

Polymeric number average molecular weight in submicron films as a tool for the manipulation of water phenomena in translucent coatings

Natalia Lopez-Barbosa*, Johann F. Osma

CMUA, Department of Electrical and Electronics Engineering, Universidad de los Andes, Cra. 1E No. 19a – 40, Bogota, DC 111711, Colombia.

*Corresponding author

DOI: 10.5185/amp.2018/900

www.vbripress.com/amp

Abstract

Absorption and desorption properties of poly(ethylene glycol) diacrylate (PEGDA) have seen to greatly vary depending on the molecular weight of the polymer, suggesting a dependence of the wetting phenomena on its molecular weight. Here, two sets of polymeric submicron films (140 and 190 nm) were fabricated by free radical polymerization using Phenylbis (2, 4, 6-trimethylbenzoyl) phosphine oxide as the photoinitiator, and PEGDA (Mn 250 or 575). The films were spin coated on glass substrates to study their wetting phenomena by dynamic contact angle analysis. All films were characterized in terms of their thickness and transmittance. PEGDA Mn 250 films (Film-250) decreased the sliding time of water drops when compared to a clean glass substrate because of a decrement in the liquid-solid interface area. Nonetheless, when using PEGDA Mn 575 films (Film-575), an improvement in the adhesion forces between the coating and the drop of water was observed, avoiding the drop to slide down the substrate and leading to its later evaporation. In addition, Film-575 drastically changed their morphology after water exposure, while Film-250 remained the same. These characteristics are of special interest in environments where a response towards small amounts of water is desired, or where water evaporation is craved. Copyright © 2018 VBRI Press.

Keywords: Polymeric films, water phenomena, average molecular weight.

Introduction

Hydrophobic coatings have become of great interest due to the protection against corrosion that they can provide. Among others, this has been mainly attained by surface texturing [1], chemical treatments [2], sol-gel methods [3], hybrid organic-inorganic compounds [4] and plasma treatment [5] of substrates. Modified hydrophobic surfaces are characterized by containing low surface energies ($\gamma < 35\text{mN/m}$) and high contact angles ($\theta > 90^\circ$) [6], which describe their wetting phenomena.

When a droplet of water is placed on a solid surface, three interfaces are encountered; liquid-solid, liquid-gas and solid-gas. The interactions between their boundaries give raise to three different surface tensions, which generate what is known as the contact angle [2]. Theoretically, if the three phases are in thermodynamic equilibrium, i.e. there is a force balance and a chemical potential matching between the three phases, and the gas phase represents the saturated vapor of the liquid, the measurement of the static contact angle between the droplet and the solid surface at any point provides enough information about the wetting phenomena of the material [7, 8]. Nonetheless, this is rarely the case, since this assumes that there exists a homogeneity among the surface of the material. Thus, the dynamic contact angle has been preferred.

The dynamic contact angle of a system can be described with an advance (θ_a) and a receding (θ_r) contact angle, which appear when the drop is moving parallel to the surface. Furthermore, dynamic contact angle measurements can provide information about the adhesion forces acting on the system [7].

Herein, two sets of polymeric submicron films (140 and 190 nm) were fabricated by free radical polymerization using Phenylbis (2, 4, 6-trimethylbenzoyl) phosphine oxide as the photoinitiator and PEGDA (Mn 250 or 575). The films were spin coated on glass substrates to study their wetting phenomena by dynamic contact angle analysis. All films were characterized in terms of their thickness and transmittance in a span of wavelengths between 300 and 700 nm, evidencing the translucency of both types of films. PEGDA Mn 250 films (Film-250) decreased the sliding time of water drops when compared to a clean glass substrate because of a decrement in the liquid-solid interface area. Nonetheless, when using PEGDA Mn 575 films (Film-575), an improvement in the adhesion forces between the coating and the drop of water was observed, avoiding the drop to slide down the substrate and leading to its later evaporation. The surface morphology of both sets of films was studied before and after water exposure with an optical transmission microscope. Film-575 drastically changed their morphology after water exposure, while

Film-250 remained the same. These differences in water phenomena and morphology could be exploited in environments where a response towards small amounts of water is desired (e.g. monitoring the state of drug packaging), or where coatings that enhance water evaporation are craved (e.g. surgery clothing, wind blades for energy generation).

Experimental

Materials and reagents

Poly(ethylene glycol) diacrylate average Mn 575, poly(ethylene glycol) diacrylate average Mn 250 and Phenylbis (2, 4, 6-trimethyl benzoyl) phosphine oxide were provided by Sigma-Aldrich, and were used with no further purification.

