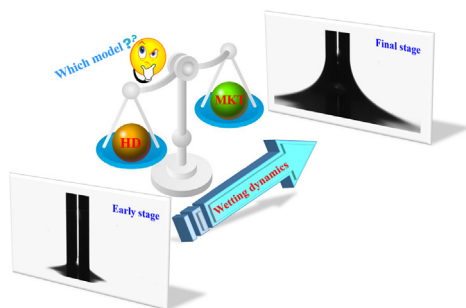Regular Article

Wetting dynamics of polydimethylsiloxane mixtures on a poly(ethylene terephthalate) fiber

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GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Hypothesis: The wetting dynamics of liquids with identical surface tensions are mostly controlled by their viscosities. We therefore hypothesized that the wetting dynamics of one- (pure liquid) and two-component (mixture) polydimethylsiloxane (PDMS) on a poly(ethylene terephthalate) (PET) fiber with similar surface tensions and viscosities should be controlled by the same underlying physical mechanisms.

Experiments: We studied the capillary rise of PDMS liquids on a PET fiber. We compared the different contact angle relaxations and characterized the transitions between the molecular-kinetic theory (MKT) and hydrodynamic approach (HD) for the PDMS mixtures and the pure liquids as a function of their viscosities.

Findings: Compared to the pure PDMS liquid with a viscosity of 20 mm^2/s that presents a contact angle relaxation following a $t^{-1/2}$ scale law in agreement with HD, the PDMS mixture with a higher viscosity (27.4 mm^2/s) shows a t^{-1} behavior predicted by the MKT. Moreover, the transition between MKT and HD appears in a regime with higher viscosities for PDMS mixtures than for pure liquids. Surface segregation of shorter PDMS chains or precursor film may be responsible for this shift.

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1. Introduction

Wetting dynamics is of fundamental importance in numerous processes, such as adhesion, secondary oil recovery, painting, liquid-based microfluidic systems, where capillary forces predominate or affect their efficiency and stability. As a consequence, wetting phenomena have been studied extensively, from both numerical and experimental aspects [1–3]. Among them, the understanding of a droplet spreading on a flat substrate is relatively well documented. However, the wetting behavior of a fiber partially immersed in a liquid bath is significantly different from that of a droplet spreading on a flat substrate due to the geometry of the fiber. For example, a fluid that can form a wetting film on a

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smooth substrate may not wet the fiber made of the same material in a similar way [4]. In fact, these different wetting behaviors stem mainly from the opposite sign of the two principal radii of curvature around the fiber [5,6]. This has been recognized when gravity is negligible. In the case of droplet spreading on a flat substrate, the radii of curvature become greater till equilibrium, reaching possibly an infinite value in the extreme case of the formation of a wetting film. This fundamental difference between the two geometries indicates that the study of the liquid-fiber system should exhibit distinctive wetting characteristics.

To describe the dynamics of wetting, two main theoretical approaches have been proposed: the hydrodynamic approach (HD) and the molecular-kinetic theory (MKT), which differ from each other mostly in the consideration of the channel of dissipation [2,3,7,8]. The first approach emphasizes the dissipation due to viscous bending generated during displacement of the contact line [8–11], and the MKT proposed by Blake and Hayes concentrates on the frictional processes occurring in the vicinity of the advancing contact line [12–16]. Since these models have already been extensively described in the literature, we will not repeat them here. When applied to the spreading of liquid droplets on a flat surface with vanishing advancing contact angle (θ_t), the two models predict slightly different power laws. Typically, θ_t varies as $t^{-3/10}$ and $t^{-3/7}$ for the HD and MKT, respectively [10,14,17,18]. It implies that the difference between these two regimes is not experimentally easily distinguishable on flat surfaces. For the case of fibers, Quéré et al. [19,20] suggested that the capillary rise along a thin vertical fiber can be characterized by $\theta_t \sim t^{-1/2}$ in agreement with the HD approach, whereas Seveno et al. [21] predicted that $\theta_t \sim t^{-1}$ when the contact-line dynamics follows the MKT model and this result has been validated by large scale molecular dynamics simulations. Besides, Vega et al. [22] have studied experimentally the capillary rise of viscous liquids round a poly(ethylene terephthalate) (PET) fiber and observed that $\theta_t \sim t^{-1}$ for low-viscosity liquids (in agreement with MKT) and $\theta_t \sim t^{-1/2}$ for high-viscosity liquids (in agreement with HD). These works suggest that, compared to flat geometry, it presents some advantages to use cylindrical fibers when the dissipation regimes have to be unambiguously distinguished.

