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Plasma and thermoforming treatments to tune the bio-inspired wettability of polystyrene

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ABSTRACT

This paper shows the effects on wettability of plasma and thermoforming treatments on 14 different polystyrene (PS) surfaces, with a comparison with a lotus leaf. Quantitative roughness analyses of PS surfaces and lotus leaf, by three-dimensional optical profilometer and scanning electron microscope, have been carried out. We characterized the water drop sliding by measuring the contact angle, sliding angle, sliding volume and sliding speed. A relevant correlation between technological treatment, surface roughness parameters and wetting measurements clearly emerges, suggesting the plasma/thermoforming treatment as a process for enhancing the hydrophilic/hydrophobic behavior of PS surfaces. Determination of the static and resistant forces of the drop sliding on the surfaces concludes the paper.

1. Introduction

Water-repellent (or super-hydrophobic) and dirt-free (or self-cleaning) natural surfaces were probably observed for the first time more than 2000 years ago; however, only in the 20th century scientists studied these two related phenomena on some natural leaves [1–10], e.g. the famous lotus *Nelumbo nucifera*, on which "raindrops take a clear, spherical shape without spreading, which probably has to be ascribed to some kind of evaporated essence", as Goethe described in 1817 [11].

In contrast to the Goethe's conjecture, the so called lotus-effect is governed more than by chemistry (Young's law [12]) by topology (Wenzel's law [13], Cassie–Baxter's law [14]) and hierarchical architectures [15,16] (similar to what we observe on the strength and toughness of materials [17–21]). The contribution of surface roughness on super-hydrophobic/self-cleaning behavior has been extensively shown in the literature [22–34]. However, in some applications, materials should be hydrophilic more than hydrophobic, e.g. in order to maximize wettability.

In this paper, we study the effects of plasma or thermoforming treatments on different polystyrene (PS) surfaces. We have considered seven PS surfaces before (A_p) or after (B_p) the plasma treatment and fourteen PS surfaces before (A_t) or after (B_t) the thermoforming treatment. All these surfaces have been analysed with a three-dimensional optical profilometer and a field emission scanning electron microscope. The hydrophilic behavior given by plasma treatment is quantified by deposing distilled water drops on PS horizontal surfaces with controlled or random volumes, showing a relevant correlation between surface roughness parameters and contact angles (CA) measurements, in accordance with Wenzel theory. The effects of the thermoforming treatment are quantified by measuring the drop contact angle, sliding angle, volume and speed. Finally, we determine the static and resistant forces of a drop sliding on the surfaces.

2. Materials and methods

2.1. Plasma treatment

A commonly applied method to increase wettability and chemical reactivity of polymeric materials (by raising surface energy) is plasma discharge treatment, also known as corona treatment. Such treatment, invented by the Danish engineer Verner Eisby in the 1950s, is particularly suitable for continuous production processes, like the extruded PS sheets constituting the subject of the present paper, being safe, economical and capable of high line speed throughput.

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Table 1
Measured roughness parameters of all PS surfaces. Note that samples $7A_p$ and $7B_p$ are used only to evaluate the effects of plasma treatment, while $7A_t$ and $14A_t$ are new samples for the determination of the effects of thermoforming treatment.