Polymeric films

Polymeric submicron films were fabricated by free radical polymerization of two different solutions. Solution I was prepared with 98 mL of PEGDA average Mn 250 and 2g of Phebylbis (2, 4, 6-trimethyl benzoyl) phosphine oxide. Solution II was prepared with 98 mL of PEGDA average Mn 575 and 2g of Phebylbis (2, 4, 6-trimethyl benzoyl) phosphine oxide.

400 μL of each solution was spin coated on a glass slide using a 150E spin coater (SPS, Netherlands) at 1500 rpm for 15 seconds. Polymerization was performed by ultraviolet A exposition for 10 minutes. Experiments were conducted by quadruplet. Here on, films from Solution I are called Film-250, and films from Solution II are called Film-575.

Polymeric films characterization

Thickness of all fabricated films was determined after all experimentation was performed and using a Dektak 3 profilometer (Veeco, USA). Translucency was confirmed by UV/VIS spectroscopy using a Genesis 10S spectrophotometer (Thermo Scientific, USA) in a span of 390 to 700 nm. A clean glass substrate was used as blank. Measurements were taken before and after water exposure to determine changes in translucency.

Dynamic contact angle measurement

Coated surfaces were placed in such way that they maintained an inclination angle of 25° . Water droplets were generated using a 1000 μL micropipette. Droplets were released at a fixed height of 3 cm perpendicular to the surface. A digital camera was horizontally aligned with the glass substrate. The camera was kept constant in terms of position and magnification, and was used to record the impact and evolution of the water droplet on the coating. Subsequent video processing was performed using software Tacker 4.90 (Open Source Physics, USA) to determine advance (θ_a) and receding (θ_r) contact angles. Experimental setup schematic is shown in **Fig. S1**.

Evaporation and expansion measurements of Film-575

A humidity sensor was used to determine changes in humidity before and after water exposure. Coated

substrates were placed inside a closed chamber with the humidity sensor above the surface. A drop of water was placed on the surface and humidity was monitored for 14 minutes. Experimental setup schematic is shown in **Fig. S2**.

A red dye was used to monitor the movement of the droplet when placed on Film-575. Covered area was determined by recording dye expansion and subsequent video processing. A correlation between droplet expansion and evaporation was determined.

Results and discussion

Polymeric films characterization

Profilometer measurements were carried out to determine the average thickness of films produced from both polymeric mixtures. Film-250 and Film-575 exhibited an average thickness of 190 nm and 140 nm, respectively.

Percentage of transmission between 390 and 700 nm was determined to confirm translucency of the coated substrates. **Fig. 1** shows the spectroscopy results for Film-250, Film-575 and a clean glass substrate. As observed, there is no significant difference between the percentage of transmittance of clean glass and coated samples.

Dynamic contact angle measurements

A video camera and subsequent video processing were used to determine dynamic contact angles in both Film-250 and Film-575. Water sliding behaviors on both surfaces differed significantly. For instance, water droplets on Film-250 slid down the substrate (**Fig. 2 left**), while water droplets on Film-575 seemed to expand their contact area and evaporate (**Fig. 2 right**).

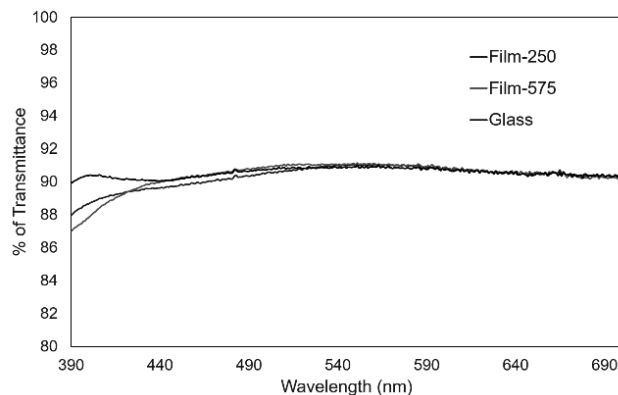


Fig. 1. UV/VIS spectrophotometric analysis for Film-250, Film-575 and a clean glass substrate.

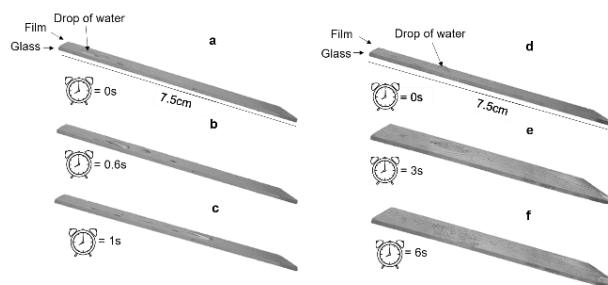


Fig. 2. Sliding properties of water droplets on Film-250 (left) and Film-575 (right) at different times.

