Experimental report

12/02/2020

Proposal: 9-11-1936 **Council:** 4/2019

Title: Study of periodic disorder in regenerated cellulose fibers by small angle neutron diffraction

Research area: Materials

This proposal is a new proposal

Main proposer: Daisuke SAWADA

Experimental team: Daisuke SAWADA
Yoshiharu NISHIYAMA

Local contacts: Lionel PORCAR

Samples: Cellulose fiber
cellulose lignin composite
cellulose chitosan composite
cellulose keratin composite

Instrument	Requested days	Allocated days	From	To
D22	2	1	26/09/2019	27/09/2019

Abstract:

Periodic disorder, composed of the repeating of crystalline and amorphous domains, sheds light on the structure of regenerated cellulose fibers. The presence of periodic disorder has been reported on two regenerated cellulose fibers, Rayon fiber (19.3 nm) and Fortisan (16.5 nm). However, in this report, the relationship between periodic disorder and the other structural parameters were unclear due to the limited number of samples. Here, we would like to propose small angle neutron scattering (SANS) experiment using Ioncell and several regenerated fibers from Lenzing AG. Ioncell is a regenerated cellulose fiber from an ionic liquid ([DBNH]OAc), and we can control the structural parameters of Ioncell by adjusting the spinning parameters. We will study these controlled samples to interconnect the periodic disorder system and structure model in regenerated fibers. In addition to standard fibers, we will apply Ioncell composite fibers with several additive polymers to pursue the change of periodic disorder. SANS with selective deuteration will be used to enhance the contrast between amorphous and crystalline cellulose.

Study of periodic disorder in regenerated cellulose fibers by small angle neutron diffraction

Daisuke Sawada[1], Yoshiharu Nishiyama[2] and Thomas Röder[3]

1. Aalto University, School of Chemical Engineering, Department of Bioproducts and Biosystems, P.O. Box 16300, 00076 Aalto, Finland. 2. Lenzing R&D, Lenzing, Austria 3. University Grenoble Alpes, CNRS, CERMAV, Grenoble, France.

Local contact: Lionel Porcar.

Introduction

The nanometric internal structures involve important parameters for the mechanical strength of fibrous materials such as morphology of crystallites, structure of amorphous phase, and linkage of crystal and amorphous region. Small angle scattering is a powerful tool to study structures at nanometer length scale. The presence of Bragg peak in meridian gives a unique information for longitudinal structure of engineering fibers. However, by small angle X-ray scattering experiments with regenerated cellulose fibers, the Bragg peak intensity was absent or very weak with considerable background noise. Therefore, a few experiments have attempted to enhance the diffraction intensity from regenerated cellulose fibers.

These previous reports showed divergent repeating distances from same cellulose fiber types, and reason of such divergence has not been addressed. Additionally, the periodic disorder has not been analyzed beyond the repeating distances probably due to the difficulty for estimating peak intensities accurately. In this experiment, we used small angle neutron scattering (SANS) with selective deuteration method to keep the original structure and to obtain the absolute intensity. We prepared several regenerated cellulose fiber types by different spinning protocols and conditions. Longitudinal structures of these fibers were studied from the 2D analysis of Bragg peak intensity.

Experimental summary

Table 1. Main samples for this experiment.

Name	Solution	Spinning type
Ioncell	DBNHOAc	dry-jet wet
Lyocell	NMMO	dry-jet wet
Fortisan	Acetone	dry
Viscose rayon	NaOH-CS2	wet
Modal	NaOH-CS2	wet
Tire cord	NaOH-CS2	wet

Vacuum dried cellulose fibers in a quartz glass tube were subjected to the airflow of argon gas containing D_2O vapor for 18 hours to increase the scattering length density (SLD) of amorphous part as previously reported [1]. The treated samples were then dried under the air flow of dry argon gas for 3 hours, and quartz tubes were sealed by wax to avoid the back-exchange to hydrogen in amorphous part. SANS data were collected from several regenerated cellulose fiber types as summarized in Table 1.

