

<sup>1</sup>School of Engineering, University of Liverpool, Liverpool, L69 3GH, United Kingdom

<sup>2</sup>Schlumberger Gould Research, High Cross, Madingley Road, Cambridge, CB3 0EL, United Kingdom

<sup>3</sup>Department of Mechanical and Industrial Engineering, University of Massachusetts Amherst, 160 Governors Drive, Amherst, MA01003-2210, USA

✉corresponding author [robpoole@liv.ac.uk](mailto:robpoole@liv.ac.uk), +44 151 794 4806

We study the sliding of drops of constant-viscosity dilute elastic liquids (“Boger fluids”) on various surfaces caused by sudden surface inclination. For smooth or roughened hydrophilic surfaces, such as glass or acrylic, there is essentially no difference between these elastic liquids and a Newtonian comparator fluid (with identical shear viscosity, surface tension and static contact angle). In contrast for embossed PTFE superhydrophobic surfaces, profound differences are observed: the elastic drops slide at a significantly reduced rate and complex branch-like patterns are left on the surface by the drop’s wake including, on various scales, beads-on-a-string like phenomena. Microscopy images indicate that the strong viscoelastic effect is caused by stretching filaments of fluid from isolated islands, residing at pinning sites on the surface pillars, of order ~30 microns in size. On this scale, the local strain rates are sufficient to extend the polymer chains, locally increasing the extensional viscosity of the solution, retarding the drop and leaving behind striking branch-like structures on much larger scales. {164 words}

Superhydrophobic<sup>1</sup> surfaces have many potential technical applications ranging from “self-cleaning” surfaces<sup>2</sup> to low-friction external surfaces (e.g. for hydrodynamically efficient ship design) or “drag-reducing” internal flows to reduce pumping costs<sup>3</sup>. Taking inspiration from nature, such as from the lotus leaf<sup>1</sup>, such surfaces are manufactured by combining hydrophobicity with some form of structural topology or roughness<sup>4</sup>. Here we create such surfaces by “hot embossing” the negative of a fine wire structure (wire diameter and spacing ~ 30 μm) onto a hydrophobic PTFE surface (static contact angle  $\theta \sim 90^\circ$ ) to create superhydrophobic surfaces ( $\theta \sim 140\text{-}150^\circ$ ) as shown in Fig. 1(a). We shall refer to such surfaces as the “xPTFE” surface. Whilst exploring such surfaces in our laboratory we have chanced upon an interesting phenomena and the purpose of this letter is to explain this effect and demonstrate its potentially broad significance. As expected for water, and indeed other Newtonian fluids, such surfaces do not wet easily and a sufficiently large droplet (volume  $\mathcal{V} \sim 50\text{-}100 \mu\text{l}$ ) placed on the surface will readily slide off when the surface is slightly inclined (at angle  $\alpha$ )<sup>5</sup>. However we found that for a class of model constant-viscosity viscoelastic liquids, a so-called Boger fluid<sup>6,7</sup>, droplets of essentially identical properties (viscosity  $\eta$ , surface tension  $\sigma$ , density  $\rho$  and static

contact angle  $\theta$ ) slide at a much reduced rate. Moreover the drops leave behind complex branch-like structures (Fig. 1(a)-(d)) on the surface and striking “beads-on-a-string” morphology<sup>8</sup> often observed in capillary break-up experiments. What is most striking about observing such extravagant viscoelastic effects is that the relevant non-dimensional group – the so-called Weissenberg number  $Wi (= \lambda \dot{\gamma})$  which is a ratio of elastic to viscous stresses and equal to fluid relaxation time ( $\lambda$ ) multiplied by a shear rate ( $\dot{\gamma}$ ) – remains small for these drops when estimated based on a typical droplet velocity ( $U \sim O(\text{mm/s})$ ) and a length scale based on the droplet nominal diameter or the capillary length ( $\sim O(\text{mm})$ ). At the same  $Wi$  for example, for smooth hydrophilic surfaces such as glass or acrylic, we find essentially no difference between the motion of these elastic liquids and the Newtonian solvent at identical Capillary number ( $Ca = \eta U / \sigma$ ) and effective Bond number ( $Bo = g^{2/3} \rho g \cdot \sin \alpha / \sigma$  where  $g$  is the gravitational acceleration).

