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Supermolecular Structure of Alginate Fibres for Medical Aplications Studied by Means of WAXS and SAXS Methods

Abstract

The main goal of the investigations presented in this paper was to determine the influence of the coagulation bath's content caused by the different levels of substitution ions Na^+ with Ca^{++} in alginate chains on the parameters of the supermolecular structure of the obtained fibres.The high mannuronic sodium alginate Protanal LF-10/60 LS produced by FMC biopolymers was used. Our research involved preparing spinning solutions from alginates of various fractions of derivatives of guluronic and mannuronic acids, and forming multifilaments to the coagulation bath, which was made of a water solution of calcium chloride, sodium chloride and/or hydrochloric acid in different concentrations respectively. The structure of fibres on their supermolecular level was evaluated by the WAXS and SAXS diffraction methods.

Key words: *alginate fibrs, medical application, supermolecular structure, WAXS, SAXS.*

Introduction

Fibrous substances are important in many biological contexts and their successful exploitation by people for food and different materials with special properties has had a millennia-long history. Although profitable technologies can evolve without accurate information about molecular or higher structures, it is certainly possible to rationalise the functional and valuable properties of manufactured materials by searching for the relationship between their properties and their atomic-level structures. This also applies to alginates.

About 50% of annual alginate output is utilised in the textile industry and 30% of it in food production [1, 2]. The residual output is consumed in the pharmaceutical, paper and cosmetic industry. Nowadays alginate fibres are being applied more and more often in the medical material industry [3]. The rising interest results from their unique properties, principally their biocompatibility to the human organism and their ability to increase blood solidification [4, 5].

Alginates are linear unbranched polymers containing β-(1→4)-linked D-mannuronic acid (M) and α-(1→4)-linked L-guluronic acid (G) residues. Although these residues are epimers (D-mannuronic acid residues being enzymatically converted to L-guluronic after polymerisation) and only differ at C5, they possess very different conformations; D-mannuronic acid is $^4C_1$ with diequatorial links between them, and L-guluronic acid is $^1C_4$ with diaxial links between them. Alginates are not random copolymers but, according to the source algae, consist of blocks of similar and strictly alternating residues (i.e. MMMMMM, GGGGGG and GMGMGMGM), each of which have different conformational preferences and behaviour (Figure 1).

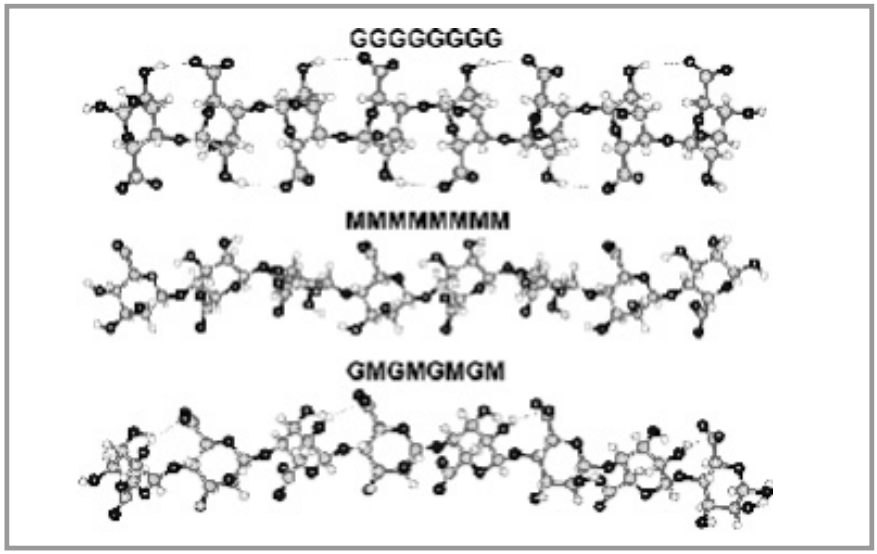

Figure 1. *Molecular structure of alginates optimised using Hyperchem and the AMBER-96 force field [6].*

Table 1. *Properties of sodium alginate Protanal LF-10/60 LS.*

Characteristic	Unit	Value
Form		powder
Content of: guluronic acid mannuronic acid	%	40÷45 55÷60
Humidity	%	10.0
Viscosity	MPa·s	52
Content of calcium	%	1.5
pH of 1% solution, 20°C		6.5
Insoluble components	%	0.01
Total content of oxygen bacteria	cfu/g	125

Alginates with a higher content of G show a greater affinity for Ca^{++} ions and form stronger, harder gels. Spinning oriented fibres from such gels has not been very successful, but they have been shown to contain the same molecular conformations as the acid forms, which can be obtained in uniaxially-oriented, polycrystalline form [7, 8]. In this paper we undertook an attempt to evaluate the transformation of the supermolecular structure of the above-mentioned alginate gels during the fibre formation process, by means of WAXS and SAXS methods.

