Rheology of emulsions with polymer solutions as the continuous phase

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\textbf{A B S T R A C T}

We investigate the effect of the addition of polymers on the flow properties of emulsions. Surfactant-stabilised 80 v\% oil-in-water emulsions, exhibiting a yield stress, with either xanthan gum (a stiff, rodlike polymer) or polyethylene oxide (PEO, a flexible, elastic polymer) in the continuous phase (concentrations between 0.005 wt\% and 0.5 wt\%) are prepared and investigated using shear rheology and confocal microscopy. The flow properties of the emulsions are very robust, and only at high concentrations of polymer (≥ 0.2 wt\%), significant changes in the flow properties are observed. In the case of xanthan gum, higher shear stresses are measured. For high concentrations the yield stress is masked by the high zero shear viscosity and shear thinning behaviour of the xanthan gum giving rise to an apparent second power law regime. In the case of PEO, an increase in the shear thinning exponent is observed, together with a decrease in the yield stress. The interaction of PEO with the surfactant SDS (sodium dodecyl sulfate) at higher PEO concentrations strongly affects the emulsion rheology, perhaps by reducing the friction coefficient between the oil droplets.

1. Introduction

Emulsions are found in a wide variety of products: for example in cosmetics, foods and paints. They are an example of complex fluids that can exhibit both solid- and liquid-like behaviour. Both from an industrial as a fundamental point of view, understanding the flow behaviour of these complex fluids is of great importance\cite{1,2}. Model emulsions with various oil/water ratios and surfactants such as sodium dodecyl sulfate (SDS) have been intensively investigated and their rheology is well characterised\cite{3–10}. However, the emulsions that can be found in foods, cosmetics and paints are often more complicated than such model systems. The dispersed phase is often a combination of various oils, the continuous phase can contain polymers or particles, and multiple additives contribute to the stabilisation of the emulsion\cite{11}. Therefore, predicting the flow behaviour of these more complex emulsions is difficult. To better understand these complex emulsions, we make a first step in changing the continuous phase of our emulsions. In many applications, polymers in the water phase are used to change the rheological properties of the continuous phase. It is very interesting to know if this also has a strong effect on the rheological properties of the emulsion. In this paper, we investigate the role of adding a flexible polymer, namely polyethylene oxide, and a rigid polymer, namely xanthan gum, to the continuous phase of the emulsion\cite{12}. Xanthan gum is a common thickening agent in all sorts of products, such as beverage emulsions\cite{13}, salad dressings\cite{14}, whipped cream\cite{15} and yoghurt\cite{16}. Its solubility and high stability over a wide range of temperatures and pH values and its high viscosity at low shear rate together with shear thinning behaviour, makes the polysaccharide very suitable for thickening food products\cite{16}. Polyethylene oxide is a hydrophilic, linear polymer available in a wide range of molecular weights. In this paper, we use a high molecular weight of $M_W = 4 \cdot 10^6$ g/mol. The advantageous characteristics of PEO, being non-toxic, easily soluble in water and insensitive to a wide range of pH values, make the polymer very suitable for the use in controlled drug delivery\cite{17,18}. The different viscoelastic behaviour of xanthan gum and PEO in solution has already been investigated extensively by Bonn and Meunier\cite{12}, showing that the flow behaviour of these solutions is largely dependent on the flexibility of the polymer. Xanthan gum shows very strong shear thinning, already at low polymer concentrations, whereas the viscosity of PEO solutions is approximately constant. Furthermore, the flexible polymer PEO exhibits large normal stress effects, in response to shear deformation, while they are almost undetectable for the stiff polymer xanthan gum\cite{12}. Highly-concentrated oil-in-water emulsions are prepared with polymer concentrations between 0.005 and 0.5 wt\% in the continuous phase. We compare the flow properties of these emulsions with the flow properties of a ‘standard’ 80 v\% oil-in-water emulsion. We observe that the rheology of emulsions is very robust, and behaves according...
to the Herschel–Bulkley model, that is a good description for the emulsions without polymers, for a wide variety of concentrations. Changing the rheology of the continuous phase initially has little effect on the flow properties of emulsions, which only change when very high concentrations (above 0.2 wt%) of polymer are added.

