

ENZYMATIC ENHANCED ADHESION OF CELLULOSIC WOVEN FABRICS COMPOSITES

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Abstract: The purpose of this work was to produce and characterize enzymatically treated fabric composites using different mixtures of two commercial cellulase enzyme solutions in dosages of 0.1% and 0.5% in order to improve the fabric's adhesion. Three cellulosic taffeta plain weave fabrics of 100% flax, cotton and bamboo viscose were used in different combinations. The properties of the woven fabrics and produced composites were characterized using several mechanical tests. The cotton & viscose composite appears to be the best materials combination, exhibiting improved breaking force (0.5% of Xylanase PLUS™) and percentage of elongation at maximum force (0.1% of Xylanase PLUS™), as well as better results on the peel adhesion test (0.5% of AlternaFuel® MAX™). The flax & cotton combination did not show any improvement for all the tested properties. Flax & viscose combination, despite not having shown peel strength improvement, exhibits remarkable elongation and breaking force (0.5% of Xylanase PLUS™). Since there is no posterior emission of volatile products, one can expect a great public acceptance. However, higher enzymatic concentrations should be studied to clarify the contribution of this parameter to the surface modification and adhesion promotion.

Key Words: biotechnology, enzymes, surface modification, pressure adherence, woven cellulosic composites

1 INTRODUCTION

Biotechnology applied to the textile processes has been an increasing tendency during the last years. Textile composites produced via enzymatic modification of the material's surface is a recent and increasing investigation field and might be the complement or the alternative to the conventional process by applying polymeric matrices. However, there are few studies about composite fabrics produced with reinforced structures from natural fibres and biodegradable matrices using enzymes [1]. Composites can be defined as multiphase materials with enhanced characteristics due to the geometric conception to maximize inherent properties of the individual components [2]. Polymer composites can be produced from a polymer matrix, by thermoset or thermoplastic or by the use of different types of binding, adjoined to the matrix in the form of fibres, yarn, mats, fabrics, foams, honeycombs, etc. [3]. The binding of the composites on synthetic materials can be done by joining polymer layers followed by consolidation of their interfaces due to pressure and heat fusion [4]. The most recurrent and increasingly important composites for structural applications consist of a polymer matrix reinforced with fibres, where a combination of high strength, relatively low weight and durability are required [5]. The consumption of composites with natural-based matrices is a small fraction of the total composites

market [3]. However, there is an increasing interest in research and development of cellulosic materials combined with man-made fibres, in which adherence is made by crosslinking polymers or selective melting of fibres and where the interaction for adherence is enhanced by the irregularity of natural fibres [6]. Cellulose is the main organic compound in the biosphere and constitutes the basic material of all plant fibres [7, 8]. The macromolecule structure is formed by linear condensation of D-anhydroglucopyranose units linked by β 1,4-glycosidic bonds [9]. The absence of side branches increases its crystallinity and leads to efficient intermolecular and intra-chain hydrogen bonding due to the hydroxyl groups, which results in dimensionally stable fibres [10]. The chemical composition on natural vegetable fibres depends on the plant's origin. Generally, plant composition can be divided in major components, such as cellulose, hemicellulose and lignin, and minor components, like protein and mineral substances, fatty and resinous acids, phenols, etc. [11, 12]. In the case of cellulosic materials, the matrix phase has to be prepared by modification of the surface, also using biotechnology approaches, unlike the thermoplastic polymers [6, 13]. The main advantage of biotechnology, compared with conventional technologies, consists in their specificity for a particular reaction over a specific substrate. Enzyme technology has the unique potential for the modification of surface of textile

and synthetic materials thanks to the high specificity of enzymes which allows diversified advanced functionalities [14]. Since the late 80's those enzymatic processes which are relevant for the textile industry have been intensively studied, with obvious results on the use of enzymes in the replacement of conventional chemical treatments [14, 15]. Enzymatic surface modification of textile materials comprises processing of fibres or biopolymers in order to change their physical and chemical surface properties, or the introduction of functional groups on the surface [14]. Cellulases are enzymes which are capable to cleave the glycosidic linkages in oligosaccharides and polysaccharides, including cellulose and hemicelluloses [16]. In order to optimize the enzymatic treatments of surface modification, enzyme mixtures were successfully conceived according to the desired effect on the fibres' or material's surface [17]. Cellulases are widely used for textile finishing of cellulosic materials as well as for development of new products [18]. There are several benefits in using cellulases or enzymes in general: its implementation is easy and the processes might be adjusted to the available equipment at different stages of the wet process; the application conditions are moderate in terms of pH and temperature; enzymes are organic compounds, so totally biodegradable, not contributing to environmental wastes; treatment with enzymes has economical advantages due to the lowest temperatures and reduction of the processing time [18]. Cellulosic materials are hydrolysed by the synergistic action of three general types of cellulases: Endoglucanases, which hydrolyse amorphous cellulose randomly into smaller polymers, thus creating new ends; Exoglucanases, which attack the extremities of the cellulose polymer, thereby producing cellobiose. Cellobiose is hydrolysed by β -glucosidase, yielding glucose [14]. There are also other species of cellulases with some importance: hemicellulases, which modify the structure of xylan and glucomannan in pulp fibres to improve chemical delignification, and endoarabinases, which hydrolyze the α -1,5-linkages of arabinan polysaccharides that are present as side chains of pectin [19].

This work is intended to study the production of composite using enzymatically modified woven cellulosic fabrics made up from fibres of cotton, linen and bamboo viscose. The adhesion of the fabric will be promoted using different mixtures of cellulase enzymes. The properties of the woven fabrics and produced composites were characterized using several standard mechanical tests.

