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Citation for published version (APA):

Tufano, C., Peters, G. W. M., & Meijer, H. E. H. (2004). *Interfacial tension and coalescence in polymer blends*. Poster session presented at Mate Poster Award 2004 : 9th Annual Poster Contest.

Document status and date:

Published: 01/01/2004

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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- The final published version features the final layout of the paper including the volume, issue and page numbers.

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Interfacial tension and coalescence in polymer blends

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Introduction

The final properties of polymer blends are, to a great extent, determined by the morphology. It's well known that interfacial tension is a key parameter in the evolution of morphology during blending. The goal of this work is to study the evolution of interfacial tension with time and temperature and the influence of such variations on drop coalescence.

Materials

Blend	Drop/Matrix	ΔR_{4h} [μm]	R_0 [mm]
A2	PB635/PDMS62700	55	1.13
B4	PBD8000/PDMS62700	0.5	1.22

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

A2 is a very diffusive system, B4 is not (see ΔR_{4h} Table1).

Results

Interfacial tension

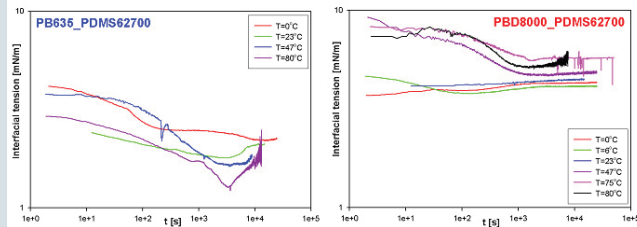


Figure 1. Interfacial tension for the two blends as function of temperature and time measured with a sessile drop apparatus.

Drop radius

Experiments for the same viscosity ratio and same temperature have been performed using SALS. The theory of Debye-Bueche gives the radius of the droplets.

$$I(q) = K\xi^3 F(q\xi); \quad F(x) = 1/(1 + x^2)^2$$

K: a function of the scattering contrast, q: scatter vector magnitude, ξ : structure correlation distance and $R^2 = 10\xi^2$, see Fig.2 and Fig.3. For system A2 the trend of the radius follows the variation of interfacial tension (see Fig.4, left). Repeating the A2 experiment after 48h: no diffusion effects left, so the trend of radii is different (see Fig.4, right).

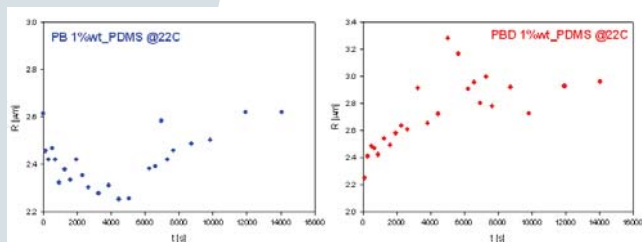


Figure 2. Drop size evolution with time at constant temperature.

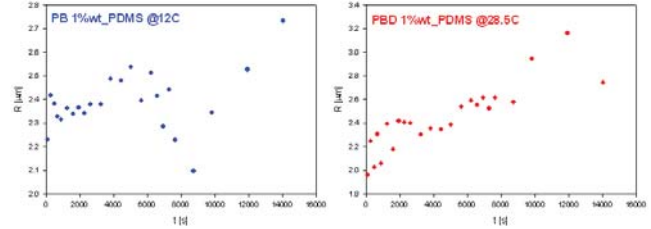


Figure 3. Drop size evolution with time at constant viscosity ratio, $\lambda = 1$.

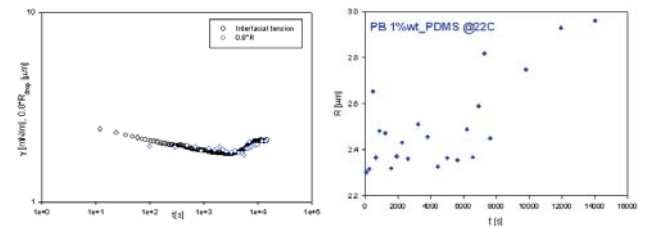


Figure 4. Left: Time evolution of interfacial tension (from [1]) and drop radius for a fresh system. Right: Drop radius evolution for an old (48h) system.

Mathematical Models

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

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

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

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

η_c : viscosity continuous phase, $\dot{\gamma}$: shear rate, σ : interfacial tension, h_{cr} : critical film thickness, p: viscosity ratio. For system A2 the initial, minimum and "plateau" value of γ have been used. For system B4 only one value of γ is used. Table2 shows the results: none of these cases is able to predict the radii values found experimentally.

	$A2_{\sigma_{in}}$	$A2_{\sigma_{min}}$	$A2_{\sigma_{plat}}$	B4
σ [N/m]	0.0024	1.70E-03	2.10E-03	4.10E-03
$R_{Imm.}$ [μm]	10.19	8.58	9.53	13.32
$R_{P.M.}$ [μm]	56.41	45.87	52.07	46.92
$R_{F.M.}$ [μm]	105.61	78.18	93.98	169
$R_{Exp.}$ [μm]	2.45	2.2	2.6	2.2 - 3

Table 2. Calculated drop radii.

Conclusions

- Diffuse interface strongly affects the morphology of the blends.
- Existing mathematical models do not apply.

References:

- [1] A. ZDRAVKOV: PhD Thesis, TU/e (2004)