

Droplet Impact Dynamics of Aqueous Polymeric Solutions

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Abstract

An experimental investigation of impact, spreading, and recoil of droplets of aqueous polymeric solutions on a horizontal hydrophobic (Teflon) surfaces is presented in this paper. The non-Newtonian aqueous polymer solutions are prepared by mixing the water-soluble hydroxyethyl cellulose (HEC) with different degrees of polymerization (QPC 300, 250 HR and 250 HHR) at different concentrations. The solution rheological and interfacial properties are characterized to understand the role of wettability, surface tension, and viscosity on the droplet surface interactions. For each polymer solution, the surface tension is measured by the maximum bubble pressure method and the static contact angle is measured using a contact angle/wettability analyzer. Intrinsic viscosities of the three polymers are determined from the viscosity measurements of their dilute solutions carried out using a capillary tube viscometer. A high speed digital camera is used to capture the droplet impact behavior at 4000 frames per second. The captured images of the droplet are analyzed by image processing and the temporal variations of the spreading factor and the flattening factor of the droplet are determined. Results show that the higher viscosity coupled with lower surface tension of the polymer solutions leads to larger spread compared to a water droplet and inhibits strong recoil on a hydrophobic surface.

Introduction

In many spray and coating processes the impact of liquid droplet on a flat surface and its post-impact spreading and recoil govern the process outcome. These include spray coating, spray cooling, inkjet printing, deposition of thermal barrier coatings, near net-shape manufacturing, aerosol drug-delivery and agro-chemical sprays. Not surprisingly, considerable work has been carried out on drop impact, spreading, and recoil behavior using analytical, experimental and computational methods (See for example a review by Yarin [1] and references therein). The drop-surface interactions are shaped by inertia, viscous, surface tension, and gravity forces. Their dynamic influences have been scaled with Weber number (We), Reynolds number (Re), Ohnesorge number ($Oh = We^{1/2}/Re$), Capillary number (Ca), and a parameter ($We \times Oh^{2/5}$), via different experimental analyses and computational modeling. The results of drop impact behavior have been generally expressed in terms of the spreading factor defined as the ratio of the instantaneous spread diameter to the equivalent drop diameter just before impact (d/D), and the flattening factor that is given by the ratio of the instantaneous drop height or liquid film thickness to the equivalent drop diameter prior to impact (h/D).

Although solutions with polymeric additives are found in a number of spray coating applications, their droplet impact behavior has received only limited attention in the literature [2-4]. Polymeric additives change the solvent rheological and interfacial properties. The rheology of polymeric solutions, governed by the molecular makeup, molecular weight, bulk concentration, and interface shear dynamics, typically exhibits a non-Newtonian behavior [5-7]. Furthermore, polymeric additives in their aqueous solutions change the liquid-gas interfacial tension and the liquid-solid wetting behavior that is time- and bulk concentration-dependent. Understanding how the changes in rheological and interfacial properties alter the drop impact dynamics can provide a mechanism to control the droplet-surface interactions (spreading, recoil, shape oscillations, rebound, column breakup, fracture, and splatter).

In this paper, we have investigated drop impact and spreading dynamics of aqueous polymeric solutions using two grades of water-soluble hydroxyethyl cellulose (HEC). The solution rheological and interfacial properties are characterized to understand the role of wettability, surface tension, and viscosity on the droplet surface interactions. A high speed digital camera is used to capture the droplet impact behavior at 4000 frames per second. The captured images of the droplet are analyzed using an image processing software (Image pro) to obtain the temporal variations of the spreading factor and the flattening factor of the droplet.

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Materials and Methods

Aqueous solutions of hydroxyethyl cellulose (HEC-QPC300, HEC-250HR, and HEC-250HHR) were prepared using distilled de-ionized water. The mixture is allowed to dissolve for about 40 hours. Only gentle stirring was employed for mixing to avoid any degradation of the polymers. The rheological and interfacial behavior is first characterized and then experiments of droplet impact are performed.

Contact angle, surface tension, and viscosity measurements: Static contact angle measurements were carried out for aqueous solutions of different concentrations by sessile drop technique, using a Kernco GI Contact angle Meter/Wettability Analyzer. A small drop is put on the substrate and allowed to reach equilibrium. The light source and the focus lens adjusted until a clear, bold and sharp drop image is gotten to ensure accurate reading. The angle was then read directly from the protractor scale of the goniometer. The reading was taken from both sides of the droplet and this is repeated four times to ensure consistency. Surface tension measurements are made by the maximum bubble pressure method using a twin orifice computerized surface tensiometer (SensaDyneQC6000). To determine the intrinsic viscosity, a capillary tube viscometer was used for viscosity measurements of dilute polymeric solutions.

