



**Experiment title:** Polymer-diblock polymer systems prepared via in-situ polymerisation of monomer: morphology control for ultimate mechanical properties

**Experiment number:**  
ME-4

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**Report:**

The brittleness of amorphous polymers is the result of strain localization in the form of crazes. Considering the network density, the intrinsic toughness of PS is expected to be higher than PC known as a ductile polymer, which deforms via shear yielding. The occurrence of crazing or shear yielding can be found in the relative extent of intrinsic strain softening and strain hardening. PS suffers from strong strain softening in combination with limited strain hardening, giving rise to localization during deformation by crazing. Maximum toughness is expected for an easily cavitating modifier, which subsequently supports the strain hardening process at higher strain. This can be obtained using a self-assembly process of block-copolymers in the monomer solution. The diblock-copolymers were synthesized by ATRP of ethylacrylate and butylacrylate using hydrogenated PB and PEO macro-initiators. The blends were prepared by bulk-polymerization. The previous study on the morphology development during in-situ polymerization showed that for a large number of systems with block copolymers based on hydrogenated PB, undesired macro phase separation occurs during the polymerization, resulting in PMMA-rich and block copolymer-rich phase, which has a structure similar to the characteristic micro-phase structure of the block-copolymer itself. Comparable results were found for all polymerizations with PBA-based diblock copolymers. Suppression of the macrophase separation can be realized by introducing

intermolecular hydrogen bonding between the matrix material and the shell block. Incorporation of a strong proton-donating unit into PS will result in controllable specific interactions between the PS-matrix and the acrylate-based copolymers. The phase behaviour has been investigated for different blends based on functionalised PS cast from different solvents. The choice of solvents was such that they are neutral or can interfere with the hydrogen bonding formation.

From Figures 1,2 and 3, it is evident that hydrogen bonding plays a prominent role in the extent of macro phase separation

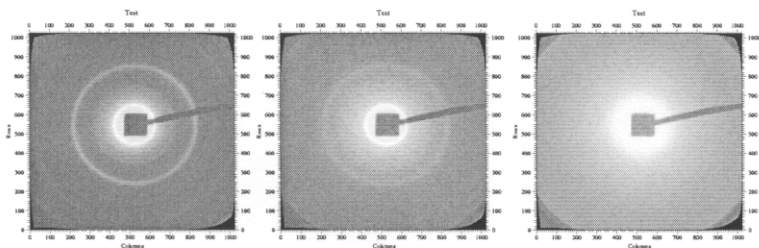


Fig1 1: Pure PB-PMA

Fig. 2: PS(OH)3 with 20% PB-PMA, casted from toluene

Fig.3: PS(OH)3 with 20% PB-PMA casted from THF

## Conclusions

The experimental results from the SAXS measurements gave more insight in the role of hydrogen bonding on the extent of phase separation and on the final morphology and thus gives a tool to suppress the macrophase separation of pre-made homopolymer/block-copolymer systems and in-situ made systems. From this point onwards, the influence of the morphology on the microscopic deformation mode during in-situ SAXS experiments can be studied.