Measurement of multi-scale deformation of polycarbonate using X-ray scattering with *in-situ* loading and digital image correlation

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ABSTRACT

Deformation of amorphous, glassy polycarbonate (PC) is characterised over a wide range of length-scales using spatially-resolved wide angle X-ray scattering (WAXS) with simultaneous digital image correlation and *in-situ* uni-axial loading. Novel observations are presented on the correlation of the evolution of the molecular structure linked to the relevant local macroscopic measures of strain as the sample deforms. This provides new insights into the mechanisms of deformation in amorphous, glassy polymers. Strains and evolving anisotropy are observed, and quantified, at different length scales identified from the WAXS measurements connected to inter- and intramolecular structures. The inter-molecular structures show permanent deformations in the form of unrecoverable stretches and reorientations, whilst intra-molecular structures show recoverable strains and unrecoverable reorientations. Such insights pave the way for development of enhanced constitutive models for amorphous glassy polymers with a correct micro-mechanical basis and calibrated evolution of anisotropy.

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1. Introduction

Polycarbonate (PC) is a glassy polymer at room temperature with good mechanical properties, such as high impact strength, good optical properties and a comparatively high glass transition temperature [1]. Due to these favourable properties it is widely used in industry and consumer products, e.g., as protective glass and equipment housing in the electronics industry. The design process for such applications requires accurate understanding of the material properties and, importantly, how the material responds and evolves under mechanical load. However, PC (as many other polymers) exhibits highly inhomogeneous deformation phenomena, e.g., necking and strain localisation, such that local deformation differs from the overall macroscopic response [2—4]. Such deformation responses are generally attributed to mechanisms occurring at the molecular-scale. As such, commonly used material models for the mechanical behaviour of PC invoke idealised representations of polymer chain networks (e.g., the "3-chain"

[5], the "8-chain" model [6], the full-network model [7] and the micro-sphere model [8]). Common to these models is that the permanent deformation, i.e., the plasticity, is modelled to occur within the individual chains. In an extension to such approaches, Harrysson et al. [9] presented a model in which plasticity originates from both stretching of polymer chains and their reorientation via an evolving chain orientation distribution function (CODF). The experimental support for the molecular-scale assumptions underlying all of these models is, however, limited. For example, it is not clear for PC if the polymer chains themselves show permanent stretching and there are very few data on the evolution of the orientation distribution function of the chains. Furthermore, due to the spatially heterogeneous nature of the deformation in PC described above, any measurement of the molecular structure and its evolution should be spatially resolved and linked to appropriate local macroscopic strain measurements.

The molecular structure in undeformed PC has been studied using neutron scattering together with numerical simulations [10—13]. Changes in the microstructure of amorphous glassy polymers due to deformation and/or heat treatment on pre-deformed specimen have been studied using wide angle X-ray scattering (WAXS) [14—16]. Neutron or X-ray scattering techniques

have also been used during *in-situ* deformation studies on semi-crystalline polymers [17–23], but not on amorphous glassy polymers. Also, in general such studies lack spatial resolution in the scattering data and use macroscopic or, at best, *ex-situ* local "full-field" deformation measurements.

Neutron and X-ray techniques, such as those described above, can provide details on the molecular-scale structures of PC and indicate the micro-/nano-scopic mechanisms of interest. However, to understand how these mechanisms are linked to overall material behaviour requires coupling to measurements at larger scales. In particular, the molecular-scale observations should be linked to macroscopic strain measurements. Further to this, the heterogeneity of the strain response requires that local "full-field" measurements are made. Spatially-resolved (full-field) mesoscopic surface deformation can be measured using optical techniques, such as digital image correlation (DIC) [24,25].

If the molecular-scale mechanisms of deformation can be linked to the macroscopic scale material response by integration of X-ray/neutron scattering and strain-field measurements, then all of the necessary ingredients are in place for developing a physically-based model to describe the mechanical behaviour. This is the ultimate objective of this work.

This paper presents new results from simultaneous, spatially resolved WAXS and full-field 3D-surface DIC measurements of *in-situ* uni-axial loading of PC, following the approach developed by Engqvist et al. [4]. This approach permits the local deformation to be studied in terms of the evolution and strain in the molecular structure linked to local macroscopic measures of strain, as the sample deforms under uni-axial loading. The experiments are first described, followed by a presentation and discussion of the results and observations at the different scale lengths before concluding on the molecular-scale origins of the observed macroscopic response of the material.

2. Experiments

The experiment described in the following involved *in-situ* tensile loading with simultaneous WAXS and 3D-surface DIC. A detailed description of the experimental set-up used in this study is given in Engqvist et al. [4]. The PC material used in the study is Makroclear®, a commercial amorphous PC manufactured by Arla Plast.

