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The Influence of Low-temperature Plasma and Enzymatic Treatment on Hemp Fabric Dyeability

Abstract

In order to study the influence of low-temperature air plasma and enzymatic treatment on the dyeing properties of hemp, "cold dyeing" of hemp fabric with acid dye (C.I. acid blue 113) and direct dye (C.I. direct red 81) was performed. In addition to the determination of dyeing kinetics, colour yield and colour fastness, assessment of weight loss, water retention and whiteness degree, as well as SEM analysis of differently treated samples was carried out. Low-temperature plasma treatment of hemp fabric caused an increase in the dyeing rate, final dye exhaustion and colour yield of dyed samples. The positive effect of plasma treatment was explained by plasma etching and oxidation effect on the hemp fibre surface. Enzymatic treatment led to a decrease in the dyeing rate in the case of C.I. acid blue 113 and slight increase in the case of C.I. direct red 81, whereas the final exhaustion of both dyes decreased. This behaviour has been attributed to a more pronounced digestion of amorphous fibre areas. All samples showed similar and low colour fastness values, which were considered as satisfactory, taking into account that the cold dyeing procedure was carried out.

Key words: *hemp, low-temperature plasma, enzyme, dyeing.*

■ Introduction

Actual fashion trends make hemp and flax fibres particularly attractive as they meet the high comfort and aesthetic standards of the modern consumer. The increasingly popular "casual style" neglects the easy creasing of hemp fabrics, which has always been implied as their main disadvantage in use. In addition, hemp fibres, like flax, have high crystallinity, causing unacceptable bending rigidity and processing difficulties [1]. However, high comfort and excellent hygienic properties have encouraged the textile industry to broaden the application of hemp fibres from traditional manufacturing (ropes, nets, carpets, cordage, etc.) to garment production.

Proper modification of hemp overcomes most of the shortcomings without deterioration of the positive fibre properties. The right choice of treatment should be governed by efficiency, economical and environmental aspects of the process applied. Thus, from an ecological point of view, low-temperature plasma treatment could be a promising option, which is already established as very efficient in the finishing of wool, cotton and synthetic fibres [2 - 5]. In the case of cellulosic fibres, most of the research has been focused on cotton and flax fibres [1 - 2]. Plasma treatment of cotton improves its mechanical properties and wettability due to changes in chemical composition and fibre surface morphology [6 - 9]. The observed increase in water retention and wetting rate of flax

is attributed to better susceptibility of fibre to water molecules as a result of plasma etching and plasma oxidation i.e. the formation of new carboxyl groups [1]. In general, plasma treatment of cellulosic fibres leads to a generation of a huge amount of free radicals on the fibre surface, making them more reactive [1, 2]. The wettability changes caused by plasma treatment induce positive effect on the dyeing of cotton and flax [1 - 9].

Though enzymes are successfully used for the finishing of various textile fibres, [10 - 12] their extensive application to cotton for imparting peculiar handle and appearance is the most dominant [13, 14]. The enzymatic hydrolysis of cellulosic materials is based on cellulase catalytic action by cleaving the β-1,4-glucoside bond of the cellulose molecule [15]. Enzymatic treatment must be strictly controlled in order to avoid unacceptable weight loss and reduction of strength. However, operating under mild conditions, bio-softening activity and positive effect on the dyeing rate of cotton [16] make enzymatic treatment particularly intriguing for research on other cellulosic fibres.

The current fashion trend dictates that the garment should maintain the natural colour and aesthetic properties of hemp. However, the expansion of hemp garment production opens some new perspectives and further requirements for dyed hemp and its mixtures with cotton and flax can be predicted. Therefore, adequate treatment of hemp prior to

dyeing must be provided. Keeping in mind the similarities in structure and chemical composition between hemp and flax fibres, it should be expected that the dyeing properties of hemp would be analogue to results obtained when dyeing flax [1]. Since there are only few papers dealing with low-temperature plasma (LTP) or enzymatic (ENZ) treatment of hemp [17 - 20], the aim of this study was to extend knowledge of the influence of these treatments on the dyeing properties of hemp fabric.

