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Interfacial tension of "immiscible" polymer blends

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Introduction

The interfacial tension, σ , is a key parameter in blending immiscible polymeric liquids. Average molecular weight of drops and matrix ($M_n^{d,m}$), asymmetry in molecular weight across the interface (ΔM_n), temperature (i.e. viscosity, $\eta(T)$) and polydispersity (p) affect the interfacial tension due to partial miscibility. The goal of this work is to study the influence of these parameters on the transient and steady interfacial tension for the blends reported in Table 1.

Materials and Methods

The materials used are polydimethylsiloxane (60K) and three different grades of polybutene.

M_n^d/M_n^m	p_d/p_m	η_d/η_m [Pa*s]	R_0 [mm]	ΔR_{4h} [μm]
PB635/PDMS	2.1/1.8	3.75/10.8	1.13	209
PB1300/PDMS	1.6/1.8	44.5/10.8	1.25	13
PB2100/PDMS	1.8/1.8	307.6/10.8	1.44	0

Table 1. Selected model components; ΔR_{4h} : drop size change in matrix after 4h at 23°C.

Higher drop M_n (i.e. smaller ΔM_n), higher η and lower p mean longer diffusion times (see Table 1). Interfacial tension is measured with a pendant apparatus [1].

Results

Transient interfacial tension

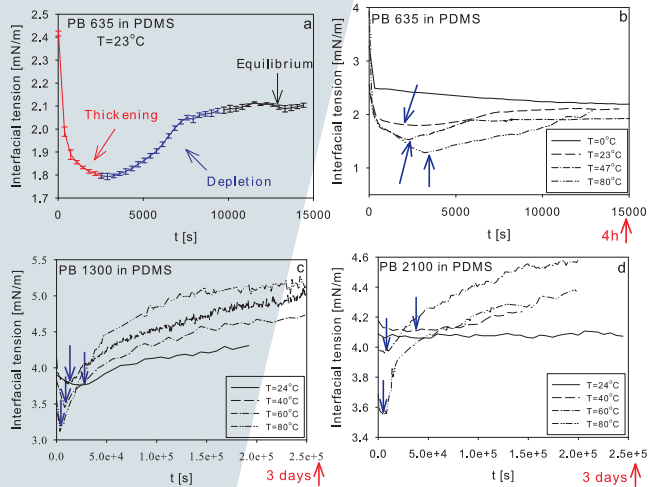


Figure 1. Transient interfacial tension as function of the temperature for different molecular weight drop phases.

Low molecular weight molecules start to diffuse generating a diffuse layer around the drop, the interface thickens ($\sigma \downarrow$). When the molecules diffuse from this layer into the matrix, depletion occurs ($\sigma \uparrow$). Due to the finite amount of molecules in the drop and the continuous transport from interface into the matrix, diffusion is exhausted and σ reaches a plateau (Fig.1a). Increasing the temperature, a higher number of molecules can migrate. Therefore, thicker layer are built

up ($\sigma \uparrow$) and it takes longer to complete the process. Increasing the M_n^d similar responses are measured, however the time scale to complete the diffusion process increases (see Fig.1c,d).

Steady interfacial tension

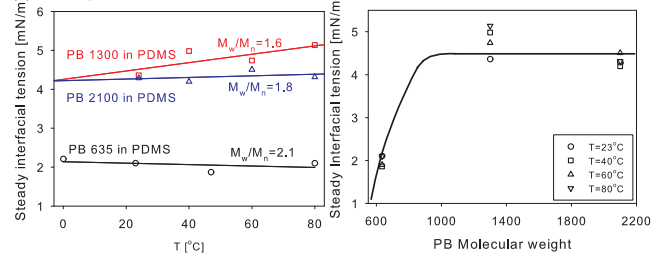


Figure 2. Influence of polydispersity, temperature and molecular weight on the steady interfacial tension.

Increasing p , the steady interfacial tension, σ_s , reduces at all the temperature investigated (Figure 2 left). With increasing M_n^d , σ_s increases and levels off, temperature has a minor effects on this trend (Figure 2 right).

Model prediction

Data are fitted with the double exponential model [2]:

$$\sigma = \sigma_s + \Delta\sigma_{s,d}e^{-(t/\tau_d)} + \Delta\sigma_{s,m}e^{-(t/\tau_m)} \quad (1)$$

where τ_d and τ_m are characteristic diffusion times of molecules moving from the drop into the matrix and vice-versa. For all the blends considered, $\tau_d < \tau_m$ (i.e. diffusion from the drop into the matrix dominates). Results are shown for the PB635 drop in Figure 3 left. With increasing M_n^d , τ_d increases (Figure 3 right). The model prediction confirms the experimental observations.

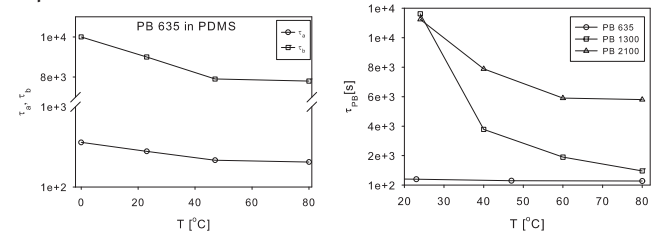


Figure 3. Calculated characteristic diffusion times.

Conclusions

- ♦ A transient σ is explained in terms of partial miscibility.
- ♦ M_n , ΔM_n , η and p affect $\sigma(t)$ and $\sigma(t \rightarrow \infty) = \sigma_s$
- ♦ Results obtained using a double exponential model are in line with the experimental results. However there is still a missing link with thickness of the interface.

References:

- [1] P. XING ET AL.: *Macromolecules*, 33, (2000)
- [2] T. SHI ET AL.: *Macromolecules*, 37, (2004)