Toughening of transparent amorphous systems via self-assembly of block copolymers

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Introduction

Modification of rigid glassy polymers by introduction of elastomeric core-shell particles is very promising to obtain nanostructured polymers with a high fracture toughness. The elastomeric core should cavitate easily and the hard shell makes the particle compatible with the matrix material.
So far, the development of tough heterogeneous amorphous systems has been focused on systems based on linear polymers. For (slightly) cross-linked polymer systems, however, more effort is needed to generalize the concept of toughening by introduction of these elastomeric particles. Once a better understanding is obtained on how to control the bulk morphology, the deformation mechanisms of thin films can be studied and compared to the bulk. On impact, the energy can be absorbed by 2 mechanisms, being shear yielding and cavitation (figure 1a and b).

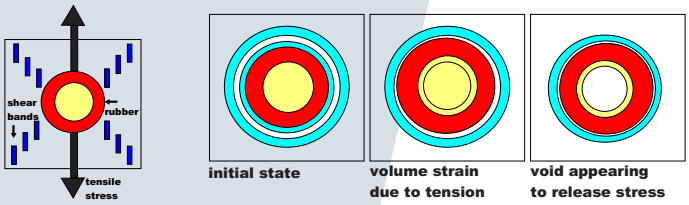

Figure 1a and b *Mechanisms of action in impact modifier particles. On the left shear yielding and on the right cavitation*

Material preparation

In order to obtain polymer micelles, di- and triblock copolymers of narrow molecular weight distribution are synthesized via ATRP. These micelles should at least have such properties that one block is soluble in the initial resin and that another block is not soluble, and in solution they should stay present as micelles at all times under curing. An example of a SAXS measurement involving hexagonally packed cylinders is represented by figure 2.

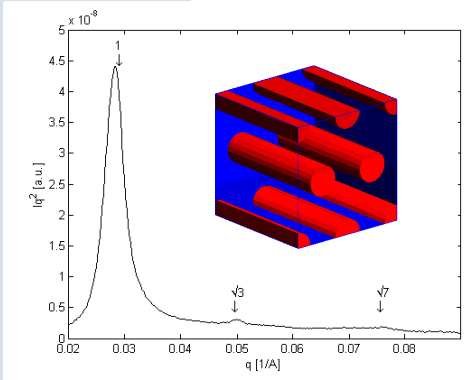

Figure 2 *SAXS data representing the presence of hexagonally packed cylinders of a PB-PBA diblock sample with Mn=23kg/mol and a block ratio of 4:19.*

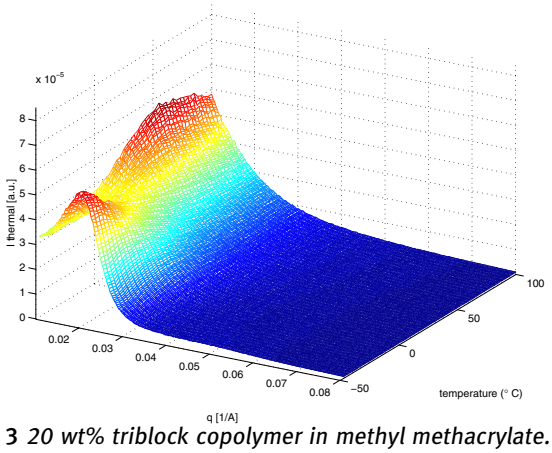

Figure 3 *20 wt% triblock copolymer in methyl methacrylate. Upon increasing the temperature the micellar ordering (visible around q=0.02 1/Å) disappears. The triblock used consists of PB-PBA-PMMA of Mn=50kg/mol in a block ratio of 4:19:27.*

Results

The morphology of the block copolymers in solution is studied by time-resolved SAXS measurements, in order to determine the optimal reaction conditions for curing. In Figure 3 the scattering pattern is depicted for a triblock copolymer at 20 wt% in MMA during a heating run. At low temperatures a micellar morphology is present. During heating from -50 °C to 100 ° the ordering decreases gradually and disappears at approximately 10 °C.

Conclusions

- Micellar structures present before reaction can be preserved when polymerization takes place at very low temperatures.

Future work

- Synthesis of polymer systems containing micellar structures at low temperatures.
- Application of modifier toughening mechanism to (slightly) cross-linked systems.
- Obtaining variations in cross-link density by using different cross-linking agents. Especially in these systems, the presence of micellar structures before cross-linking and the stabilization during cross-linking should be emphasized.
- When morphology of bulk polymer systems is controlled, a link to thin films (coatings) can be made.

References:

[1] Dean, J.M., Lipic, P.M., Grubbs, R.B., Cook, R.F., Bates, F.S.: *J Polym Sci Part B: Polym Phys 39* (2996-3010, 2001)

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