■ Experimental

Materials and chemicals

A scoured and bleached 100% hemp fabric, "honeycomb" weave, with fabric weight per unit area of 298 g/m^2 was used as a substrate. For dyeing studies, C.I. acid blue 113 and C.I. direct red 81 were used. The characteristics of dyes are presented in Table 1.

Both dyes are disulfonated. AB113 is milling acid dye, which is not commonly used for the dyeing of cellulosic fibres. However, since it has a structure similar to direct dyes, it was suitable for comparative study on the dyeing of hemp. Direct dye DR81 is typically representative of direct dyes for the dyeing of cellulosic fibres with high substantivity and relatively high rate of diffusion.

Treatments

Glow-discharge treatment of hemp fabric was carried out in a low-pressure capaci-

Table 1. *The characteristics of the dyes used.*

Dye	Manufacturer	r.m.m.	λ$_{max}$	Molecular structure
AB113 (C.I. Acid Blue 113)	Ciba, Switzerland	681.0	595	
DR81 (C.I. Direct Red 81)	Clariant, Switzerland	675.0	509.5	

Table 2. *Weight loss, water retention and CIE whiteness index.*

Sample	WL, %	WR, %	CIE whiteness Index
Untreated		68.3	17.4
LTP (2.5 min)	0.283	69.3	12.8
LTP (5 min)	0.368	74.2	11.4
LTP (10 min)	0.532	70.2	12.7
ENZ (1 %)	3.440	77.7	14.6
ENZ (3 %)	4.000	78.0	15.6
ENZ (5 %)	3.910	79.4	15.6
LTP (10 min)+ENZ (5 %)	3.680	75.0	16.9

tively-coupled RF-induced (13.56 MHz) air plasma. Treatment time was 2.5, 5 and 10 min, pressure 0.27 mbar with a power supply maintained at a constant level of 100 W. The equipment used for the plasma treatment consisted of a chamber, RF power supply, matching box, vacuum pump and gas supply with appropriate pressure gauges. The chamber was cylindrical (37 cm in diameter, 50 cm in length) with central electrode 14 mm in diameter that was powered through a matching box. Plasma was formed between the central electrode and the wall of the chamber, which was grounded. Such a asymmetric system was intentionally constructed in order to provide operating conditions under which the sheath potential was not too high, but sufficient for optimum modification of hemp fabric without diminishing positive fibre properties, thus avoiding permanent damage to the hemp [21].

Enzymatic treatment of hemp fabrics was carried out in a Polycolor (Werner Mathis AG, Switzerland) laboratory beaker dyer at 45 r.p.m. Fabric samples were treated in a bath containing 1, 3 and 5% (o.w.f.) of enzyme cellulase (Cellusoft, Color-Center, S.A., Spain) at liquor-to-hemp ratio of 20:1. A stock solution of enzyme (10 g/l) was prepared by dissolving the enzyme in a sodium acetate buffer solution (pH 4.65) at room temperature. Hemp fabric samples were immersed in the buffer solution (pH 4.65) for 5 min, then an appropriate amount of the enzyme stock

solution was added, the temperature was raised to 50 °C within 10 min and the samples treated for 1 h. Finally, the temperature rose to 80 °C during 10 min providing the deactivation of enzyme. Subsequently, samples were rinsed in water and dried at room temperature.

Methods

Weight loss (WL, %) determination was based on measuring the weight of samples (dried for 24 h at 110 °C) before (m_0) and after (m_1) plasma and/or enzyme treatment ($WL = (m_1 - m_0)/m_0 \times 100\%$).

To evaluate water retention (WR, %), samples were immersed for 24 h in distilled water, then centrifuged for 15 min and the weight of wet samples measured. Afterwards, the samples were dried for 24 h at 110 °C and water retention was calculated from the weight of wet (m_w) and dry (m_d) samples ($WR = (m_w - m_d)/m_w \times 100\%$).

SEM analysis of hemp fibres was carried out using the Leica S 360 scanning electron microscope (LEO, Germany).

