Static and dynamic wetting of porous Teflon® surfaces
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Dependence of Drop Impact Behaviour on the Addition of Polymer

This chapter discusses the impact behaviour of drops of poly(ethylene oxide) solutions in comparison with the behaviour of pure water, as described in the previous chapter.

8.1 Introduction

In the previous chapter was shown that pure water impacting on a self-cleaning surface can exhibit bouncing, break-up and splashing behaviour. The drop of water dissipates very little energy due to viscous forces or contact angle hysteresis. D. Richard and D. Quéré showed that doubling the viscosity by adding glycerol to the drop does not change the bouncing behaviour of the drop. In this research we investigated the effect of addition of small amounts of poly(ethylene oxide) (PEO) to water on the impact behaviour of drops.

PEO is a water soluble polyether which is often used in non-ionic surfactants and as a drag reducer for turbulent flows. PEO is produced by
an anionic ring opening polymerisation of ethylene oxide. A solution of PEO shows a non-Newtonian, shear thinning, behaviour. A considerable amount of research has been performed on PEO solutions. Part of this concerned the drop formation process and the liquid rupture from a nozzle under influence of gravity.\textsuperscript{63,64} A drop of Newtonian liquid normally breaks off the nozzle once it reaches a certain size. PEO solutions of high-molecular weight show necking before disconnecting from the nozzle: a thread forms connecting the solution in the nozzle with the drop.

An interesting use of PEO is the suppression of bouncing behaviour of drops of liquid.\textsuperscript{66,70} Even for low concentrations of PEO the impact behaviour changes considerably. This is particularly useful for the treatment of plants with herbicides and pesticides, since plant leaves very often are hydrophobic. While the expansion speed and maximum diameter remain the same compared to a drop of pure water, the retraction stage can be longer by several orders of magnitude.

8.2 The Viscosity of PEO Solutions

PEO solutions show shear-thinning behaviour. The shear viscosity for dilute PEO solutions equals the viscosity of water. D. Richard and D. Quéré have shown that doubling the shear viscosity of a Newtonian liquid does not influence the impact behaviour of a drop on an ultra-hydrophobic surface.\textsuperscript{44} A PEO solution is, however, a non-Newtonian liquid that can have a high elongational viscosity. An increase in the elongational viscosity can have a significant influence on the impact behaviour of a drop of liquid.\textsuperscript{67}
8.2.1 The Intrinsic Viscosity

The Mark-Houwink-Sakurada equation for the intrinsic viscosity $\eta_i$ of PEO in g·cm$^{-3}$ is given by:

$$\eta_i = 0.072M_w^{0.65}$$  \hspace{1cm} (8.1)

Knowing the intrinsic viscosity, it is possible to calculate the critical overlap concentration $c^*$ using the classification of Flory:

$$c^* = \frac{1}{\eta_i}$$  \hspace{1cm} (8.2)

For a molecular weight of $5 \cdot 10^6$ g·Mol$^{-1}$, $c^*$ has a value of 0.6 g·l$^{-1}$.

8.2.2 The Shear Viscosity

The shear viscosity is the resistance of a liquid to flow. A liquid shears because of friction between the liquid and the boundaries, resulting in a variation of the flow velocity as a function of the distance from the surface (Figure 8.1). The shear rate is the speed at which the liquid flow occurs. For Newtonian liquids the shear rate increases linearly with
an increasing shear stress. The shear viscosity of a liquid is defined by Newton’s law of viscosity:

\[ \eta_s = \frac{\sigma}{\dot{\gamma}} \]  

(8.3)

\( \eta_s \) is the shear viscosity, \( \sigma \) the shear stress, and \( \dot{\gamma} \) the shear rate. For a Newtonian liquid, the strain rate changes linearly with the shear stress and the shear viscosity is independent of the shear rate, and therefore is constant.

For a non-Newtonian liquid the viscosity is shear rate dependent. For some liquids, the viscosity increases with an increasing shear rate. Most polymers are shear thinning. For high shear rates, the polymer chains in a flow align in the flow direction, causing the shear viscosity to decrease. Many liquids show both shear-thinning and shear-thickening, depending on the shear rate. Newtonian, shear thinning, and shear thickening fluids are called power-law fluids, meaning that their behaviour can be described by a power-law:

\[ \sigma = K\dot{\gamma}^n \]  

(8.4)

\( K \) is the flow consistency index, and \( n \) is the flow behaviour index, with:

- \( n < 1 \) for a shear thinning liquid
- \( n = 1 \) for a Newtonian liquid
- \( n > 1 \) for a shear thickening liquid

At low shear rates, a so-called Newtonian plateau, where the viscosity is not shear rate dependent, can be observed for non-Newtonian liquids.\(^{71}\) The typical behaviour of these three liquids is shown in Figure 8.2.

