Supplementary Information

Partial to Complete Wetting Transitions in Immiscible Ternary Blends with PLA: The Influence of Interfacial Confinement

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1. In-situ Measurement of Interfacial Tensions and Contact Angles

A method based on the Neumann triangle method combined with a microscopy technique is used to calculate the interfacial tensions of PLA/PBS, PBS/PHBV, PLA/PHBV, and PLA/PBAT. This technique is based on the geometrical analysis of contact angles between three immiscible phases in a ternary polymer blend (Figure S1.a). The vector sum of the three interfacial tensions balanced at the line of 3-phase contact is described by a Neumann triangle which equals zero [1,2]:

$$\vec{\gamma}_{AB} + \vec{\gamma}_{AC} + \vec{\gamma}_{BC} = \vec{0} \qquad \text{(S1)}$$

At equilibrium, one can calculate the three interfacial tension ratios Γ_A, Γ_B, and Γ_C [3]:

$$\Gamma_A = \frac{\gamma_{AC}}{\gamma_{AB}} = \frac{\sin\theta_B}{\sin\theta_C} \qquad \text{(S2)}$$

$$\Gamma_B = \frac{\gamma_{BC}}{\gamma_{AB}} = \frac{\sin\theta_A}{\sin\theta_C} \qquad \text{(S3)}$$

$$\Gamma_C = \frac{\gamma_{BC}}{\gamma_{AC}} = \frac{\sin\theta_A}{\sin\theta_B} \qquad \text{(S4)}$$

This method gives relative values of the interfacial tensions between components (Γ), therefore, one can calculate the interfacial tensions when at least one interfacial tension out of the three interfacial tensions is measured with another method such as the breaking thread method.

Three melt blended ternary PLA/PHBV/PBS, PLA/PBAT/PE, and PLA/PE/PBAT systems with partial wetting morphology were prepared. AFM and SEM micrographs of the blends were used to fit geometrical constructions for a minimum 20 partially wet droplets at the interface as presented in Figure S1.c-d. Further details of the technique can be found elsewhere [4,5].

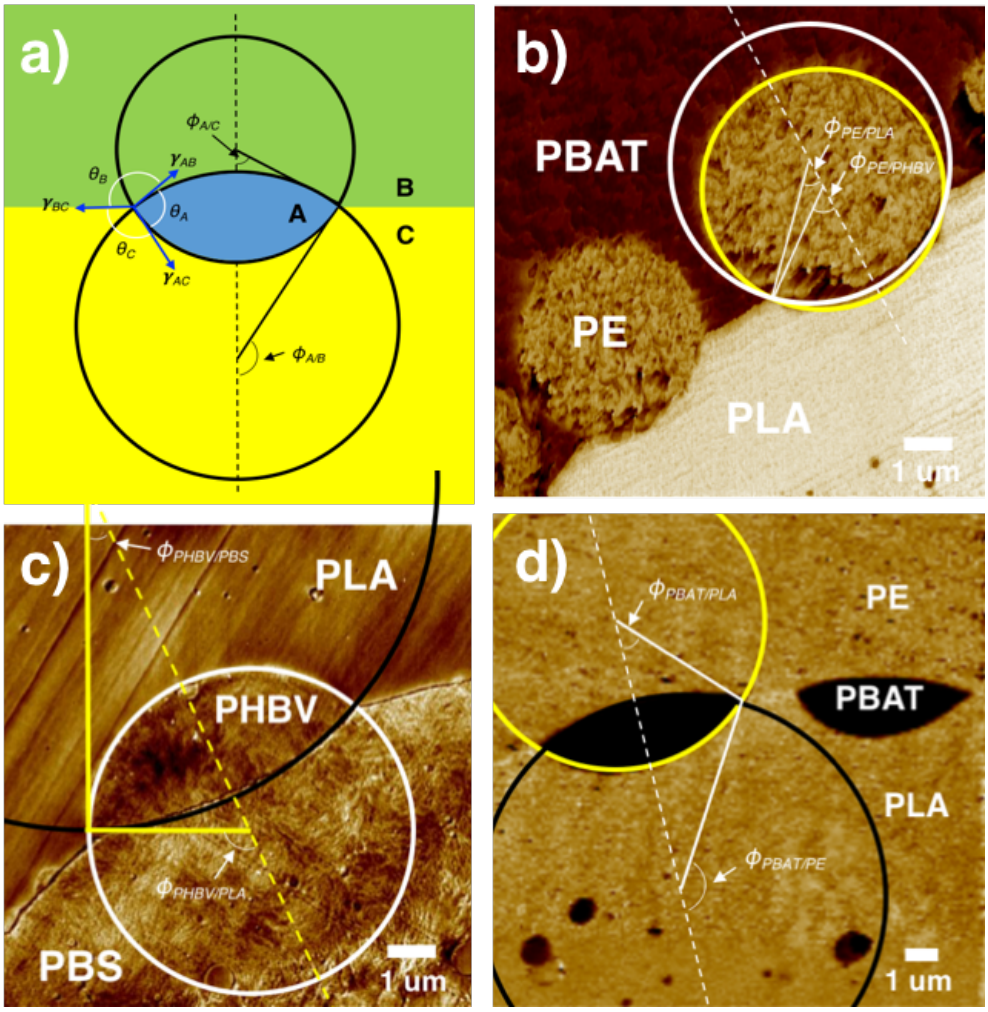

Figure S1. Geometrical constructions fitted to AFM micrographs of partially wet droplets at interface to calculate the θ contact angles in a) PLA/PHBV/PBS 50/5/50, b) PLA/PE/PBAT 50/5/50, and c) PLA/PBAT/PE 50/5/50.

