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Enzymatic Treatment of Fibres from Regenerated Cellulose

Abstract
The use of cellulolytic enzymes to modify fibres and fabrics made of regenerated cellulose is a new trend in enzyme application. Enzyme treatment improves the properties of fibres and fabrics without significantly worsening their tensile characteristics. The changes to some physical-mechanical parameters which take place in the course of enzymatic modification may improve some utility properties as well as the wearing comfort of fabrics made of enzyme treated cellulosic fibres. This emphasises that enzymatic processes are effective, require mild conditions and are safe for the environment.

Key words: *regenerated cellulose, fibres, cellulases.*

Introduction

Biotechnology currently plays a major role in industry, for example in the chemical, pharmaceutical and food sectors, as well as in environmental protection. Although industrial applications of biotechnology have been developing veryrapidly, new possibilities for its expansion may still emerge. For instance, there are many processes in the textile industry where biotechnological approach can successfully be employed.

Modern biotechnology often utilises genetically modified micro-organisms which are characterised by enhanced productivity of specific metabolites, enzymes among them. The range of novel applications of cellulolytic enzymes includes the modification of fibres and fabrics from regenerated cellulose (Figure 1), in order to improve their utility properties and wearing comfort, as well as to maintain their mechanical parameters.

In the enzymatic modification of fibres and fabrics, the quantitative and qualitative composition of cellulolytic complex, and so the type of micro-organism being produced, plays the key role. This kind of complex, which is a tailored mixture of specific enzymes, may serve as the ideal solution for creating effective, economical and technologically simple methods for modifying cellulosic fibres.

Enzymes have been used for over fifty years to remove starch-based sizes in the textile industry. During the last decade, cellulolytic enzymes have replaced the traditional stone-washing of denim garments and found applications in finishing fabrics and clothing from cotton, linen and regenerated cellulose [1]. In the modern textile industry, finishing processes which are based on biodegradable and environment-friendly enzymes can fully substitute for a wide range of chemical and mechanical operations so far used to improve the quality of textile products, and save on the energy and consumption of chemicals [2, 3].

There are several benefits resulting from the enzymatic finishing of cellulosic woven and knitted fabrics:

- smoother surface,
- more attractive appearance,
- better pilling resistance,
- gentle and soft feel,
- improved drapeability, and
- the use of environment-friendly technology.

Many studies recently carried out are focused on improving the properties of textiles by cellulase treatment. New, more specialized enzymes intended for finishing textiles from cotton, linen, viscose or Lyocell (as well as their blends with synthetic fibres) are being developed. In the biofinishing process, impurities and protruding loose fibres are removed from the surface of the fabric, while maintaining its mechanical properties at a reasonable level [4, 5].

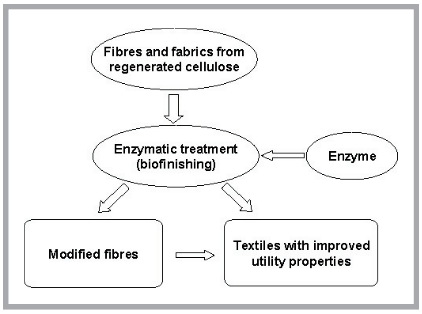

***Figure 1**. Scheme of the enzymatic treatment of fibres and textiles.*

Materials and methods

We used the commercial cellulolytic complex Econase CE (AB Enzymes), prepared from the Trichoderma reesei strain, and which is characterised by the following specific activities:

- endo-1,4-β-glucanase 2330 U/cm^3
- filter paper (FPA) 137 U/cm^3
- β-glucosidase 22 U/cm^3

and by reducing the sugar content of 20.5 mg/cm^3. It was used to treat the following cellulosic fibres:

- Celsol (IWCh, Łódź, Poland) 2.05 dtex
- AW (IWCh, Łódź, Poland) 1.70 dtex
- Viscose (ZWCh Wiskord, Szczecin Poland) 4.80 detx

Celsol and AW fibres were manufactured by a pilot scale technology line at the Institute of Chemical Fibres (IWCh), Łódź, Poland according to technologies elaborated by IWCh [6-9]. Celsol fibres were made from enzyme treated cellulose pulp, whereas AW fibres were made from hydrothermically modified cellulose pulp. Commercial viscose fibres manufactured by the ZWCh Wiskord enterprise, Szczecin, Poland.