2. Materials and methods

2.1. Polymer solutions

A 1 wt% xanthan gum solution is prepared by adding 1 g of xanthan gum (XG, $M_w = 934$ g/mol [12] from Sigma-Aldrich) to 99 g of MilliQ water. The mixture is gently stirred for 24 h to let the xanthan gum dissolve. From this stock solution, various dilutions between 0.005 and 0.5 wt% of xanthan gum are prepared by adding the right amount of MilliQ water.

Similarly, a 1 wt% PEO solution is prepared by carefully dissolving 1 g of polyethylene oxide (PEO, $M_w = 4 \cdot 10^6$ g/mol, as specified by Sigma-Aldrich) in 99 g of MilliQ water while gently stirring overnight. Dilutions with PEO concentrations between 0.005 and 0.5 wt% are prepared by adding the right amount of MilliQ water.

Since the continuous phase of the emulsions also contains 1 wt% of sodium dodecyl sulfate (SDS, from Sigma-Aldrich) as stabilising agent, we prepare polymer solutions with 1 wt% of SDS to investigate the effect of the surfactant on the rheology of the polymer solutions. Therefore, after preparation of a 1 wt% polymer solution, 1 wt% of SDS is added while stirring for 1 h. Afterwards dilutions with concentrations between 0.005 and 0.5 wt% of polymer are prepared by adding the right amount of a 1 wt% SDS solution. We use a concentration of SDS where all the surfaces are saturated, but there is little SDS in the continuous phase, to avoid complications due to the depletion interaction induced by surfactant micelles that can make the emulsions thixotropic [19]. Quantitatively, 1 wt% corresponds to 35 mM SDS; if we assume a close packing of droplets, we find that for this drop size about 2/3 of the SDS molecules are adsorbed at the oil/water interfaces, whereas 1/3 remains in solution, so the solution between the drops is at a few times the CMC (Critical Micellar Concentration) of SDS. For the calculation we use 50 Å² as the area/molecule [20].

2.2. Emulsion preparation

Various emulsions with different concentrations of polyethylene oxide or xanthan gum are prepared. We first prepare a large batch of emulsion, as a start for all emulsions. Working with a stock emulsion ensures that all emulsions have the same average oil droplet size, ruling out any variations in the flow properties due to droplet size variations. For the continuous phase, 2 wt% of SDS is dissolved in MilliQ water and then Rhodamine B (Sigma-Aldrich) is added as a dye to allow visualisation of the 2 phases under the confocal microscope. Castor oil (Sigma-Aldrich) is slowly added to the water phase while stirring at 2 krpm with a Silverson LSM-A emulsifier. Once all the oil is added, resulting in 90 v% of oil, and the oil is homogeneously distributed over the mixture, the stirring speed is increased stepwise to 10 krpm. During emulsification the sample is cooled in an ice bath to prevent heating of the sample. After mixing for 2 min at 10 krpm, a 90 v% oil-in-water emulsion with a droplet diameter of 3.4 μm with a size polydispersity of 20% is obtained.

The emulsion is divided over different vials and diluted with a solution containing either PEO or xanthan gum in a concentration between 0.01 and 1 wt%. This results in oil-in-water emulsions with 80 v% of oil, 1 wt% SDS in the continuous phase and 0.005–0.5 wt% PEO or xanthan gum in the continuous phase.

2.3. Rheology

The shear viscosity of dispersions with various concentrations of either PEO or xanthan gum, with and without 1 wt% of SDS, are measured using shear rheology tests. These shear rheology measurements are performed on a stress-controlled rheometer (Anton Paar MCR 300), equipped with a cone-and-plate geometry with a diameter of 50 mm and a cone angle of 1°. The steady shear experiments are performed by carrying out a shear rate sweep from $10^2$ to $10^{-1}$ s⁻¹ at a temperature of 20 °C set by a Peltier system.