	Sa (μm)	Sq (μm)	Sp (μm)	Sv (μm)	Sz (μm)	Ssk	Sdr (%)
$1A_p = 1A_t$	0.671 ± 0.0142	0.859 ± 0.0165	4.267 ± 0.3092	5.340 ± 1.2821	8.240 ± 0.6894	−0.274 ± 0.0118	5.583 ± 0.1041
$2A_p = 2A_t$	0.753 ± 0.0490	0.970 ± 0.0603	4.697 ± 0.9258	6.027 ± 0.1950	8.967 ± 0.3204	−0.136 ± 0.0431	5.277 ± 0.2930
$3A_p = 3A_t$	0.205 ± 0.0062	0.266 ± 0.0036	1.907 ± 1.0249	1.803 ± 0.5505	2.790 ± 0.6490	0.217 ± 0.1808	0.273 ± 0.0356
$4A_p = 4A_t$	0.086 ± 0.0093	0.126 ± 0.0162	2.160 ± 0.6907	1.863 ± 0.8615	2.833 ± 0.5776	0.821 ± 0.0993	0.108 ± 0.0242
$5A_p = 5A_t$	1.197 ± 0.1201	2.143 ± 0.1589	11.500 ± 1.1790	16.500 ± 1.9698	24.867 ± 0.7234	−2.523 ± 0.4826	11.003 ± 1.7306
$6A_p = 6A_t$	0.120 ± 0.0178	0.156 ± 0.0246	1.201 ± 0.3090	0.896 ± 0.1965	1.530 ± 0.3989	0.138 ± 0.1238	0.060 ± 0.0224
$7A_t$	0.744 ± 0.0840	0.946 ± 0.1150	3.553 ± 1.7032	4.613 ± 0.6638	6.01 ± 0.8402	−0.444 ± 0.1785	0.486 ± 0.0927
$1B_P = 8A_t$	1.730 ± 0.0954	2.203 ± 0.1250	12.963 ± 5.7969	13.927 ± 6.9070	21.300 ± 3.8626	−0.074 ± 0.1316	20.800 ± 1.3454
$2B_p = 9A_t$	1.330 ± 0.0557	1.693 ± 0.0777	6.960 ± 0.2598	9.353 ± 1.0207	14.167 ± 0.8083	−0.144 ± 0.1593	14.500 ± 0.7937
$3B_p = 10A_t$	0.921 ± 0.0093	1.187 ± 0.0115	4.403 ± 0.1950	6.657 ± 0.4466	10.080 ± 0.4703	−0.331 ± 0.0999	7.090 ± 0.1572
$4B_p = 11A_t$	1.427 ± 0.0681	1.857 ± 0.0751	8.747 ± 0.4735	9.780 ± 0.1212	16.400 ± 0.6000	−0.383 ± 0.1866	12.967 ± 0.9292
$5B_p = 12A_t$	0.939 ± 0.0302	1.213 ± 0.0351	5.627 ± 1.1371	6.733 ± 1.2595	10.473 ± 1.0403	−0.289 ± 0.2050	6.293 ± 0.7801
$6B_p = 13A_t$	1.273 ± 0.1361	1.653 ± 0.1818	6.657 ± 0.6311	9.553 ± 0.6243	14.367 ± 0.9238	−0.396 ± 0.1102	11.663 ± 1.8067
$14A_t$	0.745 ± 0.1322	0.953 ± 0.1662	4.555 ± 0.9122	4.425 ± 1.3647	6.365 ± 0.5020	−0.171 ± 0.0643	0.617 ± 0.0573
$7A_p$	0.313 ± 0.0159	0.403 ± 0.0232	2.647 ± 0.8939	2.383 ± 0.3646	3.913 ± 0.6824	0.076 ± 0.1178	0.629 ± 0.1203
$7B_p$	1.427 ± 0.1762	1.867 ± 0.2444	20.757 ± 17.4233	11.333 ± 0.7506	24.767 ± 11.8289	−0.306 ± 0.4491	15.533 ± 3.0600
$1B_t$	0.841 ± 0.2010	1.059 ± 0.2403	3.443 ± 1.3640	3.970 ± 0.2600	5.827 ± 1.0645	−0.276 ± 0.1651	0.572 ± 0.2196
$2B_t$	0.647 ± 0.0785	0.827 ± 0.0960	3.910 ± 1.2305	4.187 ± 2.0814	4.870 ± 0.3477	−0.128 ± 0.1611	0.373 ± 0.0810
$3B_t$	0.675 ± 0.0642	0.856 ± 0.0711	2.660 ± 0.5467	3.320 ± 0.3329	5.147 ± 0.3156	−0.242 ± 0.0804	0.401 ± 0.0201
$4B_t$	0.235 ± 0.0115	0.298 ± 0.0141	1.250 ± 0.0889	1.590 ± 0.5597	1.850 ± 0.0624	0.265 ± 0.2493	0.048 ± 0.0088
$5B_t$	0.359 ± 0.0654	0.463 ± 0.0883	2.020 ± 0.7544	2.020 ± 0.3724	2.837 ± 0.7211	−0.326 ± 0.1570	0.101 ± 0.0299
$6B_t$	0.518 ± 0.0474	0.644 ± 0.0551	2.123 ± 0.3204	2.553 ± 0.1701	3.757 ± 0.3988	−0.026 ± 0.0123	0.228 ± 0.0653
$7B_t$	0.602 ± 0.0762	0.757 ± 0.0993	2.917 ± 0.8153	3.133 ± 0.7427	4.413 ± 0.4332	−0.095 ± 0.1010	0.342 ± 0.0898
$8B_t$	0.933 ± 0.905	1.180 ± 0.1414	5.690 ± 0.2121	4.460 ± 1.3435	6.580 ± 0.8768	−0.044 ± 0.1061	0.724 ± 0.2531
$9B_t$	0.528 ± 0.0240	0.672 ± 0.0212	2.335 ± 0.0071	2.605 ± 0.6718	4.130 ± 0.1131	0.166 ± 0.0938	0.261 ± 0.0078
$10B_t$	0.384 ± 0.0643	0.476 ± 0.0813	2.815 ± 1.9304	1.630 ± 0.1980	2.695 ± 0.2333	0.061 ± 0.0016	0.103 ± 0.0160
$11B_t$	0.545 ± 0.0750	0.700 ± 0.1103	2.485 ± 0.5869	2.645 ± 0.6010	4.610 ± 1.1031	−0.023 ± 0.0629	0.368 ± 0.1697
$12B_t$	0.466 ± 0.0566	0.588 ± 0.0636	2.085 ± 0.0495	2.295 ± 0.1626	3.695 ± 0.0919	−0.006 ± 0.0991	0.214 ± 0.0078
$13B_t$	0.113 ± 0.0085	0.147 ± 0.0007	0.739 ± 0.3974	0.518 ± 0.0007	0.955 ± 0.1344	0.444 ± 0.6678	0.018 ± 0.0003
$14B_t$	0.616 ± 0.0827	0.786 ± 0.1209	3.010 ± 0.7637	3.275 ± 0.8697	4.605 ± 1.0112	0.018 ± 0.2737	0.336 ± 0.0849

