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Influence of interfacial tension on coalescence of polymer blends

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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

Polymer Blend	Dispersed phase/ Continuous phase	M_n
Extremely Diffusive	PB/PDMS	635/62700
Slightly Diffusive	PBD/PDMS	8000/62700
Reversed ED	PDMS/PB	62700/635
Reversed SD	PDMS/PBD	62700/8000

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:

$$\sigma (1/R_1 + 1/R_2) = \Delta P_0 + \Delta \rho g z$$

σ : interfacial tension

R_1, R_2 : radii of curvature

ΔP_0 : pressure difference in a reference plane

$\Delta \rho$: density difference

g : gravity acceleration

z : vertical height of the drop

Debye - Bauche equation:

$$I(q) = K \xi^3 [1 + (q\xi)^2]^{-2}$$

K : a function of the scattering contrast

q : scatter vector magnitude

ξ : structure correlation distance

$$R^2 = 10\xi^2$$

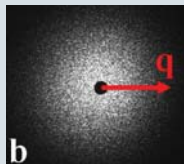
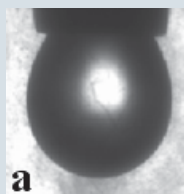


Fig. 1. a: Pendent drop configuration. b: typical SALS pattern.

Results

$M_n(\text{dispersed phase}) < M_n(\text{continuous phase})$

Short molecules diffusing from the drop into the matrix determine the interfacial tension evolution with time and this affect morphology. At constant temperature and at constant viscosity ratio, the phenomenon is more pronounced in the ED blend (Fig.2).

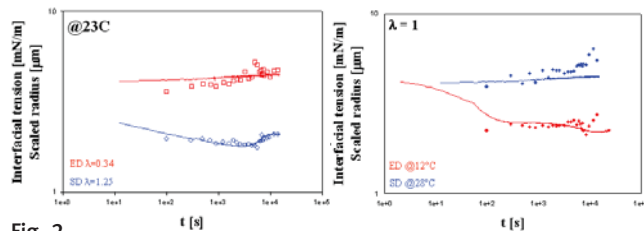


Fig. 2.

$M_n(\text{dispersed phase}) > M_n(\text{continuous phase})$

Short molecules diffuse from the matrix into the droplets but due to the fast saturation of the dispersed phase diffusion doesn't play any role and coalescence determine the morphology (Fig.3).

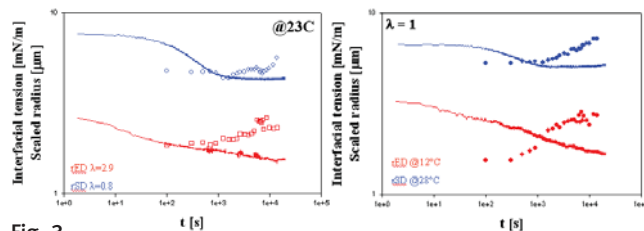


Fig. 3.

Mathematical Models

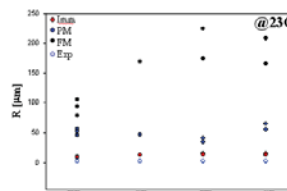
Drop radii are calculated from a drainage model. Three cases: immobile, partially mobile and fully mobile interfaces.

$$R_{Imm.} = (8/9)^{1/4} * h_{cr}^{1/2} * (\eta_c * \dot{\gamma} / \sigma)^{-1/2}$$

$$R_{P.M.} = (4/\sqrt{3} * \dot{\gamma})^{2/5} * \lambda^{-2/5} * (\eta_c * \dot{\gamma} / \sigma)^{-3/5}$$

$$R_{F.M.} * \ln(R_{F.M.} / h_{cr}) = 2/3 * (\eta_c * \dot{\gamma} / \sigma)^{-1}$$

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



η_c : viscosity continuous phase

$\dot{\gamma}$: shear rate

σ : interfacial tension

h_{cr} : critical film thickness

λ : viscosity ratio

Fig. 4. Calculated drop radii compared with the experimental values.

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.