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ABSTRACT

In pesticide and fertilizer applications, retention of spray droplets after they reach the target surface can be limited by droplets splashing, rebounding, or rolling off of the surface. In this study, a novel approach is presented for quantifying the retention efficiency. This approach enables testing of the influence of polymer additives for enhancing the retention efficiency of both real and model agricultural sprays. The results demonstrate that increasing the extensional rheology of the spray solution can increase the retention efficiency by up to 20% and in some cases achieve a total efficiency greater than 95%. The results are consistent on both synthetic surfaces and plant surfaces and suggest that for a particular polymer and surface, the extensional relaxation time alone is sufficient to predict the retention efficiency.

Published under license by AIP Publishing. https://doi.org/10.1063/5.0038391

I. INTRODUCTION

The use of agrochemicals such as pesticides and fertilizers has contributed much to improving the output and quality of agricultural crops.[1] Agrochemicals are typically dissolved in aqueous solution and delivered by spray nozzle systems on tractors or airplanes, and in the process, substantial amounts of the product may be lost to the surrounding environment. This leads to overuse of agrochemicals to achieve target levels in plants and, in turn, leads to environmental pollution and economic losses.[2] Therefore, there is a need to enhance the efficiency of agricultural spraying processes.

There are four steps where losses may occur after the atomized droplets are released from nozzles: deposition, retention, uptake, and translocation.[3] Deposition refers to the process by which droplets come into contact with the target surface, and once there, retention means that the droplets remain on the surface (rather than rolling off, for example). These first two processes depend mostly on the mechanics of the spray generation and the physicochemical properties of the spray solution and target surface, while the latter two (uptake and translocation) are more dependent on plant biology and are beyond the scope of this manuscript.

During the deposition process, studies have focused on eliminating spray drift, which is defined as the transfer of small spray droplets out of the target areas due to wind and air currents.[4–8] To prevent spray drift, a common strategy is to use nozzles that generate larger droplet sizes that are less influenced by wind.[9,10] However, larger droplets also have higher kinetic energy that may result in droplet splashing or rebound from the target surface, leading to low *retention* efficiency.[11] Unfortunately, so far it has not been possible to generate an "optimal" droplet size that is large enough to avoid drift and small enough to avoid splashing and bouncing under generalized conditions.

More and more studies are focusing on enhancing the retention of larger droplets since the use of spray nozzles that generate large droplet sizes is one of the easiest ways to reduce deposition losses during spray delivery. Adding surfactant to the spray formulation has been proposed to enhance retention by decreasing the surface tension of the spray solution and thus improving wetting.[12–16] However, splashing is more likely to occur with lower surface tension because the threshold energy required for splashing is lowered during the "radial expansion stage" of droplet impact with the surface.[17,18] Furthermore, the dynamic evolution of the surface tension becomes very important because surfactant molecules must diffuse from the bulk solution to the newly formed interfaces in a relatively short period of time after leaving the surface until landing on the plant.[19,20] It has been shown that the timescale for surfactant diffusion is often longer than the droplet contact time with the impacting surface, suggesting a limitation to the use of surfactants for increasing retention.[21,22]

Additionally, Bergeron *et al.* pointed out that adding long-chain polymers such as polyethylene oxide (PEO) can modify the rheology of the solution in a way that has been demonstrated to reduce splashing and rebound of a single droplet from a solid surface.[23] Nevertheless, to the authors' knowledge, the efficacy of this type of rheology modifier has not been demonstrated or quantified under realistic spray conditions. Other more novel approaches have also been recently proposed such as using oppositely charged polyelectrolytes or nanoparticle dispersions,[24,25] but consideration of these is beyond the scope of this manuscript.

It is clear that further understanding of the mechanisms that govern retention efficiency is needed, and various methods have been used to assess this. The majority of methods employed may be categorized either as field tests or fundamental studies. The former directly measure the benefits in application but do not provide fundamental insight.[10,26,27] The latter offer tremendous insight into the governing physics by employing highly simplified conditions in the lab (single droplets, purified solutions, etc.) but may ignore important factors that occur in the field (such as realistic droplet sizes and droplet–droplet interactions) and thus yield minimal guidance for optimizing agrochemical applications.[28–33] Therefore, there is a gap in methodology between field tests and fundamentally focused studies in the lab, and a new approach is needed that provides a link between the two.

