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Influence of interfacial tension on coalescence of polymer blends

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

Introduction
Interfacial tension of polymer blends is affected by mutual solubility which, in many cases in literature, is assumed negligible. This assumption is not completely correct if we consider a large asymmetry in molecular weights of the two components. The goal of this work is to study the evolution of interfacial tension with time as a function of molecular weight asymmetry across an interface in order to understand morphology development during mixing.

Materials

<table>
<thead>
<tr>
<th>Polymer Blend</th>
<th>Dispersed phase</th>
<th>Continuous phase</th>
<th>$M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extremely Diffusive</td>
<td>PB/PDMS</td>
<td>635/62700</td>
<td></td>
</tr>
<tr>
<td>Slightly Diffusive</td>
<td>PBD/PDMS</td>
<td>8000/62700</td>
<td></td>
</tr>
<tr>
<td>Reversed ED</td>
<td>PDMS/PB</td>
<td>62700/635</td>
<td></td>
</tr>
<tr>
<td>Reversed SD</td>
<td>PDMS/PBD</td>
<td>62700/8000</td>
<td></td>
</tr>
</tbody>
</table>

Techniques
Interfacial tension is measured with a pendent/sessile drop apparatus (Fig. 1 a). The time dependent drop shape is fitted using Gauss-Laplace equation giving the interfacial tension. The time evolution of the average radius is obtained from SALS patterns (Fig. 1 b) applying Debye-Bouche theory and from optical microscopy measurements.

Gauss-Laplace equation:

\[
\sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = \Delta P_0 + \Delta \rho g z
\]

- $\sigma$: interfacial tension
- $R_1$, $R_2$: radii of curvature
- $\Delta P_0$: pressure difference in a reference plane
- $\Delta \rho$: density difference
- $g$: gravity acceleration
- $z$: vertical height of the drop

Debye - Bouche equation:

\[
I(q) = K \xi^6 [1 + (\xi q)^2]^{-2}
\]

- $K$: a function of the scattering contrast
- $q$: scatter vector magnitude
- $\xi$: structure correlation distance
- $R^2 = 10 \xi^2$

Mathematical Models
Drop radii are calculated from a drainage model. Three cases: immobile, partially mobile and fully mobile interfaces.

\[
R_{imm.} = \left( \frac{8}{9} \right)^{1/4} \left( \frac{M_n}{\eta_c \dot{\gamma}} / \sigma \right)^{-1/2}
\]

\[
R_{pm.} = \left( \frac{4}{\sqrt{3}} \right)^{2/5} \left( \frac{M_n}{\eta_c \dot{\gamma}} / \sigma \right)^{-2/5}
\]

\[
R_{fm.} = \ln \left( \frac{R_{fm.}}{h_{cr}} \right) = \frac{2}{3} \left( \frac{\eta_c \dot{\gamma}}{\eta_c \dot{\gamma} / \sigma} \right)^{-1/5}
\]

The initial, the minimum and the "plateau" value of $\sigma$ have been plugged in the model (Fig. 4).

Conclusions
- With lower $M_n$ polymer as dispersed phase interfacial tension changes in time.
- By reversing the phases, diffusion becomes a minor phenomenon and does not play any role in defining the morphology.
- Existing mathematical models do not apply.

This knowledge can be used to understand and, moreover, to control blend morphology.