The effects of different solvents, water, ethanol, and acetone, on the nanostructure of microcrystalline cellulose (MCC) were studied using small-angle x-ray scattering (SAXS). The results indicated differences in the abilities of the solvents to diffuse inside the fibers of MCC, and that the structure of cellulose microfibrils was heterogeneous in all the studied solvents at nanoscale.

SAMPLES AND METHODS

MCC was made from cotton linter using mild acid hydrolysis in 2.5 M solution of HCl at 105°C for 1 hour. For the SAXS experiments, MCC powder was immersed in distilled water, ethanol, and acetone about 3 weeks prior to the measurements. Also, dry MCC powder was measured using SAXS to be able to compare the MCC-solvents with the dry state. The previously done wide-angle x-ray scattering (WAXS) studies revealed the crystallite dimensions (Fig. 1) and crystallinity of the MCC powder [1].

The SAXS measurements were conducted at the Department of Physics at the University of Helsinki using conventional sealed x-ray tube with Cu-anode and Bruker HI-Star area detector (Fig. 2). The intensities were set onto the absolute scale using Lupolen standard sample.

RESULTS

Using the integrated SAXS intensity curves, the specific surfaces, the radii of the gyration, and the average chord lengths of the samples were determined [2]. The specific surface increased significantly when MCC was immersed in the solvents: the values were 5.0 m²/g in dry MCC, 240 m²/g in MCC-water, 430 m²/g in MCC-ethanol and 110 m²/g in MCC-acetone.

The average chord length (L) reveals the characteristic length scale of the structure of the samples. Differences were found between the L values of the samples: 2.4 ± 0.1 nm was obtained for MCC-water, 1.6 ± 0.1 nm for MCC-ethanol, and 1.3 ± 0.1 nm for MCC-acetone. Also the radii of the gyration were different in these samples: 1.2 nm was obtained for MCC-water, 1.5 nm for MCC-ethanol, and 2.2 nm for MCC-acetone. [2]

Fig. 1 Left: SEM image of the structure of MCC made of cotton linter at micrometer level. Right: Dimensions of crystalline parts of elementary cellulose microfibrils in MCC made of cotton linter according to WAXS results [1].

Fig. 2 SAXS set-up at the University of Helsinki and the 2D SAXS patterns of microcrystalline cellulose as dry powder (left) and as immersed in water (right).

Fig. 3 Integrated SAXS intensities as a function of the length of the scattering vector (q). The both axis are in logarithmic scale. The differences in the power law behaviours indicating the fractal dimensions of the dry MCC and the MCC-solvent samples can be seen in the slopes of the curves.

CONCLUSIONS

The large increase in the specific surface values of the MCC-solvent systems compared to dry MCC indicated that all the studied solvents were able to open up the fiber bundles. According to the radius of gyration and average chord length values, water could diffuse more efficiently inside the fibrils than ethanol and acetone. The differences between the radii of gyration, the average chord lengths and the crystallite width obtained using WAXS indicated that the structure of cellulose microfibrils was heterogeneous in all the solvents.

REFERENCES