The present work aims to fill this gap by developing a spray apparatus that can examine the retention efficiency of sprays under a controlled and repeatable laboratory setting but retains several features of realistic spray conditions. In particular, the method uses real agricultural nozzles, spray pressures, and deposition rates and can be tested on both model surfaces and real plant surfaces. The utility of the apparatus is demonstrated using model solutions as well as commercial fertilizer solutions with polymer additives to test the hypothesis presented by earlier researchers that spray solutions with higher extensional viscosity can inhibit rebound and splashing processes, leading to a higher retention efficiency in spray applications.[23]

II. METHODS AND MATERIALS

A. Chemicals

The chemicals used in this study were polyethylene oxide of various molecular weights (PEO, 1 MDa, 2 MDa, 4 MDa, 5 MDa, 8 MDa), polyacrylic acid (PAA, 1.25 MDa), 2-hydroxyethylcellulose (HEC, 1.3 MDa), potassium hydroxide, and deuterium oxide (Sigma Aldrich, MO, USA). Estimates of the radius of gyration and contour length of all polymers are listed in Table I. Radii of gyration were determined according to the molecular dynamics simulation studies of each polymer based on their molecular weights,[34–37] and contour lengths were calculated by multiplying the number of repeated monomers and its length. Sodium chloride (Fisher Chemical, NJ, USA), concentrated fertilizer solution known commercially as Active Flower™ (pH = 8.623, applied after 1:40 dilution), and phosphoric acid (Active AgriScience, Saskatoon, SK, Canada) were also used.

B. Solution preparation

Concentrations of all components in the polymer solutions are given on a weight/weight basis. All polymers are water soluble, but due

TABLE I. Estimated molecular properties of the polymers studied.[34–36]

Polymer	Molecular Weight (MDa)	Radius of Gyration (nm)	Contour Length (μm)
PEO	1	18.3	6.74
PEO	2	25.9	13.5
PEO	4	36.6	27.0
PEO	5	40.8	33.7
PEO	8	51.6	53.9
PAA	1.25	8.3	2.67
HEC	1.3	84	1.98

to the large molecular weight, the powders tend to clump and form "fish eyes" when added to water. In addition, high shear may result in physical degradation of the long-chain molecules, so mixing is usually done very gently over many days.[38] To overcome the obvious impracticality in an agricultural application, a non-solvent pre-dispersion method was used to prepare the polymer solutions. For example, to make 0.1% PEO solution, a 2% dispersion was first prepared by dispersing 0.1 g PEO in 4.9 g of the non-solvent isopropanol. This 2% dispersion can be made relatively uniform by gently shaking by hand. Next, 5 g of dispersion was added to 95 g of solvent.

The solvents tested were pure DI water, aqueous solutions with varied pH and/or ionic strength, and fertilizer solution (concentrated fertilizer diluted 1:40 with water according to the manufacturers' instructions). The 100 g polymer solution was stirred at 60 rpm for 3 h using a stir bar (1 1/2 × 5/16 in, octagonal) and then placed in a roller (88 881-003, Thermo Fisher Scientific, OH, USA) for at least 12 h to guarantee uniform mixing and hydration of the polymers. Phosphoric acid and potassium hydroxide (both commonly used in fertilizers) were used to adjust the pH from 1 to 10 and sodium chloride was used to adjust the ionic strength (I) from 0.1 mol/l to 1 mol/l according to the following equation:

$$I = \frac{1}{2}\sum_{i=1}^{\infty} c_i z_i^2,$$ (1)

where c is the ion concentration and z is the valence of the respective ion.

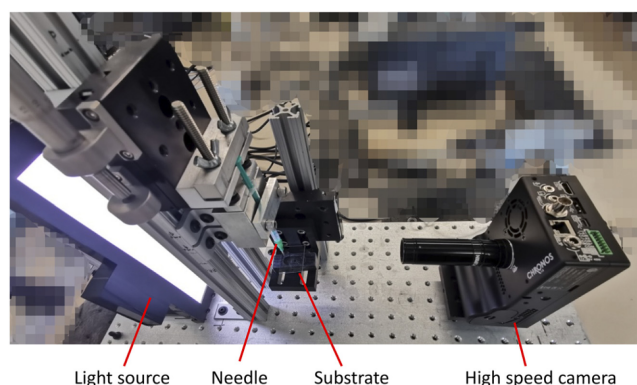### C. Surface tension, pH, and density

The surface tension of the test solutions was measured by a microbalance (Microtrough G2, Kibron, Inc. Helsinki, Finland) using the Wilhelmy rod method. The pH was measured by using a pH meter (PY-P10-2S, Sartorius AG, Goettingen, Germany), and a two-point calibration was performed using pH 4.00 and 7.00 buffer prior to measurements. The density was measured by weighing 1 ml of solution transferred via a 1000 μl pipette (5000DG, Nichipet, Japan) to a pre-tared 10 ml beaker on an analytical balance (Entris64-1SUS, Sartorius AG, Goettingen, Germany). All tests were conducted at room temperature (25 ± 2 °C). Measurements of surface tension, pH, and density were conducted in triplicate for each sample.

D. Rheology

The Dripping onto Substrate (DoS) method was used to characterize the extensional rheology of the polymer solutions.[38] The DoS setup, shown in Fig. 1, is comprised of a diffuse light source, a 5 ml syringe with a 14 gauge blunt-tipped needle, a glass substrate, and a high speed camera (1.4 CHRONOS, Kron Technologies Inc., Canada) set to record at 6000 fps and 560 × 400 resolution. The camera lens (Precise Eye, 0.25x, 0.018NA, DOF 1.59 mm, 1-6044, with 2.0x Adapter 1-61450) provides a field of view around 4 × 6 mm^2. The needle tip is positioned such that the distance between the opening and the glass substrate is ∼6 mm. A finite volume of polymer solution was released from the tip of the needle at a flow rate of ≈0.02 ml/min, and a liquid bridge was formed with a decreasing neck diameter between the needle and the glass substrate. The recorded videos were analyzed by a MATLAB R2019a code (The MathWorks, Inc., MA, USA), which detects and calculates the change in the neck diameter as a function of time. Because the solutions wetted the metal needle tip, the outer diameter was used for scaling the neck diameter and calibrating the pixel size in data analysis.