Drop impact dynamics: The droplets were carefully generated by the use of a precision syringe mounted on a vertical stand. By moving the syringe up or down the droplets could be released from different predetermined heights. The syringe diameter is varied by changing syringe orifice needle. A high speed digital camera (NAC Image Technology Version 3.0) with frame rate up to 2000 frames and shutter speed 1/4000 connected to a computer equipped with Hi-DeCam software is used to capture the droplet behavior. The lightening is provided by parabolic aluminized reflector lighting system by ARRI directed on a glossy white reflector was used for providing continuous backlighting which is reflected back on the droplet. The image is focused by the camera lens with 8 \times magnification. The camera is ensured to be perfectly inline with the targeted surface to get reliable data. Teflon was used as the hydrophobic substrate.

Analysis of the captured images provided the dynamic contact angle, instantaneous droplet spread and height, as well as drop size and velocity prior to impact. The droplet velocity was measured from the two consecutive images just before impacting the surface and by measuring the difference in the droplet position in those images and knowing the time lapse between the two frames. Each experiment was repeated four times to confirm reproducibility of the impact captured. The experimental uncertainties are outlined in Ref. [8]

Results and Discussion

The three nonionic HEC polymers considered here have different degrees of polymerization and QP 300 has the lowest molecular weight ($M = 0.6 \times 10^6$), followed by 250 HR ($M = 1 \times 10^6$) and 250 HHR ($M = 1.3 \times 10^6$). Figure 1 shows the variation of liquid-gas surface tension with concentration of aqueous solutions of the three polymers. The surface tension measurements were carried out at room temperature (23 °C). The surface tension of aqueous polymeric solutions decreases with increasing polymer concentration and attains a minimum constant value beyond the critical polymer concentration or cpc. The critical polymer concentration values for polymer solutions are determined from the asymptotic intersection point of the equilibrium $\sigma - c$ adsorption isotherm as described by Zhang [9]. The cpc value for HEC QP 300 is obtained as ~ 600 wppm, and that for HEC 250HR ~ 1350 wppm and cpc for HEC 250 HHR is ~ 650 wppm. The maximum change in surface tension is exhibited by HEC HR and is about 15% lower than water at cpc.

Figure 2 shows the variation of the equilibrium contact angle with concentration on Teflon for the three polymeric solutions. Teflon surface is hydrophobic (low surface energy) and water drop has a large equilibrium contact angle (136.5°). The lower gas-liquid interfacial tension coupled with physisorption at the solid-liquid interface changes the wettability of the substrate. With increasing polymer additive concentration the contact angle is seen to decrease until the critical polymer concentration is reached, beyond which it remains essentially constant.

Post-impact spreading, recoil, surface oscillations and column break-up are shown in Fig. 3 for water and HEC QP 300 and HEC 250 HHR solution droplets on a Teflon surface. The high-speed images of droplet surface interactions are captured at the $We \sim 40$ for all the three cases. Water and the two solutions at their critical concentration have different equilibrium surface tension. As such the droplet diameter was different in each case although the same size syringe needle orifice was used. To maintain a constant Weber number based on droplet diameter, impact velocity, and the equilibrium surface tension, the droplets were released from different heights. In all cases, the drop is seen to spread to its maximum spread diameter in about 5 ms. It is interesting to note that polymer solutions drop surface exhibits surface waves that are absent in case of water droplet. The initial spread is followed by a strong recoil, liquid column formation and column breakup for the water droplet. The polymer solutions have substantially higher viscosity compared to water. The intrinsic viscosity of each polymer was determined by measurement of vis-

cosity of their dilute solutions using a capillary viscometer and making a Huggins and Kraemer plot. The intrinsic viscosity of QP 300 is found to be 5.40 dl/g, and that of 250 HR is 6.43 dl/g while that of 250 HHR is 9.54dl/g. The higher viscosity leads to significant viscous dissipation and the viscous forces prolong the surface recoil. Spread-and-recoil oscillations are not observed for polymeric solutions.

