3. ALKALINE TREATMENT OF DIBUTYRYLCHITIN FIBRES. FLUORESCENT MICROSCOPY STUDIES

Dorota Biniaś, Stefan Boryniec, Andrzej Włochowicz, Włodzimierz Biniaś

Akademia Techniczno -Humanistyczna,
Instytut Inżynierii Tekstyliów i Materiałów Polimerowych
43-309 Bielsko-Biała, ul.Willowa 2
e-mail: dbinias@ath.bielsko.pl

1. Introduction

Dibutyrylchitin (DBCH) is obtained by the modification of chitin with butyric anhydride. It possesses fibre-forming properties and is used as an initial material to form fibres.

In this study anhydrous ethyl alcohol was used as a solvent. Spinning solutions with different polymer concentrations were prepared. DBCH fibres were formed by means of a dry-wet method. A partially solidified stream of a polymer solution coming from the spinning machine into the air was next introduced into a water bath where a total coagulation and fibre drawing took place. Due to the applied method of spinning it was possible to obtain microporous DBCH fibres. The fibres were then subjected to the alkaline treatment which resulted in obtaining fibres from the regenerated chitin and finally chitosan fibres. The fibres were examined using fluorescent microscopy and UV radiation.

2. Materials and methods

2.1. Materials

Microporous DBCH fibres were treated with kalium hydroxide in order to obtain fibres from the regenerated chitin and then chitosan fibres. In the first stage of the process, chitin fibres were obtained by applying a 5% KOH solution at the temperatures ranging from 20 °C to 90 °C. The application of a saturated KOH solution and high temperatures (70 °C to 140 °C) resulted in obtaining chitosan fibres with different deacetylation degrees. The fluorescence effects in the places of the surface and the fibre core deformations were intensified by the specific sorption of Rhodamine B used as a dye

at different temperatures (20 °C, 50 °C, 70 °C). Rhodamine B reveals no affinity to the examined fibres and therefore it is accumulated in their micropores and microcapillaries by adhesion. Obviously, due to this fact, the fluorescence effect is intensified.

2.2. Parameters of measuring system

The examination of the fibres and the recording of the microphotographs were carried out by means of a measuring set consisting of:

1. Fluorescent microscope Biolar FL, a product of PZO, Poland (source of light - mercury - vapour tube, excitation filters, barrier filter)
2. A computer system for digital image recording - a photo-video camera Panasonic KR-222, a computer video card MIRO, and a computer with Pentium II 233MHz processor.

To record longitudinal views of the fibres and their cross-sections the following magnifications were applied: 180 for the microscope, and 320 for the camera.

3. Results and discussion

DBCH fibres not subjected to the Rhodamine B dye sorption reveal a specific greenish fluorescence in UV light when the blue filters are used (Figure 1). This effect observed on the longitudinal views of the fibres reveals homogeneity of the fibre surface topography. The fibres are smooth and homogeneous with no impairments or defects. In the photograph of the cross-section of DBCH fibres (Figure 2), a clear fluorescence effect of a thin surface layer of a fibre can be seen. This phenomenon results from the specific supermolecular structure of the fibres formed using a wet-dry spinning method. The solidifying stream of the polymer is introduced into a water bath where full fibre solidification takes places.

It can be expected that the polar molecules of a solvent and those of a coagulating agent migrating through the gel layer caused radial orientation of the crystalline regions. In the deeper parts of the fibre the polymer was probably precipitated from the solution by the coagulating agent (water) in an unoriented or amorphous form.

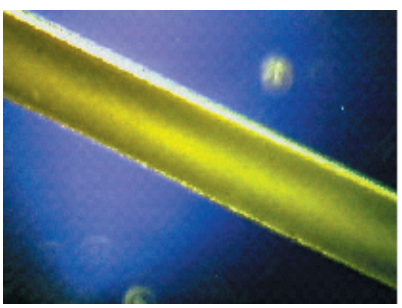

Figure 1. *Microphotograph of the surface of DBCH fibres, magnification 180×.*

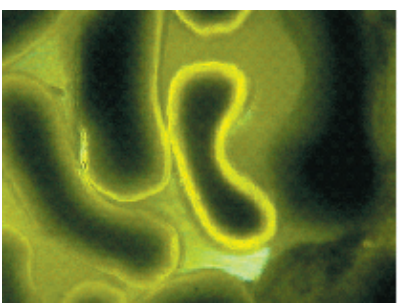

Figure 2. *Microphotograph of the cross-section of DBCH fibres, magnification 620×.*

At 50 °C (Figure 3) the dye penetrating the porous core of the fibre reveals the areas with various porosities. It is probably caused by the partial relaxation of the fibres that get swollen in an aqueous medium.The ten-minute alkaline treatment of DBCH fibres with 5% KOH solution at 70 °C (sample C1) damages the fibre skin continuity and thus its permeability grows (Figure 4). When the fibres are immersed in oil, it penetrates into their deepe areas causing a partial transparency of the fibres. Only the unmoistened parts of the core look like a string of shining beads.