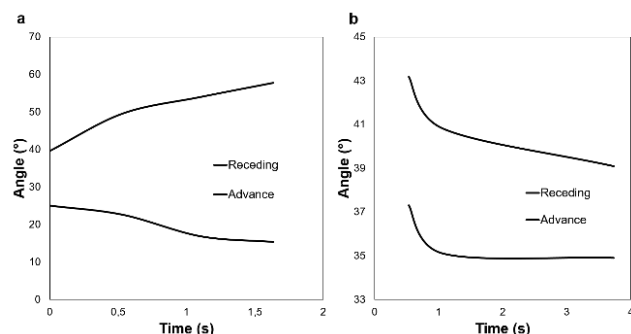


Fig. 3. Changes in advance and receding angles for (a) Film-250 and (b) Film-575.

Advance and receding angles were determined with subsequent video processing for Film-250 and Film-575 (**Fig. 3**). Receding angles decreased with time from approximately 25.6° to 15.4° and 43.2° to 24.6° , for Film-250 and Film-575, respectively. Advance angles changed from 39.6° to 57.8° and 37.3° to 33.7° , for Film-250 and Film-575, respectively. Changes in advance and receding angles were measured until no further changes were observed or until the droplet was off the surface of the substrate. This meant an approximate measurement time of 1.6 and 3.7 seconds for Film-250 and Film-575, respectively.

Evaporation and expansion measurements of Film-575

A humidity sensor was used to uphold the evaporation of water droplets on Film-575. Relative humidity inside a closed chamber was monitored as a function of time, being time 0 the instant of droplet release on the surface of the substrate. Recorded data is shown in **Fig. 4**.

Similarly, water contact area changes on Film-575 was monitored by using a dye and subsequent video processing. Recorded data is shown in **Fig. 5**.

Discussion

Reaction after water exposure of Film-250 and Film-575 was significantly different regardless of the similarity between the mixtures. Film-575 seemed to react by locally folding when in contact with the drop of water. The appearance of wrinkles increased the contact area between the droplet and the surface as confirmed by dye monitoring experiments. In the same way, the fact that both the advance and receding angles on Film-575 decreased with time, implies that the surface area of the solid-liquid interface increased, as well as the adhesion forces. These changes resulted in the impediment of water sliding down the substrate and its later evaporation. In contrast, Film-250 allowed the sliding of water droplets among their surfaces.

Proportions of polymer and photoinitiator were kept the same between Film-250 and Film-575, being the number average molecular weight (Mn) of PEGDA the only difference. The Mn of each PEGDA determined the resulting mesh size of both Film-250 and Film-575. Mesh sizes increase with Mn due to the presence of a larger PEG chain between cross-linking points [9]. The decrease of cross-linking density in Film-575, allowed a greater

penetration of water molecules, increasing interaction [10]. Similarly, the proportion between poly(acrylate) and PEG groups is higher in lower Mn PEGDA. This means, that the number of polar groups is also higher in lower Mn PEGDA, making Film-250 more affine to water than Film-575.

Previous experiments with similar free standing films [6] showed that the matrix encountered in Film-575 tend to reduce the contact area between the droplet of water and the surface by producing a mechanical folding. Nonetheless, since Film-575 is attached to a rigid substrate, attempts to fold end up in the appearance of wrinkles on the surface, which produces an increase in adhesion forces and ends up in water evaporation. This was confirmed by observing that the time of plateau of the contact area matches the quiescent period of relative humidity. These characteristics can be exploited in environments where a rapid response towards small amounts of water is desired. For example, compartments design to protect drugs from humidity could be coated with Film-575. If a significant increase in humidity is present inside the compartment, the walls will exhibit wrinkles, telling the patient not to take their medication. This technology, could also be tested in scenarios where rapid evaporation of small amounts of water is craved, such as the surface of wind blades in Eolic energy generation.

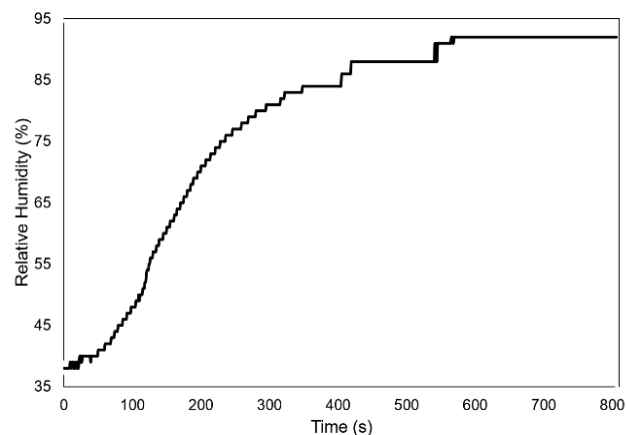


Fig. 4. Percentage relative humidity in a closed chamber after water exposure of Film-575.