Symmetrically notched specimens, with a notch radius of 5 mm and a rectangular cross section area of 8×5 mm² were machined from a sheet of 5 mm thickness, see Fig. 1. Apart from the

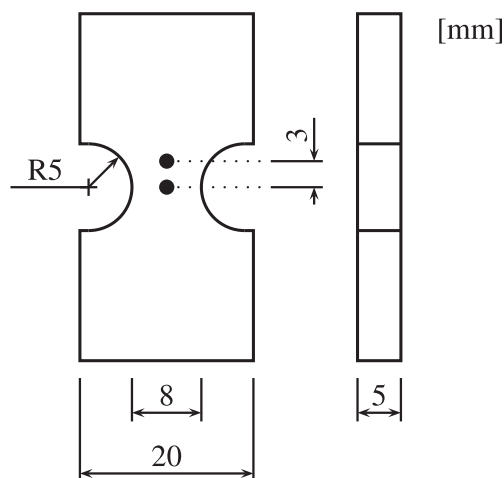machining, no additional treatments of the material were made. The specimens were loaded under uni-axial tension *in-situ* during wide angle X-ray scattering (WAXS) measurements, using a custom built tensile testing device. Both loading and unloading was performed using a constant macroscopic displacement rate of 0.01 mm/min, measured on the machine grips. The experiments were performed at the I911-SAXS beamline at the synchrotron MAX IV Laboratory (Lund University, Lund, Sweden). WAXS measurements were made using a wavelength, λ, of 0.91 Å and a sample-to-detector distance of 0.36 m giving a q-range of around 0.5–22 nm^{-1} (where $q = (4\pi/\lambda)\sin\theta$ and 2θ is the scattering angle). Q-range calibration was made using lanthanum hexaboride (LaB$_6$). A bi-dimensional hybrid pixel X-ray detector (Pilatus 1M, Dectris) was used to record the scattering data, which were corrected for: the transmission of the X-rays, the current specimen thickness (calculated from the DIC analysis) and air scattering (by subtracting the background scattering). The transmission of X-rays through the specimen was estimated using the intensity of the direct beam, measured using a pin-diode detector placed on the beamstop. The local scattering was mapped using line scans of 20 spatial points along the centreline of the specimen. The distance between the points in the line scan was 0.5 mm and the exposure time for each WAXS image was 10 s. During the experiment a total of 100 line scans were performed. The time between two consecutive WAXS measurements at the same spatial point was 300 or 510 s, where the longer time was because of a background measurement which was made after every third line scan. For clarity, only scattering data from two of the 20 spatial points of the line scans are presented: point 1 (centre point) and point 7 along the line. From here on the points are referred to as point A and B, respectively (see Fig. 3).

X-ray data are presented from the two points A and B. These points are selected to represent positions between the localisation bands (point A) and where the localisation front passes through (point B). Points far out from the localisation zone do not show any significant permanent changes in the microstructure.

3D-surface DIC was used to measure the deformation at the surface of the specimen *in-situ*, simultaneously with the scattering measurements. The synchronisation of the data from the different measurements (loading, DIC and WAXS) was achieved using a signal from the X-ray detector to the DIC-system that also was recorded in the loading system control software. A random speckle pattern was painted on the specimen using a water-based paint to facilitate the DIC. To avoid scattering by the paint, the area where
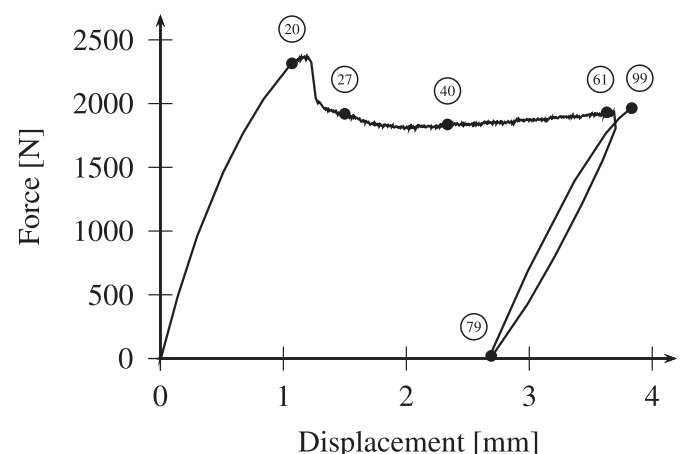

Fig. 1. The geometry of the notched specimen. The dots indicates the positions from which measured X-ray scattering data is presented.

Fig. 2. Macroscopic force–displacement curve. The symbols show six sampling points for the line scans at which DIC stretch fields are presented in Fig. 3.