For a polymer solution, the shear viscosity also depends on the concentration. The shear viscosity increases with the polymer concentration. Above the critical overlap concentration (\( c^* \)), that is, the concentration where the polymer chains effectively overlap and are entangled, the increase in viscosity is higher, as schematically shown in Figure 8.3.
Figure 8.2: The shear stress as a function of the shear rate for a Newtonian, a shear thinning, and a shear thickening liquid.

8.2.3 The Elongational Viscosity

The elongational viscosity can be described as the resistance of a liquid against elongation, and is also known as the extensional viscosity. For a Newtonian liquid, the elongational viscosity is given by $\eta_e = 3\eta_s$. Most polymer solutions show a behaviour that can be divided into three stages:71

I. The liquid shows Newtonian behaviour for low strain rates.

II. The liquid is shear thinning, but extension thickening.
Figure 8.3: The shear viscosity as a function of the polymer concentration.

III. The liquid is both shear thinning and extension thinning.

These three stages are schematically shown in Figure 8.4. The second stage is typically found for strain rates of 50 - 2000 s\(^{-1}\). These are the typical strain rates of the impacting drops investigated in this work.

In case of a drop spreading on a surface, the polymer coils have to deform because of the increase in the drop diameter (see Figure 8.5). Similar to the shear viscosity, the elongational viscosity also shows a strong increase for concentrations above the critical overlap concentration. Above the critical concentration, there is a strong interaction between the polymer chains, causing the formation and stabilisation of
Figure 8.4: The elongational and the shear viscosity for a typical polymer solution as a function of the strain rate.

polymer filaments in the liquid.\textsuperscript{72}

The ratio between the elongational viscosity and the shear viscosity is the Trouton ratio:

\[ \text{Tr} = \frac{\eta_e}{\eta_s} \]  

(8.5)

For a Newtonian liquid, \( \text{Tr} \) has a constant value of 3. For a non-Newtonian liquid, \( \text{Tr} \) depends on the applied strain rate. For PEO solutions, the molecular weight and the concentration also play an important
In the literature, values of $Tr$ ranging from 12 to more than 30 can be found for $1 \cdot 10^6$ g·Mol$^{-1}$ PEO solutions with a concentration of 0.1 g·l$^{-1}$ for the strain rates used in this work. These values are predicted to be even higher for the $5 \cdot 10^6$ g·Mol$^{-1}$ PEO solutions. These values clearly show that the extensional viscosity plays an important role in the impact behaviour of PEO solutions.

### 8.3 The Surface Tension

As mentioned before, PEO is often used as a surfactant, which lowers the surface tension of water. If a drop spreads on a surface upon impact, it increases its surface area in a very short time. Many surfactants cannot migrate to the surface fast enough to compensate for this increase in surface area. As a result, the surface tension is very close to that of pure water for the first milliseconds. This effect is called the dynamic surface tension.$^{68-70}$ An $1 \cdot 10^6$ g·Mol$^{-1}$ PEO solution needs approximately 300 ms
to reach its equilibrium surface tension,\textsuperscript{64} which is about 150 times the expansion time of a drop on impact. It takes longer for dilute polymer solutions to reach the equilibrium surface tension than for concentrated solutions.\textsuperscript{63}

The static surface tension was determined for the PEO solutions used in this study by a KSV Cam 200 drop shape analysis system. The results are shown in Figure 8.6.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure8.6.png}
\caption{The static surface tension as a function of the PEO concentration.}
\end{figure}

The surface tension influences the Weber number. A lower surface tension increases the Weber number. The effect of the surface tension on
the Weber number is shown in Figure 8.7.

![Graph showing Weber number as a function of speed at impact for two different surface tensions.](image)

**Figure 8.7:** The Weber number as a function of the impact speed for a 5 µl drop for two different values of the surface tension.

This effect is particularly relevant for high impact speeds, where the Weber numbers deviate. Because of the complication arising from the dynamic surface tension and to facilitate the comparison of different PEO solutions and pure water, the Weber numbers for pure water are used in the graphs in the remainder of this chapter.

