

# SI: Spreading of viscoelastic drop on a solid substrate

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May 2, 2024

## 1 Substrate preparation:

Two types of substrates are used in the current study, the first type being the clean hydrophilic substrates. To prepare such surfaces, the smooth glass substrates (Thermo Scientific Menzel-Gläser, Microscope Slides,  $76 \times 26$  mm) are immersed in solvents and incubated in an ultrasonic bath for 15 minutes. Tetrahydrofuran (Acros Organics Co., 99.6%), Acetone (Fisher Scientific Co., 95%) and Isopropanol (Fisher Scientific Co., 95%) are used as cleaning solvents. The contact angle of a seated water drop on a cleaned glass substrate is approximately  $15^\circ$ .

The second type of substrates are silanized hydrophobic substrates. To prepare these substrates, the cleaned glass substrates as explained before are placed in plasma cleaner device (PlasmaFlecto 10, Plasma Technology GmbH) for 10 minutes, just after plasma activation process, the substrates are incubated with  $30\mu L$  of 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane (Sigma- Aldrich Co. 97%) in a closed desiccator and placed in oven for 9 hours at  $100^\circ C$ . The contact angle of a seated water drop on a silanized glass substrate is approximately  $90^\circ$ .

## 2 Rheology measurements:

The preparation of the polymer solutions is a slow process. To obtain a homogeneous solution without changing the molar masses of the dissolved polymers, it is necessary to wait long enough to allow the polymers to diffuse into the solvent. The fully dissolved polymer solution is a transparent liquid that flows smoothly. Another important criterion to decide whether or not the polymer solution has reached equilibrium is the flow curve. The flow curve should not change over time when the polymer is fully dissolved. To illustrate this fact a solution of 3 wt% of PEO ( $10^6 \frac{g}{mol}$ ) is prepared and the flow curve over several weeks is plotted in Fig. S1 (Right) and at a constant shear rate ( $\dot{\gamma} = 10(\frac{1}{s})$ ) Fig. S1 (Left).

The flow curves after full dissolution of the polymer for all used polymer solutions are plotted in Fig. S2. The general behaviour of PEO solutions follows the Cross-model fluid (Eq. 1), the infinity viscosity ( $\eta_\infty$ ) converges to the viscosity of the base solvent (in this case water)[Cro79]. The zero shear rate viscosity ( $\eta_0$ ) is the plateau viscosity at low shear rates,  $\tau_{ve}$  is the relaxation time scale and  $m$  is the rheological exponent. For all used polymers,  $\tau_{ve}$  and  $m$  are listed in the table 1. The relaxation time of the polymer solution increases as the concentration and/or molar mass of the polymer increases.

$$\eta = \frac{\eta_0 - \eta_\infty}{1 + (\tau_{ve}\dot{\gamma})^m} + \eta_\infty \quad (1)$$

Viscoelastic materials respond to strain and this response consists of two parts, the elastic part which can be modelled by a spring and the viscous part which can be modelled by a dashpot. One of the simplest models for describing the viscoelastic behaviour of a material is the Maxwell model. The representative of this model is presented in Fig. S3, where the  $E$  is the elastic modulus of the linear spring which represents the elastic part. If we consider the applied stress as  $S$  and strain as  $\gamma$ , the relation between these two parameters in fully elastic situation can be written as  $S = E\gamma$ .  $\eta$  is also the viscosity of the liquid which is the damping parameter of the linear dashpot (the simplest model to exhibit the viscous part). In terms of stress and strain, the dashpot response would be  $S = \eta\dot{\gamma} = \eta \frac{d\gamma}{dt}$ . The Maxwell model suggests to combine the spring and dashpot in series to predict

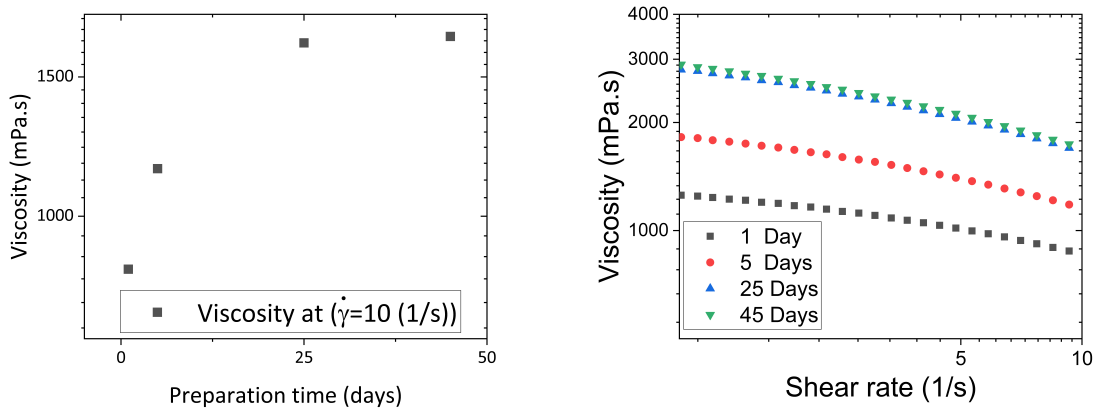


Figure S1: Dissolution kinetics of the 3 wt% PEO solution of a molar mass of  $10^6 \frac{g}{mol}$ . Left: The viscosity of sample at shear rate of  $(\dot{\gamma} = 10(\frac{1}{s}))$  as function of preparation time in days. Right: The flow curves of the polymer solution after different dissolution times.

