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Evaporation of water drops on polymer surfaces: Pinning, depinning and dynamics of the triple line

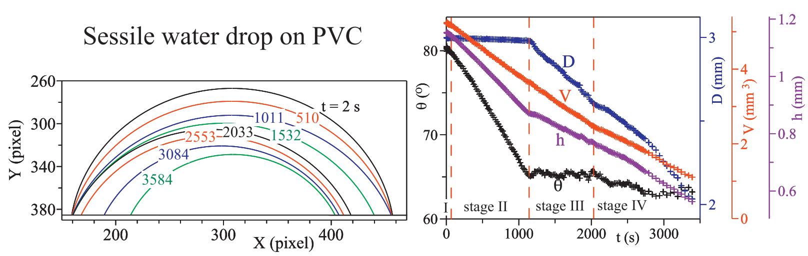
Paola G. Pittoni, Chiang-Ching Chang, Teng-Shiang Yu, Shi-Yow Lin*

Department of Chemical Engineering, National Taiwan University of Science and Technology, 43, Keelung Road, Section 4, Taipei 106, Taiwan

HIGHLIGHTS

- Study on triple line dynamics of evaporating drops on PC, ABS, PVC and PMMA.
- Pinning/depinning behavior was observed for the drops evaporation on PVC and PMMA.
- Pinning behavior was observed for the drops evaporation on PC and ABS.
- Relationship between triple line dynamics and surface topographies was detailed.
- θ, wetting diameter, height, volume and shape of the drop were deeply analyzed.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, the evaporation of water drops on four distinctive polymeric substrates, acrylonitrile butadiene styrene, polycarbonate, poly(methylmethacrylate) and poly(vinyl chloride), typified by unlike superficial morphologies, was investigated using the sessile drop method coupled with a video-enhanced image digitization technology and a best-fitting algorithm. The correlations between the observed dissimilar dynamics of the three phases contact line during the water drop evaporative process and the aforementioned surface topographies were deeply analyzed and discussed. The evaporation dynamics were measured and intensively illustrated in terms of the variation of contact angle, wetting diameter, drop height, drop volume, and drop shape. While the drops sitting on surfaces characterized by numerous defects and inhomogeneities showed a pinned triple line for almost their whole lifetime, for drops deposited on smoother substrates, after an initial pinning stage, the three phases contact line was observed receding freely until the drop disappearance.

1. Introduction

In the last two decades, the evaporation of sessile drops has been the subject of an intensive research due to its decisive role in numerous applications, such as DNA/RNA micro-arrays deposition, biochemical assays, dropwise evaporative cooling, ink-jet printing, pesticides spraying, micro/nano material fabrication, thin film coatings and manufacture of new materials [1–11]. The importance of a deep understanding of the evaporative process is demonstrated by more than 360 papers published per year on this topic in 2010 and 2011 [10]. Over the last few years especially, after the pivotal work by Deegan et al. published in 1997 [11], growing attention has been dedicated to the study of the evaporation of colloidal nanosuspensions. It is not just the analysis of morphology and size of stains created by nanoparticles during evaporation that has been a crucial topic, but also the study of effects that the presence of nanoparticles have on the evaporative process itself that has been the subject of numerous recent works [11–16].

* Corresponding author. Tel.: +886 2 2737 6648; fax: +886 2 2737 6644.
E-mail address: sylin@mail.ntust.edu.tw (S.-Y. Lin).

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In 1977, Picknett and Bexon [17] published a fundamental paper in the sessile drop evaporation research field. They described two distinct evaporative modes: at constant contact angle with decreasing wetting contact area; and at constant wetting contact area with decreasing contact angle. Afterwards a third evaporative mode, named "stick and slip" [18], has been observed for different liquids/substrates [12,19–21] and especially during the evaporation of colloidal nanosuspensions [12,13,15], since the presence of nanoparticles has been found promoting the self-pinning of the three phases contact line. This mode is characterized by a mixed behavior in which the drop, repeatedly, changes suddenly its shape, generally increasing in contact angle and decreasing in wetting diameter.

In their 1994 and 1995 works, Bourgès-Monnier and Shanahan [19,22] described four distinct stages in the evaporation of a sessile drop deposited on polymeric surfaces (smooth polyethylene and an epoxy resin with two different roughnesses). Initially (stage I), when the atmosphere near the drop was maintained saturated in water vapor, the evaporation was limited, the wetting diameter remained constant and both drop height and contact angle decreased very slightly. Then the atmosphere conditions inside the experimental chamber were altered and the relative humidity around the drop was diminished, enhancing the evaporation. This phase (named stage II or "pinned triple line" mode) was characterized by a constant wetting diameter and a decrease of both drop height and contact angle. The contact angle progressively decreased until the beginning of stage III (or "depinning" of the triple line) occurred. Stage III (named also "moving triple line" mode) was typified by a constant contact angle and a decreasing wetting diameter. In their findings, Bourgès-Monnier and Shanahan noted that the depinning was totally absent for the rougher epoxy resin, which showed directly after stage II, the occurrence of stage IV, correspondent to the final disappearance of the drop.

