.

We investigated the kinetics of this spreading using momentary contact angle measurement time graphs, which we acquired by analysing video samples frame by frame recorded during contact angle measurements. We used a simple exponential function based on the work of Dabóczi et al.⁴⁸ to fit curves on the plotted graphs (Eq. 2):

$$\theta(t) = \theta_s + (\theta_0 - \theta_s) * e^{\left(\frac{-t}{T}\right)}$$
⁽²⁾

where θ_s denotes the stationary contact angle, and θ_0 and T represent fitted initial contact angle and characteristic spreading time respectively, the values of which we acquired by fitting the function on our graphs. As we will see, the larger value of T indicates a slower rate of spreading. Since the equilibrium contact angle θ_s is 0 in our case due to near-perfect wetting, the θ_0 parameter of the fitted curves corresponds to the apparent contact angle at the start of the measurement (Eq. 3):

$$\theta(t_0) = \theta_0 \tag{3}$$

Figure 4a depicts the decline of the apparent contact angle in time during the contact angle measurement on the SHPP_LP300 sample. This fitting method was used to evaluate the behaviour of multiple samples prepared



Fig.3. High resolution XPS spectra for PP samples, C1s spectra of PP_LP300 with ageing time, (**a**) before plasma treatment, (**b**) immediately after plasma treatment, (**c**) 2 days and (**d**) 7 days after plasma treatment.

		SHPP_LP300			PP_LP300					
		С-С/С-Н	C-0	C=O	0-C=0	С-С/С-Н	С-О-С	C-0	C=O	O-C=O
	Before plasma treatment	96.1	3.3	0.5	-	91.6	6.4	1.1	0.9	-
Ageing time (day)	0	71.8	10.1	6.2	11.9	76.3	9.2	4.8	5.6	4.1
	1	76.4	8.4	5.5	9.7	80.1	8.0	4.1	4.6	3.2
	2	78.5	7.8	5.1	8.4	83.2	6.3	3.8	4.0	2.7
	3	80.6	7.4	4.5	7.4	85.7	5.4	3.6	3.3	2.0
	7	83.9	6.4	3.7	6.0	89.9	4.6	3.6	2.9	2.0

Table 4. The relative concentrations of the functional groups (%) of the fitted peaks for C1s spectra of plasmatreated roughened (SHPP_LP300) and smooth (PP PP_LP300) samples as a function of ageing time.



Fig.4. (a) Exponential function fitted to the spreading results measured on the SHPP_LP300 sample after different ageing time after the plasma treatment. (b) The fitted T values plotted as a function of ageing time for different plasma treatment parameters.

with various plasma treatment parameters and after various times of room temperature storage. The fitted T values is shown in Fig. 4b.

The hydrophobic recovery of our samples prepared with different plasma parameters can be characterized by the T parameter, as shown in Fig. 4. These results clearly show the effect of hydrophobic recovery on the spreading rate of samples that exhibit near-perfect wetting ($\theta(t_{\infty}) = 0^{\circ}$), SHPP_LP300, SHPP_LP600 and SHPP_MP300. The fitted T values increase monotonously with ageing time in these cases. This increase represents a change in wetting kinetics, or more precisely, a decrease in the absolute power of the exponential function. In contrast, sample SHPP_MP600 exhibited nearly instantaneous wetting even after one week of ageing.

The results show the effect of the intensity of plasma treatment on the rate of hydrophobic recovery experienced on the surfaces. Plasma treatment with optimal parameters results in a sample with near-spontaneous perfect wetting and slow hydrophobic recovery. Increasing plasma power above a certain point (HP samples) leads to faster recovery due to sample degradation (see Table S3 in Supporting information).

Subsequently, we also propose a qualitative explanation for the droplet-spreading behaviour on our rough hydrophilic surfaces. Plasma treatment, as previously stated, greatly increased the hydrophilicity of the PP surface. This hydrophilicity, combined with the structured surface, could potentially cause water intake via the effect known as capillary wetting. Capillary wetting caused by the morphology of the samples decreases droplet volume and increases spreading speed. Figure 5 shows a model for the change in wettability after plasma treatment.