At $We \sim 40$, the impact velocities are slightly different in each case, a more meaningful comparison can be made using dimensionless spreading factor (d/D) and flattening factor (h/D) variation with dimensionless time (time scaled with V/D) which are shown in Figs. 3 and 4, respectively. The water drop with a higher surface tension and low viscosity tends to show a smaller maximum spread and correspondingly higher flattening factor. The large spread-recoil oscillations exhibited by the water drop are absent in case of polymer solutions drops. Both QP 300 and 250 HHR solutions, with their lower surface tension, facilitate larger initial spread. However, because of high viscosity, slow and prolonged recoil with very small surface oscillations is observed with the polymer drops.

These results show that the higher viscosity coupled with lower surface tension of the polymer solutions leads to larger spread compared to a water droplet and inhibits strong recoil on a hydrophobic surface. The drop surface interactions of water drops impacting a horizontal substrate can be significantly altered using polymeric reagents.

Nomenclature

cpc critical polymer concentration
d spread diameter
D drop diameter prior to impact
h liquid film thickness
V drop velocity just before impact
We Weber number ($=\rho V^2 \sigma/D$)
 ρ density
 μ viscosity
 σ gas-liquid interfacial tension

Subscripts

e equilibrium

Acknowledgment

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References

1. Yarin, A. L. 2006 Drop Impact Dynamics: Splashing, Spreading, Receding, Bouncing. *Annual Review of Fluid Mechanics* 38, 159-192.
2. Bergeron, V., Bonn, D., Martin, J. Y., and Vovelle, L. 2000 Controlling Droplet Deposition with Polymer Additives. *Nature* 405, 772-775.
3. Cooper-White, J. J., Crooks, R. C., and Boger, D. V. *Colloid and Surfaces A: Physicochemical and Engineering Aspects* 210:105-123 (2002).
4. J. Lampe, DiLalla, R., Grimaldi, J., and Rothstein, J. P., *Journal of Non-Newtonian Fluid Mechanics* 125:11-23 (2005).
5. Birdi, K. S. (ed.) *Handbook of Surface and Colloid Chemistry*. New York, NY: CRC Press, 2003.
6. Holmberg, K., Jönsson, B., Kronberg, B., and Lindman, B. 2003 *Surfactants and Polymers in Aqueous Solution*. New York, NY: Wiley, 2003.
7. Manglik, R. M., Wasekar, V.M. and Zhang, J. *Experimental Thermal and Fluid Science* 25:55-64 (2001).
8. K.P. Gagne, Jog, M. A., and Manglik, R. M. 2006 *ASME International Mechanical Engineering Congress and Exposition*, Chicago, IL, Nov. 2006, Paper No. IMECE2006-14699, 2006.
9. Zhang, J., and Manglik, R.M., *Journal of Heat Transfer* 127:684-691 (2005).