2. AFM micrographs of the ternary PLA/PBS/PBAT system

The ternary PLA 47.5%/PBS 5%/PBAT 47.5% blend were prepared to show formation of a completely wet layer of PBS at the interface of the PLA/PBAT. This system consists of components with very low interfacial tensions.

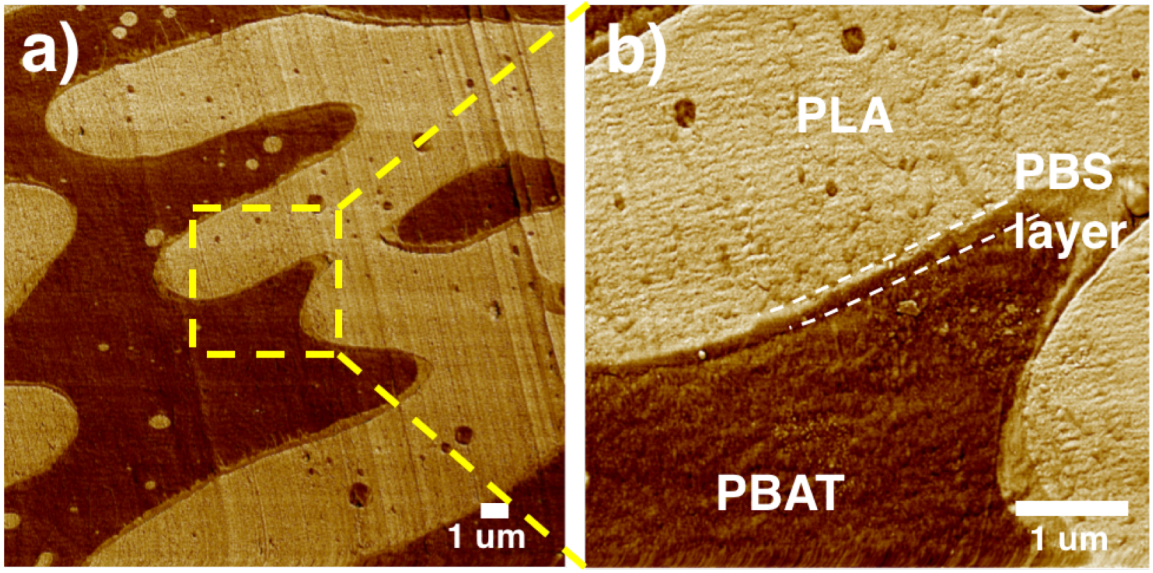

Figure S2. a, b) AFM micrographs of the PLA/PBS/PBAT 50/5/50 system with complete wetting morphology.

3. Rheology of pure components

The results of the complex viscosities of the neat polymers examined at 190°C are presented in Figure S3.

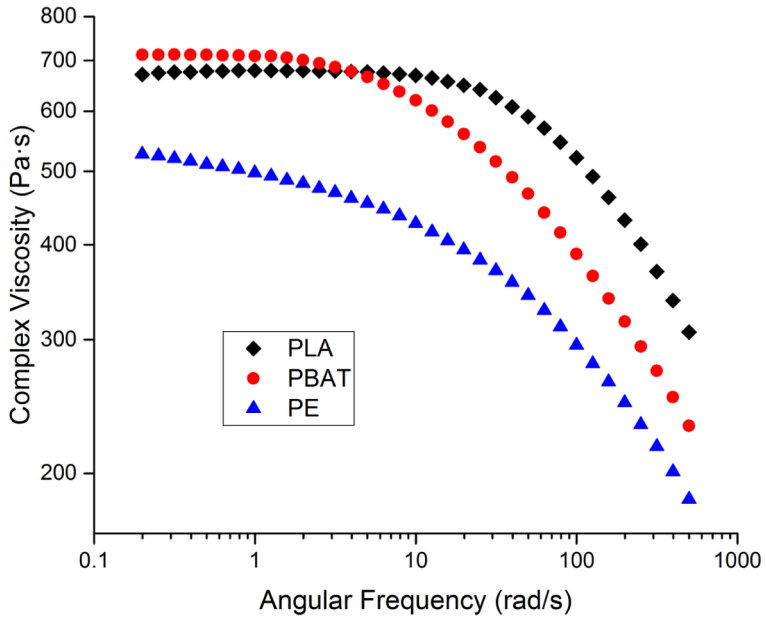

Figure S3. Complex viscosity vs. frequency of pure homopolymers used in this study at 190°C.

References:

[1] D. Li, A.W. Neumann, Phase rule for capillary systems, Adv. Colloid Interface Sci. 49 (1994) 147–195.

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[4] S. Horiuchi, N. Matchariyakul, K. Yase, T. Kitano, Morphology development through an interfacial reaction in ternary immiscible polymer blends, Macromolecules. 30 (1997) 3664–3670.

[5] N. Virgilio, P. Desjardins, G. L'Esperance, B.D. Favis, In Situ Measure of Interfacial Tensions in Ternary and Quaternary Immiscible Polymer Blends Demonstrating Partial Wetting, Macromolecules. 42 (2009) 7518–7529.