Experimental report

24/11/2023

Proposal: 9-12-688 **Council:** 10/2022

Title: Aggregation of dye in semicrystalline polyamide films and hair and its influence on polyamide film morphology

Research area: Materials

This proposal is a new proposal

Main proposer: Wenke MUELLER

Experimental team: Wenke MUELLER

Local contacts: Ralf SCHWEINS

Samples: Polyamide film with dye

Instrument	Requested days	Allocated days	From	To
D22	3	1	04/07/2023	05/07/2023

Abstract:

The self-aggregation of three industrially relevant dyes in polyamide (PA) films (PA-6 and PA-(6,6)) and in goat hair will be studied. Dye molecules are expected to diffuse into the amorphous regions of the PA film and subsequently change the morphology of the whole film. The scattering length density of the amorphous phase will be varied by introducing H2O and D2O at varying ratio into this phase. This permits to collect data on the same system but at variable contrasts. This will generate a better understanding of dye diffusion, adhesion and morphological changes in the PA film and in hair and help to quantify phenomena that limit literature-described models for diffusion during dyeing processes.

Experimental Report Proposal Number 9-12-688

DOI: 10.5291/ILL-DATA.9-12-688

Abstract: The structure of dyed polyamide films and dyed goat hair was studied with small-angle neutron scattering (SANS) at different contrasts. The absorption of either of the three investigated dyes Yellow, Blue or Red into the substrate does not change the structure of the substrate, but slightly varies contrast conditions in neutron scattering.

Scientific Background: Polyamide (PA) fibres and their coloration are of significant importance for the textile industry. They are used to produce synthetic yarns, which are contained in clothes and textiles. PA polymers can furthermore be used as a model system to study hair coloration, because they contain amide groups, which make up the backbone of proteins, and because of their semi crystallinity. The process of efficient PA- or hair dyeing could be hampered by dye self-aggregation outside or within the substrate. The goal of this work was to study dye self-aggregation in hair and in PA films as a model system.

Materials and Methods

Materials: Polyamide 6 (PA 6) and Polyamide 6,6 (PA 6,6) films with a film thickness of 0.5 mm (± 20 %) were obtained from Goodfellow (France). Goat hair samples were provided by KAO Germany GmbH. Blue (HC Blue 18, ≥ 99.8 %), Yellow (HC Yellow 16, ≥ 99 %) and Red (HC Red 18, ≥ 99 %) were provided by KAO GmbH (Germany). The buffer salts sodium carbonate Na_2CO_3 (≥ 99.8 %) and sodium bicarbonate $NaHCO_3$ (≥ 99.7 %) were obtained from Sigma Aldrich Chemie GmbH, Germany. Buffer solutions contained $NaHCO_3$ at a concentration of 21 mM and Na_2CO_3 at a concentration of 79 mM, resulting into pH = 10.5 if H_2O was used as a solvent or into pD = 10.7 if D_2O was used as a solvent. Three different buffers with the same $NaHCO_3/Na_2CO_3$ composition, but with different H_2O/D_2O ratios were made and used to prepare dyeing solutions: (1) 100 % H_2O/0 % D_2O , (2) 79 % H_2O/21 % D_2O, (3) 100 % D_2O. MilliQ water was used as H_2O. D2O (99.90 % D) was obtained from Eurisotop, France or Sigma Aldrich Chemie GmbH, Germany.

Dyeing of PA: PA films were cut into rectangles with a size of 2 cm x 3 cm for dyeing. They were inserted into a solution containing the respective dye at a concentration of either 0 mM, 0.1 mM, 1 mM or 10 mM in a $NaHCO_3/Na_2CO_3$ buffer, which was prepared in the given H_2O/D_2O mixture. Dyeing solutions had a volume of 25 mL. PA films were dyed for 14 days at a temperature of 40 °C. The dyeing solution was exchanged every 3 days for a fresh solution. After dyeing, PA films were taken out of the solution. Residues of dye on the film surface were washed off by inserting the film into a H_2O/D_2O mixture with the same H_2O/D_2O composition as the dyeing solution and quickly taking it out. This was repeated 2 times with a fresh solution of the same composition. PA films were stored in sealed boxes, which contained an open vial with a H_2O/D_2O mixture at the same ratio as the dyeing solution. Samples were stored at room temperature.

