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Protocols

Plasma treatment switches the regime of wetting and floating of pepper seeds

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ABSTRACT

Cold radiofrequency plasma treatment modified wetting and floating regimes of pepper seeds. The wetting regime of plasma-treated seeds was switched from the Wenzel-like partial wetting to the complete wetting. No hydrophobic recovery following the plasma treatment was registered. Environmental scanning electron microscopy of the fine structure of the (three-phase) triple line observed with virgin and plasma-treated seeds is reported. Plasma treatment promoted rapid sinking of pepper seeds placed on the water/air interface. Plasma treatment did not influence the surface topography of pepper seeds, while charged them electrically. Electrostatic repulsion of floating plasma-treated seeds was observed. The surface charge density was estimated from the data extracted from floating of charged seeds and independently with the electrostatic pendulum as $\sigma \approx 1-2\ \mu C/m^2$.

1. Introduction

Plasma treatment is a widespread method of modification of surface properties of organic materials [1–7] and results usually in pronounced hydrophilization of organic surfaces [1,2,8–10]. The obvious advantage of plasma treatment of organic materials is that surface properties such as wettability and adhesion can selectively be modified without affecting the bulk characteristics of the materials [1,2,11–13]. The depth of influence of plasma treatment remains debatable, but it is definitely no more than 10 nm [14,15]. This makes plasma treatment extremely useful for treatment of seeds, due to the fact that this kind of treatment does not influence DNA. Various groups study plasma treatment of seeds by plasma discharges [16–24]. Generally, researchers concentrate on the impact exerted by plasmas on seed germination rate and homogeneity [16–22]. In our present research, we concentrated on the hydrophilization of pepper seeds by plasma treatment [23–26], switching the mode of their floating. It is noteworthy that plasma treatment of natural organic tissues is different from that of organic polymers because plasma-treated natural surfaces do not restore their initial hydrophobicity, as it occurs when synthetic polymers are exposed to plasma treatment [27–31]. The reported switching of the mode of floating of pepper seeds is important in a view of their priming [32,33]. The priming is a form of seed planting preparation, in which the seeds are pre-soaked before planting [32,33]. It influences the temporal homogeneity of rate of germination of seeds [32,33]. The density of a variety of seeds is smaller than that of water, thus the success of the priming depends strongly on the regime of their floating. We demonstrate that plasma treatment changes this regime, promoting the submergence of seeds.

2. Experimental

Pepper seeds were exposed to plasma treatment according to the following protocol:

Pepper seeds (*Capsicum annuum*, Roni-272) supplied by Hazera Co. (Israel) were selected and exposed to the inductive radio frequency plasma discharge with the following parameters: the frequency was 13.56 MHz; the pressure was 0.5 Torr; the power of plasma discharge was varied from 6.8 to 18 W; and the time span of irradiation was 120 s. After that, the seeds were mixed by shaking the Petri dish and exposed to plasma for another 120 s.

The plasma treated seeds were placed onto the water surface and were floating. Every two hours they were slightly shaken. The

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control group of non-treated seeds was also placed onto the water surface. The regime of floating of the seeds was visualized and captured with a Nikon 1 J5 camera.

The true density of seeds was established as $645 \pm 11\,kg/m^3$ using the toluene displacement method, as described in detail by Üçer et al. in Ref. [34]. Weighted pepper seeds were immersed into toluene and the displaced volume was measured.

The apparent contact angles of water on seeds were measured with a Ramé-Hart goniometer (model 500) at room temperature by placing a water drop of a volume of 1 μL on a seed surface. For the establishment of impact of the time of irradiation on the apparent contact angles of irradiated seeds, the time span of irradiation was varied from 5 s to 240 s. Ten measurements were taken to calculate the mean apparent contact angles. Bi-distilled water (resistivity $\rho \cong 1\,M\Omega\,cm$) was used in the experiments. The measurements of thnt contact angles. Bi-distilled water (resistivity $\rho \cong 1\,M\Omega\,cm$) was used in the experiments. The measurements of the apparent and advancing contact angles (performed with the inclined plane method) were carried out under the ambient conditions.

Wetting regimes inherent to non-treated and plasma-treated pepper seeds were studied with FEI Quanta 200FEG ESEM at wet-mode. A water drop of 1.5 μL was placed onto the seed surface prior to the ESEM pump down process. The ESEM vacuum system was then pumped down to 5.3 Torr that provided relative humidity of 100% for a sample temperature of 2 °C. The imaging was focused on a comparable study of the shape of triple line for both treated and untreated pepper seeds. Furthermore, a comparable study of the evolvement of triple line under equilibrium conditions was carried out for similar time-scales. Prior to the wetting experiment, the surface morphologies of the various seeds were compared under ESEM high vacuum conditions using gold/palladium thin film coating.