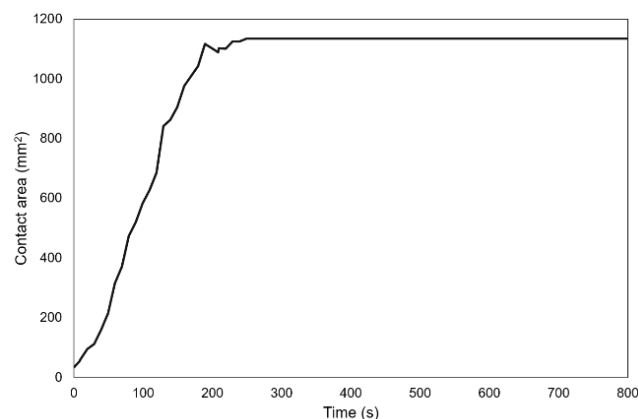


Fig. 5. Water contact area changes as a function of time after water exposure of Film-575.

Conclusion

Changes upon the interaction between water droplets and coatings produced by PEGDA Mn 250 and PEGDA Mn 575 were observed. The decrease on the cross-linking density and thus the proportion of poly(acrylate) to PEG groups in Film-575, produced an increase in surface area of the solid-liquid interface and in the adhesion forces after water exposure. This lead to subsequent water evaporation as evidenced by an increase in local relative humidity. These characteristics are of special interest in environments where a response towards small amounts of water is desired (e.g. monitoring the state of drug packaging), or where coatings that enhance water evaporation are craved (e.g. surgery clothing, wind blades for energy generation).

Acknowledgements

The authors would like to thank the cleanroom from the Department of Electrical and Electronics Engineering at Universidad de los Andes for the financial support.

Author's contributions

Conceived the plan: N. Lopez-Barbosa, J. F. Osma; Performed the experiments: N. Lopez-Barbosa; Data analysis: N. Lopez-Barbosa, J. F. Osma; Wrote the paper: N. Lopez-Barbosa. Authors have no competing financial interests.

Supporting information

Supporting informations are available from VBRI Press.

References

1. Beckford S, Langston N, Zou M, Wei R (2011) Fabrication of durable hydrophobic surfaces through surface texturing. *Appl Surf Sci* 257:5688–5693.
DOI: [10.1016/j.apsusc.2011.01.074](https://doi.org/10.1016/j.apsusc.2011.01.074)
2. Gao S-H, Gao L-H, Zhou K-S (2011) Super-hydrophobicity and oleophobicity of silicone rubber modified by CF 4 radio frequency plasma. *Appl Surf Sci* 257:4945–4950.
3. Kumar D, Wu X, Fu Q, Ho JWC, Kanhere PD, Li L, Chen Z (2015) Hydrophobic sol-gel coatings based on polydimethylsiloxane for self-cleaning applications. *Mater Des* 86:855–862.
4. Holubová B, Cílová ZZ, Kučerová I, Zlámál M (2015) Weatherability of hybrid organic-inorganic silica protective coatings on glass. *Prog Org Coatings* 88:172–180.
5. Múgica-Vidal R, Alba-Elías F, Sainz-García E, Ordieres-Meré J (2014) Atmospheric plasma-polymerization of hydrophobic and wear-resistant coatings on glass substrates. *Surf Coatings Technol* 259:374–385.
6. Lopez-Barbosa N, Zuluaga N, Jumah S, Osma JF (2015) Fabrication of folding polymeric thin films with hydrophilic properties. *Novos Saberes* 2:71–83.
7. Bertola V, Wang M (2015) Dynamic contact angle of dilute polymer solution drops impacting on a hydrophobic surface. *Colloids Surfaces A Physicochem Eng Asp* 481:600–608.
8. Bonn D, Eggers J, Indekeu J, Meunier J, Rolley E (2009) Wetting and spreading. *Rev Mod Phys* 81:739.
9. Ross AE, Tang MY, Gemeinhart RA (2012) Effects of Molecular Weight and Loading on Matrix Metalloproteinase-2 Mediated Release from Poly(Ethylene Glycol) Diacrylate Hydrogels. *AAPS J* 14:482–490.
DOI: [10.1208/s12248-012-9356-3](https://doi.org/10.1208/s12248-012-9356-3)
10. Yañez-Soto B, Liliensiek SJ, Murphy CJ, Nealey PF (2013) Biochemically and topographically engineered poly (ethylene glycol) diacrylate hydrogels with biomimetic characteristics as substrates for human corneal epithelial cells. *J Biomed Mater Res Part A* 101:1184–1194.