Although a number of studies have investigated the sliding<sup>9-11</sup> (or rolling<sup>5</sup>) of liquids drops on various surfaces, including on superhydrophobic surfaces<sup>5</sup>, no studies have previously investigated the sliding of viscoelastic drops on superhydrophobic surfaces. Following the Newtonian study of Le Grand et al<sup>10</sup>, who studied the shape and motion of millimetre-sized drops down an inclined plane for three different silicon oils on partially wetting surfaces ( $\theta \sim 50$  deg), Morita et al<sup>11</sup> conduct a similar investigation using two polymer solutions (a polystyrene of  $M_w = 280,000$  g/mol in acetophenone). In both studies<sup>10,11</sup>, the shape of the droplets were essentially identical being round at low Bond number with the development of more complex shapes including a so-called “corner” transition and then onto “cusps” and then “pearling” at higher droplet velocities (similar to shapes observed in dewetting<sup>12</sup>). A small difference was that Morita et al<sup>11</sup> showed the polymer solutions move *faster* at equivalent Capillary number (i.e. the *opposite* of what we observe here). However this may be a consequence of the shear-thinning nature of the solutions and the use of the zero shear rate viscosity in the estimation of the Capillary number.

Many studies<sup>13-15</sup> have shown that a superhydrophobic surface can be produced by creating roughness or patterned structures on polytetrafluoroethylene (PTFE) substrates. In this study we make use of a rather simple and inexpensive method to create superhydrophobicity on PTFE surfaces. The underlying idea is to use a very fine stainless steel mesh, the diameter and spacing of the mesh wire being approximately 30 microns, as a model and emboss this structure directly onto the PTFE sheet to create a regular topology of surface features. To do so, firstly the PTFE sheet was sanded by sandpaper<sup>14</sup> to soften the surface prior to the embossing process. Then the mesh was placed directly onto the PTFE sheet, sandwiched between two stainless steel plates of 12 mm thickness, before 10 G-clamps were applied to fasten together the plates and provide a high contact pressure and uniform embossing. The sample was heated in an oven at 350°C, slightly higher than the quoted melting point of PTFE (327°C), for 3 hours and then allowed to cool down

to room temperature over a period of about 8 hours. In this manner, superhydrophobic xPTFE sheets (maximum size of 15 cm by 15 cm) with regular brick-like micro-structure, as shown in Figure 1(a), could be uniformly and repeatedly created. Finally, scanning Electron Microscopy imaging was undertaken to confirm that the embossing process does not significantly change the PTFE structure on top of the pillars/bricks when compared to the native PTFE sheet (see e.g. images of smooth PTFE in Nilsson et al.<sup>14</sup>)

Aqueous polymer solutions with constant shear viscosity ( $\eta = 285$  mPa.s) yet exhibiting elasticity were prepared by adding 500 ppm (w/w) of a high-molecular-weight polymer (polyethylene oxide 'PEO' of  $M_w = 4 \times 10^6$  g/mol) to a more concentrated 45% (w/w) aqueous solution of the same polymer but of a much lower molecular weight (polyethylene glycol 'PEG'  $M_w = 8000$  g/mol)<sup>7</sup>. These fluids are specifically designed for use in free surface experiments as they are superior to more traditional Boger fluids made using sucrose or glycerine solutions (which can form a skin or absorb water from the atmosphere respectively). The Newtonian fluid comparator used is a 47% (w/w) aqueous solution of the low molecular weight PEG. In this way, as illustrated in Table I, we are able to essentially match all of the traditional fluid and contact angle characteristics between the two fluids (with the obvious exception of the relaxation time which is, by definition, zero in the Newtonian fluid). Thus, for the same droplet diameter and inclination angle we should expect identical Capillary and Bond numbers. The relaxation time is measured using a Capillary Break Up Extensional Rheometer<sup>16</sup> and estimated to be  $\lambda \sim 2.5 \pm 0.5$  s (similar to that measured in oscillatory shear<sup>7</sup>). The CaBER technique also allows the extensional viscosity to be estimated ( $\sim 10,000$  Pa.s) which gives a Trouton ratio  $\sim 3 \times 10^4$  (i.e. very similar to those observed in Oliveira and McKinley<sup>8</sup>).

