

Chapter 2

Experimental Part

“There is need of a method for finding out the truth.”
...René Descartes

2.1 SAXS Setup

Three types of materials are studied in order to cover a relatively wide range of materials with different structures and properties. Samples are subjected to uniaxial deformation and the nanostructure evolution is monitored by SAXS. Figure 2.1 presents schematically the experimental setup. Small-angle X-ray scattering (SAXS) is carried out at the synchrotron beamline A2 at HASYLAB, Hamburg, Germany. The X-ray path is perpendicular to the sample. The sample-detector distance for a SAXS study is generally about 2000–3100 mm. The wavelength of radiation is 0.15 nm. Scattering intensity is collected by a 2D marccd 165 detector (Marresearch, Norderstedt, Germany) in binned 1024×1024 pixel mode (pixel size: $158.2 \mu\text{m} \times 158.2 \mu\text{m}$). Thus for the typical long period of 20 nm a variation of the peak position by one pixel causes a long period variation of below 1 %. The intensities of the primary beam before the sample and of the transmitted beam after the sample are recorded in order to calculate the absorption factor of the material.

Tensile testing is done in a home-made [1] stretching-machine. The machine performs symmetric drawing in order to maintain the position of the beam on the sample. Signals from load cell and transducer are recorded during the experiment. The macroscopic deformation is determined close to the beam position to ensure accurate comparison of the mechanical data with the nanostructure evolution. For this reason a precise method has been developed [2]. In this method a pattern of fiducial marks is stamped on the sample. The sample is monitored by a TV-camera. Using the fiducial marks the local strain $\varepsilon = (\ell - \ell_0)/\ell_0$ is computed automatically

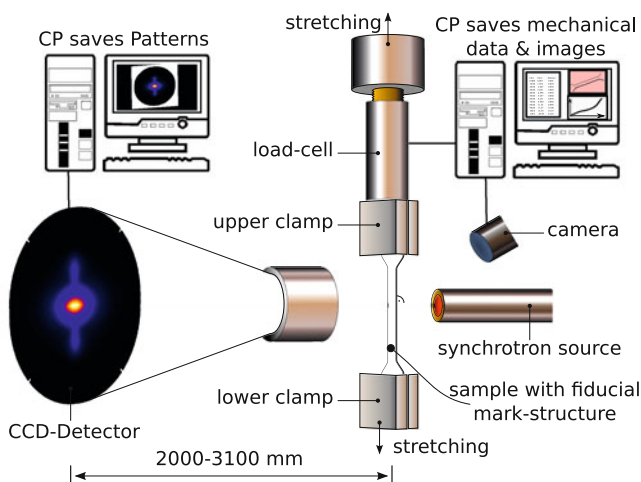


Fig. 2.1 Schematic presentation of the experimental setup used for in-situ SAXS measurements during mechanical deformation. The original drawing has been provided by Courtesy of C. Schloen

from the average initial distance, ℓ_0 , of the fiducial marks and the respective actual distance, ℓ . More details will be presented in Chap. 3.

Details about the sample preparation and experimental conditions of each group of the studied materials are presented in the following three sections.

2.2 Thermoplastic Polyurethane Elastomers

Material. A thermoplastic polyurethane (TPU) is injection molded from melts of different temperature. The material is a commercial grade polyester based thermoplastic polyurethane (TPU) with 94 Shore A durometer hardness from Huntsman Inc., e.g. for sealing applications. The TPU has been polymerized in a one-step process and is provided in granular form ground from cast film.

Injection molding.¹ Samples for the SAXS measurements have been processed directly from the received material. Dumbbell shaped specimens type 5 A according to DIN ISO 527 are injection molded. The nominal dimensions in the central zone of the specimens are 4 mm × 1 mm. Injection molding is carried out in an Arburg 220 S Allrounder 150-30 from pellets dried at 90 °C for 4 h. The screw diameter is 15 mm. Specimens have been molded in a 2-cavity mold and gated with film gate (0.8 mm thick). The mold is kept at a temperature of 60 °C. The injection speed has been set to 25 cm/s where the maximum injection pressure has been 1600 bar. Different kind

¹ This part has been done by A. Frick et al. at IPSP, Aalen University.

of samples are produced, the temperature at the nozzle of the injection unit is set to 205, 215 and 235 °C, respectively.

Test bar characterization.² The injection-molded test bars are characterized by optical microscopy and by differential scanning calorimetry (DSC). Light microscopy is carried out in a Zeiss Axioplan 2 equipped with an AxioCam camera. The specimens are cross-sections cut from the centers of the test bars. They are 10 μm thick. Slicing is carried out at −70 °C using a rotary cryo-microtome Leica RM 2165. A Mettler–Toledo DSC 821^e is employed. Sample mass is 5.0 ± 0.1 mg. The samples are studied under nitrogen flux, cooled to −100 °C and heated to 280 °C at a rate of 20 K/min.

In-situ SAXS-stretch measurements. The clamping distance is 45 mm. A 500 N load cell is used. Continuous stretching is performed at cross-head velocity of 1 mm/min for the monitoring of SAXS. Video frames are grabbed every 10 s. The sample-detector distance is 2488 mm. The cycle-time is 60 s (50 s exposure).