After solvent treatment, the originally smooth surface of extruded sheets had microscale and nanoscale roughness resulting a porous surface structure (Figs. 1b,d). When the samples (smooth and roughened) were exposed to plasma treatment, hydrophilic groups formed at the outermost surface through plasma oxidation and no morphological changes were detected. The porous surface structure of the surface-modified sample and the possible capillary imbibition are schematically shown in Fig. 5. Plasma exposure can mostly impact the accessible outermost surfaces of the sample and hardly diffuse into the pores. The surface of the spherulites in the deeper layers of the porous structure were subject to reduced plasma exposure because they were shielded by the spherulites on the outermost surface. However, the hydrophilic groups were also introduced in deeper



Fig.5. A schematic of wettability phenomena observable on plasma-treated PP surfaces depending on roughness and ageing time.

layers to a lesser extent, which enabled the imbibition of water droplets into the pores below the surface and thus helping the fast spreading of water droplets and the formation of film-wetting.

Due to the porous surface structure and the high surface energy created by hydrophilic groups, the surface became superhydrophilic, leading to almost complete film wetting. Moreover, samples treated with high-power and long plasma treatment showed signs of degradation, especially at the outermost surface of the modified layer. The increased spreading time of droplets to reach complete wetting after the plasma treatment results from the rearrangement of polar groups toward the bulk phase to reach a more stable state. The concentration of the polar groups decreased over ageing time, thus more time was needed for the drop to reach its equilibrium wetting state. As Fig. 5 shows, presumably only the surface energy changes during recovery while the roughness remains constant, which might enable the application of PP over a wider time interval.

Conclusions

This study presents a novel method for precisely controlling the wetting properties of hierarchically structured PP surfaces, transitioning between superhydrophobic and superhydrophilic states. The manipulation of surface wettability on roughened polypropylene surfaces, ranging from superhydrophobic to superhydrophilic, is known. However, the achievable wettability range can vary depending on the selected methods. The presented solvent treatment enabled us to achieve an advancing contact angle greater than 150°. The morphology of the created surface layer consists of hierarchically structured porous surface layer that composed of spherulites and a dense top layer of PP over the porous surface layer. Removing the top layer, we can the porous surface layer. The structure of the porous layer shows deviation from the mesh-like structure of PP membranes⁴⁹. Hierarchically structured PP surfaces with superhydrophobic characteristics were induced to transition into superhydrophilic wetting regime via air plasma treatment. With the optimal treatment parameters, we successfully developed a superhydrophilic surface that exhibited no measurable hydrophobic recovery effect even after one week of ageing in air.

A detailed study, using XPS and WCA measurements uncovered a strong correlation between surface composition on the plasma-treated roughened PP surfaces and wetting kinetics specifically in the context of droplet spreading speed over different ageing periods. The roughness of the surface, influenced by capillary effects and the reorientation of oxygen-containing functional groups over time, played a key role in controlling the reduced speed of droplet spreading. These findings provide new insights into the surface modification of commodity polymers like PP, significantly enhancing their applicability in new markets.

Moreover, the introduced simple model for the characterization of droplet spreading behaviour on superhydrophilic, roughened PP surfaces was used to describe the spreading time of droplet as a function of ageing time. The proposed model, which shows good agreement with experimental data, offers a novel method for comparing the droplet spreading behaviour on plasma-treated roughened surfaces. The proposed model can be used in the industries where the monitoring of long-lasting surface wettability of plasma treated surfaces plays a crucial role.

Data availability

Data is provided within the manuscript or supplementary information files.

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Author contributions

Csenge Vámos, Máté Füredi and Zoltán Hórvölgyi were responsible for conceptualizing the experiments and methodology. Csenge Vámos wrote the manuscript. Csenge Vámos and Tamás Bárány conducted the formal analysis. Csenge Vámos, Olga Krafcsik and Kiss Gábor prepared the investigations. Botond Béla Marosfői helped with the project administration. All authors reviewed and edited the manuscript.

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Competing interests

The authors declare no competing interests.

Additional information

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