Dyeing of goat hair: Goat hair tresses were inserted into a solution containing the respective dye at a concentration of either 0 mM, 0.1 mM, 1 mM or 10 mM in a $NaHCO_3/Na_2CO_3$ buffer, which was prepared in the given H_2O/D_2O mixture. Dyeing solutions had a volume of 25 mL. They were dyed for 24 h at a temperature of 40 °C and subsequently taken out of the dyeing solution. Goat hair tresses were not washed or rinsed, but immediately dried using a paper towel and transferred to a sealed box, which contained an open vial with a H_2O/D_2O mixture at the same ratio as the dyeing solution. Samples were stored at room temperature.

SANS measurements: Measurements were performed at the SANS instrument D22. Samples were mounted in closed boxes that were connected to a constant stream of N_2 gas, which was saturated with a H_2O/D_2O mixture. The H_2O/D_2O ratio corresponded to the H_2O/D_2O ratio in the dyeing solution. Measurements were performed at a temperature of 25 °C. Goat hair samples were felted before mounting to remove any alignment, which would cause an anisotropic scattering signal. A circular neutron beam with a diameter of 10 mm was used. The D22 instrument possesses two detectors: The front detector, which was at a fixed distance of 1.4 m to the sample and a rear detector. Measurements were carried out at two sample-to-rear-detector distances: 4 m (collimation 4 m) and 17.6 m (collimation 17.6 m) at a neutron wavelength of 6 Å to cover a q-range of 0.0033 $Å^{-1}$ to 0.7 $Å^{-1}$. Neutrons were detected with two ^3He

detectors (multi-tube detector consisting of vertically aligned Reuter-Stokes tubes, with 128 tubes for the rear and 96 tubes for the front detector, all with a diameter of 8 mm and a pixel size of 8 mm x 8 mm. Detector images were corrected to the transmission of the direct beam, scaled to absolute intensity and azimuthally averaged using the GRASP software.

Goat Hair: Figure 1A displays the SANS curve emerging from a goat hair sample, which was only treated with the buffer solution in 100 % D_2O. The SANS curve is dominated by an $I_q \propto q^{-4}$ slope, but oscillations, which are caused by the appearance of diffraction peaks, are clearly discernible in the range of 0.01 $Å^{-1}$ < q < 0.3 $Å^{-1}$. These diffraction peaks arise due to the organization of intermediate filaments within the hair fibre.[1] To facilitate the identification of diffraction peak positions, the A_0q^{-4} contribution was subtracted from the SANS curve. The result is shown in Figure 1B. The obtained values agree with literature.[1] A similar analysis was performed on SANS curves from goat hair samples, which were dyed in solutions containing either Yellow, Blue or Red in a $NaHCO_3/Na_2CO_3$ buffer in 100 % D_2O. However, no significant change in the position of diffraction peaks was observed. This signals, that the uptake of dye does not significantly change the hair structure. Diffraction peaks were not visible any more in SANS curves from hair tresses, which were treated or dyed in a $NaHCO_3/Na_2CO_3$ buffer that was prepared in a solution containing 21 % D_2O and 79 % H_2O. This could be attributed to a reduction in contrast of the intermediate filaments relative to their matrix. Furthermore, the SANS curve from the reference sample and the dyed sample overlayed, suggesting no detectable dye self-aggregation within the hair and a negligible change in contrast due to dye uptake for all three dyes.

Polyamide 6: Figure 2 shows SANS curves from PA 6 films that were treated or dyed in buffers or dyeing solutions, which were prepared with H_2O and D_2O at varying rations. The diffraction peak, which appears due to crystalline regions in the semicrystalline PA 6 polymer, is matched at a solvent composition of 21 % D_2O and 79 % H_2O. No scattering signal, which would point towards dye self-aggregation, is revealed upon variation of the D_2O/H_2O ratio (Figure 2B). Figure 3 shows SANS curves from PA 6 films, which were dyed at variable concentration of the dye Blue in the dyeing solution. From Figure 3 it is visible, that an increase in the concentration of dye in the dyeing solution and therefore in the PA 6 film results in an increased contrast between amorphous and crystalline domains in the PA 6 film. This can be understood in terms of the change of the scattering length density of amorphous domains upon inclusion of the dye. This observation and the size of crystalline domains will be analysed by fitting the data with a suitable model.[2]