While the DoS method enables detailed analysis of extensional rheology, in this work, we have elected to quantify differences in extensional rheology using the extensional relaxation time because it is essentially constant for these solutions. For a more detailed description of the method, we refer the reader to Dinic et al.,[38] but, briefly, the extensional relaxation time is calculated from the slope of the logarithm of neck radius normalized by the needle diameter vs time elapsed from when the data enter the elasto-capillary regime. The beginning of the elasto-capillary regime is marked by a sudden change from a negative curvature to a constant, and more shallow, slope. The relaxation time is then equal to $-1/(3m)$, where m is the slope in this regime. In some cases, after a period of time with a constant slope, the slope begins to decrease again when the polymer reaches the limit of finite extensibility, and data after this point were not included in the measurement of relaxation time.[38,39] Measurements of extensional relaxation time were conducted in triplicate for each sample.

Shear viscosity was measured using a Modular Compact Rheometer MCR 302 (Anton-Paar, Austria) in a parallel plate configuration (measuring system PP50, diameter 50 mm and inset I-PP50/SS, diameter 50 mm; stainless steel Cat.no.16222) at 25 °C with a temperature resolution of ±0.1 °C. The shear rate was set at 10 s^{-1}, and tests were conducted in triplicate.

E. Nuclear magnetic resonance (NMR) spectroscopy

Proton NMR tests were performed to detect the presence of chemical reactions between the commercial fertilizer and the polymer. Fertilizer solution, aqueous PEO solution (0.1% of 1 MDa PEO), and fertilizer solution with PEO (also 0.1%) were tested with deuterium oxide as the aqueous phase used to disperse the polymer and dilute the fertilizer. The three samples were placed into separate Norell 5 mm, 7 in. standard tubes (Sigma Aldrich, USA) that were capped, sealed with parafilm tape, and sent to NMR facilities in Department of Chemistry at UBC. ^{1}H NMR spectra were obtained using a Bruker Avance 300 spectrometer. Peak intensities and areas were measured using the Brucker-NMR software.

F. Spray apparatus for retention efficiency

Experiments were conducted using a specially designed apparatus to measure the retention efficiency, defined here as the mass of the spray that stays on the surface divided by the mass of the spray that *reaches* the surface. As shown in Fig. 2 the spray apparatus is composed of a pressure regulator (AR20-B, pressure range 0-100 psi, SMC Corporation, Japan), a 2 Quart pressurized tank (model 7004, Sharpe Manufacturing Company, USA), a push button directional control valve (normally closed, PXBB4131BC2, Parker Hannifin Corporation, USA), and a nozzle (see Table II). Commercial nozzles were provided by Active AgriScience (Saskatoon, SK, Canada), and the specifications of each are listed in Table II. Droplet size classification was developed by the American Society of Agricultural and Biological Engineers (ASABE), and it should be noted that this classification is based on spraying water. In all cases, the nozzle was positioned 18 in. above the samples and operated at a pressure of 45 psi (gauge).

FIG. 1. DoS setup composed of a light source, a needle, a substrate, and a high speed camera.
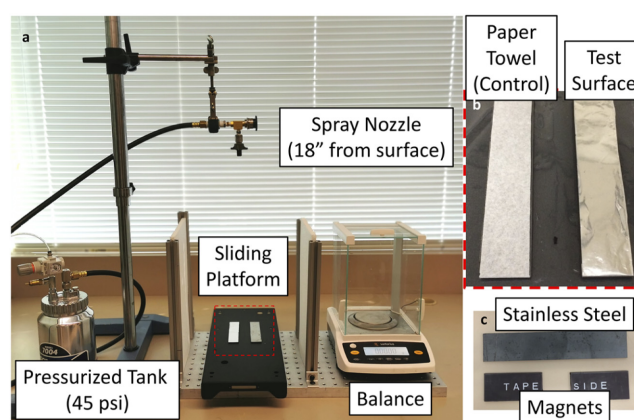
FIG. 2. (a) Specially designed spray apparatus consisting of a pressurized tank for spray solution, a spray nozzle, a sliding platform with test surfaces on it, and a balance. (b) Test surface and control (paper towel) under the nozzle of 5 in. length, 1 in. width, and 1 in. in between two surfaces. (c) Surface holders made of stainless steel and magnets.

TABLE II. Spray nozzles and droplet size category in volume median diameter (VMD). The range in VMD indicates the values that can be produced by adjusting the spray pressure, rather than the droplet size distribution.