For the flow behaviour of the emulsions, a roughened cone-and-plate geometry is used to prevent slip. The geometry has a diameter of 50 mm and a cone angle of 1°. The gap at the truncation is 25 μm, this is still much larger than the average drop size. All samples are pre-sheared at a shear rate of 50 s⁻¹ for 30 s, followed by a rest period of 30 s. This allows to create a controlled initial state for every sample. The measurements are performed at a temperature of 20 °C set by a Peltier system. The rotational tests are performed by doing shear rate sweeps from $10^3$ to $10^{-3}$ s⁻¹.

Normal stress measurements are also performed with the roughened cone-and-plate geometry, but with a different protocol: the first normal stress difference, $N_1$, is measured over 60 s at a fixed shear rate, followed by a rest period of 30 s at zero shear rate. The first normal stress difference is then defined as the difference between the equilibrium $N_1$ at the imposed shear rate minus $N_1$ at zero shear rate, since, due to residual trapped stresses, the first normal stress difference can differ from zero at zero shear rate. We tested our method outlined here against more reliable but very cumbersome AC measurements of the normal stresses [21], and found that this is the best way to correct for drift of the normal force transducer.

2.4. Confocal microscopy

All emulsions are studied with a Leica TCS SP8 laser scanning confocal microscope system to investigate the effect of additives in the continuous phase on the average droplet size. Therefore, we use a typical slice thickness of approximately 50 μm. A 488 nm Ar laser is used for excitation of the fluorescent Rhodamine B in the water phase. Measurements are performed with a Plan Apochromat oil-immersed objective with a magnification of 100x and a NA of 1.40.

3. Results and discussion

3.1. Solutions and emulsions with xanthan gum

The flow properties of aqueous xanthan gum solutions with different concentrations of polymer are shown in Fig. 1. The concentration of polymer increases from 0.005 wt% (lightest red) to 0.5 wt% (darkest red). Fig. 1a shows that with increasing xanthan gum concentration, the viscosity increases. Furthermore, the solutions, especially with higher concentrations of xanthan gum, show shear thinning behaviour. Fig. 1b shows the flow properties of xanthan gum solutions with addition of 1 wt% of SDS. We use a concentration of SDS for which in the emulsion all the surfaces are saturated, but there is little SDS in the continuous phase, to avoid complications due to the depletion interaction induced by surfactant micelles that can make the emulsions thixotropic [22]. Comparing the two graphs, we do not observe large differences. This is also made clear in Fig. 1c, showing the ratio between the viscosity with and without 1 wt% SDS. The curves are relatively flat and close to 1. The observation that the viscosity ratio can go below unity is probably due to the addition of ions from the SDS that make the xantan chains slightly less stiff [23]; the side chains of the polysaccharide contain pyruvic acid residues that make xanthan gum a polyelectrolyte. Especially at higher concentrations of xanthan gum (≥ 0.1 wt% of xanthan gum), the viscosity curves are very similar, and agree with values from the literature [24] for xanthan of the same manufacturer; as
xanthan is a bioproduct, samples from different manufacturers typically have a different rheology. At lower concentrations of xanthan gum (≤ 0.1 wt% of xanthan gum), the viscosity curves with SDS show slightly lower viscosities and do not show strong shear thinning behaviour. The inset of Fig. 1b shows the viscosity curves for the higher concentrations of xanthan gum (with SDS) at low shear rates ranging from $10^{-3}$ to $10^{3}$ s$^{-1}$. For the other concentrations, the viscosity is too low to be measured at such low shear rates. However, since these solutions do not show shear thinning behaviour in the measured range, we can assume that the viscosity remains similar at low shear rates. We observe that for the highest concentrations of xanthan gum (0.5 wt%), a zero shear viscosity of 200 Pa s is reached, which is about a factor $10^4$ higher compared to the lowest concentrations of xanthan gum (0.005 wt%).

