Characterization of mono-ethylene-glycol based industrial polyurethanes samples by fast-neutron radiography and neutron tomography

Massimo Rogante¹ and Stefan Söllradl²

¹ Rogante Engineering Office, Contrada San Michele n. 61, 62012 Civitanova Marche, Italy
² Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II), Lichtenbergstrasse, 85747 Garching, Germany

main@roganteengineering.it

Abstract. A complicated structural organization of polyurethanes may have a strong influence on the materials functional properties. Under particular conditions such as mechanical and thermal loading and aging, it leads to the material degradation, even in fresh-prepared bulk polymers and especially if defects are present in the material. Unwanted bubbles can be observed, which form during the expansion of the mixture during its chemical reaction and remain present in the final product. These macro-, micro- and nano-bubbles influence the material's performance. In this work, neutron radiography and tomography have been adopted to characterize at a macro-scale level the bulk of commercially available polyurethane samples, obtained from dissimilar-mixture ratios with different densities and branching levels as well as from different zones of the production mould. The characterisation allowed an estimation of the different dense materials - as they are used, e.g., in soles of shoes - as well as the invisible defects like pores and cracks, responsible for the materials fracture by mechanical loading. The obtained information are expected to be useful for various industrial sectors such as automotive and footwear industry. It will be completed by applying SANS, which has already proved to characterize the microstructure of the bulk-polymer with respect to nano-pores, micro-cracks and their arrangement in the polymer matrix.

1. Introduction
Polyurethanes are polymers containing the urethane linkage in their backbone chain and are made by reacting di-isocyanates with di-alcohols. Since polyurethane chains form easily from the hydrogen bond, these polymers can be very crystalline. This is one reason, why they are frequently used to compose block copolymers (having the properties of thermoplastic elastomers) with soft rubbery polymers. This material is mostly adopted in different industrial sectors (e.g. footwear, automotive, interior design and building). In the footwear industry, e.g. they are used to produce micro-cellular shoe soles. Typical shoe-sole systems utilize a single surfactant. Other novel surfactants are actually under consideration to reduce the soles density while maintaining its physical properties.
The combination of two diverse surfactant chemistries has recently improved the dimensional stability, surface characteristics and, in general, various macroscopic characteristics and physical properties of the final product. A complex structural organization of polyurethanes, including crystalline and amorphous domains, may have a strong influence on the materials functional properties. It leads under particular conditions - such as mechanical and thermal loading, or aging - to the material degradation. This may happen also in the case of fresh-prepared bulk polymers and, in particular, if defects are present in the material [1].

Unwanted bubbles can be detected, which form during the expansion of the mixture while its chemical reaction and remain present in the final product. These macro- (i.e. having size from 0.5 mm and larger), micro- (i.e. having sizes of 1-500 µm) and nano-bubbles (i.e. having sizes of 1-1000 nm) influence the performance of the polyurethanes. Variables as mixture composition, injection speed, injection power, melt temperature, and melt viscosity influence the appearance of those bubbles (e.g. size distribution, interface area, concentration, and volume fraction). In particular, the interface area plays a key role in the polymer material’s strength and durability. The spatial distribution of the mentioned bubbles in the bulk material is not homogeneous and depends on the different zones of the mould. A change of one parameter has influences on other production parameters and the knowledge of those parameters is fundamental for the understanding and improvement of the materials performance.

Thermal neutron radiography and fast neutron gauging measurements have been already adopted to evaluate the feasibility of detecting macro voids in polyurethane products and were used to determine its uniformity[2]. A very high citation index exists concerning polymers (for instance, in Macromolecules, Polymer Content, Physical Review), but no investigations related to neutron imaging were performed yet. Refs. [1-7] can be considered, e.g. related to neutron beam investigations of different types of polymers.

In the frame of our study, representative samples were selected for the investigation with respect to their attenuation coefficient and inner defects such as bubbles at the instrument NECTAR [8, 9] at FRM-II. Three cylindrical PU samples were investigated and the attenuation coefficients for fission neutrons (1.8 MeV) determined with respect to the density of each sample. To confirm the determined attenuation components from transmission experiments, computed tomography was performed on those samples. In addition, computed tomography was performed at the example of a defective safety shoe to study, down to which size defects such as cavities can be identified in bulk PU materials with fission neutrons. Due to the low interaction of fission neutrons with matter in general, while it has a high interaction with elements like hydrogen it is especially suitable for the investigation of materials like polyurethane, especially if hydrogen-rich samples exceed thicknesses of more than 5 cm compared to cold- and thermal neutron radiography.