Sample	$\tau_{ve}$ (s)	$m$
Water + PEO (2%, 300k)	0.000108	0.9187
Water + PEO (3%, 300k)	0.0002186	0.7374
Water + PEO (4%, 300k)	0.0005521	0.719
Water + PEO (2%, 600k)	0.0007864	0.676
Water + PEO (3%, 600k)	0.004355	0.6068
Water + PEO (4%, 600k)	0.02218	0.534

Table 1: The rheological parameters deduced by fitting the Cross-model to the flow curves.

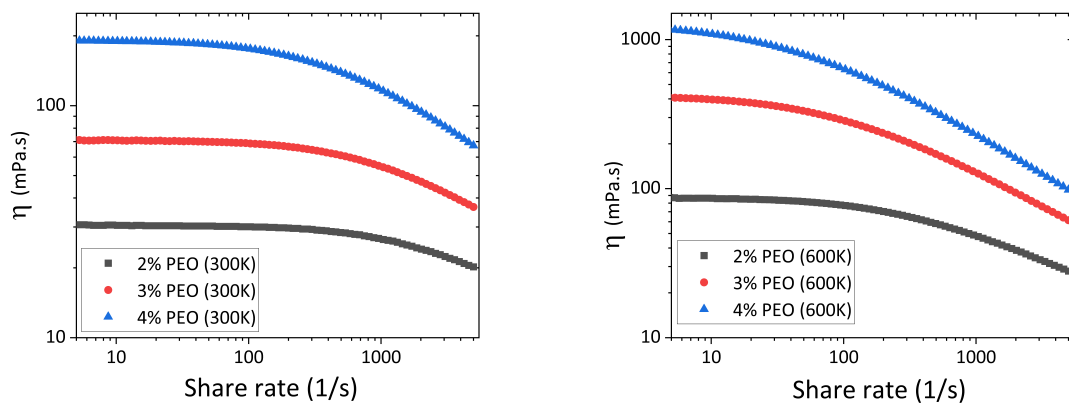


Figure S2: Left: The flow curve of different concentrations of PEO ( $300 \times 10^3 \frac{g}{mol}$ ). Right: The flow curve of different concentrations of PEO ( $600 \times 10^3 \frac{g}{mol}$ ).

the system viscoelastic response, Fig. S3. If a stress applies to the system, the stress would be equal in each element since the spring and dashpot are in series ( $S = S_s = S_d$ ). On the other hand, the total strain would be sum of the strain in each element ( $\gamma = \gamma_s + \gamma_d$ ). By considering all the equations, the governing equation for the system would be the ( $\eta\dot{\gamma} = \frac{\eta}{E}\dot{S} + S$ ). Now if we stretch the material and holds that (a situation similar to the drop spreading), the left hand side of previous equation is zero ( $\dot{\gamma} = 0$ ). By solving the equation for the remaining terms and considering  $\tau_{ve} = \frac{\eta}{E}$ , the time dependent response of material would be as (Eq. 2):

$$S(t) = E\gamma_0 \left[ e^{-\frac{t}{\tau_{ve}}} \right] \quad (2)$$

In this formula,  $\tau_{ve}$  is the relaxation time of polymer, in short time scales ( $t \ll \tau_{ve}$ ), the system behaves like pure elastic system and if the time scale of measurement is long enough ( $t \gtrsim \tau_{ve}$ ), the viscous part plays a role and the system relaxes (Fig. S3). This simple model shows that only if the time scale of drop spreading is long enough one can observe the effect of viscoelasticity.

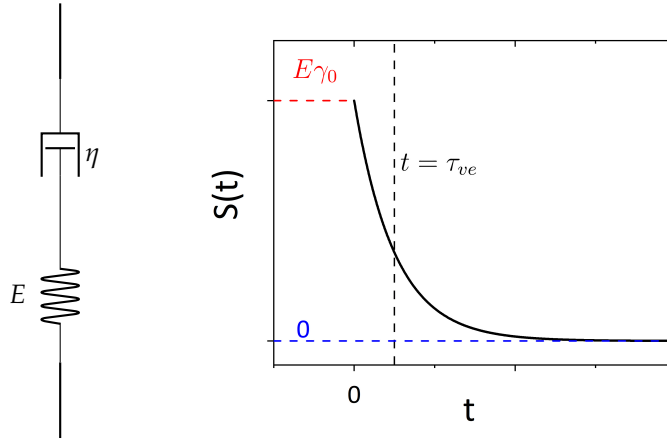


Figure S3: Left: Representative of Maxwell model. Right: The response graph of an applied shear  $E\gamma_0$  based on Eq. 2.

