

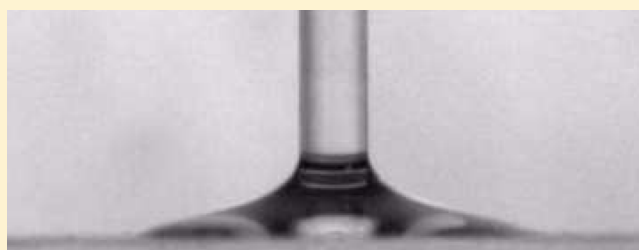
# Origin of Contact Line Forces during the Retraction of Dilute Polymer Solution Drops

M. I. Smith\* and J. S. Sharp

School of Physics and Astronomy and Nottingham Nanotechnology and Nanoscience Centre, University of Nottingham, University Park, Nottingham NG7 2RD, U.K.

## Supporting Information

**ABSTRACT:** The forced dewetting of water and dilute poly(ethylene oxide) solution (PEO) drops is investigated for syringe-driven flow. Comparisons are made with the free dewetting observed during drop impact. We provide strong evidence that during droplet retraction, polymer deposited on the substrate results in a velocity-dependent force at the contact line. These findings are in stark contrast to previous studies which attributed dissipation to bulk viscoelastic effects or normal stress effects at the contact line.



## INTRODUCTION

Control of the wetting of liquid drops is an important consideration in a number of technological applications including contact dispensing,<sup>1</sup> inkjet printing,<sup>2</sup> spray cooling,<sup>3</sup> and the application of agrochemicals.<sup>3,4</sup> The deposition of drops during these processes involves a rapidly moving contact line, often initiated by a drop impacting a surface. A number of strategies have been investigated to provide the necessary control, including altering the surface wettability,<sup>5</sup> electro-wetting deposition,<sup>6</sup> or liquid bridge breakup.<sup>1</sup> While the drop impact dynamics of simple fluids have been extensively studied,<sup>5</sup> there is increasing research effort to understand the influence of additives such as nanoparticles, surfactants, and polymers.<sup>4,7,8</sup> These additives can influence the dynamic wetting and dewetting of droplets via a variety of mechanisms such as pinning of the contact line,<sup>7</sup> dynamic surface tension effects,<sup>8</sup> or simply altering the physical properties (such as the shear viscosity) of the droplet.

One dramatic example of the effects of additives occurs when an  $\sim 100 \mu\text{g mL}^{-1}$  high- $M_w$  polymer, such as poly(ethylene oxide) (PEO), is added to water. If a water drop impacts a hydrophobic surface, it expands to form a flat disc ( $V_{\text{spread}} \approx 1000 \text{ mm s}^{-1}$ ) before contracting under the action of surface tension ( $V_{\text{retraction}} \approx 200 \text{ mm s}^{-1}$ ). If insufficient viscous dissipation has occurred, then the drop will rebound from the surface. Drops containing long polymer chains also spread rapidly but then retract an order of magnitude more slowly ( $V_{\text{retraction}} \approx 20 \text{ mm s}^{-1}$ ). A PEO solution drop is therefore much less likely to rebound from a surface.

Initially, the energy dissipation mechanism in impacting dilute polymer solution drops was thought to be caused by a transient increase in the extensional viscosity. It was believed that velocity gradients, generated in the fluid, stretched the polymer chains, leading to increased energy dissipation and slow retraction.<sup>4</sup> However, it has recently been shown that the

slowing of the retracting fluid is dominated by the properties of the contact line rather than bulk flow.<sup>3,9–11</sup>

