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Experiment Report Form

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

(next page)

DUBBLE	**Experiment title:** Toughness improvement of brittle glassy polymer matrices by incorporation of cavitating triblock copolymer structures	**Experiment number**: **26-02-243**
Beamline: BM26B	**Date(s) of experiment**: From: 25-02-2005 To: 28-02-2005	**Date of report**: 27 - 09 - 2005
Shifts: 9	**Local contact(s)**: Dr. F. Meneau	
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Background

Triblock copolymers consisting of a crystallizable, a rubbery, and a glassy part might form under the right conditions a toughness improving modifier for brittle glassy polymers. Due to phase separation, crystallizable domains are formed in the matrix. The size of these crystallizable domains strongly determines, together with the cooling rate, the type of nucleation that might occur, i.e. homogeneous or heterogeneous. If the domain size is relatively large, then enough heterogeneities are present, which might act as a nucleation site for crystallization and heterogeneous crystallization occurs. If the domain size is small, the number of nucleation sites might be smaller than the number of domains present, leading to crystallization at supercooled temperatures. In the latter case, homogeneous crystallization will occur. Whether heterogeneous and/or homogeneous nucleation occurs depends on the processing conditions.

For toughness improvement, cavitation is required for stress delocalization. During loading, the amount of crystallization and type of crystals will determine how the sample will deform. Upon sufficient loading, the crystallized domain will cavitate and delocalize the stress around these domains.

Triblock copolymers synthesis and characterization

PCL-PBA-PMMA triblock copolymers were prepared as follows: at first PBA is prepared by controlled radical polymerization of BA. The second acrylate block (PMMA) was then added by subsequential polymerization of MMA onto the previously formed macroinitiator, which still is living. This diblock copolymer (PBA-PMMA) is then coupled with hydroxyl-functional PCL to obtain the desired triblock copolymer. The three blocks in PCL-PBA-PMMA had a molar mass of approx. 10, 18, and 75 kg/mol, respectively. The triblock copolymer was not pure, since only 50 % of triblock could be obtained. The remainder was acrylate diblock copolymer (PBA-PMMA) and homopolymer PCL. However, the presence of these residual contamination is not always detrimental, it might even lead to more stable structures.

Experimental results

Tensile tests combined with X-ray scattering measurements provide insight in the local deformation mechanism. For example, PMMA shows at low strains already a scattering streak in the vertical direction (90 and 270°), which is a strong indication of crazing. Strong scattering at 0 and 180° is caused by shear yielding, whereas scattering around 90 and 270 ° is caused by crazing.

Figure 1 shows the SAXS pattern of the triblock copolymer upon deformation. It can be seen that the peaks at 90 and 270° are less sharp than for samples deformed by crazing. Delocalization takes place, which can be seen from the widening of the peaks at 90 and 270°. Blending the triblock copolymer with 50 % of PMMA homopolymer improves the properties of PMMA significantly. Clearly, cavitation can be distinguished, as can be seen from the increase of the scattering intensity over the whole azimuthal angle range around Frame

60 in Figure 2. Compared to PMMA homopolymer, the 50/50 (w/w) blend also has improved mechanical properties, i.e. the tensile strength at break is improved.

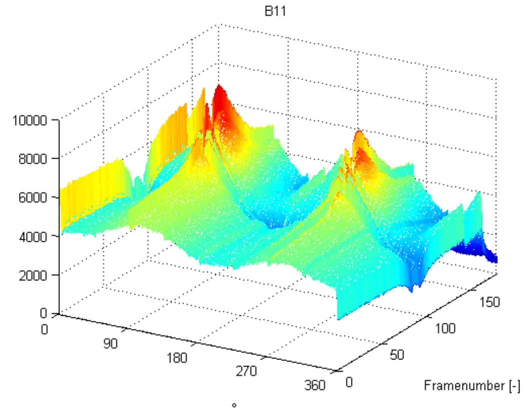

Figure 1: *Pure triblock TL 0616*

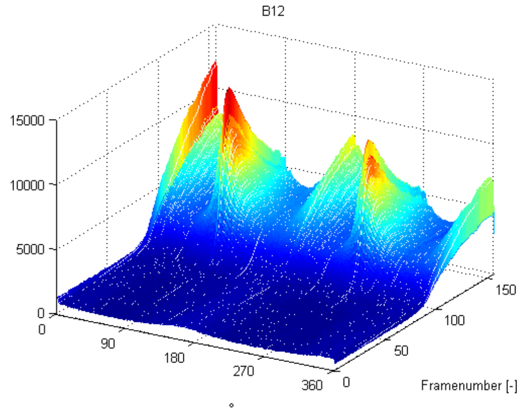

Figure 2: JK 0705 blend 50% PMMA (6N)