The surface tension does also have an effect on the maximum diameter a drop achieves. Research by Rioboo *et al.* has shown that the diameter increases by 10 % when the surface tension is reduced by a factor of 3.56
8.4 Experimental

The same setup was used as in the previous chapter. A second high-speed camera was also used because of the failure of the Kodak EktaPro EM Motion Analyzer. A Kodak EktaPro HS 4540 camera was used instead, at a frame rate of 1125 fps, compared to 1000 fps for the Kodak EktaPro EM Motion Analyzer.

The experiments described in this work were performed using PEO with a molecular weight of \( 5 \cdot 10^6 \text{ g} \cdot \text{Mol}^{-1} \) supplied by BDH Chemicals Ltd. Dilute solutions in reversed osmose water were made, with concentrations of 0.005 g l\(^{-1}\), 0.01 g l\(^{-1}\), 0.05 g l\(^{-1}\), 0.1 g l\(^{-1}\) and 0.5 g l\(^{-1}\). Solutions with a concentration above the critical overlap concentration were also investigated, but useful results could not be obtained because filament formation dramatically decreased the impact velocity. As a second experimental system poly(ethylene glycol) solutions with molecular weights ranging from 600 g \( \cdot \) Mol\(^{-1}\) to 20,000 g \( \cdot \) Mol\(^{-1}\) and concentrations up to 5 g l\(^{-1}\) were studied, but these solutions did not show an impact behaviour that significantly differed from pure water. The elongational viscosity of these solutions was probably not high enough to change the behaviour upon impact.

8.4.1 Quantitative Description of the Behaviour of the Drop Impact

The impact behaviour exhibited by the PEO solutions is more diverse than the behaviour of pure water, mainly because PEO solutions can form filaments. Several additional morphologies were observed. The first is “tree bouncing”, where the drop remains connected to the surface by a thick filament. This filament gives the rebounding drop the appearance of a tree crown on its trunk. A second possibility is that the drop remains initially connected to the surface by a filament, but the filament breaks at a later stage. In that case, a small drop stays behind on the surface.
In this thesis, that morphology is referred to as “tree break-up”. A third morphology is reminiscent to the splashing behaviour, but in this case the fingers stay connected to the main drop, and no satellite drops are ejected. This behaviour is referred to as “tree splashing”. Examples of these three different kinds of impact behaviour are shown in Figure 8.8.

Figure 8.8: Different types of drop impact behaviour: a) tree bouncing, b) tree break-up, and c) tree splashing.

Figure 8.9 categorises the impact behaviour of drops of PEO solutions as a function of the Weber number and the PEO concentration. The lowest concentration of 0.005 g·l$^{-1}$ shows a similar behaviour as pure water, but break-up and splashing occur at higher impact rates. For the 0.01 g·l$^{-1}$ solution, tree break-up is observed rather than normal break-up. Tree break-up is observed for the 0.05 g·l$^{-1}$ solution. Bouncing does not occur for this concentration. For high impact rates, tree splashing
is observed. For the 0.1 g·l⁻¹ solution, deposition occurs for low impact rates, the drop with a Weber number of 50, shows tree bouncing, break-up occurs for Weber numbers of 90 and 220, and for a Weber number of 290 tree splashing occurs. The 0.5 g·l⁻¹ drops only show deposition behaviour.

![Graphical representation of the behaviour of drops on impact for pure water and 0.005 g·l⁻¹, 0.01 g·l⁻¹, 0.05 g·l⁻¹, 0.1 g·l⁻¹, and 0.5 g·l⁻¹ PEO solutions in water.](image)

Figure 8.9: A graphical representation of the behaviour of drops on impact for pure water and 0.005 g·l⁻¹, 0.01 g·l⁻¹, 0.05 g·l⁻¹, 0.1 g·l⁻¹, and 0.5 g·l⁻¹ PEO solutions in water.

For a value of the Weber number of 220, only pure water shows splashing. The addition of PEO suppresses splashing even at very low concentrations. Images of impacting drops at their maximum diameter are shown in Figure 8.10. The pure water drop is clearly the most unstable.
Figure 8.10: Images of drops on impact at their maximum diameter for a Weber number of 220 for a) pure water b) a 0.005 g·l$^{-1}$, c) a 0.01 g·l$^{-1}$, d) a 0.05 g·l$^{-1}$, e) a 0.1 g·l$^{-1}$, and f) a 0.5 g·l$^{-1}$ PEO solution.