### 3 Dependency of drop spreading on zero time definition

One of the experimental difficulties to study the spreading radii versus time is to determine the exact time of the contact. Three solutions have been used to tackle this issue. On transparent substrates, adding a bottom view camera has proven to be a good and stable solution [EWS13]. Alternatively, a phase space plot was suggested, i.e., to plot the contact line velocity versus the spreading radius ( $r/R$ ). [HFW<sup>+</sup>21] The third option would be to define a fitting parameter as  $t_0$ , this parameter can pop up in the fitting function  $r = B(t - t_0)^\alpha$ . For all of our experiments, this parameter is in the order of few frames  $t_0 \sim 0.0001s$ . In all the graphs in the main manuscript, the data points of the first four frames are omitted to be sure that the definition of first contact point time has no influence on the fitting.

The advantages of the phase-plot method is that we get ride of time dependency, the contact line velocity is plotted versus the wetted radius in Fig. S4. In this figure, we re-plot the data shown in Fig.2a of the main manuscript as phase-space plot. The exponent in this case,  $\delta$ , is related to the spreading exponent by  $\alpha$ , this relation can be written as  $\delta \sim (\frac{1}{\alpha} - 1)$ . Fig. S4 shows that the differences in the behavior are independent of the definition of  $t = 0$ .

### 4 Transition from early stage of drop spreading to Tanner regime

As mentioned in the main text, the drop spreading of intermediate molar mass polymer solutions ( $300 - 600 \times 10^3 \frac{g}{mol}$ ) as well as Newtonian liquids exhibits an early regime and this follows by a

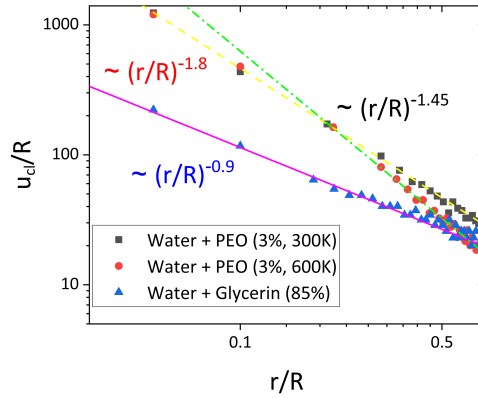


Figure S4: Phase-space plot of the contact line velocity versus the wetted area radii.

viscous dominated regime (known as Tanner law regime). These two regime and cross over between them are shown for one of the samples (PEO (3%,  $300 \times 10^3 \frac{g}{mol}$ ) in Fig. S5.

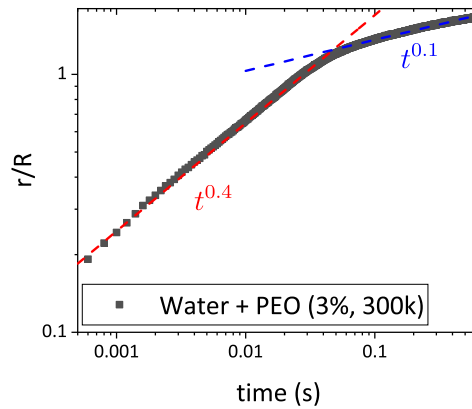


Figure S5: Radius of the wetted area ( $r$ ) normalized by initial radius of drop ( $R$ ) as a function of time, for water and PEO (3%, 300k) on hydrophilic substrate. The early stage of drop spreading is followed by a second regime (known as Tanner law regime).

## 5 Spreading of high molar mass polymer solutions

As mentioned in the main text, the drop spreading of high molar mass polymer solutions ( $1000 - 8000 \times 10^3 \frac{g}{mol}$ ) exhibits an additional regime in the first few milliseconds. This regime is shown for one of the samples (PEO (0.25%,  $8000 \times 10^3 \frac{g}{mol}$ ) in Fig. S6.



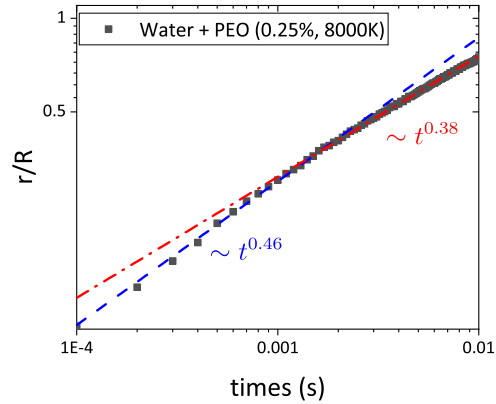


Figure S6: Radius of the wetted area ( $r$ ) normalized by initial radius of drop ( $R$ ) as a function of time, for water and PEO (0.25%, 8000k) on hydrophobic substrate. The early stage of drop spreading is divided into two regimes, which is not the case for low molar mass drop spreading.

## References

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