The experimental set-up is quite simple. On the same surface, two droplets (one Newtonian and the other viscoelastic) of known volume (both  $\vartheta = 50$  and  $100 \mu\text{l}$  have been studied) are placed along a "horizontal" line separated by some distance, typically a few cm. The surface is then impulsively tilted to the desired angle and the droplet motion recorded using a camera (Nikon D5300). Typical images of how these droplets spread and then slide under gravity are shown in Fig. 2(a) multimedia view for glass ( $\theta \sim 30^\circ$ ) and for xPTFE ( $\theta \sim 145^\circ$ ) in Fig. 2(c) multimedia view. Each experiment is repeated at least three times and then the data post processed to determine the droplet velocity ( $U_N$  for the Newtonian drop and  $U_V$  for the viscoelastic) as shown in Figs. 2(b) and (d). For the partially wetting glass surface, the droplet spreads, flows slowly and leaves a wide thin film. Both the Newtonian and Boger fluid "drops" flow at the same speed (up to  $0.6$  mm/s at the highest inclination angle). If plotted as Ca versus Bo, all of the data sets collapse for this glass surface. For the xPTFE superhydrophobic surface, in marked contrast, the Boger fluid is slowed down significantly, sliding at a much slower rate ( $U_V/U_N \sim 0.17$  for  $\vartheta = 100 \mu\text{l}$  and  $U_V/U_N \sim 0.13$  for  $\vartheta = 50 \mu\text{l}$ ) as shown in Fig. 2. (c)-(d). Concomitantly, small ( $\sim 10$ - $100 \mu\text{m}$ ) branch-like structures are left on the surface (Fig.1(c)-(d) and Fig. 3(d))

coupled with beads-on-a-string like (more correctly “beads-on-a-tail” like) larger scale structures (~mm) as shown in a side view, in Fig. 3(b) and Fig. 3(c) (top-down view). We note that for the smaller drops on the xPTFE surface the droplet speeds are roughly comparable to those of the larger drops on the glass surface, where no effects of elasticity is observed. This suggests that a “global” Weissenberg number based on drop speed and a length scale based on either a typical droplet radius (~2-4 mm), or the capillary length (~2.2 mm) cannot fully explain such pronounced viscoelastic effects on the xPTFE surface as even though the Weissenberg number is order one on both the smooth and superhydrophobic surfaces, the dramatic viscoelastic effects are only observed for the superhydrophobic case. In order to gain mechanistic insight into the possible causes of such differences, we used light microscopy (Nikon Epiphot TME) to probe the branch-like structures (Fig. 1(c)-(d)) and, as is shown very clearly in fig. 3(a), filaments between droplets isolated on the pillars that form the microstructure, of order ~30 microns in size, remain. We therefore suggest that such filaments exist dynamically between wetted pillar tops and the main body of the sliding drop as the drop moves. We hypothesize that, on this scale, the local strain rates are sufficient to extend the polymer chains, locally increasing the extensional viscosity of the solution, retarding the drop and leaving behind striking branch-like structures. Results from Kumpfer and McCarthy<sup>16</sup> on similar superhydrophobic surfaces, but for water, have shown a similar physical mechanism for the production of water microdroplets at pinning sites on such surfaces which rapidly evaporate. In the current case, the high extensional viscosity of the Boger fluid causes these fluid islands to remain attached to the main drop via ligaments which provide a tensile resistive force to the drop thus significantly retarding its sliding speed. For the ligaments in Figure 3 to survive, the ligament break-up time,  $\tau_b \approx \eta_E d / \sigma$ , must be longer than the time required to reach the next island,  $\tau_c = w / U$ . Here  $w = 2d$  is the spacing between islands. As a result a minimum extensional viscosity of  $\eta_E > 2\sigma / U \approx 100$  Pa-s is needed to develop stable ligaments in these experiments: CaBER measurements estimate  $\eta_E$  to be two orders of magnitude larger than this minimum requirement for the Boger fluid used here. Assuming all the islands produce ligaments, a sliding resistance resulting from the fluid’s extensional viscosity can be approximated as  $F_{EV} = \eta_E \dot{\epsilon} A$  where  $\dot{\epsilon} \approx U / w$  is the extension rate in the ligament and  $A = \pi d^2 n / 4$  is the area of the islands connected to the drop through ligaments where  $n = D / 2w$  is the number of islands along the receding contact line of the drop. The force thus becomes  $F_{EV} = \pi U D \eta_E / 32 = (\pi \sigma D / 32) Tr Ca$  where  $Tr = \eta_E / \eta$  is the Trouton ratio. The resulting extensional forces is on the same order of magnitude of the gravitational force, resulting in an additional resistance force in addition to the capillary forces and shear stresses developed as the drops slide down the incline. The larger beads-on-tail morphology arises from the differential slowing of the drop, elongating the tail to form long strands which then undergo an instability similar to that observed in capillary break-up experiments<sup>8</sup>: such effects are most readily observed from viewing the embedded