For more precise differentiation between plasma and/or enzyme treatment effects, "cold dyeing" at 60 °C was intentionally chosen. Fabrics were dyed in a bath containing 0.5% (o.w.f.) dye and 5% (o.w.f.) Na_2SO_4 at liquor-to-hemp ratio of 100:1 for 120 min. Isothermal dyeing of fabrics was carried out in a laboratory dyeing machine - Dyemaster (John Jeffreys Ltd.,

UK) with vertical motion of 30 r.p.m. After dyeing, the samples were rinsed, squeezed and dried at room temperature. Dye exhaustion was determined from the absorbance of dye solutions measured at the beginning and after 5, 10, 15, 20, 30, 45, 60, 90 and 120 min of dyeing. The absorbance at λ$_{max}$ was measured by a 160A UV/VIS spectrophotometer (Shimadzu, Japan).

Kubelka–Munk values (K/S), selected as the indirect parameters of colour yield of dyed samples, were measured on a Datacolor SF300 (Germany). The same instrument was used for evaluation of colour fastness (shade change, ΔE and Grey scale grade) of dyed samples after washing (50:1, 2 g/L NaDBS, 1 g/L Na_2CO_3) at 60°C for 30 min, and determination of CIE whiteness index (CIE D65).

■ Results and discussion

LTP treatment of hemp resulted in weight loss of fabric likely due to severe interaction between different high-energy plasma particles and fibre surface (i.e. plasma etching) [1, 22]. Although the values of weight loss (Table 2) are low, it is obvious that prolongation of treatment time caused a slight increase in weight loss. ENZ treatment resulted in a remarkably higher weight loss of fabric, which was more prominent at higher enzyme concentrations. LTP treatment (10 min) prior to enzyme (5%) application induced weight loss comparable to that of the ENZ treated sample for the same enzyme concentration.

The increase in water retention of LTP treated fabrics (Table 2) can be attributed to plasma etching of the fibre surface. An even higher increase in water retention was evident in the case of ENZ treated samples, which could be attributed to the removal of non-cellulosic hydrophobic components from the fibre surface [1]. LTP+ENZ treated fabric showed the water retention value which lies between the values of LTP and ENZ treated samples.

SEM images of untreated, LTP treated, ENZ treated and LTP+ENZ treated fibres are presented in figure 1. No significant difference in fibre topography between untreated and LTP treated sample (10 min) is noticed. This could be expected since SEM analysis seems to be a powerful tool for surface morphology assessment of LTP treated bast fibres only after longer exposure times. This

is in accordance with literature data as the formation of pits and holes, that can reach microscopic dimensions after oxygen or argon plasma treatments of flax, became noticeable by SEM or ESEM only after longer treatment times [23]. The existence of pits and cracks likely causes the macroscopic porosity changes in hemp fibre and increase in specific surface area, making the hemp more accessible to water molecules i.e. enhancing the water retention of the fibre. SEM analysis revealed that the surface of ENZ treated fibres became smoother.

The oxidation of fibre surface induced by plasma is probably responsible for the yellowing of hemp fabric, though the exact reason for the reduction of whiteness is not known yet [1]. The values of CIE whiteness are shown in Table 2. ENZ treatment caused a slight decrease in CIE whiteness as compared to LTP treated samples. However, the application of enzymes after LTP treatment led to an increase in fabric whiteness approaching the level of the untreated sample. Such effect was also present in the case of flax [1].

Dye-exhaustion curves of untreated, LTP treated, ENZ treated and LTP+ENZ treated samples are shown in Figure 2 (AB113) and Figure 3 (DR81). LTP treatment induced a remarkable increase in the dyeing rate and final dye exhaustion. The longer the LTP treatment time, the higher the final exhaustion was. Dyeing with DR81 is considerably slower as compared to AB113. However, prolongation of LTP treatment time in the case of DR81 showed no significant influence on dye exhaustion and obviously dye-exhaustion curves overlapped.