Manufacture of cellulosic fibres

The cellulosic fibres were formed by the wet spinning technique on a laboratory spinning line. The alkaline cellulose solution was forced through a Pt-Rh spinneret with 1000 60-μm holes into a spinning bath containing 120-150 g/dm^3 of sulphuric acid and 150 g/dm^3 of sodium sulphate. The temperature of the spinning bath was 15 °C. the freshly-formed cellulosic fibres were stretched in hot water (85 °C), rinsed with water at 40 °C, passed through a spin finish bath containing 7 g/dm^3 of Berol Fintex, dried on heated rotating drums at a temperature of 85-90 °C, and finally wound onto the spools with a take-up speed of 20-50 m/min.

Enzymatic treatment of cellulosic fibres

Cellulosic fibres devoid of the spin finish agents and wound onto perforated spools were subjected to enzyme treatment in the Econase CE solution (endo-1,4-β-glucanase activity 0.9 U/cm^3) in an 0.05M acetate buffer at pH 4.8. The temperature of the process was 50 °C and the duration was 15 minutes. After the enzyme treatment, the fibres were thoroughly washed with hot distilled water (90-95 °C), and subsequently with cold distilled water; they were then dried on the spools at 25 ±2 °C.

Analytical methods

The specific activities of the enzymatic complex were estimated colorimetrically with DNS [6], based on the amount of reducing sugars liberated [7] in the reaction with the following substrates: carboxymethylcellulose (CMC) for endo-1,4-β-glucanase, salicin for β-glucosidase, and some Whatman filter paper No.1 for FPA.

The average degree of polymerisation ($\overline{DP}v$) of the fibres was estimated by the viscometric method ($\overline{DP}v$) in an alkali sodium-ferric-tartrate solution (EWNN) [12] (the results presented in Table 1), and by GPC method ($\overline{DP}w$) (the results presented in Table 2). The water retention value (WRV) was determined gravimetrically [13]. The α-cellulose content was estimated according to the method

***Table. 1.** Some properties of cellulosic fibres' material before and after enzymatic treatment by cellulase Econase CE.*

Type of fibre		Fibre material properties			
		α-cellulose content	DP_v	WRV	Weight loss
		%		%	%
Celsol	untreated	85.9	342	111.1	-
	modified	92.0	328	112.0	2.0
AW	untreated	84.3	325	101.8	-
	modified	91.6	319	113.0	1.2
Viscose	untreated	96.3	300	85.0	-
	modified	89.6	292	86.5	0.2

***Table 2.** Molecular parameters of cellulose in Celsol and AW fibres before and after enzymatic treatment by cellulase Econase CE.*

Type of fibre		Molecular parameters						
		Mn	Mw	Mw/Mn	DPv	Percentage of DP fraction		
						200>DP	200<DP>550	DP>550
		kD	kD	−	−	%	%	%
Celsol	untreated	16.9	36.5	2.2	225	60	33	7
	modified	15.5	35.3	2.3	220	62	31	7
AW	untreated	16.3	35.9	2.2	221	60	33	7
	modified	14.3	33.7	2.3	208	63	31	6

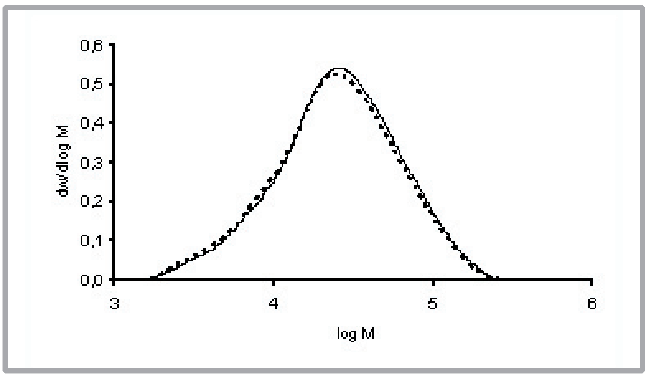

***Figure 2.** Molecular weight distribution curves of cellulose in Celsol fibres. Solid line – untreated fibres, dotted line – fibres modified by cellulase Econase CE.*