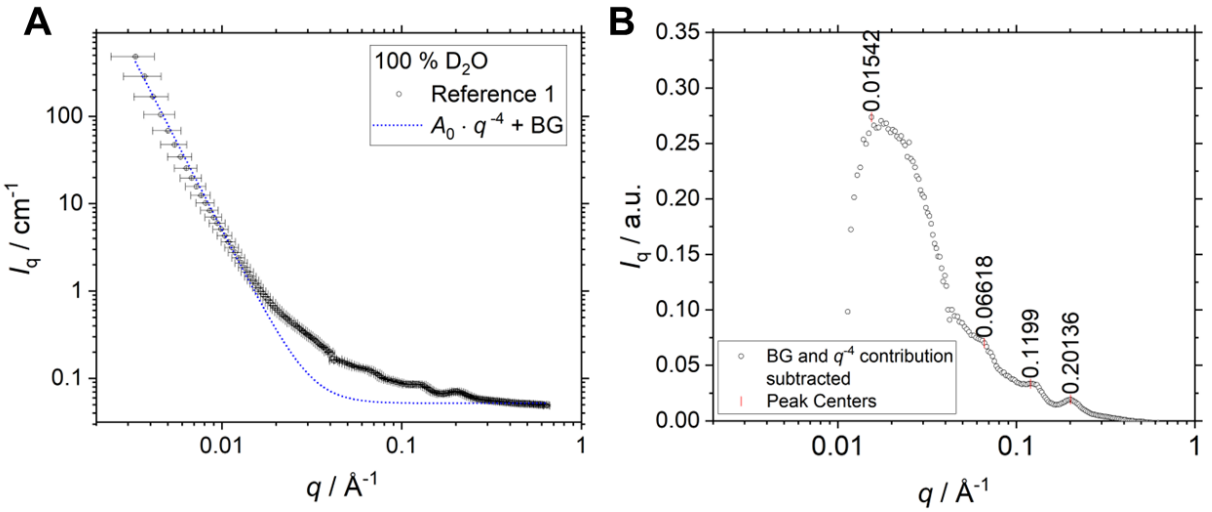

Figure 1: **A** SANS curve of a goat hair sample, which was treated with a $NaHCO_3/Na_2CO_3$ buffer solution in 100 % D_2O (Reference 1) and q^{-4}-dependent contribution to total scattering from submicron structures at the hair interface and pores. **B** Difference between the SANS curve shown in **A** and the q^{-4} dependent contribution and peak centres.

