In–situ study of crazing in different polymers as a function of temperature and elongation

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Abstract. The deformation behaviour of various polymers was investigated by USAXS during straining at room temperature and elevated temperatures with the aim to correlate it with deformation structures observed by means of transmission electron microscopy during “in situ” straining of semithin sections. Different materials (isotactic and syndiotactic polypropylene, long chain branched and syndiotactic polystyrene, cyclic olefin copolymers and SBS block copolymers with various architectures), known to be brittle or ductile, or to change their deformation modes as a function of temperature were chosen. Simultaneously the samples were videotaped. In a second series of experiments the samples were strained until crazing started, and then craze propagation was monitored as a function of time. Measurements were performed in October 2003. Data evaluation is in progress.

Experimental. Measurements were performed at HASYLAB, beamline BW4. Samples were strained in a straining stage with a temperature chamber (Figure 1). 2D USAXS images were collected by a Gabriel detector. The sample–to–detector distance was 12.54 m. As a function of scattering power the data acquisition time was chosen between 1 s and 300 s. The accessible data range was $-0.05 \text{ nm}^{-1} < s_1, s_3 < 0.05 \text{ nm}^{-1}$. Temperature stability inside the chamber was better than 1 °C. On the other hand, temperature can only be preset coarsely ($\pm 4 ^\circ C$).

Data were pre–evaluated using pv–wave: Detector response was considered, data were normalized to constant incident flux, empty scattering was subtracted. Insensitive areas (beam stop, beam stop...
support, detector flaws) were masked. The center of the patterns was determined, the patterns were centered and properly aligned. Finally the patterns were rescaled in units of the scattering vector \( |s| = (2/\lambda) \sin \theta \).

**Some Results.** A typical result of the craze evolution experiment is shown in Figure 2 considering as example a cyclic olefin copolymer (COC). Crazing starts with a primary craze direction and an indication of an “equatorial streak”. Then a secondary craze direction is developing. Finally there is no more change in the scattering pattern between elongations of 0.65 vertical direction of the scattering patterns. They are related to crazes that are extended almost perpendicular with respect to the straining direction. The faint equatorial streak is related to needle–shaped voids that are extending in the direction perpendicular to the primary craze direction. Embrittlement was observed with increasing norbonene content in the COCs.

![Figure 2: Craze propagation in a cyclic olefin copolymer (COC) as observed by USAXS as a function of elongation. Each image shows the region -0.05 nm\(^{-1} < s_1, s_3 < 0.05\) nm\(^{-1}\). Straining direction \( s_3 \) is vertical.](image)

Similar diffraction patterns were taken during deformation of polystyrene (PS) at room temperature. With increasing temperature up to 80°C (still below \( T_g \)), transition from the formation of homogeneous crazes to fibrillated crazes in long chain branched PS was observed, which is in agreement with our previous TEM results. After a quantitative evaluation of the data we expect also to confirm the formation of coarser fibrils and greater distances between the fibrils in both linear and long chain branched PS, as found during “in situ” straining in TEM.

In the opposite direction evolves the deformation behaviour with temperature in a semicrystalline type of PS (syndiotactic polystyrene, sPS). Above 60°C a decreasing tendency to form crazes with temperature was found. Already at 80°C sPS shows a scattering pattern comparable to that recorded from syndiotactic polypropylene (sPP), which deforms predominantly via shear bands (simultaneously monitored with the TV camera).

In SBS block copolymers and their blends with homo PS the changes in the morphology and the transition from ductile to brittle deformation behaviour with increasing PS content were investigated. Additionally the effect of extrusion direction on the deformation behaviour (i.e. parallel and perpendicular to the lamellae formed by the two components) was studied.