Nozzle	Category	VMD (μm)
Lurmark 02F110	Fine	145–225
Lurmark 03F80	Medium	226–325
TeeJet AIXR 11002	Coarse	326–400
Agrotop airmix 110-05	Very coarse	401–500

Positioned directly below the nozzle is a sliding platform, with two sample holders, each consisting of a stainless steel plate (thickness 0.75 mm, width 1 in., length 5 in.), and two magnets (thickness 0.186 mm, width 1 in., length 2 in., Dongguan Maghard Flexible Magnet Co., Ltd., China) used to hold the sample in place. All samples were cut (and arranged, if applicable) to be 7 in. long and 1 in. wide so that they could be wrapped around the sample holders and held in place by the magnets under the steel plate so that only the sample material was exposed to the spray. Next to the spray apparatus, an analytical balance (Entris224-1S, Sartorius AG, Goettingen, Germany) was used for weighing the samples before and after each spray.

1. Materials for retention efficiency

A paper towel (thickness 0.49 mm, Western Family Foods, Tigard, OR, USA) was used as the control sample for all tests. Low density polyethylene (LDPE) plastic (thickness 0.17 mm, P1525 Frost King, Thermwell Products Co., Inc., NJ, USA) and aluminum foil (thickness 0.01 mm, Handi-Foil Corporation, IL, USA) were used as model sample surfaces that are highly reproducible in terms of surface properties. Wax paper (thickness 0.03 mm, Reynolds Kitchen, IL, USA) was also tested as a potential sample surface.

Leaves from six randomly selected plants on campus were also tested for comparison with the model surfaces. The collected leaves were placed on and covered with a dry paper towel, without overlapping them, and pressed with heavy books for five days for drying. Fresh corn leaves were also collected from corn plants provided by Active AgriScience (Saskatoon, SK, Canada) for tests on a live leaf

surface. In the case of the corn leaves, they were cut immediately prior to testing, and a wet paper towel was used to cover the cutting edge to prevent excess water evaporation. For all leaves tested, care was taken to cut the sample from the same position on the leaf. Systematically investigating the "hairy" structure [Fig. 3(b)] observed on some leaf surfaces is beyond the scope of this paper but certainly could affect retention of spray droplets.[40]

2. Spray test for retention efficiency

In each spray experiment, ~100 ml of spray solution was added to the pressurized tank. One control sample (paper towel) and one test sample were placed on the two sample holders, respectively, and weighed separately on the analytical balance. It was assumed that all droplets reaching the paper towel would be absorbed and therefore serve as a reference for the mass of droplets reaching each sample under a given set of spray conditions. The sample holders were positioned symmetrically under the nozzle, with 1 in. in between. The spray was then started, and the sliding platform translated manually at ≈3 in./s. The sample holders were designed to be 5 in. in length so that they are long enough to accommodate local variability in the spray and samples while still being of a practical size.

After each spray, the control and test surface were weighed again and retention efficiency ϵ was calculated by

$$\epsilon = \frac{s - s_0}{c - c_0}, \tag{2}$$

where s and c are the masses of the test and control samples after spraying, respectively, and the subscript 0 indicates the mass before spraying. The position of the control sample and test sample was switched within each replicate to reduce the chance of systematic bias in the event of a potential asymmetry in the spray pattern. All spray tests were conducted in triplicate, switching control and the test surface included within each replicate, resulting in six trials for each permutation of the nozzle, test solution, and test surface. All experiments were conducted under ambient laboratory conditions, and evaporation of water from the samples was found to be less than 10% of the weight over a period of 35 s, and all weights were measured in less than 10 s after completing the spray.
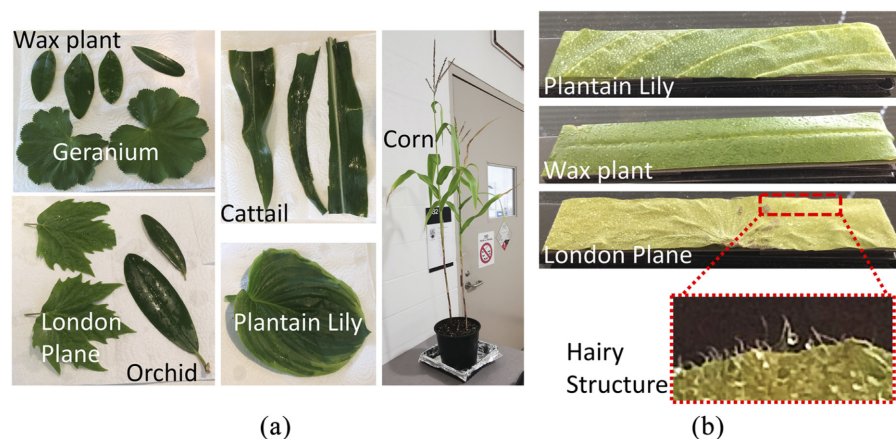
FIG. 3. (a) Six leaf surfaces collected, pressed, and dried for comparison with model surfaces and fresh corn leaves for the real leaf surface test. (b) Representatives of dried leaf surfaces; hairy structure could be seen.
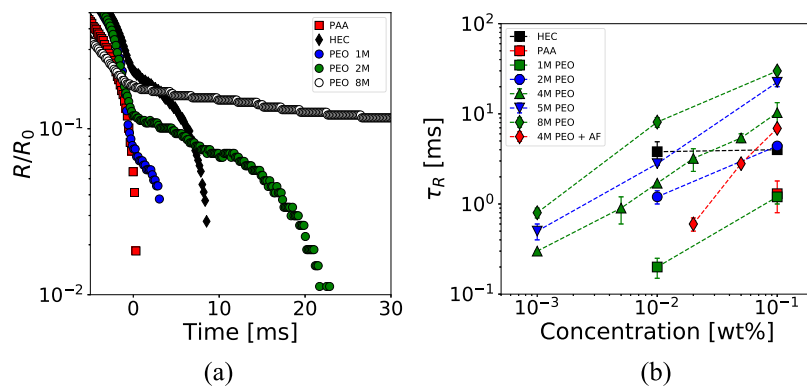
FIG. 4. (a) Neck radius evolution from DoS experiment for the aqueous polymer solutions at 0.1% concentration, with the time axis shifted so that the transition point t_c between inertia-capillary (IC) region and elasto-capillary (EC) region is at zero. (b) Extensional relaxation time τ_R of aqueous polymer solutions as a function of polymer concentration. (Data for repeats not shown for clarity, dashed lines are guides to the eye.)