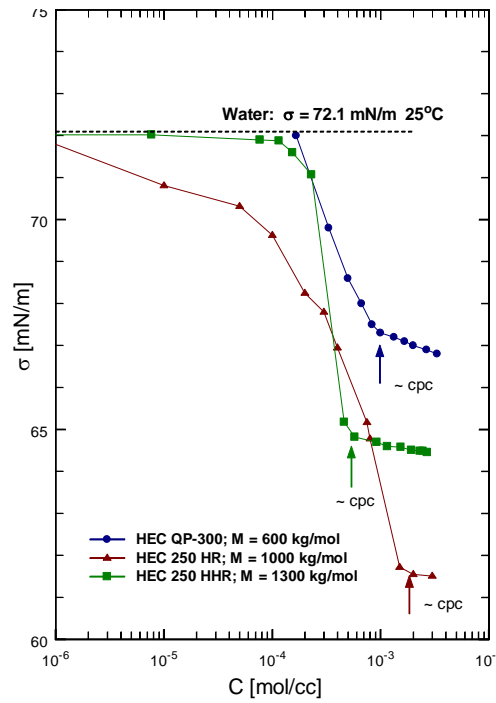


Figure 1. Variation of surface tension with concentration

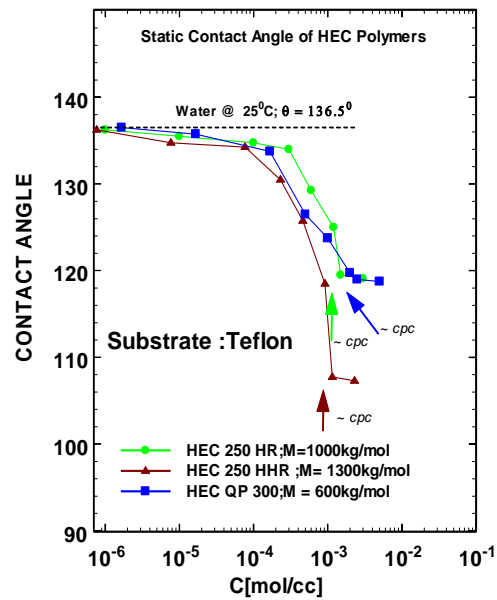


Figure 2. Contact angle measurements on Teflon substrate

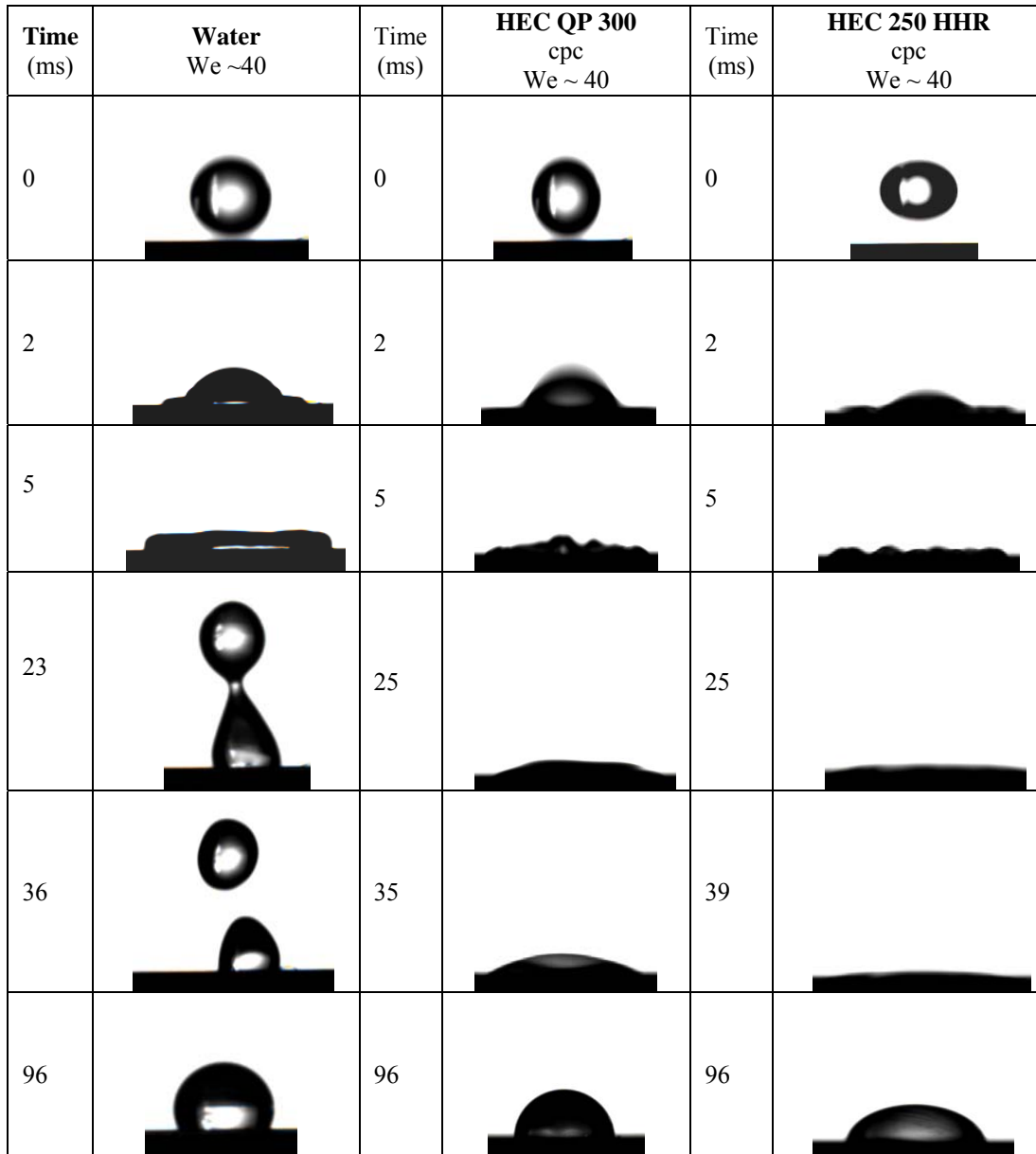
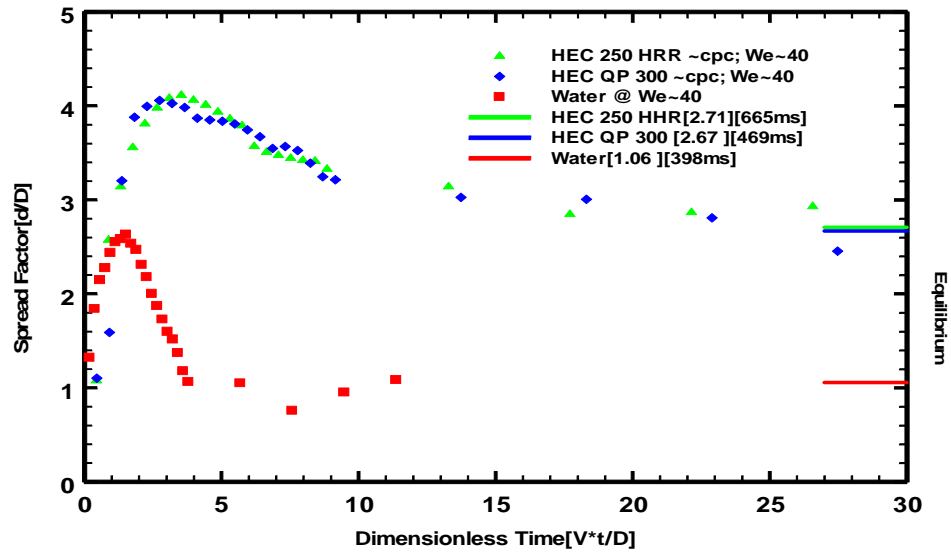
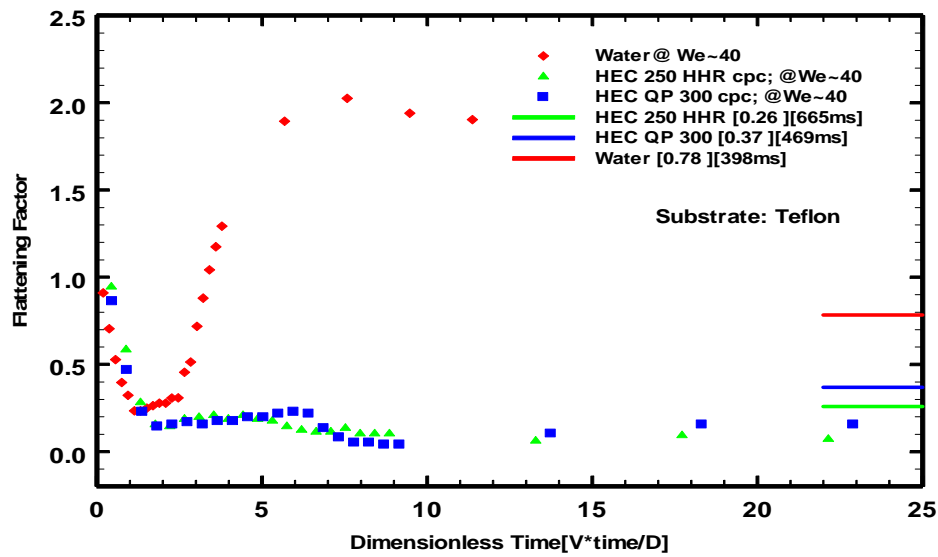


Figure 3. Impact dynamics of drops of water, aqueous HEC QP 300 and HEC 250 HHR on a Teflon surface. Water drop: $D_e=2.724\text{mm}$, $V_e=1.033\text{ m/s}$, $\sigma_e=73$. HEC QP 300, *cpc*, $D_e=1.5\text{mm}$, $V_e=1.374\text{ m/s}$, $\sigma_e=67.3$. HEC 250 HHR, *cpc*, $D_e=1.5\text{mm}$, $V_e=1.32\text{ m/s}$, $\sigma_e=65$.



(a)



(b)

Figure 4 (a) Temporal variation of the spread factor and (b) the flattening factor during post-impact evolution of droplet surface for drops of water and aqueous solutions of HEC QP 300 and HEC 250 HHR on a Teflon surface. Water drop: $D_e=2.724\text{mm}$, $V_e=1.033\text{ m/s}$, $\sigma_e=73$. HEC QP 300, *cpc*, $D_e=1.5\text{mm}$, $V_e=1.374\text{ m/s}$, $\sigma_e=67.3$. HEC 250 HHR, *cpc*, $D_e=1.5\text{mm}$, $V_e=1.3$, $\sigma_e=65$.