Other studies have considered the role of the substrate during the retraction of drops of dilute polymer solutions. Drops impacting small targets and drops impacting hot surfaces (such that a Leidenfrost layer developed between the drop and surface) were shown to rebound and not to exhibit the reduced retraction velocities observed for the same drops on solid surfaces.<sup>12,13</sup> However, the significance of these results must be carefully interpreted since by removing the surface, the flows inside the drop may also have been altered. Bartolo et al.<sup>3</sup> have suggested that the antirebound effect relies upon the no-slip boundary condition provided by the substrate in order to generate a shear flow in the vicinity of the contact line. They argue that the resultant velocity gradient generates normal stresses in the polymer solution which leads to enhanced energy dissipation. These authors obtained indirect evidence which suggested that polymer deposition was not the origin of the phenomenon by observing the impact dynamics of water drops on substrates which had been previously dipped into dilute polymer solutions. The role of the surface was therefore believed to be the generation of a shear flow at the contact line of the drop and not a direct interaction with adsorbed polymer chains. However, more recently the biopolymer  $\lambda$ -DNA was observed to suppress drop rebound weakly. These polymer chains were observed to stretch at the retreating contact line and were deposited on the substrate in a stretched conformation.<sup>9</sup> This suggests that an interaction between substrate and polymer chains does exist and that it may play an important role in the antirebound effect. The confusion over the role of the surface generated by these contradictory

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results<sup>3,9,10</sup> requires additional consideration and is the focus of this article. However, the wider issues of dynamic wetting in additive-containing droplets addressed by this study are likely to be of broader interest.

## MATERIALS AND METHODS

To investigate the role of the substrate in the antirebound phenomenon, we simulated drop impact using a syringe pump. A glass capillary was placed close to a hydrophobic surface, and 0.5 mL of fluid was dispensed. Upon reaching the maximum dispensed volume, the direction of pumping was reversed, sucking the drop back into the capillary. This results in a maximum retreating contact line velocity which is comparable to that observed during drop impact experiments of dilute polymer solutions ( $V_{\max} \approx 16 \text{ mm s}^{-1}$ ).

A series of measurements were performed in which the drops were spread on the surface using a flow rate of  $485 \mu\text{L s}^{-1}$  and then retracted at constant flow rates of 485, 345, 165, 55, 21, and  $6 \mu\text{L s}^{-1}$ . The radial symmetry of the drops means that a constant volume flow rate resulted in a contact line velocity that varies with the radius. Movies of the expansion and retraction of each drop were captured using a Dalsa Genie HC640 equipped with a  $10\times$  Macro lens at frame rates varying from 5 to 200 fps. The macroscopic contact angles and diameter of the drops in each frame were then measured using image-processing software written in Matlab (see Supporting Information 1).

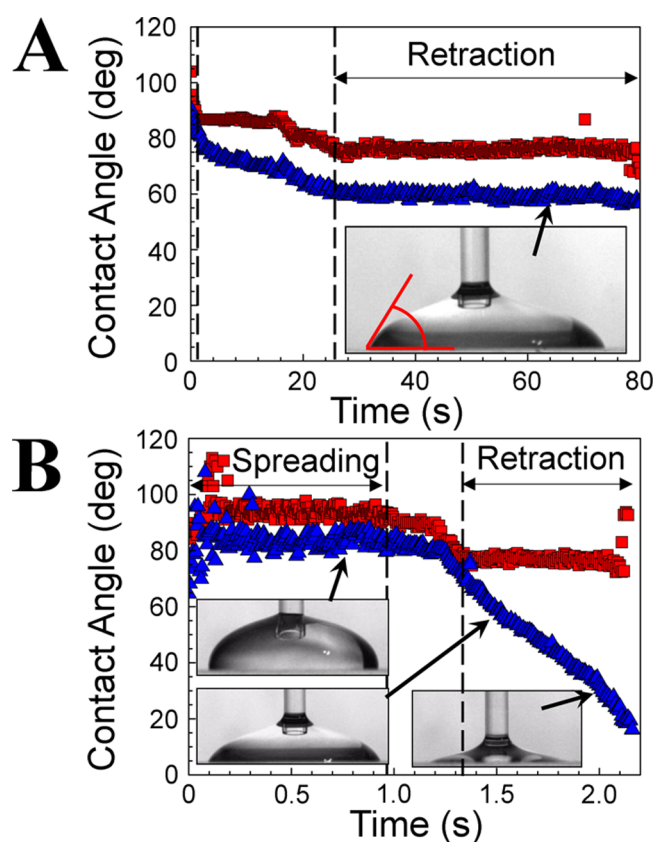
The experiments were performed with solutions of pure water and  $200 \mu\text{g mL}^{-1}$  PEO ( $M_w \approx 4 \times 10^6$ , Sigma) dissolved in deionized water. The surface tension of water drops and the PEO solution drops was measured using the pendant drop technique<sup>14</sup> and found to be  $72 \pm 2$  and  $64 \pm 3 \text{ mN m}^{-1}$ , respectively, consistent with literature values.<sup>3,12,13</sup> Drop retraction experiments were performed on glass slides spin coated with a 120-nm-thick polystyrene (PS) film. The rms roughness of a spin-cast PS film was measured to be  $\sim 1 \pm 0.4 \text{ nm}$  over a  $20 \mu\text{m}^2$  area using atomic force microscopy.