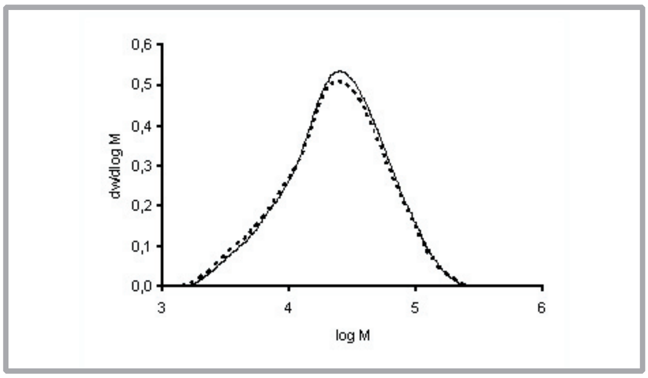

***Figure 3.** Molecular weight distribution curves of cellulose in AW fibres. Solid line – untreated fibres, dotted line – fibres modified by cellulase Econase CE.*

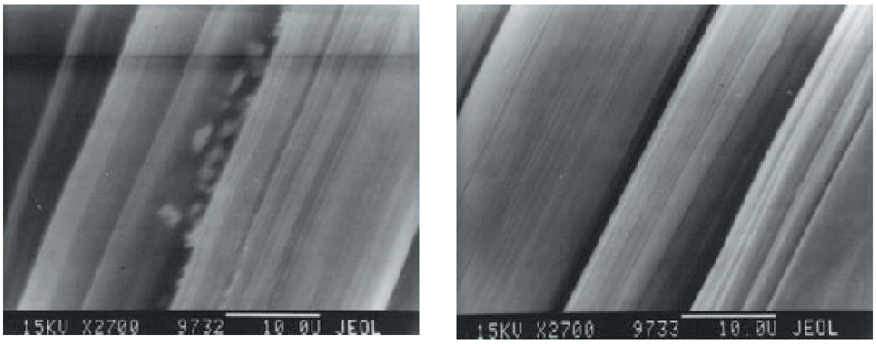

Figure 4. *SEM photographs of Celsol fibres; a) – untreated, b) – modified by cellulase Econase CE.*

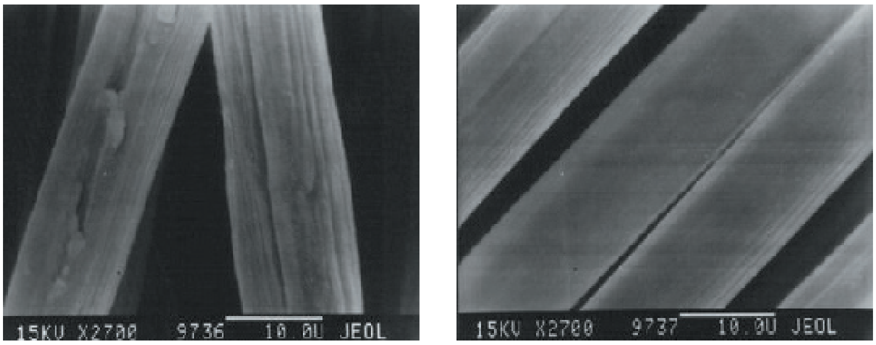

Figure 5. *SEM photographs of AW fibres; a) – untreated, b) – modified by cellulase Econase CE.*

described in standard [14]. Molecular weight distribution was determined by the GPC method [15] using the Hewlett-Packard system. The fibres' mechanical properties were estimated according to appropriate standards [16-21] the longitudinal rigidity and contact angle were determined by methods described elsewhere [22]. The appearance of fibres before and after enzymatic treatment was examined using a JEOL JSM-35C scanning electron microscope.