For the measurement of the surface charge density, a simple experimental set (similar to the electrostatic pendulum) was used, composed of two vertical capacitor plates with a distance of 5 cm between them. Two seeds were suspended on polycaprolaktam wires (the diameter and the length of wires were 46 μm and 205 mm respectively) inside the capacitor (see Fig. 1). The voltage between plates was varied on the scale of kilovolts; the maximal voltage was 6 kV.

3. Results and discussion

3.1. SEM and ESEM study of wetting of virgin and plasma-treated pepper seeds

The results of the comparative SEM study of surface topography of virgin and plasma-treated pepper seeds are depicted in Fig. 2. The SEM study resulted in two important conclusions: (1) the micro-scaled relief is inherent to pepper seeds with the characteristic dimension of roughness *ca.* 10–50 μm; (2) plasma treatment did not influence the surface topography of pepper seeds under the plasma parameters, supplied in the Experimental Section.

Wetting of nano- and micro-roughened surfaces, such as represented in Fig. 2, typically takes place within homogeneous or heterogeneous regimes described respectively by the Wenzel or Cassie-Baxter models, as shown schematically in Fig. 3 (see Refs. [36–38]). In the Wenzel wetting regime, the liquid penetrates into grooves and pores constituting a roughened surface (see Fig. 3a). In contrast, in the Cassie wetting regime, air is entrapped between the liquid and the solid surfaces (see Fig. 3b) [36–38]. More complicated "mixed" wetting scenarios have also been reported [38].

The Wenzel and Cassie-Baxter models are valid when the characteristic dimension of a droplet (the contact radius) is much larger than the pores forming a relief.

We performed an ESEM study of wetting of virgin and plasma-treated pepper seeds in order to examine the true wetting state (regime) of water on these micro-structured surfaces. The ESEM study was carried out in two series of experiments: (1) comparative study of the fine structure of the triple (three-phase) line; (2) comparative study of water condensation on virgin and plasma-treated pepper seeds.

Study of the fine structure of the triple line demonstrated two main effects, the first of which is the meandering of the triple line (see Fig. 4), due to its strong pinning by defects, addressed in detail in Refs. [39–45]. The second conclusion is that water fills grooves and pores of both virgin and plasma-treated seeds, promoting the Wenzel regime of wetting, as recognized from Fig. 4.

The water condensation on the surfaces of virgin and plasma-treated pepper seeds was different. When water was condensed on virgin plasma seeds, micro-scaled water droplets were registered, as shown in Fig. 5a, whereas the same condensation process resulted in formation of a thin water film on the surface of plasma-treated seeds (see Fig. 5b), thus evidencing hydrophilization of the

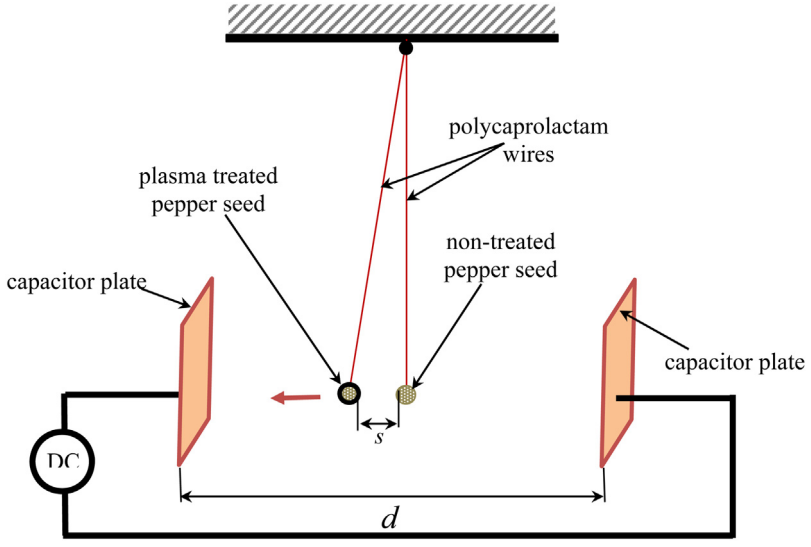

Fig. 1. Experimental set used for the electrostatic measurements of the specific surface charge density of plasma treated pepper seeds.