Experimental

Materials

We used the high mannuronic sodium alginate Protanal LF-10/60 LS (Tab. 1), produced and delivered by FMC Biopolymers (Drammen, Norway) to obtain investigated fibres.

Formation of alginate fibres

The spinning solution of sodium alginate (concentration 6% by weight) was placed in a pressure container, and then a specified amount of solution was supplied to the spinning head by means of the spinning pump. The head was equipped with a platino-rhodium spinneret with 300 holes of a diameter of 80mm. The spinning solution was brought to the coagulation bath through a spinneret. There the fibre-forming polymer was precipitated in the form of fibres. The coagulation bath was made of a water solution of calcium chloride, sodium chloride and/or hydrochloric acid in suitable concentrations. The temperature of the coagulation bath was 40°C. Filaments formed in the coagulation bath were then brought to a water bath of a temperature of 40°C and afterwards to another bath of a temperature of 80°C. The fibres were spun with a take-up velocity of 21.2 to 26.7m/min, and were drawn in water baths with a total draft R=50%. The alginate fibres which formed were taken up wet, and were then dried in the air, either in the tension-free conditions or under tension on heated godets.

Analytical methods

WAXS

Wide-angle X-ray scattering investigations were carried out with a HZG-4 Seifert diffractometer. CuK_α radiation was used at 40kV and 30mA. Monochromatisation of the beam was obtained by means of a nickel filter and a pulse-height analyser. A scintillation counter was used

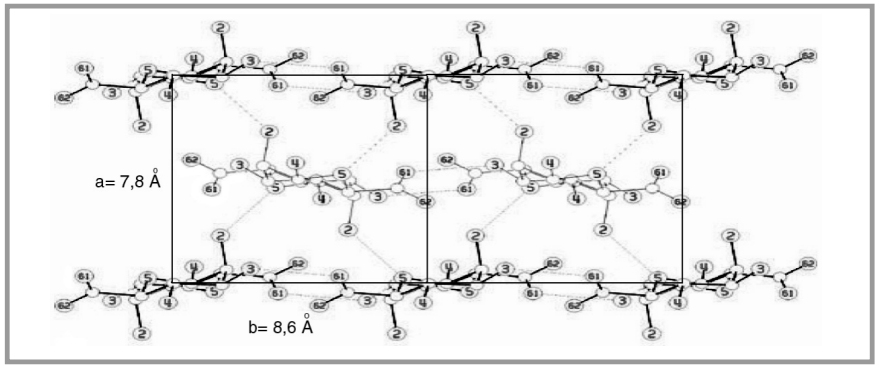

Figure 2. *View of the crystal structure of mannuronan - the c axis projection with a vertical, again showing the inter-sheet O2···O5 H bonding of the anti-parallel sheets of parallel molecules with intra-sheet O3···O61 H-bonding.*

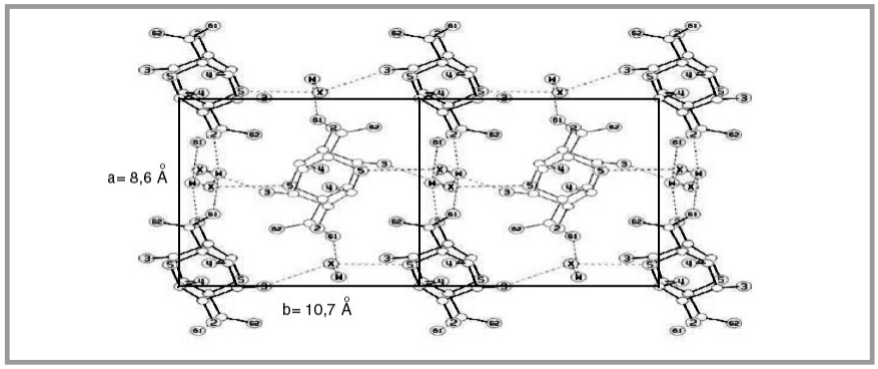

Figure 3. *View of the crystal structure of hydrated guluronan the c axis projection of two complete unit cells with a vertical, the central diamond shows all the O···water···O bridges that glue the matrix together – the O61···W···O2 bridges vertically and the O3···X···O5 bridges horizontally.*