2. Materials and methods

Different commercially available polyurethane samples - manufactured with varied known reactant mixture ratios with dissimilar branching levels and obtained from different zones of the production mould - have been investigated. These specimens are made of the following two main polyester based polyurethanes systems: A) for compact parts such as shoe treads; B) for expanded parts such as intermediate shoe soles. The chemical composition is the following: polyol polyester; 4,4'-diphenylmethane diisocyanate; tertiary aliphatic amines, and chain extenders. Table 1 reports the main macroscopic (mechanical) characteristics of these polyurethanes.

| Characteristics       | A        | B        |
|-----------------------|----------|----------|
| density (kg/m³)       | 1100     | 420-450  |
| hardness (Shore A)    | 62-65    | 46-50    |
| traction (MPa)        | 15.0     | 5.7      |
| elongation (%)        | 600      | 390      |
Fast-neutron radiography and -tomography have been adopted with the main goal to benchmark the capability to identify macro-scale internal bubble structures in bulk material. Fast neutrons with a mean energy of 1.8 MeV were used and the investigation was carried out with a collimated beam (circular collimator of 10 mm) [9], resulting in an \( L/D = 233 \). A 2.4 mm PP/ZnS scintillator was used with 30\% of ZnS to convert the fast neutrons to light. As detector system an Andor DV434-BV CCD camera was used, maintained at a temperature of -50°C with 1024 \( \times 1024 \) pixel\(^2\) and a field of view of 317x317 mm\(^2\).

Three homogeneous samples with cylindrical shape (diameters between 50 mm and 60 mm) of PU with different densities were investigated means of radiography and tomography (see Figure 1).

\[
\frac{\mu}{\rho} = -\ln \left( \frac{I}{I_0} \right) \rho d
\]

where \( \mu \) is the attenuation coefficient, \( \rho \) is the density, and \( d \) is the transmission of a single beam of neutrons through the sample, the mass-attenuation coefficient was determined.

In addition, computed tomography was performed to determine the average-attenuation coefficient for polyurethane with the fission neutron beam available at NECTAR. The tomography was executed with 357 projections, acquired according to the “golden ratio” approach [11] according to equation:

\[
\varphi = \left( 2\pi \ i \frac{1 + \sqrt{5}}{2} \right) \mathrm{mod} (2\pi)
\]

where \( \varphi \) is the angle of the \( i \)-th projection acquired. The acquisition was stopped after a good compromise between visible details (e.g. bubbles) and acquisition time was reached after regular
reconstructions during the data acquisition. All projections are reconstructed using the software Octopus [12] and evaluated using Python [10] scripts. In addition, the tomography of a defective safety shoe was acquired using the golden ratio approach with 325 projections as details in the size of two voxels were visible. The projections were reconstructed using the software Octopus [12] for the reconstruction and VG Studio Max [13] for visualization.

3. Results
The transmission through polyurethane cylinders with different densities was investigated. Fig. 2 shows the radiographs of the investigated cylinders, where Fig. 2a represents the images of Sample 1 (low-density PU) and Sample 3 (high-density PU) in direct comparison and Fig. 2b shows the radiograph of Sample 2 (high-density PU). The black rectangles in the images indicate the origin of the transmission profiles as plotted in Fig. 3. Based on the known thickness of the samples as well as the determined transmission, the attenuation coefficients were calculated depending on the Lambert-Beer Law for attenuation of radiation in matter (Eq. 1).

![Fig. 2. The radiographs of Sample 1 (upper sample, low density) and Sample 3 (lower sample, higher density) in Fig. 2a and of Sample 2 (higher density) in Fig. 2b). The inside area of the rectangles indicates the region, where the intensity profiles were determined.](image)

![Fig. 3. The transmission profiles averaged over 6 rows of pixels per column. Each profile corresponds to the indicated section from rectangular sections of Fig. 2.](image)

From the obtained data, a clear dependence of the transmission through low-density PU materials (blue line) and high-density PU material (green and red lines) is shown, even if the basic material is
the same and the concentration of gas inside the samples determines its density. While a transmission of 76.6% was achieved in Sample 1 through a material thickness of 57 mm, only 42.8% transmission was measured through Sample 2 with a thickness of 50 mm, and 46% in Sample 3 with a thickness of 54 mm.