Now that we know the flow properties of the xanthan gum solutions, we investigate the flow properties of SDS-stabilised 80 v% oil-in-water emulsions with various concentrations of xanthan gum in the continuous phase. Fig. 2a shows the flow curves of the different prepared emulsions. We can immediately see that for low concentrations of xanthan gum (≤ 0.1 wt%), there are only small changes in the flow curves. These flow curves indicate that a factor 10–100 increase in viscosity of the continuous phase due to addition of xanthan gum (see Fig. 1b) has little effect on the shear rheology of the emulsions.

At higher concentrations of xanthan gum (≥ 0.2 wt%), the flow behaviour is different. It is immediately obvious that these curves do not show a clear yield stress plateau, see Fig. 2a. Rather, it looks like there are two different power law regimes, a faster decaying part at higher shear rates and a slower decaying part at lower shear rates. At these high concentrations of xanthan gum, the continuous phase itself is shear thinning and reaches high viscosities of 10 Pa s at $10^{-3}$ s$^{-1}$ for 0.2 wt% xanthan gum and even 200 Pa s at $10^{-3}$ s$^{-1}$ for 0.5 wt% xanthan gum (see Fig. 1b). So, the strong shear thinning behaviour of the continuous phase appears to mask the yield stress behaviour of the emulsion itself. Confocal microscopy images of the emulsions show that structural changes are not at the origin of the different flow behaviour. Fig. 2b, c shows very similar confocal images for 0.005 wt% of xanthan gum and for 0.5 wt% of xanthan gum. No surprising features can be seen and the average droplet size also does not change with changing xanthan gum concentration.

To better understand the flow properties of the emulsions with xanthan gum, we use two different models to fit the data. First, the Herschel–Bulkley model, which is very commonly used to describe the shear stress as a function of shear rate for concentrated emulsions [25]:

$$\sigma = \sigma_0 + K\dot{\gamma}^n$$  \hspace{1cm} (1)

where $\dot{\gamma}$ is the shear rate, $\sigma$ is the shear stress and $\sigma_0$ is the yield stress. The consistency $K$ and flow index $n$ are adjustable model parameters. Since we do not observe a plateau value for the emulsions with higher concentrations of xanthan gum, indicating two different decaying regimes, we also fit the data with a double power law:

$$\sigma = A\dot{\gamma}^p + B\dot{\gamma}^q$$  \hspace{1cm} (2)

where we take that $p > q$. Fig. 2d shows a few examples of both the Herschel–Bulkley fitting (solid line) and a double power law (dashed line) for emulsions with low (0.005 wt%) and high (0.4 and 0.5 wt%) xanthan gum concentrations. Whereas the Herschel–Bulkley model nicely fits the data for lower polymer concentrations, at higher concentrations the model does not capture the shear stresses at low shear rates. This suggests that the shear thinning behaviour of the xanthan gum masks the yield stress. Fig. 2e shows the goodness of the fits, represented by the R-squared value, here plotted as a function of xanthan gum concentration. On average, the higher the R-squared value, the more accurately the fit describes the data. Since a double power law contains four parameters, whereas the Herschel–Bulkley model contains only three, a double power law gives a better fit. However it should be noted that the power-law in fact has less than 4 completely adjustable parameters, since the power-law must be contained between 0 and 1. The Herschel–Bulkley model (orange squares) at low polymer concentrations nicely fits the data, however the R-squared value decreases at higher concentrations: the emulsions with high concentrations of xanthan gum (≥ 0.2 wt%) are better described with a double power law. The second exponent that arises is probably due to the shear thinning of the xanthan gum itself and becomes more significant for higher concentrations of xanthan gum. Not only the emulsion itself is shear thinning, but the continuous phase also contributes on a different shear rate range. Although a second shear thinning component is not very surprising, the apparent disappearance of the yield stress is. This characteristic feature of highly-concentrated oil-in-water emulsions stems from jamming of the oil droplets above the critical packing fraction of 64 v%. This jamming does not disappear, since the oil concentration does not change. We have also done an alternative fitting with the inclusion of a yield stress, where we use the yield stress at very low polymer concentration as a constant, in order not to add a fitting parameter. The fit is equally good, suggesting that the yield stress is in fact still present, but is masked by the shear thinning of the continuous phase.