movie files of the droplet motion (links provided in Fig. 2 multimedia view). Experiments on roughened hydrophilic surfaces (on both sanded acrylic, where the roughness is random, and hot-embossed acrylic where the surface topology is the same as the xPTFE surface), not shown for conciseness, exhibit results identical to the smooth glass surface indicating that roughness alone is insufficient to create this mechanism but that the combination of hydrophobicity with surface topology, i.e. the hallmark of superhydrophobic surfaces, are both required to observe such striking phenomena.

Our results indicate that elastic fluids, even those judged only weakly elastic on a macroscopic scale as measured in a conventional rheometer for example, may exhibit significant elastic effects on superhydrophobic surfaces due to the pinning of microdroplets and correspondingly large strain rates reached. In addition to the interesting pattern formations observed here, these results may have significant technological applications as many practical coating flows fluids are viscoelastic, as are many biological liquids. {1949 words}

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**Table I:** Fluid properties {70 WORDS}

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Fluid	Shear Viscosity (mPa.s)	Surface tension (mN/m)	Fluid density (kg/m <sup>3</sup> )	Static contact angle glass {xPTFE} (°)	CaBER relaxation time (s)
PEG (Newt)	285±2	53.3	1082	29±2.0 {146±4.0}	-
PEG/PEO (Boger)	285±5	53.3 <sup>^</sup>	1080	31±2.0 {145±4.0}	2.5±0.5

<sup>^</sup>assumed same as solvent

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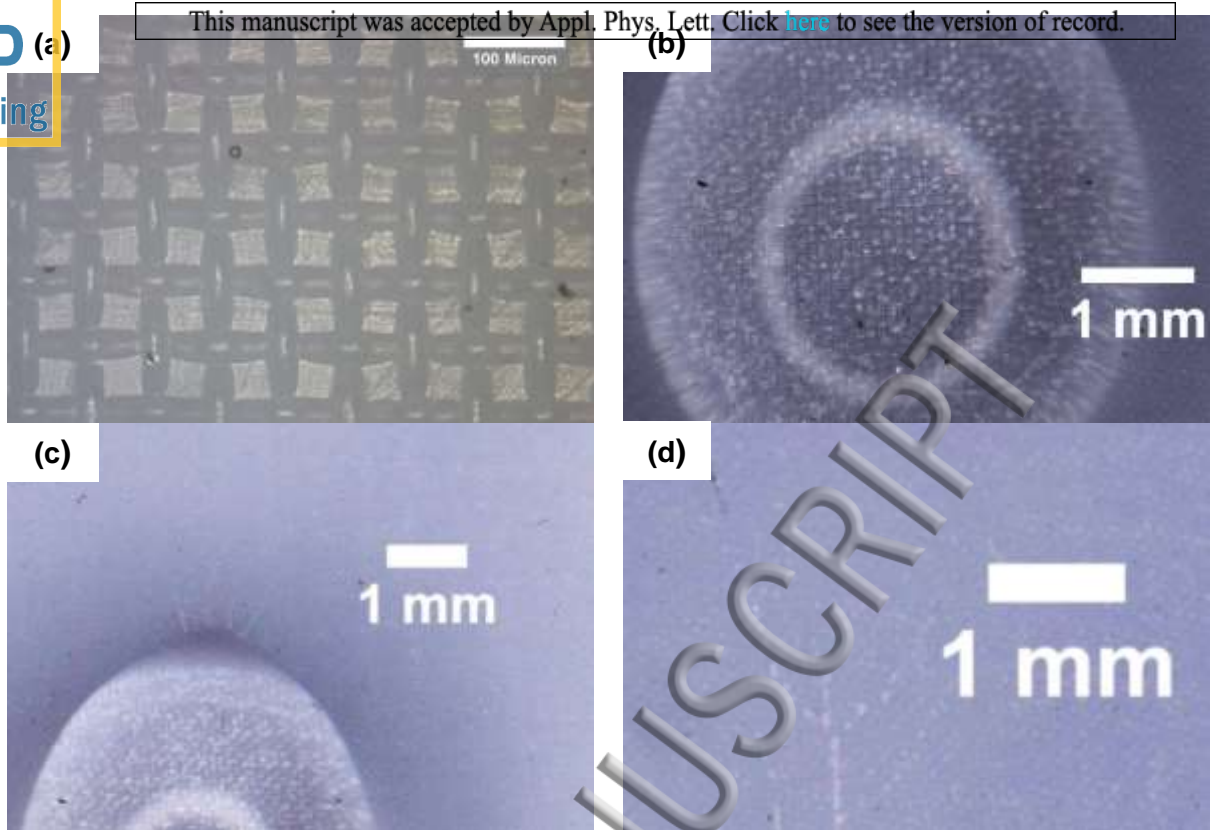