Based on those data, the attenuation coefficient $\mu$ was determined from the radiographs as a function of the investigated material. For all three samples $\mu$ was normalized with the density of the material and the mass attenuation coefficient $\mu/\rho$ determined as shown in Table 2.

| Sample       | Attenuation coefficient (tomograph) $\mu$ [1/cm] | Density $\rho$ [g/cm$^3$] | Mass attenuation coefficient (tomograph) $\mu/\rho$ [cm$^2$/g] | Mass attenuation coefficient (radiograph) $\mu/\rho$ [cm$^2$/g] |
|--------------|-----------------------------------------------|---------------------------|---------------------------------------------------------------|---------------------------------------------------------------|
| Sample 1 (low-density) | 0.05 (1)                                      | 0.31 (1)                  | 0.132 (3)                                                     | 0.16 (6)                                                      |
| Sample 2 (high-density) | 0.16 (1)                                      | 0.96 (1)                  | 0.145 (1)                                                     | 0.18 (7)                                                      |
| Sample 3 (high-density) | 0.14 (1)                                      | 0.89 (1)                  | 0.134 (1)                                                     | 0.16 (6)                                                      |

The values, determined from the computed tomography of the test samples are shown in Fig. 4. Fig. 4(a-c) illustrates the reconstructed shapes of the investigated PU samples with their corresponding attenuation coefficients. In addition, the histograms corresponding to the inner sections of the white rectangles are plotted in Fig. 4d. The mean attenuation coefficient of each sample and the corresponding mass attenuation coefficient were determined, which were well in accordance with the values determined by the radiograph. However, due to the better statistics of the computed tomography, the uncertainty was significantly reduced.

Fig. 4. Reconstructed shapes of the investigated PU samples 1 (a), 2 (b) and 3 (c) with their corresponding mass attenuation coefficients. The rectangles indicates the area, which data are plotted in the histogram shown in (d).
Fig. 5 shows a photograph of the investigated safety shoe in comparison with the reconstructed volume of the computed tomography. Two non-planar sections of the that volume were clipped along the red lines (Fig. 5d) and are illustrated in Fig. 5b and Fig. 5c. The red circles indicate larger defects (more than 2 voxels at a voxel size of 0.29 mm along each edge), observed from the reconstructed volume. Those were confirmed destructively after the experiment by opening the corresponding sections of the sole as shown in Fig. 5a. Based on the determined correlation between attenuation coefficient and density of the samples illustrated in Fig. 4, the density of the different sole components was found to be 0.06 cm\(^{-1}\) (0.35 g/cm\(^3\)) for the yellowish part and 0.13 cm\(^{-1}\) (0.78 g/cm\(^3\)) for the greenish part, respectively.

![Fig. 5.](image)

**Fig. 5.** Photograph of the cut shoe successive to the investigation (physical cut sections to confirm the results) with selected defective sections marked with red circles (a). False colour image of the different attenuation coefficients, cut along a non-planar surface of the sole onto the intersection between the high-density (green) and low-density (yellow) material. Defects can clearly be identified as black sections in the tomography (b). Cut along a non-planar surface parallel to the sole into the mainly low-density part of the sole in a deeper section with defects shown (c). Overview (d) of the shoe with a cut perpendicular to the surfaces illustrated in b) (right line) and c) (left line).
4. Discussion and conclusions
The obtained information about the cavities will be completed by applying SANS, which allows a microstructural characterisation of the bulk-polymer structure with respect to nano-pores, micro-cracks and their arrangement (grouping) in the polymer matrix. SANS, having less Q value than SAXS (∼0.005Å⁻¹, or less, if necessary) allows the investigation of objects with larger sizes compared to SAXS. In particular, SANS allows the detection of H inside the bubbles, while SAXS detects only N and C [1]. The sizes of the investigated bubbles can be different, due to the molecular orientation around the same bubbles (internal surface effect). The approximate size of bubbles that can be investigated is in the range 0.5-2 microns. In comparison, fast neutron radiography and tomography is capable of identifying macroscopic defects in the size of 0.58 mm which corresponds to the size of two neighbouring voxels at least. Thus, neutron radiography and tomography, SANS, and SAXS are in this case, complementary.

The macro-, micro- and nano-properties can be analysed and compared to macroscopic characteristics (e.g., strength, density and bending resistance). The results can give an important contribution to the attainment of the main industrial objectives, which are:
- surface improvements with the reduction or the elimination of bubbles
- dimensional stability to control and predict the functional properties, strongly depending on the size and amount of defects as well as on their total area
- to replace expensive components of the mixture with new low cost components, which allow the product to maintain its original characteristics and performances.

The obtained information are expected to be useful for various industrial sectors such as footwear and automotive industry. For the latter, the presence of macro-bubbles in parts such as polyurethane gaskets or seat upholstery may represent starting points of rupture processes, thus information on the internal distribution of bubbles can contribute to the improvement of the production process of these parts.

An industrial application of neutron radiography and tomography has been described, showing the usefulness of this neutron technique in the polymers field. In particular, diverse commercially available polyurethane samples adopted in the footwear sector were successfully investigated, obtaining information on the internal macro-porosity, which could be useful either for the materials improvement, or for the control and estimate of the functional characteristics.

4. References
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