



	Experiment title: In-situ studies on the local deformation mechanisms during mechanical drawing of toughened polymers.	Experiment number: 26-02-91
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Shifts: 12	Local contact(s): Wim Bras	<i>Received at ESRF:</i>
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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 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. Suppression of the macrophase separation was realized by introducing intermolecular hydrogen bonding between the matrix material and the shell block. The phase behaviour has been investigated for different blends based on partially functionalised PS. As the dispersed phase diblock copolymers as well as triblock copolymers are used. From Figures 1 - 3, it is evident that hydrogen bonding plays a prominent role to suppress macro phase separation. A second way to avoid undesired macrophase separation is by polymerizing the diblock copolymer/ MMA solution at -40°C with an UV-initiator. Decreased mobility may result in fixation of the micellar morphology. The SAXS-patterns of the blends indicate the presence of core-shell like structures, however, further research (modeling) is necessary to study the ordering and sizes of the dispersed phase, figure 4.

Preliminary tensile testing experiments have been performed with our home-built device. To test our equipment and the procedure to analyze the data, commercial available systems like HIPS and Kraton PS-PEP copolymers were tested. Furthermore, we investigated the

mechanical response of our blends and triblock copolymers based on PMMA. A distinction could be made between the brittle behavior as a result from crazing and a more homogeneous deformation behavior, but more experimentation is required to get more detailed information on the microstructural deformation and on the detailed data analysis.

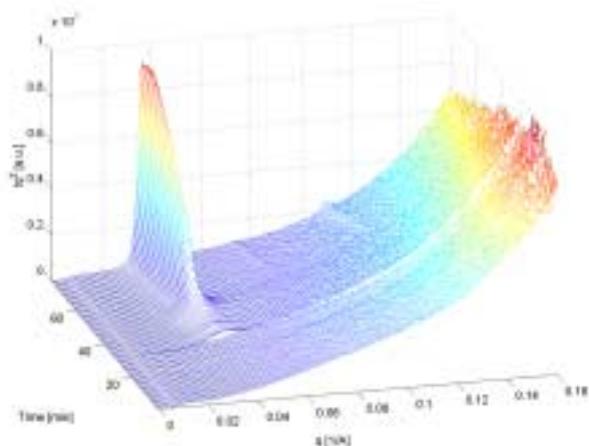


Fig. 1: Time-resolved SAXS patterns recorded during the polymerization of styrene with 10% PB-PMA at 100°C. No hydrogen-bond interaction.

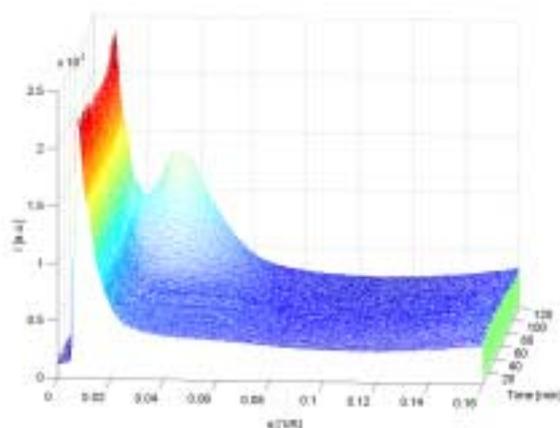


Fig. 2: Time-resolved SAXS patterns recorded during the polymerization of styrene and 5wt % p-(hexafluoro-2-hydroxyisopropyl)styrene with 10% PB-PMA at 100°C. Due to hydrogen bond interaction no macrophase separation could be observed

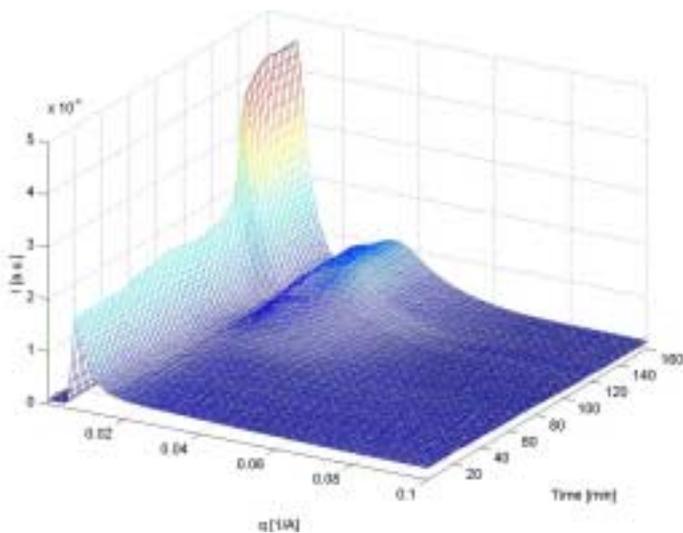


Fig. 3: Time-resolved SAXS patterns recorded during the polymerization of styrene and 5wt % p-(hexafluoro-2-hydroxyisopropyl)styrene with 10% PB-PMA-PMMA at 100°C.

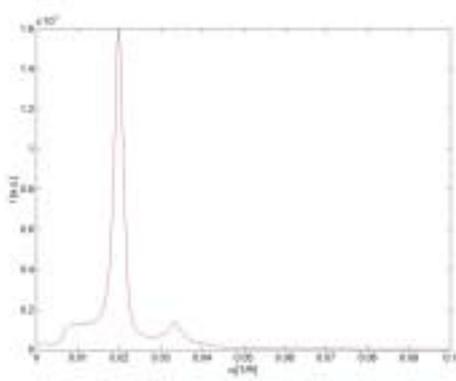


Fig. 4: SAXS pattern of PB-PBA-PMMA triblock copolymer

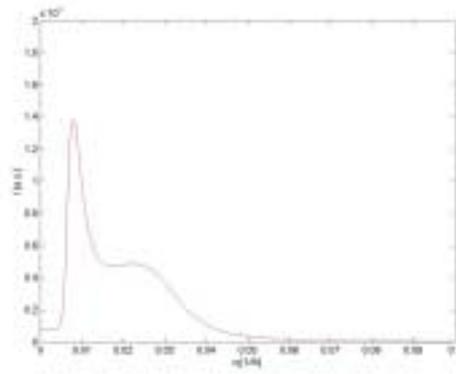


Fig. 5: SAXS pattern of a PMMA blend with 10% PB-PBA-PMMA, polymerized at -40°C .

Conclusions

The experimental results from the SAXS measurements gave more insight in the role of hydrogen bonding and polymerization conditions 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, of which the preliminary results showed a combined crazing and cavitation mode as local deformation mechanism.