3.2. Solutions of and emulsions with polyethylene oxide

Fig. 3 shows the viscosity of various PEO solutions as a function of shear rate. The concentration of polymer increases from 0.005 wt%
0.2 wt%), also a significant change in the measured yield stress values at around 0.05 wt% of PEO, see Fig. 4 c. At even higher concentrations of PEO (0.05 wt% and 0.1 wt% of PEO still show similar flow behaviour as the emulsion without PEO. However, a fit with the Herschel–Bulkley model results in a higher flow index

Examples of these fittings at low and high concentrations of PEO are shown in Fig. 4 a. Similarly to the xanthan gum, we do not see significant differences in the flow curves for low concentrations (< 0.05 wt%) of polymer. The flow curves nicely follow the Herschel–Bulkley model, with a yield stress of approximately 17 Pa and a flow index of around 0.51. This is not surprising, since the viscosity of the continuous phase also does not show a significant increase at these low concentrations (see Fig. 3c). This jump in viscosity is likely due to an interaction between the SDS and the PEO, such as e.g. the complexation of SDS micelles and the long PEO chains [27,28]. Similar observations are described by Martinez Narvaez et al. where the PEO concentration is fixed at 0.1 wt% and the SDS to the PEO solutions, the viscosity significantly changes, as can be seen in Fig. 3c. This jump in viscosity is due to a decrease in shear stress and the normal stress, \( \sigma \), gives the effective friction

\( \mu \).

\( N_1 \).

\( \frac{\sigma}{\mu} \) gives the effective friction

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Fig. 3. Viscosity of PEO solutions for various concentrations of polymer. (a) Viscosity curves as a function of shear rate for PEO solutions with concentrations between 0.005 (lightest blue) and 0.5 (darkest blue) wt%. Since these viscosities are very close to that of water, it is difficult to obtain reproducible results for very low shear rates and polymer concentrations due to edge effects in the rheometer caused by the surface tension of the solution. (b) Viscosity curves as a function of shear rate for PEO solutions with 1 wt% of SDS. (c) Ratio between the viscosity with and without 1 wt% SDS as a function of shear rate. The colours in (a), (b) and (c) represent the same PEO concentrations.

Fig. 4. Flow properties of 80 v% oil-in-water emulsions with various concentrations of PEO in the continuous phase. (a) Flow curves of the emulsions with concentrations between 0.005 (lightest blue) and 0.5 (darkest blue) wt% of PEO. (b) Herschel–Bulkley fits of the flow curves of emulsions with three different concentrations of PEO. (c) Herschel–Bulkley fit parameters as a function of concentration. The black squares show the yield stress $\sigma_0$ (left y-axis), whereas the red circles show the flow index $n$ (right y-axis). (d) Confocal microscopy image of an 80 v% oil-in-water emulsion with 0.005 wt% PEO in the continuous phase. The scale bar is 5 $\mu$m. (e) Confocal microscopy image of a 80 v% oil-in-water emulsion with 0.5 wt% PEO in the continuous phase. The scale bar is 5 $\mu$m. Both images are taken with the same scanning parameters and no image manipulation is performed afterwards. (f) Friction coefficient, defined as the ratio between the shear stress and the normal stress, $\frac{\tau}{N}$, as a function of the shear rate for an 80 v% oil-in-water emulsion, and an 80 v% oil-in-water emulsion with 0.5 wt% of PEO.