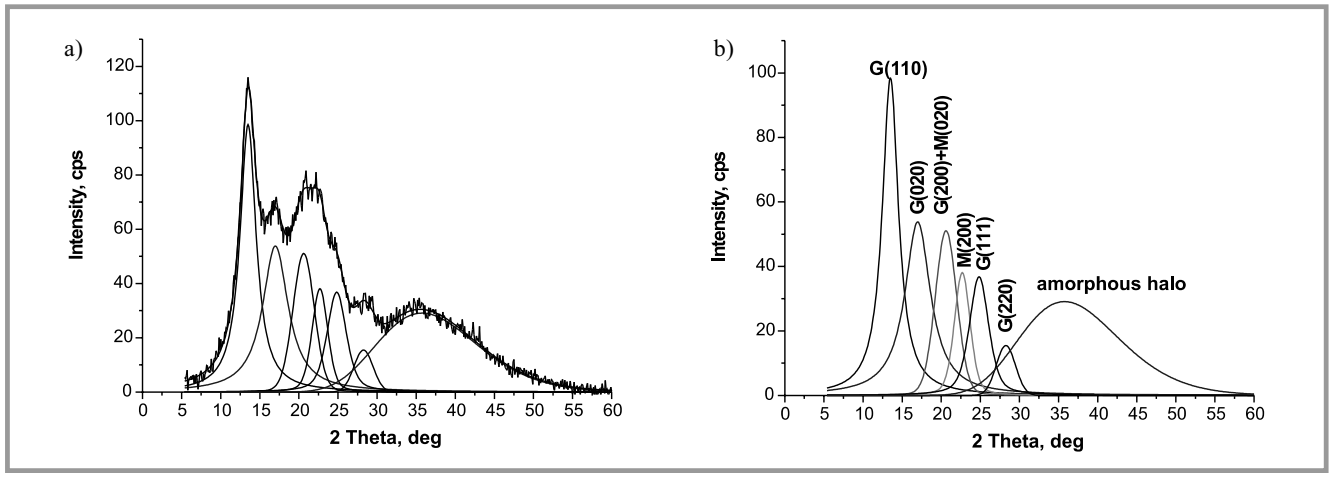

Figure 4. *An example WAXS curve for a sample of alginate filament (fibres precipitated in the coagulation bath without $CaCl_2$) a) curve resolved into individual peaks,b) diffraction reflexes with adequate Miller indices.*

as a detector. Investigations were performed over the range of angles from 5° to 60° with a step of 0.1°. Each diffraction curve was corrected for polarisation, Lorentz factor, and incoherent scattering.

SAXS

Small-angle X-ray scattering investigations were performed by means of an MBraun camera, which utilises a conventional Kratky collimation system. The front of the camera was directly mounted on the top of the tube shield of a stabilised Philips PW 1830 X-ray generator. The X-ray tube was operated at a power of 1.5kW. CuK_α radiation was used; monochromatisation was performed by a Ni β filter and a pulse–height discriminator. The entrance slit was set at 50μm. Scattered radiation was recorded over an acquisition time of 900s by means of a MBraun linear position-sensitive detector, model PSD 50. The detector had 1024 channels with a channel-to-channel distance of 52mm. The experimental SAXS curves were corrected for sample absorption and de-smeared from collimation distortions by means of the 3DVIEW computer program supplied by MBraun.

Results and discussion

In our WAXS investigations, we made full use of the recent works of Arnott et. al. [9] on mannuronan and guluronan structures (Figure 2, 3)

The X-ray diffraction patterns obtained from a particular alginate sample will depend on its chemical composition, especially on the relative lengths and positions of the polymannuronic (M) and polyguluronic acid (G) blocks. The diffraction signals of polymannuronic acid were indexed on a two-chain orthorhombic unit cell with dimensions of a=0.76nm, b=0.86nm and c=1.04nm (chain direction). The X-ray diffraction pattern of polyguluronic acid (G) can be indexed on a two-chain orthorhombic unit cell with parameters of a=0.86nm, b=1.07nm and c(chain axis)=0.87nm, in space group $P2_12_12_1$.

There are therefore only two variable polymer-packing parameters, a molecular translation along the c direction and an orientation about c.

Based on the structures elaborated, we resolved the experimental WAXS curves into individual peaks (Figure 4a, b) using the OPTIFIT software [10].