Also the sorptive properties of sample C1 change when the sample is subjected to the alkaline treatment. It can be observed even at such a low temperature (20 °C). Rhodamine B is permanently bound with the fibre and causes its red colouring (Figure 5).

It can be suggested that the sorption of the dye is affected both by the change of the chemical affinity and by the formation of micropores in the skin of the fibre. The micropores result from kalium butyrate diffusion which is also responsible for the defects of the polymer mass in the near surface fibre layers.

The accumulation of the dye Rhodamine B in the places where the fibre skin is damaged results from the sorption process at 50 °C (Figure 6). The more developed the skin surface, the more intensive dye accumulation is. At the same time strong fluorescence of the dye can be observed in the form of bright lines and dye aggregations along the fibre axis. The dye sorption rises as the temperature of dyeing grows. At 70 °C a complete penetration of the fibre interior by Rhodamine B takes place. The dye fills the porous core and strong fluorescence of the whole fibre can be seen. Under such conditions especially longitudinal defects on the fibre skin are demonstrated as brightly shining belts of different thicknesses and lengths.

The fibres from the regenerated chitin after full debutyrylation in 5% KOH at 70 °C for 180 minutes (sample C6) manifest weak fluorescence (Figure 7). Small fluorescent dots in the fibre interior may come from the unreacted macromolecules of DBCH.

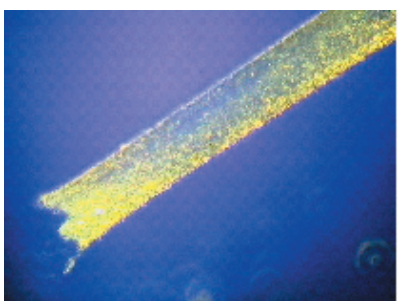

Figure 3. *Microphotograph of the surface of DBCH fibres containing Rhodamine B introduced at 50 °C, magnification 180×.*

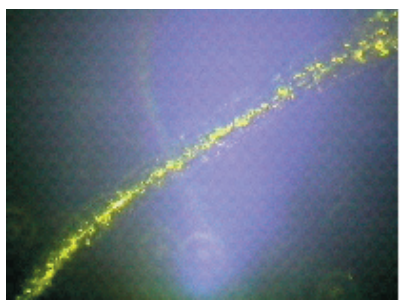

Figure 4. *Microphotograph of the surface of DBCH fibres after 10 min. of alkaline treatment with 5% KOH solution at 70 °C, magnification180×.*

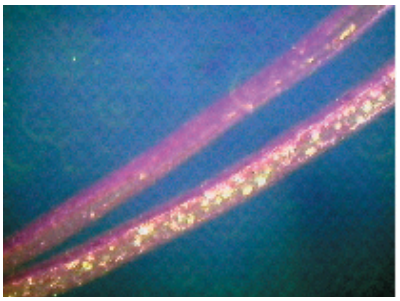

Figure 5. *Microphotograph of the surface of DBCH fibres after 10 min. of alkaline treatment with 5% KOH solution at 70* °C *containing Rhodamine B introduced at 50* °C*, magnification 180×.*

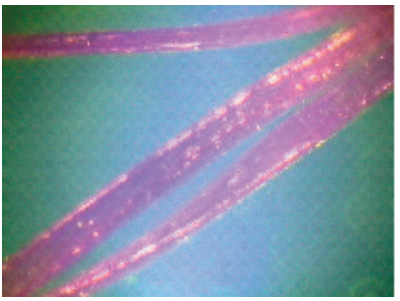

Figure 6. *Microphotograph of the surface of DBCH fibres after 10 min. of alkaline treatment with 5% KOH solution at 70* °C *containing Rhodamine B introduced at 50* °C*, magnification 180×.*

The dye absorbed at 20 °C by the fibres from the regenerated chitin (sample C6) is uniformly distributed on the fibre surface (Figure 8). Swelling and full conversion of DBCH probably result in the uniform shrinkage of the fibre in its whole cross-section, which leads to obtaining a homogeneous structure of the fibre surface on a macroscopic scale. The fibres "dyed" at higher temperatures are characterized by a larger diameter, which proves that they get strongly swollen under the influence of such temperatures. On the surface of the fibres small fluorescent dots can be seen (Figure 9).