2.3 Polypropylene/Montmorillonite Nanocomposites

Materials. Nanocomposites from metallocene polypropylene (HM562S, Lyondell-Basell) and nanoclay (hydrophilic montmorillonite, MMT) are studied. The MMT is obtained from Laviosa Chimica Mineraria, Italy (3.8 wt.-% aq. dispersion of montmorillonite). A compatibilizer is added to two of the materials in order to intercalate the MMT. The compatibilizer is an amphiphilic block copolymer (ABC) made³ by atom-transfer radical polymerization (ATRP) [3, 4]. It consists of a hydrophobic block of hydrogenated polybutadiene, i.e. poly(ethylene-co-1,2-butylene) monoalcohol (trade name: Kraton L-1203 from Kuraray Co., Japan) with molecular weight 7000 and PDI = 1.05, and a hydrophilic block of quaternized dimethylaminoethyl methacrylate. Modified nanoclays with 4.7 and 8.0 wt.-% of the ABC have been prepared. Table 2.1 describes the composition of the studied materials. Sample PP is the pure polypropylene. Sample PP+MMT is a blend of polypropylene and the freeze-dried hydrophilic MMT. The samples PP+lcMMT and PP+hcMMT are composites that contain MMT with low compatibilizer amounts and high compatibilizer amounts, respectively. In order to prepare the nanocomposites, modified lcMMT and hcMMT have first been freeze-dried and, second, blended⁴ with the PP.

Test bars S2 according to DIN 53504 are injection molded in a MiniJet II (Thermo Scientific) from a melt of 200 °C. Mold temperature: 30 °C, molding pressure: 650 bar, molding time: 45 s. holding pressure: 100 bar. Holding time: 20 s. The cross-section of the parallel central part is ca. 4 mm × 2 mm.

² See footnote 1.

³ The compatibilizer has been prepared by K. Jankova et al. at Danish Polymer Center, Technical University of Denmark.

⁴ Blending has been performed by J. de Claville Christiansen et al. at Aalborg University.

Table 2.1 PP/MMT Nanocomposites based on metallocene polypropylene (PP)—HM562S (Lyon-dellBasell) and montmorillonite (MMT) (Laviosa)

Sample	Composition
PP	Pure polypropylene
PP+MMT	PP + 3 wt.-% freeze-dried MMT
PP+lcMMT	PP + (3 wt.-% MMT + 4.65 % ABC)
PP+hcMMT	PP + (3 wt.-% MMT + 8.0 % ABC)

The compatibilizer is an amphiphilic block copolymer (ABC)

In-situ SAXS-stretch measurements. The clamping distance is 45 mm. A 500 N load cell is used. The machine is operated at a cross-head speed of 0.5 mm/min. Video frames are grabbed every 10 s. In the continuous stretching experiments necking starts after a draw path of ca. 3.5 mm. The experiment is stopped after the neck is fully developed. In the load-cycling experiments the samples are pre-strained by 2 mm. After that the cycling starts. In each cycle the samples are strained by 1 mm and retracted by the same draw-path thereafter. Thus strain-controlled load-cycling instead of stress-controlled cycling is performed. The sample-detector distance is 3031 mm. Scattering patterns are recorded every 30 s with an exposure of 20 s.

2.4 Microfibrillar Composites

Materials. Microfibrillar composite (MFC) precursors are made⁵ from high density polyethylene (HDPE) as the matrix and polyamide 6 (PA6) or polyamide 12 (PA12) as the reinforcing phase. Two samples contain the commercial compatibilizer Yparex[®]8102. The HDPE is produced by Borealis [PE VS4531[®]; density 0.94 g/cm³; melt flow index: 0.6 g/10 min (2.16 kg, 190 °C); melting point by DSC: 133 °C]. The PA6 is made by Lanxess [Durethan[®] B30S; density: 1.14 g/cm³; melt volume flow rate: 110 cm³/10 min (5 kg, 260 °C, ISO 1133); melting point by DSC: 220 °C]. The PA12 is produced by EMS-GRIVORY [Grilamid[®] L25; density: 1.01 g/cm³; melting point by DSC: 178 °C; M_w = 60 kg/mol; M_n = 31 kg/mol]. Yparex[®]8102 is made by DSM. It is a copolymer of HDPE and maleic anhydride. Its melt flow index is 2.3 g/10 min (2.16 kg, 190 °C); melting point by DSC: 125 °C; M_w = 120 kg/mol; M_n = 15 kg/mol. Quantities of granulate have been premixed in the proportions as indicated in Table 2.2.

Each mixture has been melt-blended in a laboratory twin-screw extruder. The extrudate has been cooled to 12 °C and a slight drawing has been applied in the first haul-off unit of the extruder line to stabilize the strand cross-section. Further drawing has been performed in the second haul-off unit after heating the strand in a water bath of 97–98 °C. A third haul-off unit has applied the last drawing causing the diameter of the strand to decrease from 2 mm (at the die out-let) to about 0.6–0.9 mm. Details

⁵ Samples have been prepared by Z. Denchev et al. at University of Minho.

Table 2.2 Composition (in wt. %) of oriented blends

Sample code	PA6	PA12	HDPE	Yparex
P6HY(20/80/0)	20	—	80	0
P6HY(20/70/10)	20	—	70	10
P12HY(20/80/0)	—	20	80	0
P12HY(20/70/10)	—	20	70	10

In the coding P6, P12, H and Y stand for polyamide 6, polyamide 12, HDPE, and the compatibilizer Yparex, respectively

concerning the principle of the preparation [5] and the design of the extruder line [6] have been published elsewhere.

In-situ SAXS-stretch measurements. Load-cycling tests are performed. After approaching different pre-strains (ca. 5.5 % and ca. 8–10 % engineering strain for low-cycling and high-cycling, respectively) the sample is cycled between two fixed distances of the cross-heads. In the experiments the strain rate, $\dot{\epsilon}$, is close to $\pm 1.5 \times 10^{-4} \text{s}^{-1}$. Video frames are grabbed every 10 s. Sample-detector distance is 2542 mm. Scattering patterns are recorded every 30 s with an exposure time of 23 s.

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