Just as blending bulk polymers to obtain a desired physical property [23], addition of a second component to a liquid can help to tailor wetting properties [24,25]. Compared to one-component systems, the number of works related to two-component ones is rather limited despite their adjustability and versatility [26–28]. The root of this issue might be due to the fact that one faces some tough issues in this endeavor. For example, the mutual compatibility of two components has to be taken into account [29]. Besides, the simultaneous variation of surface tension and viscosity makes it difficult to distinguish the roles of these two factors for processes driven by wetting [30]. This indicates that the problem requires some clarification.

In the present work, we report on the spreading dynamics, from an infinite reservoir, of one- and two-component polymer liquids around a PET fiber. The primary aim is to explore the possible existence of the different dissipation mechanisms that may appear in two-component systems, and to provide insight into the role of short polymer chains in the wetting process. Two types of polydimethylsiloxane (PDMS) with viscosities of 5 mm²/s (PDMS5) and 500 mm²/s (PDMS500) were selected. First, according to the work of Vega et al. [22], PDMS500 and PDMS5 respectively follow the HD model and the MKT. Besides, the solubility parameter, ~14.9 MPa$^{1/2}$ [31,32], of PDMS liquids is nearly independent on viscosity or molecular weight, so that a mixture of these two liquids is thermodynamically compatible according to the Hildebrand-Scatchard equation [33]. Their compatibility is also supported by the experimental work of Fondecave and Brochard-

Wyart [34]. Additionally, the viscosity of the two-component PDMS systems can be tailored by their ratio, simultaneously maintaining a nearly constant surface tension. These characteristics offer a way to study the dissipation mechanisms of the liquids with various viscosities, and also open the door to a better understanding of the role of short polymer chains in two-component polymer systems.

2. Materials and methods

2.1. Materials

The fiber is a PET monofilament fiber with 0.8 mm diameter from Goodfellow. The polymer liquids are linear PDMS provided by Sigma-Aldrich Chemical Co. and used as received. The PDMS5 liquid, with short chains, has a number-average molecular weight of around 800 g/mol, and its counterpart, PDMS500, with long chains has a number-average molecular weight of around 17,300 g/mol. Both molecular weights are below the critical molecular weight for entanglement (Mc ≈ 29,000 g/mol) [31], for which reptation is expected [35]. Therefore, the polymer chains of the PDMS5 and PDMS500 liquids can be represented by Rouse chains without consideration of entanglement as well as disentanglement when short and long chains are combined.

The 2-component PDMS mixtures were prepared by magnetic stirring for more than 16 h with mass ratio (PDMS5/PDMS500) of 75%/25%, 70%/30%, 65%/35%, 60%/40%, 55%/45%, 50%/50% and 25%/75%. For the sake of brevity, the solutions with those ratios are referred to 75/25, 70/30, 65/35, 60/40, 55/45, 50/50 and 25/75 liquids. The mixtures were always used just prior to their mixing preparations, so these liquids were assumed to be homogenous. Surface tensions were measured by the pendant drop method using a Krüss drop-shape analyzer (DSA100) at 20 °C. Dynamic viscosities of all liquids, including the pure PDMS5 and PDMS500, were measured with a Brookfield DV-II + PRO digital viscometer at the same temperature. Kinematic viscosity (the ratio of the dynamic viscosity to the density of liquid) is also presented for comparison with the work of Vega et al. [22]. The surface tension and viscosity values are shown in Fig. 1. It indicates that surface tension values are nearly constant while the viscosity values increase dramatically with addition of PDMS500. Table S1 (Supplementary material) lists the capillary length of the liquids ($a = \sqrt{\gamma/\rho g}$, with γ the liquid-vapor surface tension, ρ the liquid density, and g the gravitational acceleration), the Bond number
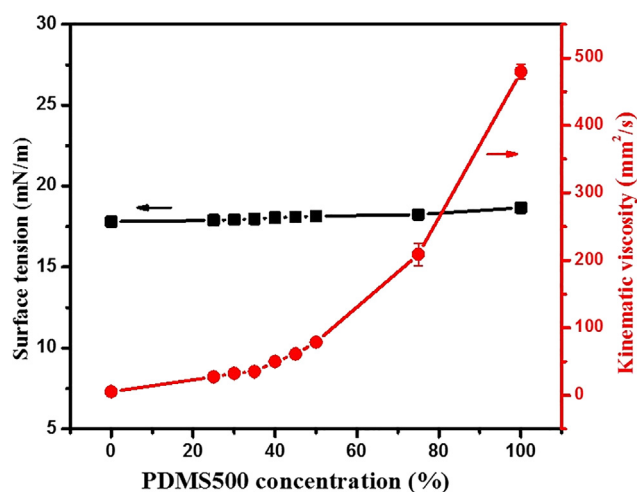

Fig. 1. Surface tensions and viscosities of the one- and two-component PDMS liquids versus PDMS500 concentration.