Compatibilization of Immiscible Polymers by Addition of Random Copolymer

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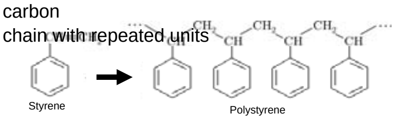
Introduction

Polymer

Polymerization of a monomer to form a long carbon chain with repeated units

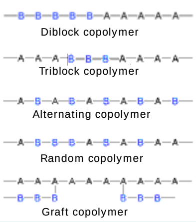


Immiscible polymers

- Have a low entanglement density at interface
- Phase separate to form different morphologies

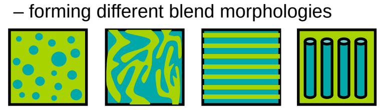
Copolymers

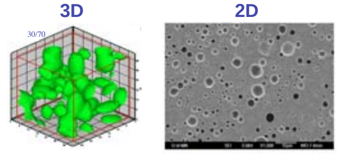
- Created by covalent bonding monomers of the two polymers
- Prefers to be at the interface of immiscible polymers
- Acts as a bridge between phases



Blend Morphology

- Immiscible polymers phase separate when mixed – forming different blend morphologies





Droplet Morphology

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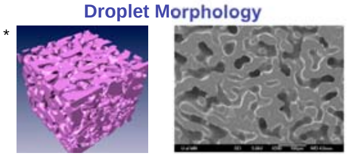


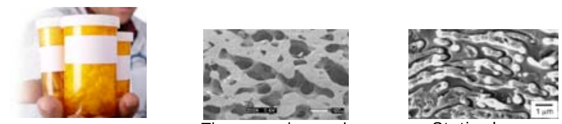
Cocontinuous Morphology

* Pyun et al., *Macromolecules* **2007.**

Cocontinuous Blends

- A cocontinuous morphology is a mutual interpenetration of two phases
- Range of cocontinuity - Usually near 50/50 compositions
- One way to form cocontinuous blends is through melt blending
- Cocontinuous blends are NOT in thermodynamic equilibrium and coarsen during annealing/post processing
- Compatibilizers can stabilize morphology during annealing

Applications



Moisture absorbing packaging (Capitol Specialty Plastics, U.S. Patent 5,911,937) | Tissue engineered scaffolds (Washburn et al., J Biomed Mater Res, 2002) | Static charge control (Stat-Rite®, Lubrizol; PermaStat®)

Effects of Annealing

- Microstructure coarsens dramatically upon annealing
- Coarsening rate

$$\frac{dR}{dt} \sim K\frac{\Gamma}{\eta}$$

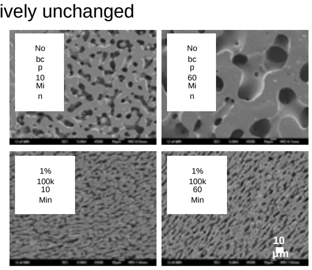
Γ ← Surface Tension; η ← Viscosity

Doi and Ohta, *J Chem Phys* **1991**.

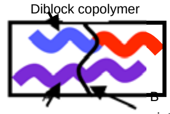
- Rate can be slowed by adding an optimal copolymer

SEM images of 45/55 PS/PMMA blends

- No bcp shows a dramatic increase in phase size
- 1% 100K block copolymer shows phase size is relatively unchanged



Hypothesis



- Known: PS-b-PMMA, diblock copolymer, improves adhesion between phases in PS/PMMA system
- PRD770 is a random copolymer of PMMA and poly butyl methacrylate (PBMA) – there is no PS in the copolymer

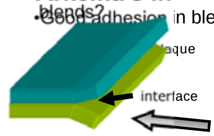
Claim: PRD770 improves adhesion between phases in a polystyrene (PS)/ polymethyl methacrylate (PMMA) system

Goals

- Verify PS and PMMA have good adhesion with the addition of PRD770 in PMMA
- Cocontinuous blends?

Arkema's Inc. Adhesion Test

- Good adhesion in blends that contain >7% PRD770 in PMMA

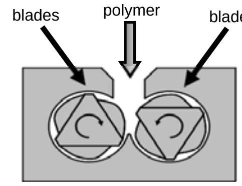


- Press plaques of PS and PMMA with and without the copolymer
- Laminated plaques at temperatures from 230-250˚C
- Physically pulled the layers apart at the interface and gave an adhesion rating of: Excellent, Good, Fair, or Poor

Prepared Samples

- Blended polymers in a Haake batch mixer
- Mixed polymers for 10 min at 50 RPM
- Mixer temperature 220ºC
  - above glass transition of polymers
- Quenched blends in liquid N_2
- Prepared blends
  - 10% PRD770 in PMMA
  - 50% PRD770 in PMMA

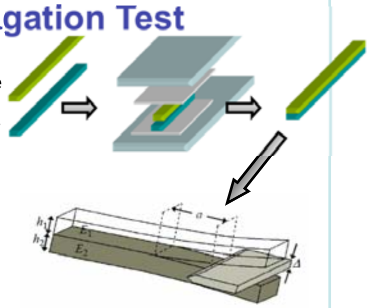
Schematic of Haake Batch Mixer



Maric, *Poly. Eng. and Sci.* **2001.**

Dual Cantilever Beam Crack Propagation Test

- Pressed beams of PS and PMMA with and without the copolymer
- Laminated beams together at temperatures of 220˚C and 250˚C
- Inserted a blade at the interface to create a crack in between the layers



Critical interfacial fracture toughness (G_c) or the critical strain energy release rate

$$G_c = \frac{3\Delta^2 E_1 E_2 h_1^3 h_2^3}{8a^4}\left[\frac{C_1^2 E_2 h_2^3 + C_2^2 E_1 h_1^3}{(C_1^3 E_2 h_2^3 + C_2^3 E_1 h_1^3)^2}\right]$$

$$G_c \sim \frac{1}{a^4}$$

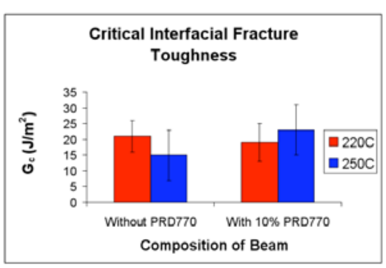
Δ = blade thickness
E_i = elastic modulus
h_i = beam thickness
$C_i = 1 + 0.64\,(h_i/a)$
a = crack length

Cretin et al. *Macromolecules*, 1992.
Cole PJ. *Ph. D Thesis* 2002.

Results

250˚C	G_c (J/m²)	St. Dev.
Without PRD770	15	6
With 10% PRD770	23	8

220˚C	G_c (J/m²)	St. Dev.
Without PRD770	21	6
With 10% PRD770	19	5



Conclusions

- Dual Cantilever Beam Crack Propagation (DCB) test, within standard deviation, shows there is no statistical improvement in adhesion with the addition of PRD770
- Expected to see DCB test show an increase in G_c by a factor of 2
- Cannot confirm Arkema's results

This may be due to:
- Difference in test set up - Adhesion rating vs. DCB test
- Difference in types of materials used

Possible Future Work

- Arkema saw improved adhesion with high impact polystyrene (HIPS). Use HIPS, instead of PS, for a DCB test
- Use Arkema coextruded PS and PMMA for DCB test
- Try DCB test on plaques prepared by Arkema

Acknowledgements

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