Drop impact experiments were also performed with the same solutions and surfaces. Droplets were formed at the end of a blunt 21G hypodermic needle and dropped onto a PS surface from a height of 12 cm. The dynamics were filmed with an Optronics CL 600  $\times 2$  high-speed camera at 500 fps.

## RESULTS AND DISCUSSION

Drop impact studies and syringe-driven flows have important differences, but they both exhibit the same key features of interest to this study, namely, a retreating contact line moving across a hydrophobic surface at comparable velocities (for PEO solution drops). The use of syringe-driven drop retraction also provides two big advantages. First, the motion of the retreating contact line can be carefully controlled. This enables slow retraction velocities to be investigated, which are experimentally inaccessible in drop impact experiments. Second, oscillations of the bulk drop shape (which can obscure some of the details of the contact line motion in drop impact<sup>9</sup>) are not present in a syringe-driven drop retraction. In this article, we elucidate some of the key aspects of the dewetting of dilute polymer drops using syringe-driven flows before confirming the applicability of these results to droplet impact phenomena.

Figure 1A shows example plots for a water drop ( $\square$ ) in which the fluid is retracted at the slowest flow rate of  $6 \mu\text{L s}^{-1}$ . On the time scale of these experiments, evaporation is negligible ( $0.004 \mu\text{L s}^{-1}$ ) and therefore not expected to play a significant role. A similar plot is shown for the maximum flow rate of  $485 \mu\text{L s}^{-1}$  in Figure 1B. PS is hydrophobic with equilibrium contact angles for water and  $200 \mu\text{g mL}^{-1}$  PEO of  $\theta_{\text{eq}} \approx 87 \pm 3$  and  $\sim 76 \pm 3^\circ$  respectively. During the spreading of water drops, we observed an approximately constant advancing contact angle ( $\theta_{\text{A}} \approx 97 \pm 3^\circ$ ). Upon reaching the maximum radius, the pump flow direction is reversed (left-hand

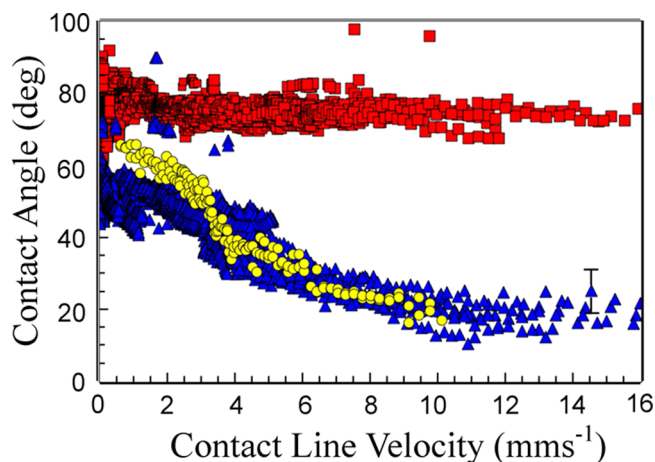


**Figure 1.** Syringe-driven flows of water and PEO solution drops. Contact angle measurements for spreading at  $485 \mu\text{L s}^{-1}$  and the retraction of drops of water ( $\square$ ) and  $200 \mu\text{g mL}^{-1}$  PEO ( $\Delta$ ). The retraction flow rate is (A) 6 and (B)  $485 \mu\text{L s}^{-1}$ .