We observe that the addition of PEO lowers the friction coefficient of the emulsion, meaning that the system is more slippery. PEO is commonly used as a lubricant as it results in slippery surfaces [34]. Whereas the rheology of emulsions is normally determined by the deformation of the droplets, addition of PEO can result in rheology that is dominated by sliding of the droplets in the emulsion, due to a lubricated layer generated by the presence of polymer. The deformation of droplets is well described by the Herschel–Bulkley model, with a flow index $n \approx 0.5$. Sliding of the droplets enhances the shear thinning, and can bring the flow index to 1 eventually. For our emulsions with the highest concentrations of PEO, we find a flow index with a value exactly in between, a strong indication that both deformation and sliding contribute to the flow behaviour of the emulsions. How the PEO/SDS interaction exactly contributes to the decrease of the yield stress remains an open question.

coefficient between the drops, in analogy with granular materials [33]. For granular systems, it is observed that when the contacts between particles are purely frictional, a normal stress is measured, whereas no normal stress is measured in the case of lubricating contacts. It should be noted here that measurement of the normal force in yield stress materials is notoriously difficult, see [21], who found a quadratic dependence on the shear stress, in line with the decreasing ratio as a function of shear rate found here. There are however very few reliable measurements from the literature to compare with, because of the difficulty of measuring this.

Whereas the rheology of emulsions is normally determined by the deformation of the droplets, addition of PEO can result in rheology that is dominated by sliding of the droplets in the emulsion, due to a lubricated layer generated by the presence of polymer. The deformation of droplets is well described by the Herschel–Bulkley model, with a flow index $n \approx 0.5$. Sliding of the droplets enhances the shear thinning, and can bring the flow index to 1 eventually. For our emulsions with the highest concentrations of PEO, we find a flow index with a value exactly in between, a strong indication that both deformation and sliding contribute to the flow behaviour of the emulsions. How the PEO/SDS interaction exactly contributes to the decrease of the yield stress remains an open question.
4. Conclusion

We have prepared surfactant-stabilised highly-concentrated oil-in-water emulsions with various concentrations of either xanthan gum or polyethylene oxide (MW = 4 - 10^6 g/mol) in the continuous phase. We observe that the flow properties of the emulsions are very robust and behave according to the Herschel–Bulkley model. At low concentrations of polymer (≤ 0.1 wt%), no significant change in the flow curves is observed as compared to the emulsion without added polymer. We measure an enhanced shear stress for the emulsions with higher concentrations of xanthan gum (≥ 0.2 wt%), since xanthan gum solutions with these concentrations have a high zero shear viscosity. The shear thinning behaviour of these xanthan gum solutions results in an additional power law exponent at lower shear rates, whereas the shear thinning behaviour of the emulsion itself results in an exponent of approximately 0.5 independent of the xanthan gum concentration. Surprisingly, the yield stress seems to disappear for these high xanthan gum concentrations.

The emulsions with PEO in the continuous phase show significantly different behaviour at high concentrations of PEO (≥ 0.2 wt%). A decrease in the yield stress is measured with increasing PEO concentration, together with an increase in the shear thinning exponent. Confocal microscopy reveals the presence of PEO/SDS complexes at the surface of the oil droplets. This changes the elastic properties of the oil droplets, by lowering the friction coefficient of the emulsions. The rheology of the emulsions with high concentrations of PEO is not only determined by the deformation of the oil droplets, but also by the sliding of the oil droplets due to the slippery surface. This explains the increased shear thinning, whereas the decrease in yield stress remains not understood by now.

We previously performed a very systematic study of the effect of oil volume fraction on the rheology of emulsions; this part of emulsion rheology is now by well understood [35,36]. What we focused on here is the changes such emulsions undergo when polymers are added to the continuous phase. From our findings, we expect those changes to be observed also for other volume fractions, so we have focused on a relatively low one that still has an appreciable yield stress; for higher volume fractions the changes would be more difficult to observe because of the higher viscosity of the emulsions themselves.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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