The resolved curves indicate that the structure created during the formation process of alginate fibres have a relatively high order (the crystallinity index evaluated for fibres precipitated in the coagulation bath without $CaCl_2$ is about 70%).

By comparison of the WAXS curves obtained for alginate fibres with the different Ca^{++} ions content (Figure 5), we can conclude that the increase of calcium chloride content in the coagulation bath changes the shape of these curves. The intensity of the peaks from crystalline planes, particularly of guluronan (110), (020) and (200) decreases. This proportion of diffraction reflex intensities changes when the Ca^{++} ion content grows continuously.

Thus, we obtained the maximum of WAXS reflexes for filaments precipitated in the coagulation bath containing hydrochloric acid only (0% of Ca^{++} ions content in fibres). Based on the earlier study of the formation process, a distinct deterioration in the coagulation was found for this kind of fibre. Moreover the take-up velocity had to be reduced from 26.7 to 21.2m/min, and the draft was decreased from 50% to 15%. The tenacity of these fibres was lower than 10cN/tex, and the finishing of fibres required the application of a considerable amount of ethyl alcohol (dehydrating agent).

On the other hand, we obtained the optimum of mechanical properties (also with a very stable precipitation process) for alginate filaments, which were formed in the coagulation bath, including calcium chloride of a concentration of 25g/l (9% of Ca^{++} ion content in fibres), which corresponds to the very weak intensities of WAXS reflexes.

The comparison of SAXS curves obtained for the fibres investigated in the direction parallel to the fibre axes (Figure 6) show the existence of the guluronan and mannuronan blocks' structure.

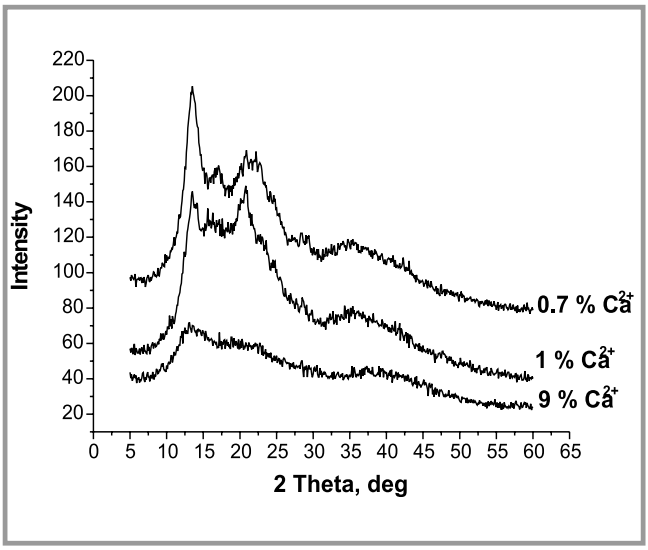

Figure 5. WAXS curves for alginate filaments with the different Ca^{++} ions content (fibres formed in coagulation baths with the different concentration of calcium chloride).

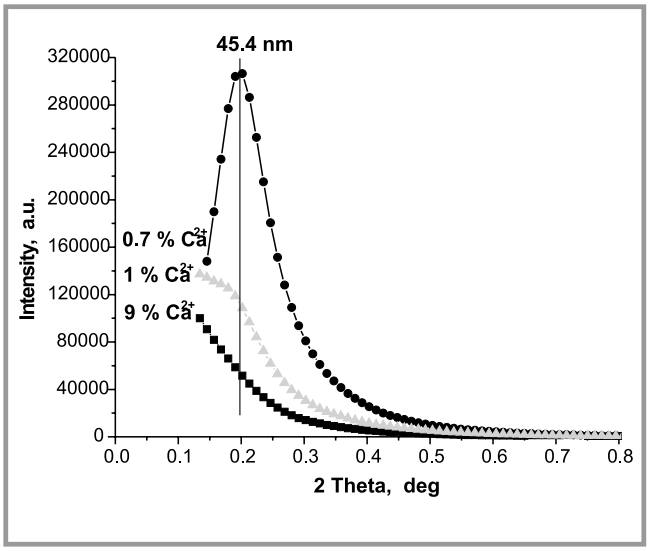

Figure 6. The comparison of SAXS curves (in the direction parallel to the fibres' axes) for alginate filaments with the different Ca^{++} ion content.

The long period of this structure (calculated from Bragg's law) corresponds to the maximum visible on the curve registered for sample of fibres without Ca^{++} ions. The distinct peak of alternating GM blocks (at a distance of about 45.4nm) corresponds to the inflection point on the curve registered for fibres of 1% calcium ion content. The long spacing effect described the complete disappearances on the SAXS curve obtained for fibres with the substitution of Ca^{++} ions at the level of 9%.