dashed line in Figure 1A). Initially, the contact line remains static with a steadily decreasing contact angle. At a receding contact angle ( $\theta_{\text{R}} \approx 76 \pm 2^\circ$ ), the contact line begins to move (right-hand dashed line in Figure 1A). In the case of water, this contact angle  $\theta_{\text{R}}$  is found to vary by approximately  $6^\circ$  over the velocity range studied here (Figure 2).<sup>15,16</sup> However, the uncertainties associated with the determination of the contact angles are comparable to the observed changes (see experimental scatter in Figures 1 and 2).

The macroscopic advancing and receding contact angles of PEO solution drops ( $\Delta$ ) were found to be lower than for water drops. This is due to the different balance of interfacial energies associated with the drops. At the lowest flow rate ( $6 \mu\text{L s}^{-1}$ ) we observe strong qualitative similarities between the behavior of water and PEO solutions (Figure 1A). Upon reaching the maximum radius, the drop contact angle slowly decreases following a change in the flow direction. At a critical contact angle, the contact line begins to move and the contact angle is only weakly dependent upon velocity (see movie S1 (la5005159\_si\_002.avi)).

At the maximum flow rate ( $485 \mu\text{L s}^{-1}$ ), the onset of retraction in the PEO solution drop occurs at approximately the same contact angle of  $\sim 63^\circ$  observed for slower retraction velocities (Figure 1B). However, from this point onward the behavior of drops containing PEO deviates significantly from that of the corresponding water drop. Once the drop edge has begun to move, the contact angle rapidly decreases as the velocity of the contact line increases (see movie S2 (la5005159\_si\_003.avi)).



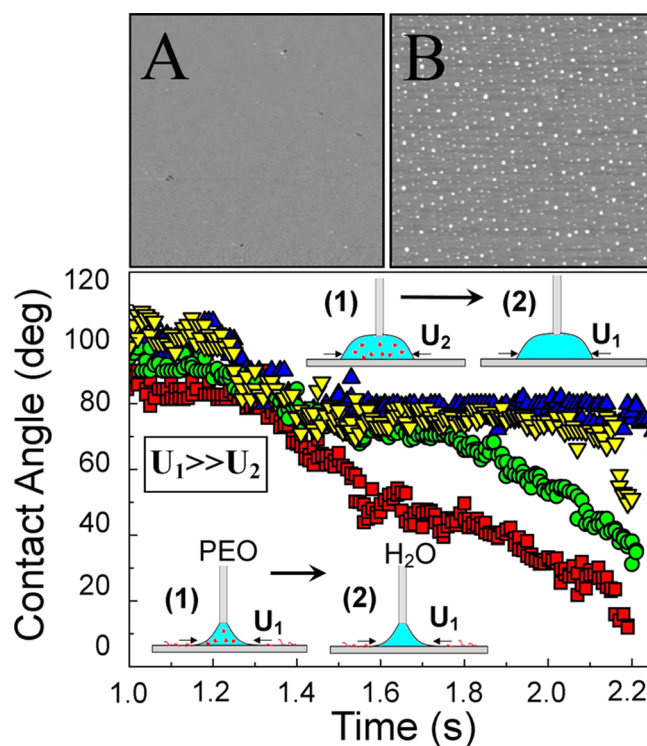
**Figure 2.** Contact-angle dependence on contact line velocity. The contact angle during the retraction phase of drops of water ( $\square$ ) and  $200 \mu\text{g mL}^{-1}$  PEO solution ( $\Delta$ ) on a polystyrene surface. The changes in the PEO solution drops' contact angle indicates a resistive force that increases with velocity. Also shown is data for a two-stage experiment. Droplets of water were retracted on a surface upon which a PEO drop had previously been retracted ( $\circ$ ).