Corona treatment is based on a high-frequency and high-voltage electrical discharge. The discharge is generated between an electrode and a counter electrode. The corona discharge has such a powerful impact on the substance surface that the molecular structure changes in a way that improves the surface wettability. In the presence of a high voltage discharge in an air gap, air ionization occurs. If a plastic material is placed in the discharge path, the electrons generated in the discharge impact the surface with energies two or three times larger than that necessary to break the molecular bonds. This creates very reactive free radicals that, in presence of air oxygen, can react rapidly to form various chemical functional groups on the substrate surface. An evolution of the system, particularly efficient for the higher activation potential, is the plasma jet system, where by means of high-voltage discharge (5–15 kV, 10–100 kHz) a pulsed electric arc is generated. A process gas, usually oil-free compressed air flowing past this discharge section, is excited and converted to the plasma state. This plasma then passes through a jet head to arrive on the surface of the material to be treated. The jet head is at earth potential and in this way largely holds back potential-carrying parts of the plasma stream. Corona surface and plasma jet treatment modifies only the surface characteristics without affecting material bulk properties [35–37].

Corona discharge treatment is commonly applied in cooling appliance industry: refrigerator insulation systems are typically constituted by polyurethane foam, reticulated *in situ* within cavity designed by purpose. To ensure mechanical and thermal stability of the final assembly, and thanks to the strongly modified surface topology due to the plasma treatment, adhesion of polyurethane foam over surrounding surfaces, i.e. PS liner surface and external case, must be maximized. For the purposes of the present paper, PS extruded slabs have been treated with the industrial "Ferrarini and Benelli" corona discharge system, integrated within refrigerators production line at Indesit Company; main characteristics of the equipment are: nominal power (7.3 kVA), corona discharge power (6.5 kW), corona discharge device working frequency (30 kHz), achievable surface energy after treatment ($(4.2–5.6) \times 10^{-2}$ N/m), material temperature in treatment area (80 °C), performance test method (ASTM Standard Test Method D2578-84, "Wetting Tension of Polyethylene and Polypropylene Film").

2.2. Thermoforming treatment

Thermoforming is the technology almost universally applied for refrigerator cabinet liner and door internal surface manufacturing; such technique allows high throughput production, together with a very good net shape surface finishing. Main phases of the process are: pre-heating (100 °C), peak temperature (180 °C), final temperature (70 °C).

After thermoforming, thickness reduction can exceed 90% in some areas: a careful control is needed to verify that sheet is kept robust (e.g. no breakage of aesthetic or functional layer), tuning the process and the material characteristics.

2.3. Surface characterization

The characterization of PS surfaces was performed with a three-dimensional optical profilometer, Talysurf CLI 1000, equipped with the CLA Confocal Gauge 300HE or a mechanical cantilever with 300 μm range and 10 nm vertical resolution or with 546 μm range and 10 nm vertical resolution from Taylor Hobson, Leicester, UK. The parameters tuned during the analysis are the measurement speed equal to 200 μm/s, the return speed equal to 1 mm/s or 500 μm/s, the sampling rate equal to 150 Hz or 40 Hz, the measured area equal to $500 \times 500\ \mu m^2$ and the resolution in the "xy" plane equal to 2.5 μm, leading to a final resolution of 201 points/profile. All parameters were referred to a 250 μm cut-off. See [38–40] for a detailed explanation of the classical roughness parameters extracted (Sa, Sq, Sp, Sv, Sz, Ssk, Sdr).