FIG 1. (a) Newly made xPTFE surface; (b) Static drop of elastic fluid on same surface clearly highlighting surface features; (c) Drop motion initiation (d) Zoomed view showing development of “branch-like” structure left in wake of drop {SINGLE COLUMN = 250 WORDS}

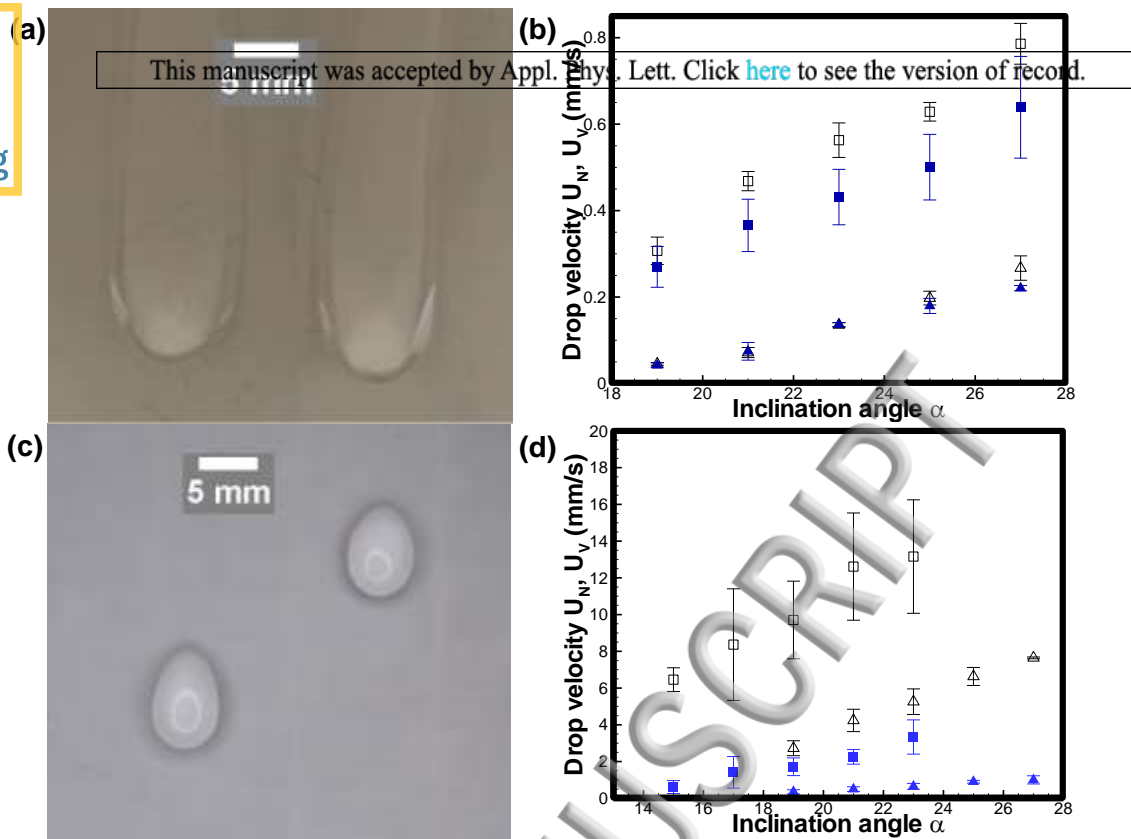


FIG 2. Sliding drops on glass surfaces (a) left hand side Newtonian; right hand side Boger fluid (multimedia view) (b) Drop velocity versus inclination, Newtonian ( $U_N$ ) drops (open symbols), Boger ( $U_V$ ) (closed symbols)  $\Delta$  50  $\mu\text{l}$ ,  $\square$  100  $\mu\text{l}$ ; (c) Sliding drops on xPTFE surfaces image left hand side Newtonian; right hand side Boger fluid (multimedia view), (d) Drop velocity versus inclination symbols same as (b). {SINGLE COLUMN = 230 WORDS}