For a simple water drop, the retracting contact line begins to move once  $\theta(t) \approx \theta_R$ . Any initial resistance to contact line motions arises due to surface roughness and heterogeneity.<sup>17,18</sup> Further decreases in contact angle  $\theta(t) < \theta_R$  originate from additional forces ( $f$ ) acting per unit length along the contact line, where<sup>19</sup>

$$f = \gamma_{LV}(\cos \theta(t) - \cos \theta_R) \quad (1)$$

Although strictly valid only at equilibrium, the above equation is approximately correct since the retraction rate is slow enough for inertial effects to be neglected. Figure 2 shows a plot of the contact angle against contact line velocity during the retraction phase for all of the data collected. The contact angle for pure water drops (squares) is found to be largely independent of velocity. However, for drops of PEO solution (triangles) the contact angle decreases with increasing contact line velocity, indicating the presence of a velocity-dependent force which resists the motion of the contact line. Equation 1 provides an estimate that the additional contact line force per unit length for PEO solution drops, retracting at  $16 \text{ mm s}^{-1}$  is  $\sim 33 \text{ mN m}^{-1}$  (see Supporting Information).

To determine whether the altered contact line dynamics in PEO solution drops are caused by the interaction of the fluid and adsorbed polymer chains, we performed a series of experiments that were designed to isolate the effects of surface-adsorbed polymer molecules. In the first instance, we performed tapping-mode atomic force microscopy (AFM) measurements on polystyrene (PS) films following the spreading and retraction of PEO drops to determine whether PEO is actually deposited at a surface by a retreating contact line (details in Supporting Information 4). Figure 3 shows  $10 \times 10 \mu\text{m}^2$  AFM phase images for samples prepared using retraction rates of 6 and  $485 \mu\text{L s}^{-1}$ . At the slow retraction rate, no structure is observed. However, at the fast retraction rate, long, closely spaced chainlike structures were observed which were aligned ( $\pm 20^\circ$ ) with the radial direction corresponding to the drop center. These structures are reminiscent of those observed previously for DNA chains.<sup>9</sup>



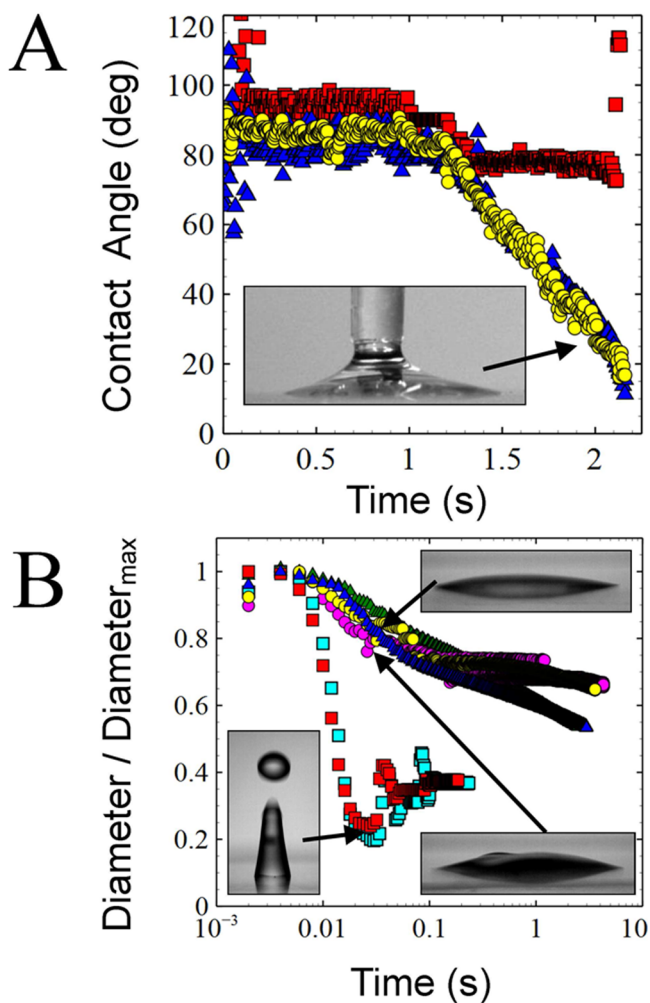
**Figure 3.** Deposition of polymer during contact line retraction. (Top) AFM phase images ( $10 \times 10 \mu\text{m}^2$ ) were taken after a  $200 \mu\text{g mL}^{-1}$  PEO drop was spread and then retracted at flow rates of (A) 6 and (B)  $485 \mu\text{L s}^{-1}$ . (Bottom) Two-stage experiment. Stage 1: drops of  $200 \mu\text{g mL}^{-1}$  PEO were spread and retracted at different flow rates. Stage 2: pure water drops were spread and retracted at a flow rate of  $485 \mu\text{L s}^{-1}$  at the same location. The figure shows the contact angles during the retraction of these water drops. The PEO drops used to prepare the surfaces were retracted at flow rates of  $485 \mu\text{L s}^{-1}$  ( $\square$ ),  $278 \mu\text{L s}^{-1}$  ( $\circ$ ),  $56 \mu\text{L s}^{-1}$  ( $\nabla$ ), and  $6 \mu\text{L s}^{-1}$  ( $\Delta$ ). The difference in behavior is indicative of different amounts of polymer being deposited at the interface.