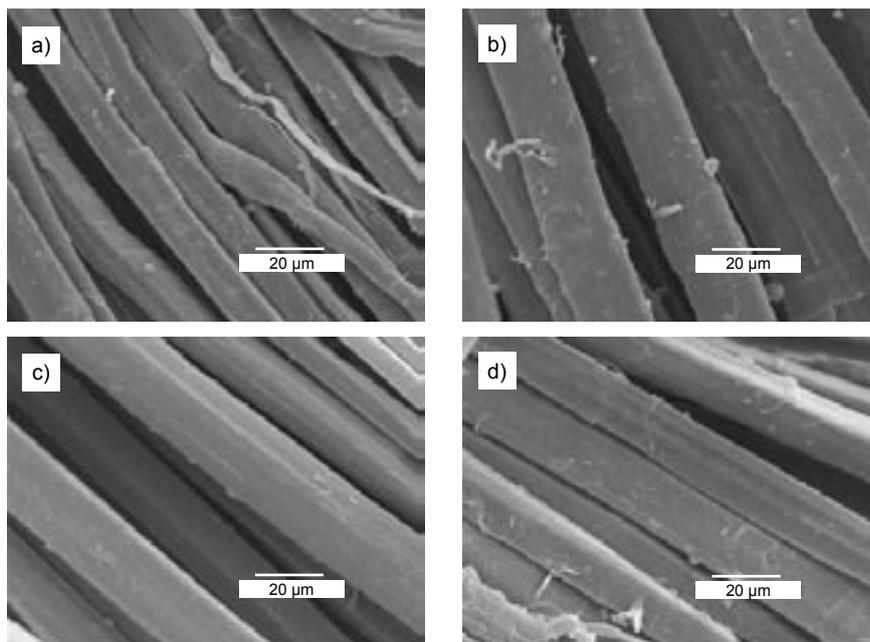Enhanced dye exhaustion and higher dyeing rates of LTP treated samples

Figure 1. *SEM images of: a) untreated; b) LTP treated; c) ENZ treated and d) LTP+ENZ treated hemp fibers.*

are attributed to plasma etching and oxidation [1]. It is likely that etching increased fibre porosity and induced minor topographical changes that make hemp fibre more susceptible to dye and water molecules. Easier diffusion of dye into the fibre caused by LTP treatment is not sufficient for an increase in dye exhaustion as it is also considerably influenced by the structure, molecular weight and state of the dye in a dyeing bath. Therefore, DR81 as a dye with high substantivity and rate of diffusion is easily bound to the active sites of the fibre and consequently it is poorly affected by prolongation of LTP treatment time. On the contrary, acid dye exhibits low substantivity and dyeing is mainly controlled by diffusion which is remarkably promoted by LTP treatment.

ENZ treatment induced a significant decrease in the dyeing rate and final exhaustion of AB113. The initial dyeing rate of DR81 in the case of ENZ treated hemp was of the same order as the LTP treated sample. After 45 min of dyeing, ENZ treated samples exhibited reduced dyeing rates as compared to LTP treated samples, though they were still higher when compared to untreated hemp. However, final exhaustion of the ENZ treated sample was slightly lower in comparison with an untreated sample. The decrease in final exhaustion of both the investigated dyes is suggested to be due to the enzymatic hydrolysis of hemp and digestion of amorphous regions that are responsible for fibre dyeability [1]

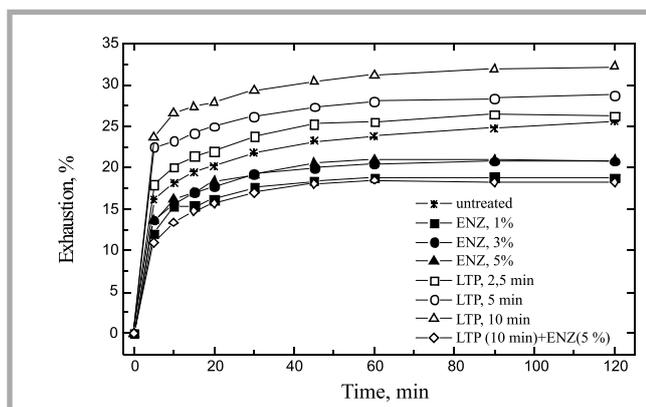LTP+ENZ treated hemp showed a similar dyeing pattern to that of the ENZ treated