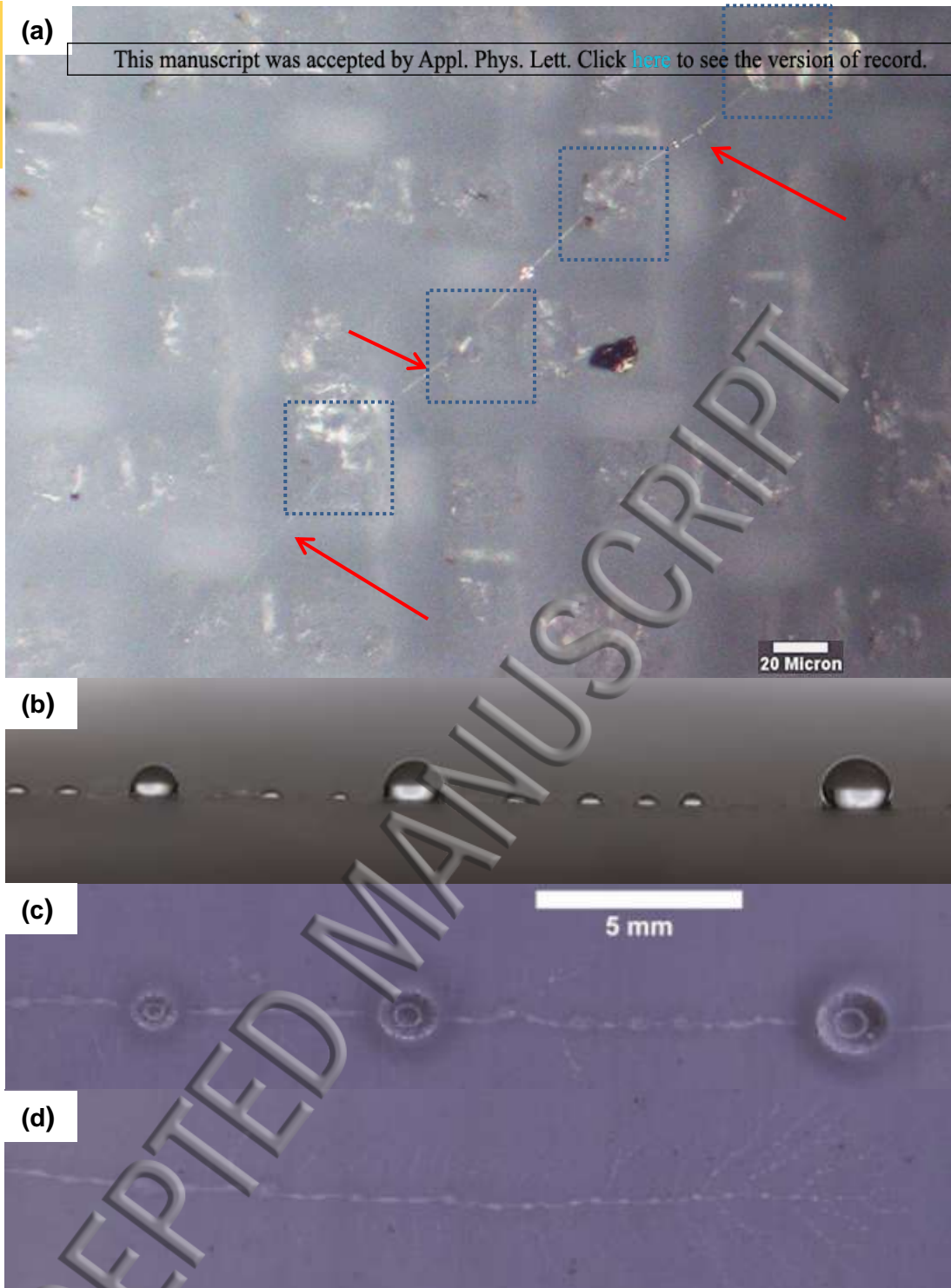
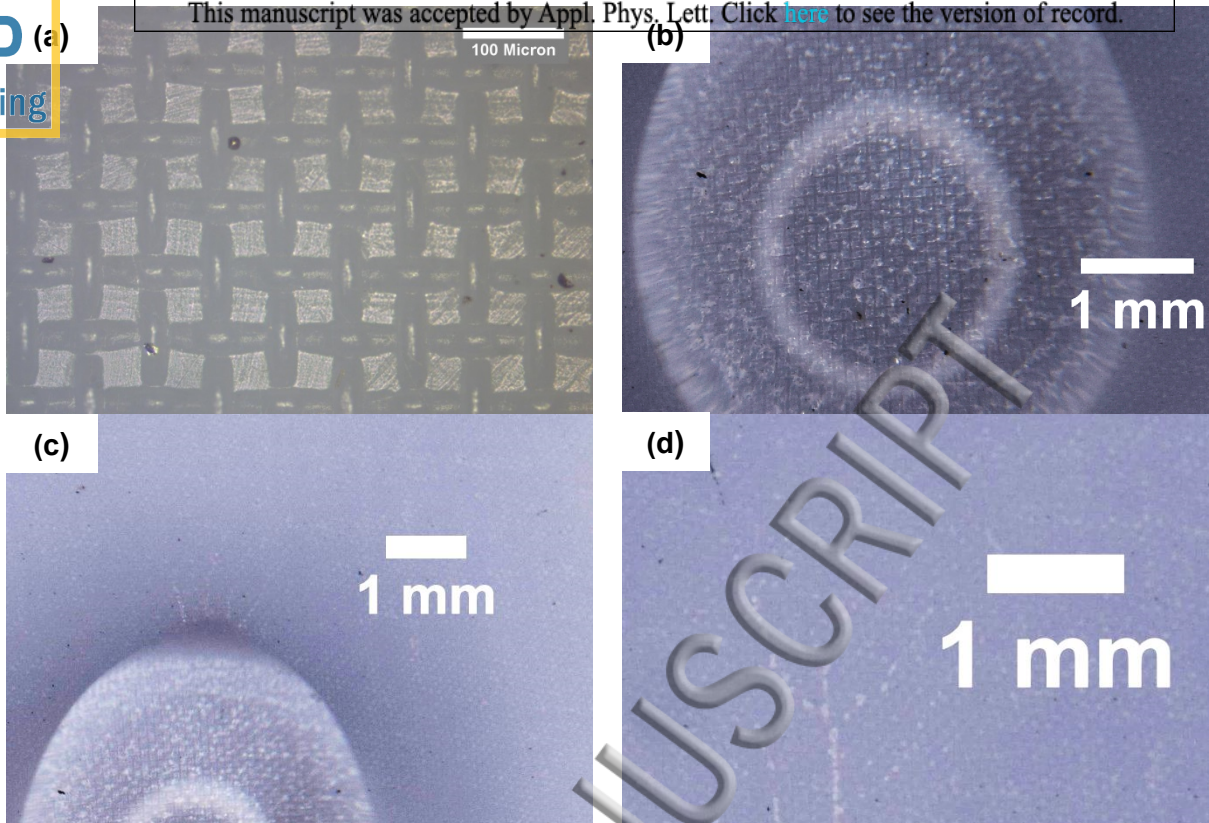