To determine the role of the deposited PEO, we then performed a two-stage experiment. Stage one: drops of  $200 \mu\text{g mL}^{-1}$  PEO were spread at  $485 \mu\text{L s}^{-1}$  and then retracted at flow rates of 485, 278, 56, and  $6 \mu\text{L s}^{-1}$  on glass slides coated with PS films. The capillary was positioned above a cross marked on the reverse side of the slide to enable the location of drop deposition to be easily determined. Following this, the substrates were rinsed thoroughly with deionized water and dried with  $\text{N}_2(\text{g})$ . Stage 2: a capillary of pure water was then positioned above the mark on the same glass slide, and an experiment was performed in which both spreading and retraction occurred at the maximum flow rate of  $485 \mu\text{L s}^{-1}$ .

Figure 3 shows the retraction dynamics for water drops in the two-stage experiment. When the substrates were prepared with a PEO solution drop that had been retracted slowly, the behavior of the water drops in stage 2 was very similar to that of a water drop spreading on a clean PS surface. However, when the substrate was prepared with a PEO solution drop retracted at high speed, the subsequent retraction dynamics of the water drop resembled those of a drop containing PEO. This may explain why dipping substrates in PEO solutions, performed in a previous study,<sup>3</sup> did not alter the subsequent water droplet dynamics. Regardless, this simple observation provides extremely strong evidence that the deposition of polymer chains on a surface has a significant effect on the contact line dynamics in retracting liquid droplets. This is the

case even when there is no polymer dissolved in the bulk of the drops.

From these combined experiments it is clear that the interaction between the droplet and the polymer deposited on the surface is the dominant energy dissipation mechanism during the retraction of PEO solution drops. Figure 4a shows a



**Figure 4.** Role of predeposited polymer in dissipation at the contact line. (A) Comparison of the contact line dynamics for syringe-driven flows. Three types of droplets are shown spreading and retracting at  $485 \mu\text{L s}^{-1}$ . A water drop on a PS surface ( $\square$ ), a  $200 \mu\text{g mL}^{-1}$  PEO drop on a PS surface ( $\Delta$ ), and a two-stage experiment in which the data shows a water drop retracting on a PS surface upon which a PEO drop had been previously spread and retracted ( $\circ$ ). (B) Comparison of the dynamics for the same three types of experiments performed using drop impact.

comparison of the dynamics observed for three different droplet experiments all retracted at a flow rate of  $485 \mu\text{L s}^{-1}$ . A comparison of the plots for the PEO solution drop on fresh PS surfaces and that of a water drop in the two-stage experiment shows that the retraction dynamics are indistinguishable in these two cases within the limits of experimental uncertainty. Figure 2 also shows the equivalent contact angle against velocity data to be very similar. This provides strong evidence that polymer adsorbed to the surface can modify the contact line dynamics of a water droplet in the same way as is observed in droplets containing PEO.