III. RESULTS AND DISCUSSION

A. Polymer selection

To enhance spray retention, three types of polymer, PEO, PAA, and HEC, were evaluated due to having previously been established as generating aqueous solutions with high extensional relaxation time τ_R.[38,41,42] As outlined in the Introduction, a high extensional relaxation time is expected to improve droplet retention. On the other hand, a high shear viscosity is undesirable since that would alter the performance of the pumping and spray generation system, which would be impractical in an agricultural setting.[43] The polymer must also be compatible with commercial fertilizer solutions that often have high ionic strength and a wide range of pH, so the rheology of polymer solutions with different different pH and ionic strength was also examined.

Representative data from DoS measurements of extensional rheology are plotted in Fig. 4(a), and three different regimes of filament thinning are observed. These regimes are well-described in the literature[38,44] and will only be reviewed here briefly. First, we see the inertio-capillary regime that appears non-linear as plotted, and the end of this regime is used to define the point when time is equal to zero. Note that essentially all of the data for PAA fall into this regime, meaning that the extensional rheology is not measurable with our experimental setup.

After the inertio-capillary regime, we see the elastocapillary regime where the data become linear on this plot. The slope of the line in this regime is inversely proportional to the extensional relaxation time such that shallower slopes correspond to higher relaxation times. Note that all of the data shown after time equals zero for 8 MDa PEO fall into this regime. Finally, we see a change from a linear, back to non-linear data in the terminal visco-elastocapillary regime, where it is understood that the polymers in solution have reached the limit of their ability to stretch and dissipate energy. This limit is reached for the data shown for HEC, 1 MDa PEO, and 2 MDa PEO with the duration of the elastocapillary regime varying in each case.

To extract the extensional relaxation time τ_R from the curves in Fig. 4(a), we simply fit the data in the elastocapillary regime and use the slope to calculate τ_R.[38] In Fig. 4(b), it can be seen that PEO solutions have higher extensional relaxation times than PAA and HEC at a similar molecular weight and at the same concentration. As expected, the extensional relaxation time increases with increasing molecular weight due to the longer contour length (Table I).[38,39] Note that no

values are reported for 0.001% HEC or 0.001% and 0.01% PAA because they were below the measurement resolution of the DoS setup and they are excluded from further experiments.

The shear viscosity of the polymer solutions (reported at 10 s^{-1} in Table III) also increases with increasing concentration and molecular weight, but in this case, the PEO solutions tend to have a lower shear viscosity compared to those with HEC or PAA. Under the spray conditions used in this study, polymer solutions with shear viscosity larger than 3 mPa s resulted in poor spray quality with non-uniform droplet patterns. Therefore, 3 mPa s was set as the upper limit for acceptable shear viscosity, and this (combined with the results of extensional rheology) precludes the use of PAA and the highest concentration of several other polymers. Therefore, 4 MDa PEO was selected for use in further testing in this study since it produced the highest extensional relaxation times without exceeding the cutoff for the shear viscosity. The shear viscosity of a commercial fertilizer, Active Flower, was measured as 0.95 mPa s and 1.01 mPa s when 0.01% of 4 MDa PEO is added, and the extensional relaxation time for solutions of Active Flower with 4 MDa PEO is shown in Fig. 4.

In terms of environmental impact, PEO is considered safe for the environment and is widely used for cosmetics and in biomedical applications.[45] For plants, PEO with a molecular weight larger than 1 kDa has been reported to be difficult to absorb[47] and is compatible with living cells.[46] In terms of chemical compatibility of PEO with common

TABLE III. Shear viscosity (mPa s) measured at 10 s^{-1} of aqueous polymer solutions at different concentrations at 25 °C. The designation following the polymer abbreviation indicates the molecular weight (e.g., 1M = 1 000 000 Da).