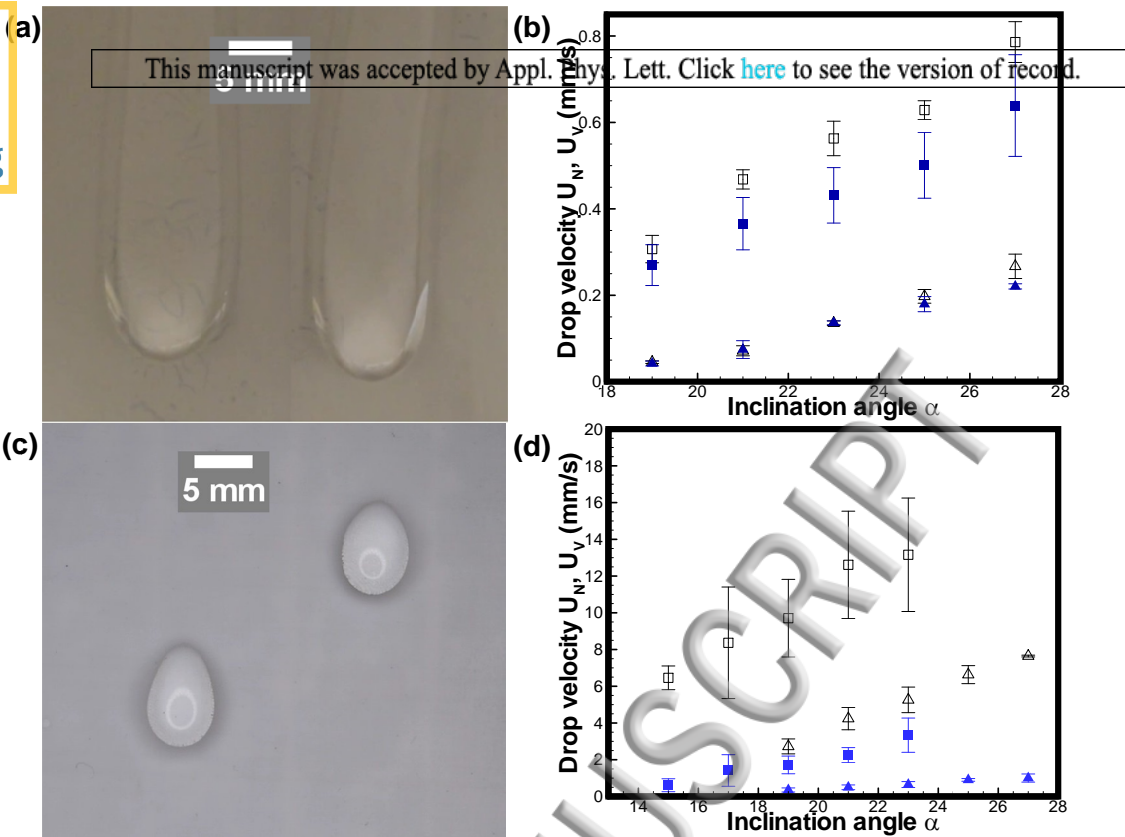