Figure 2. *Dye-exhaustion curves of untreated, LTP and/or ENZ treated hemp fabrics (C.I. acid blue 113).*
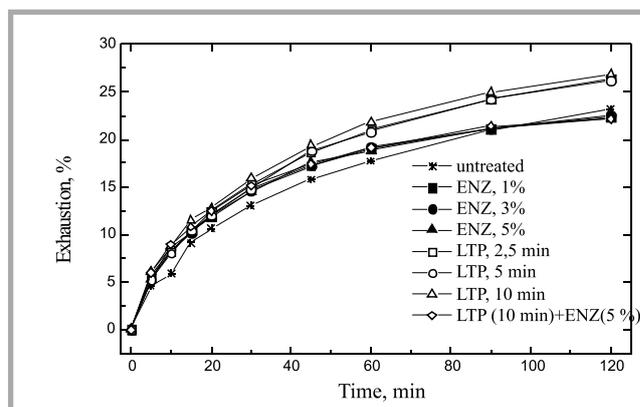

Figure 3. *Dye-exhaustion curves of untreated, LTP and/or ENZ treated hemp fabrics (C.I. direct red 81).*

Table 3. *Kubelka-Munk values (K/S) of dyed samples.*

Sample	K/S	
	Direct Red 81	Acid Blue 113
Untreated	3.56	2.90
LTP (2.5 min)	3.74	3.27
LTP (5 min)	3.90	3.18
LTP (10 min)	3.90	3.19
ENZ (1 %)	3.28	2.36
ENZ (3 %)	3.37	2.71
ENZ (5 %)	3.29	3.73
LTP (10 min) + ENZ (5 %)	3.36	2.66

samples, though the dyeing rate and final exhaustion of both dyes were much lower compared to all other investigated samples. Such behavior can be attributed to plasma action prior to ENZ treatment. The appearance of cracks and holes makes the fibre surface more accessible to enzymes, promoting easier digestion of amorphous regions [1].

The changes in hemp dyeability after LTP, ENZ and LTP+ENZ treatments are also illustrated with K/S values presented in Table 3. The K/S value presents an indirect parameter of the colour yield of the dyed sample and it is correlated to the dye concentration on hemp fibre. K/S values are in good correlation with results corresponding to dyeing curves.

The colour fastness of dyed samples is presented in Table 4. Obviously, there is no significant difference in Grey scale grade between untreated and LTP treated samples. However, since the cold dyeing procedure was carried out and a specific type of dye was used, the results of colour fastness, particularly for DR81, could be considered as satisfactory. Better colour fastness of samples dyed with DR81 is likely due to higher substantivity.

Table 4. *Color fastness of dyed samples; *1: great change, 2: considerable change, 3: noticeable change, 4: slight change, 5: no change.*

Sample	Colour fastness			
	Direct Red 81		Acid Blue 113	
	ΔE	Grey scale grade*	ΔE	Grey scale grade*
Untreated	4.35	2-3	16.1	1
LTP (2.5 min)	3.93	3	17.4	1
LTP (5 min)	4.22	2-3	17.1	1
LTP (10 min)	4.89	2-3	16.3	1
ENZ (1 %)	3.35	3	15.1	1
ENZ (3 %)	3.07	3	14.5	1
ENZ (5 %)	4.21	2-3	14.6	1
LTP (10 min) + ENZ (5 %)	4.09	3	17.5	1

Conclusion

- Low-temperature plasma treatment has a positive effect on hemp dyeability since the dyeing rate and final exhaustion of both the investigated dyes (C.I. acid blue 113 and C.I. direct red 81) significantly increased compared to untreated hemp.
- Enzymatic treatment leads to a decrease in the dyeing rate in the case of C.I. acid blue 113 and a slight increase in the case of C.I. direct red 81, whereas the final exhaustion of both dyes decreased.
- Low-temperature plasma+enzyme treated samples showed a further decrease in final exhaustion and reduction of dyeing rate compared to all other investigated samples. This could be attributed to more a pronounced digestion of the amorphous areas of the fibre that became considerably more accessible to enzymes after plasma etching.
- Although all investigated samples show rather low colour fastness, we consider it as satisfactory, bearing in mind that the cold dyeing procedure was carried out.

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