Polymer	0.001%	0.01%	0.1%
PAA 1.25M	1.10	1.66	40.4
HEC 1.3M	0.94	1.21	5.44
PEO 1M	0.97	0.98	2.35
PEO 2M	0.99	1.03	2.20
PEO 4M	1.04	1.07	2.88
PEO 5M	1.04	1.20	5.25
PEO 8M	1.06	1.22	7.62

agrochemicals, we tested several potential effects. Proton NMR results did not show any significant sign of chain breaking or chemical reactions when 0.1% 4 MDa PEO was mixed with Active Flower (which contains 10 active ingredients). Furthermore, no significant changes were observed in the shear rheology. However, a large decrease in the extensional rheology was observed when PEO was added to Active Flower as compared to DI water.

To understand this effect, we systematically varied the pH and ionic strength of aqueous solutions of PEO and measured the extensional relaxation time. The range of ionic strength tested was from zero to 1.0 M using physiological ionic strengths (0.1M–0.2M NaCl or KCl) and the ionic strength of Active Flower (0.17M) as a reference point.[48] pH from 1 to 10 were tested, given that different fertilizers from Active AgriScience (Active Build[TM] pH = 1.051; Active Flower pH = 8.623) fall in this range.

In Fig. 5, the extensional relaxation times τ_R of 0.1% 4 MDa PEO solutions vs pH and ionic strength are shown, with data of 0.1% 4 MDa PEO in DI water and diluted Active Flower for reference. Both the pH and ionic strength had significant impacts on τ_R. In Fig. 5(a), higher pH was observed to cause a decrease in τ_R, with a slightly sharper decrease above pH 7. Surprisingly, in Fig. 5(b), τ_R is found to show a non-monotonic behavior with a local maximum at lower and local minimum at higher ionic strengths. One reason for this that might be proposed is that the hydroxide ion and salt ion concentrations influence the arrangement of the polymer backbone by electrostatic interactions and alter its ability to stretch during extensional deformation.[49–51] Unfortunately, this explanation does not seem to apply here since the polymer is non-ionic. At this stage, we are not able to offer a convincing explanation for these trends, and this is the topic of an ongoing study in our laboratory.

By comparing data of 0.1% 4 MDa PEO in DI water and diluted Active Flower, we may conclude that for PEO in this fertilizer, pH seems to have a stronger influence than ionic strength on τ_R. Additionally, even though surfactants were not intentionally added to the solutions in this experiment, they are ubiquitous in many commercial fertilizers, including Active Flower. It has been suggested that high ionic strength could facilitate screening of micelles and other particles attached to the polymer chain, resulting in fewer pre-stretched and more extensible chains.[49] However, further studies are needed to examine the intrinsic mechanisms underlying this behavior to provide more insight for optimizing the additive polymer for a particular agrochemical formulation.

The density and pH of the solutions were measured before and after the polymer was added with no significant change observed, which is expected due to the relatively low polymer concentration. The surface tension is not significantly different due to addition of PEO (Active Flower = 70.1 mN/m, 0.1% of 4 MDa PEO in Active Flower = 69.4 mN/m), though the measurements show that the fertilizer contains a small amount of surface active species and is reduced slightly by PEO. It is well known that reducing the surface tension will lead to smaller droplets in the spray and can also enhance retention efficiency, but that effect is not the subject of the present work.

B. Model sample-surfaces

While testing on real plant surfaces would be the most ideal for comparison to field applications, the use of model surfaces is important for standardizing measurements between laboratories and isolating experimental variables. Here, we evaluate the use of aluminum foil, low density polyethylene (LDPE) plastic film, and wax paper since they are inexpensive and commonly available, mass-produced materials. The retention efficiency from a spray of DI water was measured for each model surface along with a range of plant leaf surfaces. In Fig. 6, each data point represents an individual spray experiment.

The scatter in the data is believed to be, in part, due to the fact that the sliding platform that holds the samples is actuated manually and a future version of the device will automate this step to improve repeatability. It can be seen that in terms of retention efficiency, the model surfaces show a retention efficiency similar to plant surfaces. Wax paper was also tested but showed a higher retention efficiency than expected due to absorption of water droplets in regions of the paper that were not saturated with wax. Based on these results, we conclude that aluminum foil and LPDE sheets can reasonably be used as surrogates for plant leaves for testing the impact of changing fluid properties on retention efficiency.
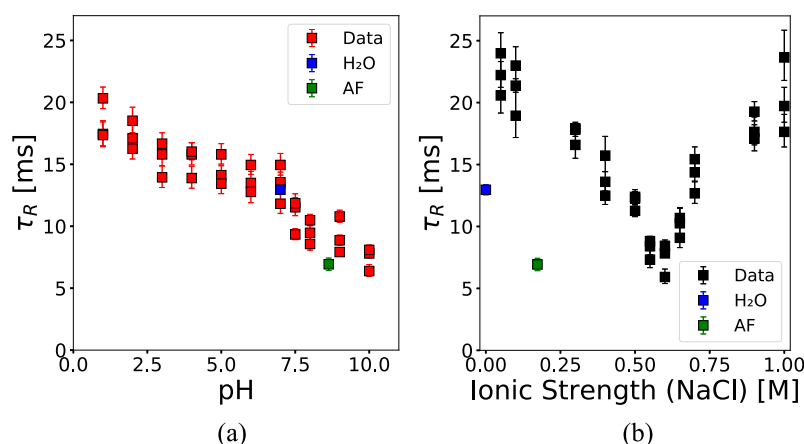