Small-angle neutron scattering data were collected at the D22 instrument at ILL. The glass tubes were aligned side by side along direction in a sample holder. A configuration was used for a wave-vector range, q of ca. 0.01–0.1 $Å^{-1}$, achieved by utilizing sample-to-detector distances of approximately 5.2 m at 6 Å neutron wavelength. Neutron was exposed 5 or 10 minutes for each sample.

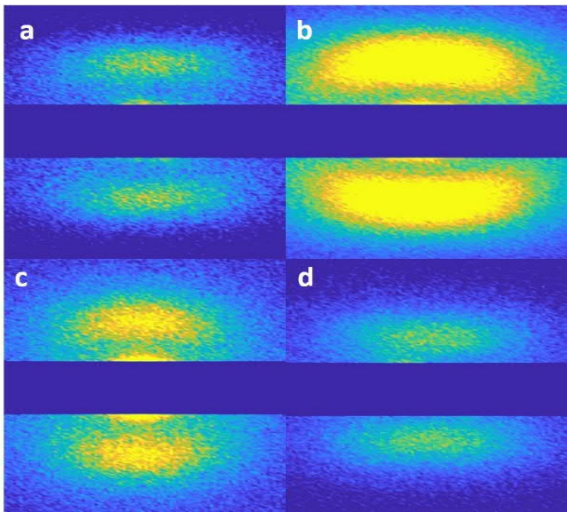

Figure 1. The small angle neutron diffraction pattern of (a) Fortisan, (b) Modal, (c) Viscose Rayon and (d) Tire cord (Super3).

Results

Bragg peaks in meridian from viscose type cellulose fibers and Fortisan were shown in Figure 1. These wet-spun fibers and dry-spun fiber showed two diffraction spots. We analyzed the repeating distance (L) from the scattering vector (Q):

$$L = \frac{2\pi}{Q}$$

The L value of Fortisan, Modal, Viscose Rayon and Tire cord were 184, 171, 181 and 226 Å, respectively. The long repeating distance of tire cord indicates the high aspect ratio of elementary fibrils, which may explain its superior tensile properties. Unexpectedly, regenerated cellulose fibers from dry-jet wet spinning, namely Ioncell and Lyocell, showed off-meridional diffraction pattern (four-point pattern) as shown in Figure 2. The four-point pattern enabled us to characterize these fiber types with repeating distance between crystallites, the tilt angle of oblique crystallites [2], and volume fraction of amorphous phase [3].

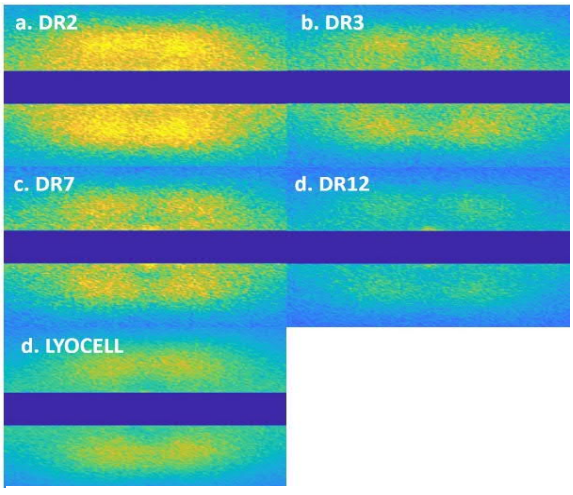

Figure 2. The small angle neutron diffraction pattern of Ioncell from (a) DR2, (b) DR3, (c) DR7, (d) DR12 and (e) Lyocell.

We performed 2D gaussian fitting to obtain these structural parameters from the Bragg peak intensity.

Although the tensile strengths of these fibers showed positive relationship with the spinning parameter of draw ratio (DR), the structural parameters did not linearly increase nor decrease. In other words, we did not find simple correlation between tensile properties and any of these structural parameters. Further experiments will be performed to link these structural parameters and the tensile properties of these fibers.

References

1 Fisher et al. *Macromolecules.* **11**, 213-217 (1978)
2 Murthy, N.; Grubb, D. *J Polym Sci Pol Phys* **44**, 1277-1286 (2006)
3 Nishiyama et al. *Biomacromolecules* **4**, 1013-1017 (2003)