FIG 3. (a) Branch structure left on the xPTFE (400x magnification) illustrating islands of elastic fluid marooned on pillars of structure (highlighted by dotted lines) connected by very thin ( $\sim 1$  micron) fluid bridges indicated by arrows. Note “beads-on-a-string” phenomenology often observed in capillary break-up experiments. (b)–(d) Beads on a string morphology at “drop” scales (all images at same scale, drop has slid right to left). Side (b) and top view (c) of the same experiment whereas (d) indicates branch-like structures left behind from initial position of drop. {DOUBLE COLUMN = 880 WORDS}



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(a)

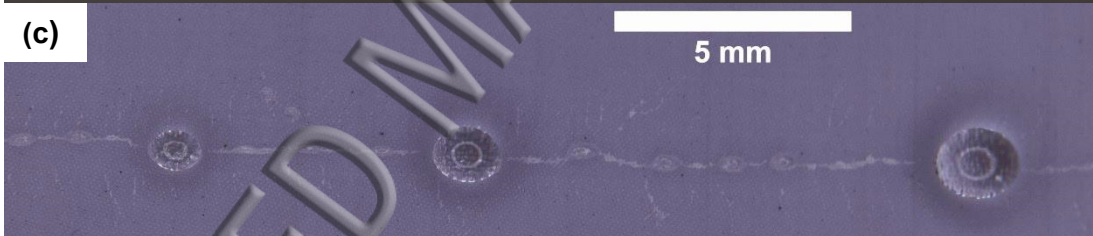
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(b)



(c)



(d)



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