FIG. 5. (a) Extensional relaxation time τ_R of 0.1% 4 MDa PEO solutions as a function of pH (red square); the ionic strength is 0.5M for all solutions. Data of 0.1% 4 MDa PEO in DI water (blue square) and diluted Active Flower (green square) were shown for reference (N = 3). (b) Extensional relaxation time τ_R of 0.1% 4 MDa PEO solutions as a function of ionic strength (black square); pH is 7 (N = 3).
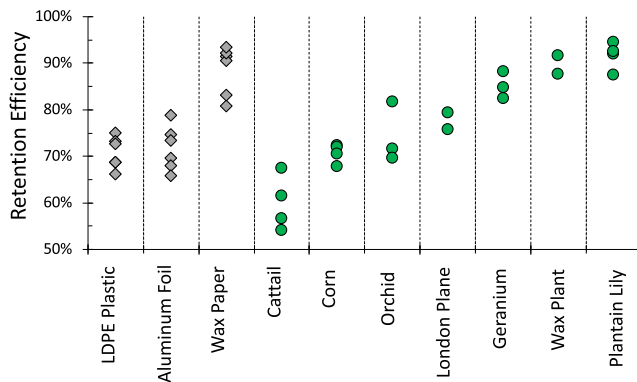
FIG. 6. Comparison of retention efficiency of model surfaces (diamond) and real plant surfaces (circle).

C. Effect of droplet size and extensional relaxation time

Having established that model surfaces exhibit realistic retention efficiencies, the effect of droplet size from the spray and extensional relaxation time τ_R were investigated on the model surfaces. First, the retention efficiency of DI water sprayed onto two model surfaces using four different nozzles is shown in Fig. 7(a). As expected, it can be seen that smaller droplet sizes result in higher retention efficiency on both model surfaces. This result is in accordance with other studies under both single-droplet and multi-droplet conditions.[29,32,33,52]

Next, the retention efficiency of aqueous polymer solutions (4 MDa PEO) sprayed onto the same surfaces with the same four nozzles is plotted as a function of τ_R in Fig. 7(b). PEO was added at various concentrations to generate this range of τ_R. The results show that for both model surfaces and all four nozzles, higher τ_R results in higher retention efficiency. This supports the hypothesis that long-chain polymer additives can increase the retention efficiency of agrochemical sprays and—for the first time—we quantify the effect using commercial spray nozzles. Interestingly, when those data are plotted on semi-log axes as in Fig. 7(b), the slope of the data appears to be nearly constant and consistent for each type of material. This suggests that there may be underlying material properties of the surface that can be used to develop predictive models in future work.

It is also worth noting that with the increased extensional relaxation time, there is an accompanying increase in the droplet size due to the mechanics of spray formation.[53] This increase in droplet size increases the inertia of the droplets colliding with the surface, which should lead to increased splashing and rebound and a decrease in retention efficiency [see Fig. 7(a)]. Nevertheless, despite the increase in the droplet size, the retention efficiency is still increasing with increasing extensional relaxation time. This shows that the influence of the extensional rheology on the droplet's impact with the surface is more significant than the influence on atomization for determining the retention efficiency.

D. Live plant surfaces and fertilizer solutions

While the results with model surfaces are promising, it is important to verify that the same trend exists for live plant surfaces and commercial fertilizers. Corn leaves were chosen due to their more hydrophobic nature and also because corn is one of the target plants for Active Flower. Figure 8 shows that similar to the model surfaces (blue squares and green diamonds), higher retention efficiency is also achieved with higher τ_R with aqueous solutions on live corn leaf surfaces (black circles). Retention efficiencies on both model surfaces are higher than that on corn leaf surfaces, and this is likely due to differences in surface chemistry and morphology. Fertilizer solution was also sprayed on corn leaves, showing a 72.7% retention efficiency (red dotted line), which is slightly higher than pure water (green dashed-dotted line). This suggests that one or more of the ingredients in the fertilizer formulation marginally improves the retention efficiency in this case. This could be due to smaller droplets generated because of lower surface tension, but more systematic studies in the future are needed to elucidate this effect.