8.4.2 Evolution of the Drop Diameter

The evolution of the drop diameter after impact has been monitored for the different PEO concentrations. A typical result is shown in Figure 8.11.

It is interesting to see that the maximum diameter upon impact does not significantly differ for pure water and the PEO solutions. This result is in agreement with results found in the literature.$^{66}$ The receding motion starts directly after the maximum diameter has been reached for all concentrations. As mentioned in the previous chapter, this is related to a low contact angle hysteresis. Another interesting phenomenon for
Figure 8.11: The relative diameter after impact for a Weber number of 220 for different PEO concentrations.

the 0.5 g·l⁻¹ solution is the long retraction time compared to the other concentrations. The retraction speed for the investigated PEO solutions is shown in Figure 8.12.

While the retraction speed increases with increasing Weber number for pure water and PEO solutions up to 0.1 g·l⁻¹, it does not significantly change for the 0.5 g·l⁻¹ solutions. This implies that the drop retraction time increases with increasing Weber numbers. This most likely is linked to the fact that the elongational viscosity increases with the strain rate and therefore with an increasing Weber number. In Figure 8.12, dashed lines are shown as an indication where transitions in the drop impact
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Figure 8.12: The retraction speed as a function of the Weber number for several PEO solutions.

behaviour occur. The reason for the different behaviour of the 0.5 g·l$^{-1}$ solution compared to the more dilute solutions, is probably that the concentration is near the critical concentration, and therefore has a much higher and more non-Newtonian elongational viscosity.

V. Bergeron et al. found a very low retraction speed for a 0.1 g·l$^{-1}$, 4·10$^6$ g·Mol$^{-1}$ PEO solution on a surface with a contact angle of 120°. Drops of this solution had retraction times that were several orders of magnitude longer than drops of pure water. This very slow retraction behaviour has not been observed for the self-cleaning surface investigated.
in this work. The retraction speed decreases upon the addition of PEO, but this effect is clearly not as dramatic as in this reference.\textsuperscript{66}

8.4.3 The Elasticity of a Bouncing Drop

For sufficiently dilute PEO solutions, bouncing behaviour of drops was observed. The drop elasticity for these solutions was determined, in similarity to the pure water case of the previous chapter. The results are shown in Figure 8.13. When considering the coefficient of restitution for

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure8_13.png}
\caption{The coefficient of restitution as a function of the Weber number for several PEO solutions.}
\end{figure}
a value of the Weber number of 7, a decrease with an increasing PEO concentration was found. This behaviour was not unexpected, because the elongational viscosity increases with increasing PEO concentration. However, for higher values of the Weber number, the addition of PEO enhances the bouncing behaviour of the drops for some of the samples. This is most significant for a value of the Weber number of 220. The water drop dissipates a large fraction of its energy by splashing, while the 0.005 g·l$^{-1}$ and 0.01 g·l$^{-1}$ PEO solution drops stay intact, and have therefore a higher coefficient of restitution. The 0.05 g·l$^{-1}$ solution consistently shows tree break-up, except for a Weber number of 290 where the drop splashes. This accounts for the reasonably constant coefficient of restitution for this solution. The speed on second impact as a function of the Weber number is shown in Figure 8.14.

The loss of kinetic energy by ejecting satellite drops is reduced in the case of the PEO solutions compared to pure water. This is primarily due to the fact that satellite drops are less likely to form, and when they occur, the total ejected volume is smaller compared to drops of pure water.

8.5 Conclusions

This chapter discusses the change in the impact behaviour of water drops upon the addition of PEO with a molecular weight of $5 \cdot 10^6$ g·Mol$^{-1}$. An important characteristic of PEO solutions is the high elongational viscosity. At low concentrations, the drops bounce off the surface. Splashing behaviour occurs at higher impact rates compared to pure water. At high concentrations, drop bouncing is suppressed. The retraction speed of the drop decreases with an increasing PEO concentration. The extension speed and the maximum diameter do not significantly differ from those of pure water.

The high elongational viscosity reveals itself by filament formation.
Figure 8.14: The speed at second impact as a function of the Weber number for several PEO solutions.

This filament formation can also be observed during the rebound of drops of PEO solution. The drops on rebound have a tree shape morphology. For concentrations of 0.01 and 0.05 g·l$^{-1}$ the filament is very thin and breaks, leaving behind a small drop on the surface.