One possible objection to the above is that the polymer might redissolve in the fluid during spreading, influencing the rheology of the fluid. Two lines of evidence rule out this possibility. First, estimates based upon the AFM images show that if all of the polymer on the surface and in contact with the base of the water drops were to redissolve in the fluid then the hypothetical polymer concentration would not exceed  $\sim 0.25 \mu\text{g mL}^{-1}$  (See Supporting Information 6). This excludes any potential fluid rheology effects as a possible mechanism because such low concentrations would be expected to have little or no effect on droplet dynamics.<sup>9</sup> Furthermore, when these experiments were performed the surfaces were rinsed with water following PEO drop retraction and prior to the water drop measurement, thus ensuring that any polymer that could potentially redissolve had been removed from the surface.

Having established the origin of the dissipative forces at the contact line of retreating PEO drops, we now show that such results are also applicable to droplet impact phenomena. First, we confirmed that polymer is deposited at the surface following PEO drop impact using AFM (Figure S1). Second, a series of experiments, analogous to those conducted with the syringe pump, were conducted. Three types of drop impact experiments were performed. Upon impact on clean PS surfaces, water drops ( $\square$ ) were observed to spread and retract rapidly ( $\sim 10$  ms), resulting in a partial rebound from the surface in which approximately half of the droplet was ejected. In contrast, the impact of a  $200 \mu\text{g mL}^{-1}$  PEO drop ( $\Delta$ ) resulted in a retraction that was  $\sim 2$  orders of magnitude slower (see Figure 4b). In the final drop impact experiment, a single drop of PEO was allowed to impinge and retract on a clean PS surface. The surface was then rinsed thoroughly with deionized water and dried. A droplet of pure water was then deposited on exactly the same spot that the PEO drop had been previously deposited ( $\circ$ ). Movie S3 (la5005159\_si\_004.avi) shows an example of each type of experiment (the spreading and retraction dynamics are also plotted in Figure 4b). It is clear that the dynamics of the water droplet, dropped onto a surface pretreated with a PEO drop, is very similar to that of a PEO drop on a clean PS surface, i.e., the rebound effect observed for pure water on clean PS is suppressed by depositing a PEO drop first. This verifies that the forced dewetting experiments can be used to probe the physics of drop retraction of polymer-loaded drops under conditions that are comparable to those observed in drop impact studies.

## CONCLUSIONS

Forced dewetting of droplets using a syringe pump was used to probe the origin of contact line forces during the retraction of PEO drops. It was shown that the force at the contact line increases with increasing retraction velocity. This force was shown to be correlated with the deposition of polymer chains at the surface. A novel two-stage experiment in which pure water droplets were retracted on the same spot that a PEO droplet had previously been retracted was then performed. These water droplets displayed quantitatively similar dynamics to the PEO drops, suggesting that the dissipation arising at the contact line can be explained in terms of polymer deposited at an interface by the retreating contact line rather than in terms of the fluid rheology. Finally, using drop impact experiments we were able to confirm that our results are more generally applicable and provide a key insight into the mechanism responsible for the well-known antirebound effect observed in drops of dilute polymer solution.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Three movies: Spreading and retraction of 200  $\mu\text{g mL}^{-1}$  PEO droplets at low and high speed. A side-by-side comparison of the droplet impact of a water drop, a 200  $\mu\text{g mL}^{-1}$  PEO drop, and a two-stage experiment (details described in the main text). One pdf: contains additional details of methods, supporting calculations, and an AFM image of polymer left behind on the surface after a PEO drop impact experiment. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [mike.i.smith@nottingham.ac.uk](mailto:mike.i.smith@nottingham.ac.uk)

### Notes

The authors declare no competing financial interest.

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