After N-deacetylation for 6 hrs. in a saturated KOH solution at 140 °C, the fibres (sample N H4) also reveal weak "self-fluorescence" (Figure 10) but they demonstrate strong deformations on the fibre surface as can be seen in the photographs of the fibre cross-sections (Figure 11). As a result of the partial N-deacetylation, a distinct skin-core structure can be observed. Probably a chitosan ring is formed around the chitin core. The next microphotographs (Figures 12 - 14) illustrate the adsorption of Rhodamine B by sample N H4 at 20 °C, 50 °C and 70 °C. The formed morphological structure of the fibres after partial N-deacetylation is so stable, that no defects caused by swelling or dye-absorption irregularities are visible. Nor the discolouration of the fibres is revealed in the microscope observations.

Figure 15 presents the microphotographs of the longitudinal views of sample N H7 (chitosan fibres from the regenerated chitin subjected to N-deacetylation in a saturated KOH solution for 240 min). The fibres not affected by Rhodamine B are characterized by a moderate fluorescence in comparison with the other samples. Irregularly distributed light-coloured spots indicate that the fibre surface is wrinkled.

Figures 16 - 18 show the effect of "dyeing" the fibres at the growing temperatures. At 20 °C the dye distribution on the fibre surface is uneven with stronger local colouring. At 50 °C, the dye is distributed more evenly but the colour saturation is weaker. At 70 °C, the fibres swell strongly and the dye is almost completely extracted from them by the immersion oil.

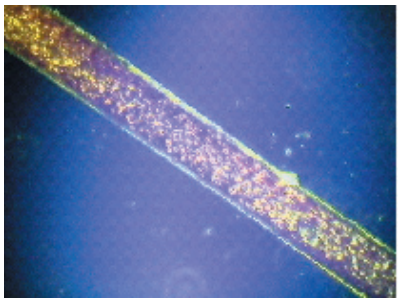

Figure 7. *Microphotograph of the surface of regenerated chitin fibres containing Rhodamine B introduced at 20 °C, magnification 180×.*

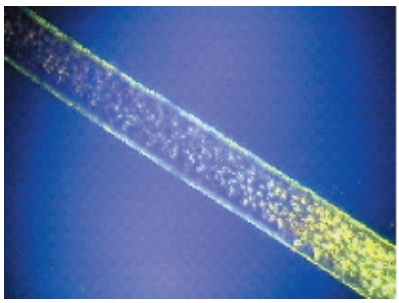

Figure 8. *Microphotograph of the surface of regenerated chitin fibres containing Rhodamine B introduced at 50 °C, magnification 180×.*

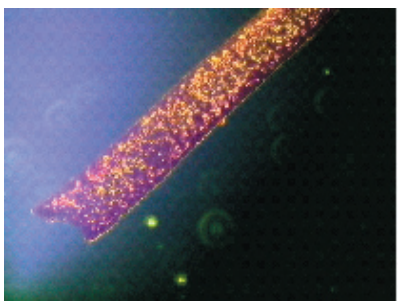

Figure 9. *Microphotograph of the surface of regenerated chitin fibres containing Rhodamine B introduced at 70 °C, magnification 180×.*

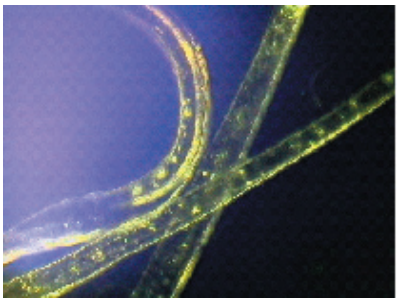

Figure 10. *Microphotograph of the surface of chitosan fibres (DD=84), magnification 180×.*

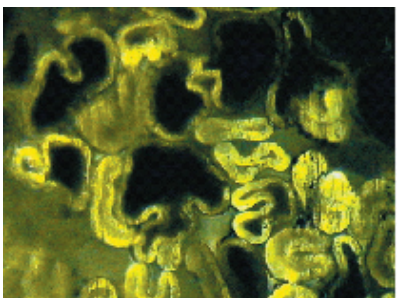

Figure 11. *Microphotograph of the cross-section of chitosan fibres (DD=84), magnification 320×.*