Conclusion

- Based on both WAXS and SAXS results, it was found that a relatively high level of substitution with the calcium in alginate fibres, which causes an improvement in their mechanical properties, in the applied conditions of the precipitation process, distinctly deteriorates the structure of these fibres on the supermolecular level.

Acknowledgment

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The 60th Anniversary of the Textile Research Institute (IW) in Łódź, Poland

The two-day celebration began on September 12, 2005 at the New Theatre in Łódź with a ceremonial meeting which was attended by invited guests, as well as former and present employees of the Institute. The official part of the meeting was opened by Jolanta Mamenas, the managing director of the Institute, who presented the Institute's foundation and history, its main achievements, and the outstanding researchers who have worked there since its foundation. Many congratulatory addresses followed, including from Stefan Krajewski, the Voivode of Łódź (provincial governor of the Łódź region), Marek Bartosik, the Ministry of Scientific Research and Information Technology, Prof. Jan Krysiński, the Rector of the Technical University of Łódź, Prof. Tadeusz Więckowski, the Rector of the Technical University of Wrocław, Prof. Tadeusz Kulik, the Rector of the Technical University of Warsaw, Prof. Janusz Szosland, the Honorary Chairman of the Polish Textile Association, Prof. Eckhard Schollmeyer, Prof. Henrik Wenzel, Prof. Marc van Parys, Dr. Victoria Vlasenko, and Dr Tatyana Chibisova, representatives of the Deutsches Textilforschungscentrum Nord-West e.V, Krefeld (Germany), the Technical University of Denmark; the Technical University of Ghent and UNITEX (Belgium), the Kiev National University of Technology and Design, Kiev (Ukraine), and the Nonwovens Research Institute, Serpukhov (Russia) respectively, and Prof. Izabella Krucińska, the Dean of the Faculty of Textile Engineering and Marketing, Technical University of Łódź.

Jadwiga Sójka-Ledakowicz Ph. D., Eng., the Institute's vice director responsible for scientific research, was awarded the Gold Cross of Merit, and Bogna Goetzendorf-Grabowska Ph. D. Eng., & Halina Królikowska M. Sc. Eng. –were awarded the Silver Cross of Merit; and 28 former & present employees were awarded congratulation letters.

The official part of the meeting was followed by the comedy '*Mayday'* written by Ray Cooney, and by a dinner-party. The second day of the Anniversary celebration took place at the

International Scientific Symposium 'New Vision of Textile Industry and Economic Needs'

at the Dobieszków Conference Hall. The following lectures were presented:

- **'Nanotechnology to Functionalisation of Textile Materials'** by *Prof. Eckhardt Schollmeyer, DTNW, Krefeld, Germany.*
- **'Perspectives for Material Engineering at the Beginning of the 21st Century'** by *Prof. Krzysztof J. Kurzydłowski, Technical University of Warsaw.*
- **'Biotechnology in the Textile Industry'** by *Dr Jadwiga Sójka-Ledakowicz, Textile Research Institute, Łódź .*
- **'Our Engineering Is Your Change to Innovations'** by *Prof. Mark van Parys, I. Garez, M.Eng., A. Deraeve, M.Eng., Technical University of Gent, Belgium.*
- **'Microporous Polyurethane Membranes as a Basic Component of Multilayer High-tech Composite'** by *Prof. Stefan Brzeziński, IIMW, Łódź.*
- **'Current Multifunctional Multiplayer Textiles: Unlimited Possibilities of Their Application'** by *Dr Victoria Vlasenko, EKMA, Kiev, Ukraine.*
- **'Research and Innovation in Textile Industry: the Role of Technological Centres'** by *Dr Jan Laperre, Centexbel, Ghent, Belgium.*
- **'Textile Dyes: Past, Present and Future'** by *Prof. Wojciech Czajkowski, Technical University of Łódź.*
- **'Savings of Water and Energy by Process Integration in Polyester Dyeing: Latest Achievements and Perspectives'** by *Prof. Henrik Wenzel Christensen, IPU, Lyngby, Denmark.*
- **'Modern Methods of High Quality Yarn Production'** by *Prof. Tadeusz Jackowski, Dr Danuta Cyniak, Dr Jerzy Czekalski, Technical University of Łódź.*

An open-air party ended the anniversary celebrations.

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