Results

The studies of the enzymatic treatment process included the influence of the enzymatic treatment on the physical-chemical, molecular and utility characteristics of selected cellulosic fibres.

Some physical-chemical properties of cellulosic fibres before and after enzymatic treatment are presented in Table 1.

In all the types of fibres tested (Table 1), weight loss did not exceed 2.0%. There was some decrease in the average polymerisation degree ($\overline{DP}_v$), an increase in α-cellulose content and also a slight increase in water retention value (WRV) observed for the cellulosic fibres after the enzymatic treatment.

In order to investigate the influence of enzymatic modification on the molecular structure of selected cellulosic fibres, the molecular parameters ($\overline{M}n$, $\overline{M}w$, $\overline{DP}v$, percentage of DP fractions) as well as the molecular weight distribution curves were determined by the gel permeation chromatography (GPC) method. Changes in the fibres' surface appearance before and after enzymatic treatment were investigated by scanning electron microscopy (SEM). The obtained results are presented in Table 2 and in Figures 2-5.

On the basis of the results obtained (Table 2, Figures 2, 3), it was found out that after 15 minutes of enzyme treatment, there was only a slight decrease in the average molecular weight of the material of the tested fibres. There were also no distinct changes in the DP fraction percentages. On these grounds, it can be concluded that the enzymatic treatment process does not affect the molecular structure of the cellulosic AW and Celsol fibres. From SEM photographs (Figures 4, 5) it can be seen that the untreated fibres have rough surfaces with some cellulose debris on them. The enzyme-treated fibres are characterised by smooth, even surfaces and a lack of any impurities.

Investigations were also conducted to assess the influence of enzymatic modification on some physical-mechanical properties of cellulosic fibres. The results obtained are presented in Table 3.

Table 3. *Some physical-mechanical properties of cellulosic fibres before and after enzymatic treatment by cellulase Econase CE.*

Type of fibre		Tenacity	Elongation at break	Loop tenacity	Initial modulus	Elasticity degree at 5% elongation	Fibre-fibre friction coefficient	Longitudinal rigidity
		cN/tex	%	cN/tex	cN/tex	%	-	cN
Celsol	untreated	18.4	9.3	1.7	690	70.5	0.620	282
	modified	16.6	7.5	1.6	652	73.0	0.525	256
AW	untreated	17.7	27.0	2.4	722	65.0	0.416	116
	modified	17.8	23.0	1.8	636	65.0	0.592	102
Viscose	untreated	18.1	11.0	7.0	643	74.0	0.628	290
	modified	16.0	11.0	6.3	588	81.0	0.510	267

The results obtained (Table 3) show minor decreases in tenacity, loop tenacity and elongation at break of the enzyme-treated cellulosic fibres compared to the untreated ones. It can also be concluded that during the enzymatic treatment process, the following changes take place in some physical-mechanical parameters of the tested fibres:
- an increase in elasticity degree at 5% elongation (viscose, Celsol);
- a decrease in initial modulus (viscose, Celsol, AW);
- a decrease in fibre-fibre friction coefficient (viscose, Celsol);
- a decrease in longitudinal rigidity (viscose, Celsol, AW).

The above parameters may influence the improvement of some of the utility properties and wearing comfort of the fabrics made from enzyme-treated cellulosic fibres. For instance:
- Fabrics made from fibres with low initial modulus, increased elasticity and decreased longitudinal rigidity are characterised by good drapeability and ability to recover their original shape when the load applied is released.

- Fabrics made from fibres with a decreased friction coefficient may be have better elastic recovery, wrinkle resistance and a soft, 'silky' feel.

Conclusions

The enzymatic treatment does not affect the molecular structure of cellulosic AW and Celsol fibres. The tensile properties of the modified fibres generally remain at acceptable levels. The changes to some physical-mechanical parameters which take place during the enzymatic modification of selected cellulosic fibres may improve the utility and comfort properties of fabrics such as pilling and wrinkle resistance, wettability, dyeability, drapeability and soft feel. Further studies seem to be necessary in order to examine if the changes of modified fibres' parameters have any effect on the improvement of utility properties of fabrics made from those fibres.

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