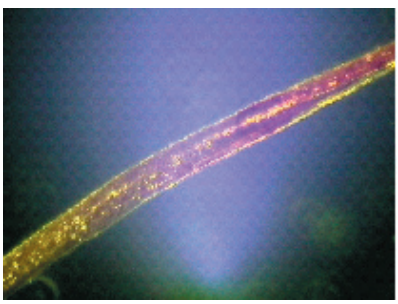

Figure 12. *Microphotograph of the surface of chitosan fibres (DD=84), containing Rhodamine B introduced at 20 °C, magnification 180×.*

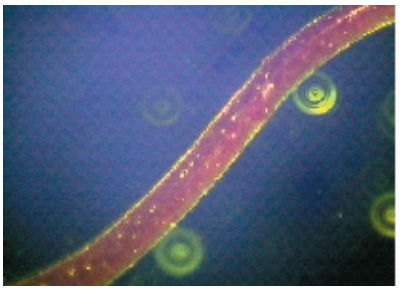

Figure 13. *Microphotograph of the surface of chitosan fibres (DD=84), containing Rhodamine B introduced at 50 °C, magnification 180×.*

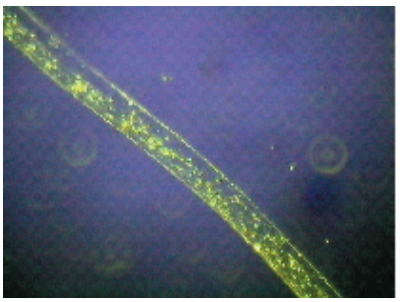

Figure 14. *Microphotograph of the surface of chitosan fibres (DD=84), containing Rhodamine B introduced at 70 °C, magnification 180×.*

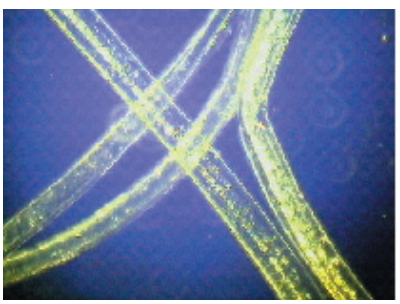

Figure 15. *Microphotograph of the surface of chitosan fibres (DD=93), magnification 180×.*

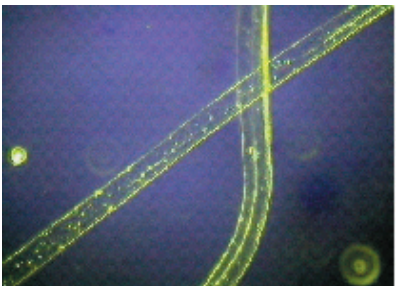

Figure 16. *Microphotograph of the surface of chitosan fibres (DD=93), containing Rhodamine B introduced at 20 °C, magnification 180×.*

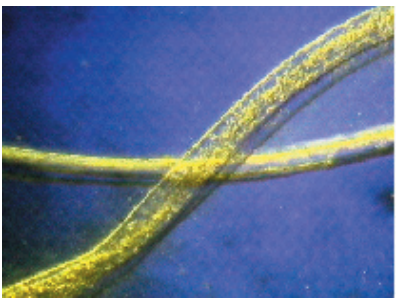

Figure 17. *Microphotograph of the surface of chitosan fibres (DD=93), containing Rhodamine B introduced at 50 °C, magnification 180×.*

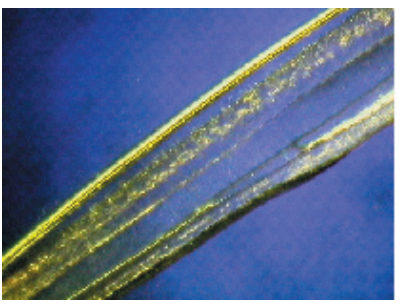

Figure 18. *Microphotograph of the surface of chitosan fibres (DD=93), containing Rhodamine B introduced at 70 °C, magnification 180×.*

4. Conclusions

1. Fluorescent microscopy creates extra possibilities to examine morphology of fibres.
2. Application of Rhodamine B with no affinity to the fibres under examination enabled the observation of the micro-slits penetrated by small dye molecules.
3. Fluorescent microscopy pictures revealed a specific skin-core structure of DBCH fibres, preserved in the whole course of the alkaline treatment.

5. References

1. **Biniaś D.:** Badania zmian struktury włókien z dibutyrylochityny spowodowanych jej chemiczną modyfikacją, Praca doktorska, 2004.
2. **Biniaś W., Włochowicz A., Biniaś D., Boryniec S.**: Sposób wytwarzania włókien dibutyrylochitynowych Patent application nr P 359883, 2003.