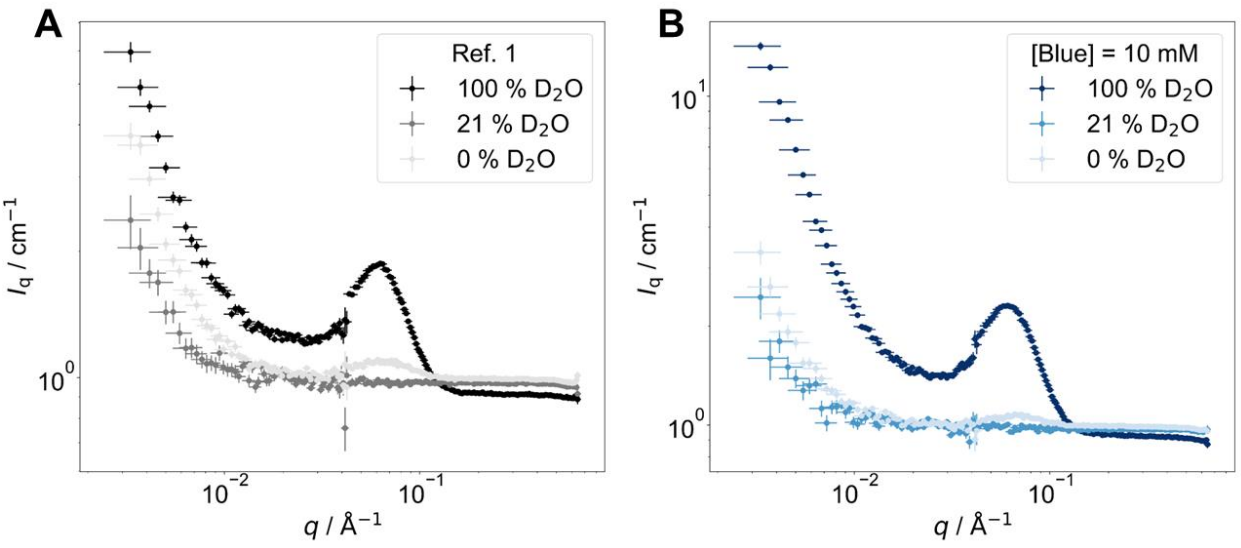

Figure 2: **A** SANS curve from PA 6 films, which were treated with a $NaHCO_3/Na_2CO_3$ buffer solution, which was prepared in a H_2O/D_2O mixture containing the indicated volume fraction of D_2O (Reference 1). **B** SANS curve from PA 6 films, which were treated with a solution containing the dye Blue at a concentration of 10 mM. A $NaHCO_3/Na_2CO_3$ solution, which was prepared in a H_2O/D_2O mixture containing the indicated volume fraction of D_2O served as a solvent for the dyeing solution.

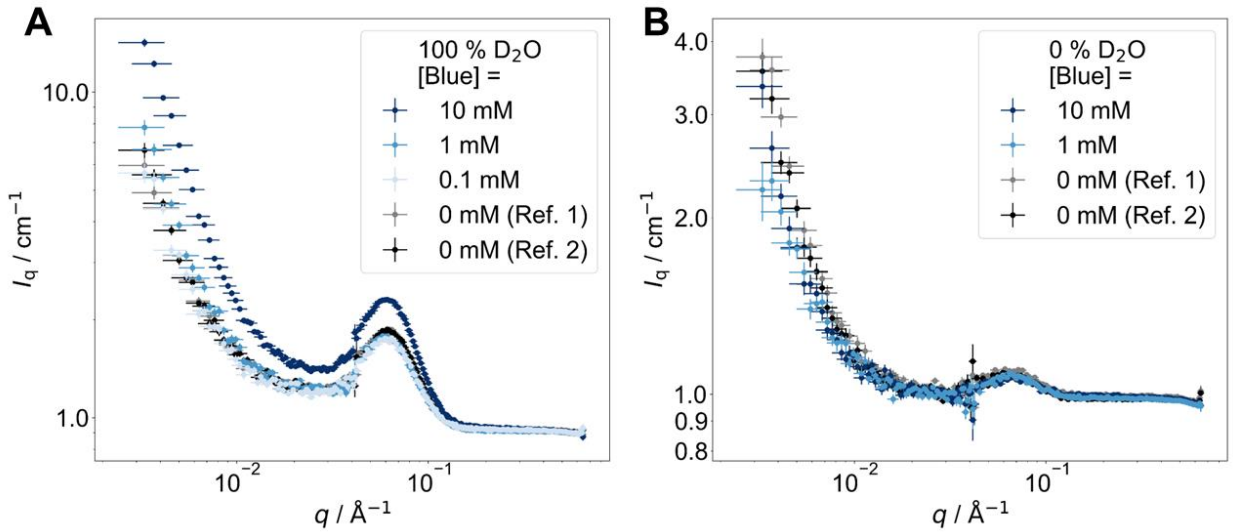

Figure 3: **A** SANS curves from PA 6 films, which were treated with a solution containing the indicated concentration of the dye Blue. A $NaHCO_3/Na_2CO_3$ buffer, which was prepared in D_2O, served as a solvent for the dyeing solution. **B** SANS curves from PA 6 films, which were treated with a solution containing the indicated concentration of the dye Blue. A $NaHCO_3/Na_2CO_3$ buffer, which was prepared in H_2O, served as a solvent for the dyeing solution.

References

(1) Murthy, N. S.; Wang, W.; Kamath, Y. Structure of Intermediate Filament Assembly in Hair Deduced from Hydration Studies Using Small-Angle Neutron Scattering. *Journal of Structural Biology* **2019**, *206* (3), 295–304. https://doi.org/10.1016/j.jsb.2019.04.004.

(2) Murthy, N. S.; Akkapeddi, M. K.; Orts, W. J. Analysis of Lamellar Structure in Semicrystalline Polymers by Studying the Absorption of Water and Ethylene Glycol in Nylons Using Small-Angle Neutron Scattering. *Macromolecules* **1998**, *31* (1), 142–152. https://doi.org/10.1021/ma9707603.