As a final test, the retention efficiency of a fertilizer spray (Active Flower) with 0.02%, 0.05%, and 0.1% 4 MDa PEO additive was measured (red circles). Interestingly, these data points fit neatly into the trend of the data for aqueous polymer solutions. This suggests that extensional relaxation time may be sufficient as a parameter for predicting the retention efficiency for a given surface and polymer despite the presence of surfactants that alter the surface tension or ions that alter the extensional rheology, but further tests are required to conclude this more strongly. Note that for this particular fertilizer solution, it would be difficult to achieve higher values of τ_R using PEO without exceeding the 3 mPa s limit set earlier. This lower value of τ_R
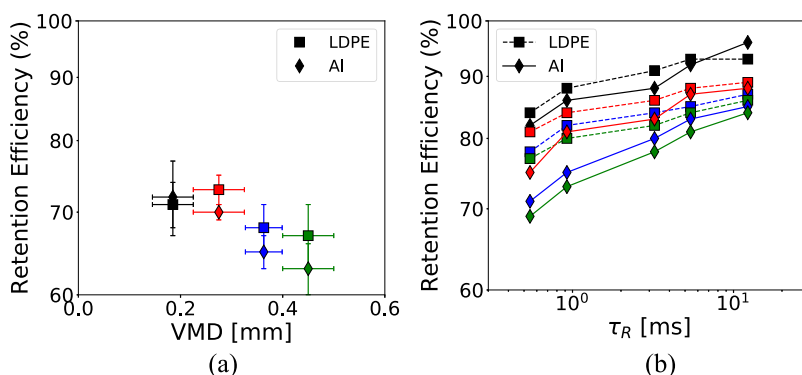

(a)

(b)

FIG. 7. (a) Retention efficiency of DI water droplets on two selected model surfaces, aluminum foil (diamond, solid line) and LDPE plastic (square, dashed line), sprayed using different nozzles that generate fine (black), medium (red), coarse (blue), and very coarse (green) droplet size (N = 3). (b) Retention efficiency of polymer solution as a function of the extensional relaxation time τ_R of the polymer solution (N = 3). [Error bars and data for repeats not shown for clarity; the length of error bar is similar to Fig. 7(a).]
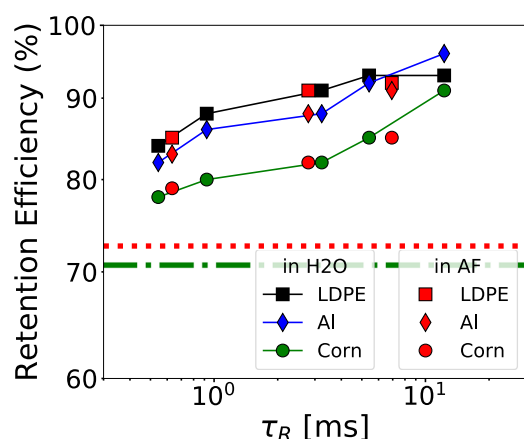
FIG. 8. Preliminary spray tests on the corn leaf surface using aqueous 0.001%, 0.005%, 0.02%, 0.05%, 0.1% 4 MDa PEO solution (green circle). Results from aqueous 4 MDa PEO solution on two model surfaces, LDPE plastic (black square) and aluminum foil (blue diamond), were shown for comparison. Spray tests on these three surfaces using 0.02%, 0.05%, 0.1% 4 MDa PEO in Active Flower solution are shown in red points. Retention efficiency of DI water (green dashed-dotted line) and Active Flower (red dotted line) without additive polymer on the corn leaf surface was 70.6% and 72.7%. Nozzle Lurmark 02F110 was used to generate fine droplets (N = 3). (Error bars and data for repeats not shown for clarity.)

in diluted Active Flower fertilizer is consistent with the decrease in τ_R at higher pH (Fig. 5). Therefore, future experiments could assess other polymers that can produce higher τ_R with lower shear viscosity for fertilizers.

IV. CONCLUSION

A series of experiments was conducted to characterize polymer solutions and screen polymers with five different molecular weights and three chemical structures to generate solutions with high extensional relaxation time τ_R and low shear viscosity for use in agricultural spray applications. A simple spray apparatus and methodology were developed and shown to be effective for quantifying the retention efficiency of spray solutions under realistic, but highly controlled conditions. From the results, PEO at 4 MDa was selected as the most suitable additive; however, the extensional relaxation time τ_R was found to be sensitive to pH and ionic strength of the solution, which can vary significantly between fertilizer formulations.

Experiments using the spray apparatus proved that retention efficiency is enhanced with increasing extensional relaxation time τ_R and decreasing droplet size on all surfaces tested. In addition, preliminary tests on corn leaf surfaces and using commercial agrochemical solutions with PEO additive also showed increased retention efficiency with higher extensional relaxation time. This represents a useful platform for future investigations to quantitatively examine the effects of changes in other fluid properties (due to surfactants, nanoparticles additives, etc.) as well as differences in the chemistry and morphology of different surfaces on retention efficiency. From a practical point of view, the results may also lead to the development of commercial spray formulations with enhanced retention efficiency, resulting in less pesticides or fertilizers applied and more environmentally friendly application, and may also lead to improvements in other spray-coating applications.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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