In the study of sessile drops, particularly concerning dynamic processes, special attention is needed in defining what is intended for "contact angle". There are three different important contact angles which can be measured: the advancing contact angle, θ_{ad}, observed when the liquid advances on a dry surface; the receding contact angle, θ_{rec}, observed when the liquid recedes on a previously wetted substrate; and the equilibrium contact angle, θ_{eq}, defined by Young's equation. This equation is defined for an ideal substrate that is chemically homogenous, rigid, perfectly flat, and on which chemical processes, such as chemical reactions or diffusion, are not present. Theoretically, when all these conditions are respected, just θ_{eq} would be measured. Obviously, real substrates are far from being ideal and differences between the measured angles and θ_{eq} can always be observed. Specifically, the difference between the advancing and the receding contact angle is termed contact angle hysteresis. The major causes of hysteresis are due to the surface deviation from the ideal conditions: they can be either chemical, such as the presence of chemical heterogeneities on the substrate or chemical bonds between liquid and solid; or physical, such as the roughness of the substrate, the molecular reorientation or random local defects present on the solid surface [23–29].

Great heedfulness is required in defining these angles during the evaporative process, especially in reference to the receding contact angle. Picknett and Bexon [17] pointed out that stage III starts when the contact angle has reached the value of the "conventional" receding contact angle, obtained by mechanical withdrawal of the liquid from the drop. However in most of the posterior works [10,19,22,30], it has been reported that the contact angle reached at the end of stage II was generally lower than the θ_{rec} measured by forced dewetting or using the tilting plane method. Moreover, stage III was not detected during the drop evaporation on various rough substrates [12,19,22], or on substrates which showed ionic, covalent or metallic bonds on the surface in the order of 1 eV [21,24], wherein which the drop evaporated, decreasing its contact angle until completely disappearing.

When θ_{rec} has been determined through manual forced dewetting by removing the liquid from the drop by means of a syringe, quite different values have been reported [10,30]. It has been pointed out that the probable major cause of these discrepancies was the different rate of liquid withdrawal used during the experiments recorded in literature [31]. On an ideal surface, as previously described, the three phases contact line should recede steadily. However, during measurements on real surfaces, a very slow withdrawal of liquid does not correspond to a sudden movement of the triple line. The rate of the withdrawal is thus essential for evaluating correctly the receding contact angle. The reported differences in receding contact angle values are even more enhanced if the titling plane method is used for the experiments, since this method is greatly affected by the drop volume [23]. In this respect, the drop evaporative process allows a minimum and kind of "standardized" rate of liquid withdrawal and this, obviously, affects the measurement of θ_{rec} [19,22,30]. For these reasons, in the present work, we did not refer to the dynamic angle measured during the drop evaporation as "receding contact angle" or θ_{rec}, but as "dynamic contact angle" or, simply, "contact angle", θ.

In this study, the evaporation of water drops on four distinctive polymeric substrates, namely acrylonitrile butadiene styrene, polycarbonate, poly(methylmethacrylate) and poly(vinyl chloride), was investigated using the sessile drop method coupled with a video-enhanced image digitization technology and a best-fitting algorithm. To the best of our knowledge, apart from some results published for the evaporation of water droplets on poly(methylmethacrylate) [30,32–34], the polymer substrates used in our measurements have never been reported in literature.

The four polymer surfaces, analyzed by a scanning electron microscope, were typified by unlike superficial morphologies. Thus, the aim of this work was, specifically, to deeply examine the possible correlations between the observed dissimilar dynamics of the three phases contact line and these surface topographies during the water drop evaporative process. The evaporation dynamics were measured in terms of the variation of the contact angle, the wetting diameter, the drop height, the drop volume, and drop shape.

2. Experimental

2.1. Apparatus

A similar apparatus of the video-image enhanced sessile drop tensiometer used in the present study has been detailed in Lin et al. [32]. The equipment was used to create the silhouettes of the sessile drop, take video-images of these silhouettes, and digitize the images. The apparatus consisted of an image forming and recording system, a drop forming system, an air thermostat and a humidity system, and a video-image profile digitizer, as schematized in Fig. 1.

The image forming and recording system consisted of a light source (a halogen lamp with constant light intensity; Oriel, QTH No. 63200), a lens system for producing a collimated beam, an objective lens (effective focal length 60 mm, f/no. 7.1), a video recorder, and a solid-state video camera (MS-4030 CCD, Sierra, Scientific Co.). The lens system consisted of two plano-convex lens, a quartz ND filter, and a pinhole. The samples were installed on adjustable stages (with freedom of XYZ, rotation, and tilting) placed on a vibration isolated workstation.

The drop forming system consisted of a stainless-steel needle connected to the normally closed port of a three-way miniature solenoid valve (Lee Co.) via 1/16 in. i.d. Teflon tubing. The common port of the valve was connected to a gas-tight Hamilton syringe