Confined flow of polymer blends

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C. Tufano, G.W.M. Peters, and H.E.H. Meijer
Eindhoven University of Technology, Department of Mechanical Engineering

Introduction
The trend toward miniaturization leads to processes in which the characteristic sizes of device and morphology are comparable. The goal is to study the influence of a confinement on the steady state morphology of two emulsions, differing in mutual miscibility and interfacial tension (Table 1).

Materials and Methods

<table>
<thead>
<tr>
<th>Blend</th>
<th>$M_n^\text{blend}/M_n^\text{const}$</th>
<th>$\eta_d/\eta_m$ ($\text{Pa.s}$)</th>
<th>$\sigma_{\text{steady}}$ ($\text{mN/m}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBD8K/PDMS60K</td>
<td>1.6/1.8</td>
<td>44.5/10.8</td>
<td>4.2</td>
</tr>
<tr>
<td>PB635/PDMS60K</td>
<td>2.1/1.8</td>
<td>3.75/10.8</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Table 1. Selected model components.

Three weight concentrations (10%, 20%, 30%) are investigated. Samples were sheared between parallel plates (gap spacing H=40 $\mu$m) in a range of shear rates at which the transition from "bulk" behavior towards "confined" behavior was observed. Results are compared to the Maffettone-Minale model (MM model), as a function of the capillary number $Ca$, for bulk flows to detect deviations from bulk behavior.

$$L_p$$ and $W$ are measured; $r_p = L/B$ is calculated:
$$L_p^2 = B^2 + (L^2 - B^2 \cos^2 \theta); \text{LBW} = 8R^3$$

$\theta$ predicted by MM model, and $\theta = 0$ are used.

$$\theta_{\text{MM}} = \frac{1}{2} \arctan \left( \frac{c_1}{c_2} \right); f_1 = \frac{40(p+3)}{(2p+3)(19p+16)}$$

$Ca = \frac{\eta_m \dot{\gamma} R}{\sigma}$; $R$=drop radius

Results
Drop deformations ($r_p$) are fairly well predicted by the MM model for high enough shear rates. At lower shear rates (i.e. higher degree of confinements, $2R/H$), better agreement is found by considering $\theta = 0$ (Figure 2 and 3, $r_p$ vs $Ca$ curves).

The partially miscible PB/PDMS system
For the PB/PDMS system, $W$ vs $Ca$ becomes constant at concentrations higher than 10% and for a larger degree of confinement.

Morphology: strings
The dependence of the length $L$ and the width $B$ of the drops on $Ca$ was investigated for the 20 wt% systems by fitting the experimental data with $L \propto Ca^l, B \propto Ca^b$. The strong dependence of $L/B$ on $Ca$ is unique feature of strings in confined emulsions (Figure 4).

Conclusions
By decreasing the shear rate, for each blend the same morphology evolution is encountered:

- droplets arrange into two layers, move to a single layer at a critical degree of confinement lower than 0.5 and finally superstructures, like ordered pearl necklaces and strings, form.
- The MM model does not fully predict the morphology evolution in the confined geometries.
- An unique condition to identify strings is proposed.


PO Box 513, 5600 MB Eindhoven, the Netherlands