Solvent-cast triblock copolymers have a much better developed morphology. Compared to the extruded triblock copolymers, these polymers show also cavitation (Figure 3, around frame 60) and also scattering in the directions 0 and 180°, originating from shear yielding of the matrix. Solvent-cast triblock copolymers are crystallized by heating above the glass transition temperature (T = 100°C) of PMMA and subsequently cooled to -60 °C. During this cooling crystallization occurs. After heating to room temperature, these samples were also mechanically tested. The scattering pattern presented in Figure 4 shows a strong resemblance with Figure 3, indicating that cavitation occurs but at lower deformation (at frame 50). Annealing of the samples, however, is catastrophic for the properties of the samples. The samples craze upon loading, as can be seen form Figure 5 and 6: scattering streaks at 90 and 270 ° can be observed.

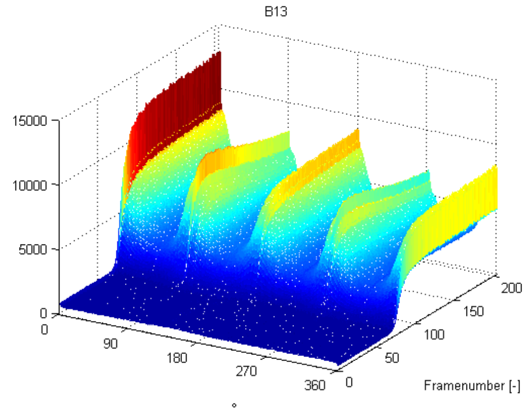

Figure 3: TL 0706 solvent cast (=TL 0616 solvent cast)

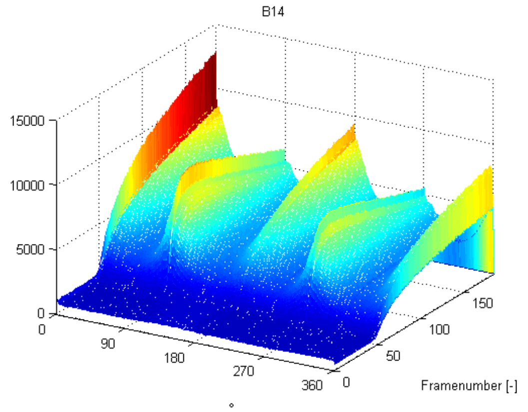

Figure 4: TL 0706 cryst (=TL 0616 solvent cast and crystallized)

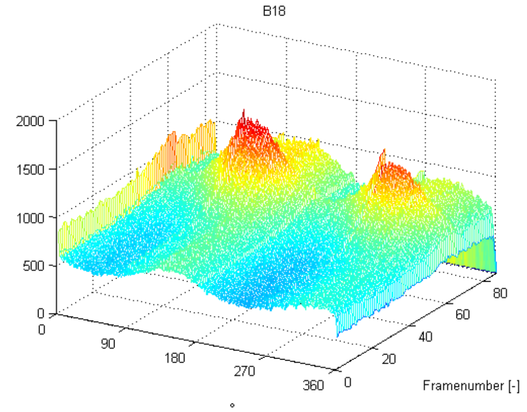

Figure 6: TL 0616 after annealing

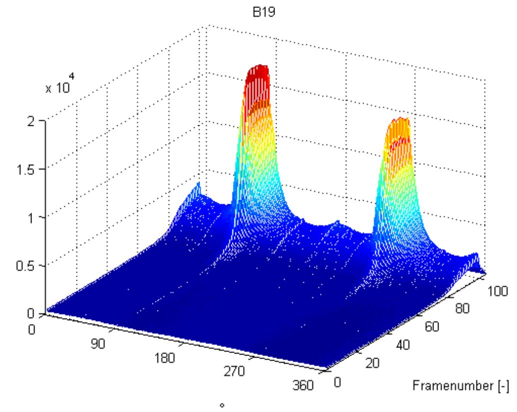

Figure 7: JK 0705 blend 50% PMMA (6N) after annealing

In future studies, different triblock copolymer systems will be studied, prepared by different synthetic approaches, consisting of better defined triblock copolymers and less impurities (diblock copolymer or homopolymer). These triblock copolymers will be studied in their pure form and also blended with a brittle

PMMA matrix polymer. Also, samples will be subjected to different thermal histories to investigate the influence on crystallization type and percentage on the deformation mechanism.