2 EXPERIMENTAL

Materials

The composites were conceived by combining three taffeta weaved woven fabrics: 100% linen, 177 g/m²; 100% cotton, 156 g/m²; 100% bamboo viscose, 133 g/m². Two commercial enzymatic formulations were used. AlternaFuel® MAX™ (Dyadic International, USA) a liquid cellulase preparation produced from *Myceliophthora thermophila*, which converts lignocellulosic substrates into glucose. Dyadic Xylanase PLUS (Dyadic International, USA) a concentrated liquid acid-neutral endo-1,4- β -D-xylanase produced by *Trichoderma longibrachiatum*. All other reagents were of analytical grade purchased from Sigma-Aldrich and used without further purification.

Enzymatic treatment process

Cleavage of the glycoside bonds of the polymers' surfaces were achieved by hydrolysis with the two commercial cellulase preparations opportunely diluted in 0.1 M phosphate buffer. Fabrics of flax, cotton and viscose (3.16 g, 2.89 g, 2.41 g, respectively) with the dimensions of 30 x 6 cm were incubated in a liquor rate of 1/20 and with two cellulase enzymatic dilutions of 0.1 and 0.5%. The solutions with the immersed fabrics were processed under continuous agitation at the temperature of 50°C for 30 minutes. After the treatment, each sample was rinsed with 250 mL of distilled water, at room temperature, with slight agitation, for 10 seconds. Excess water was removed by compression of the sample wrapped on a tweezers, against beaker walls. The control test has also been made by immersion of the three samples in the buffer solution, using the same treatment conditions but without enzyme formulation. Parameters of enzyme dosage preparations are outlined in Table 1.

Table 1 Enzyme dosage [mg], sample mass [g] and volume of solution [mL] in a liquor rate of 1:20 for sample dimension of 30 x 6 cm

Materials	Solution [mL]	Sample mass [g]	Enzyme formulation			
			AlternaFuel® MAX™		Dyadic® Xylanase PLUS	
			0.10%	0.50%	0.10%	0.50%
Enzyme dosage [mg]						
Flax	127	3.16	10.1	49.9	10.2	49.6
Cotton	116	2.89	11.7	50.0	10.4	49.1
Viscose	96	2.41	10.4	10.7	51.2	51.6

Adhesion of composites

The combinations of fabrics that were made for the development of textile composites can be seen in Table 2. All sample-composites were pressed for 10 minutes after the enzyme treatment. Then, the adhesion was promoted by compression in a uniaxial hydraulic press under the load of 10 tonnes at 200°C for 60 seconds.

Table 2 Enzyme and fabrics combinations for composite production and respective codex

Composites	Enzyme formulation			
	Alternafuel® MAX™		Dyadic® Xylanase PLUS	
	0.10%	0.50%	0.10%	0.50%
Flax&Cotton	B	D	A	C
Flax&Viscose	F	H	E	G
Cotton&Viscose	J	L	I	K

Fabric characterization

The three woven fabrics were characterized by physical tests as per following standards: Determination of mass per unit area using small samples (NP EN 12127:1999); Determination of number of threads per unit length (ISO 7211-2: 1984 modified; NP EN 1049-2: 1995); Determination of crimp of yarns in fabrics (NP 4115: 1991); Determination of linear density of yarn removed from fabric (NP 4105: 1990); Determination of thickness of textiles and textiles products (NP EN ISO 5084: 1999); Standard Test Method for Breaking Force and Elongation of Textile Fabrics (Strip Method, ASTM D5035: 93); Standard Test Method for Pilling Resistance and other Related Surface Changes of Textile Fabrics (Martindale Pressure Tester Method, ASTM D 4970–89).

Composite characterization

The composites were characterized by physical tests as per following standards: Determination of thickness of textiles and textiles products (NP EN ISO 5084: 1999); Standard Test Method for

Breaking Force and Elongation of Textile Fabrics (Strip Method, ASTM D5035: 93); Standard Test Method for Peel or Stripping Strength of Adhesive Bonds (ASTM D903: 93); Standard Test Method for Pilling Resistance and other Related Surface Changes of Textile Fabrics (Martindale Pressure Tester Method, ASTM D 4970–89).

3 RESULTS AND DISCUSSION

The physical properties of a textile product are vital to its performance, determining its suitability for the intended application [20, 21]. On the original materials as well as on the final composite products, basic characterization physical tests and mechanical strength tests were made, as stated in the following tables.

Yarn characterization demonstrates that there tends to be a major dispersion of results in linen yarns when compared with viscose (Table 3). This can be understood due the fibres' different origins - due to the manufacturing process of viscose, these fibres present a greater uniformity, hence the lower value of the coefficient of variation on the ring spun yarns.

The results of the test of Determination of Peel or Stripping Strength of Adhesive Bonds in the flax & cotton composite show lower values than in the control, which can indicate that treatment conditions are not favourable for this combination (Table 4). The results of the testing of Breaking Force and Elongation of Textile Fabrics were also worse than for the control composite. Mass per unit surface was not determined due to the contamination of the composite samples by a large amount of solid particles during the pressing process. The results of the test of Determination of Peel or Stripping Strength of Adhesive Bonds on the flax & cotton composite show lower values than in the control, which can indicate that treatment conditions are not favourable for this combination. The results of the testing of Breaking Force and Elongation of Textile Fabrics were also worse than for the control composite.

Table 3 Characterization of woven fabrics

	Flax	Cotton	Viscose
Mass per unit area [g/m ²]	177.01±0.28	155.76±4.75	132.91±0.35
Number of threads (warp) [N°/cm]	19.6±0.6	17.8±0.5	48.7±2.5
Number of threads (weft) [N°/cm]	19.4±0.9	15.6±0.5	33.7±0.6
Crimp (warp) [%]	5.7±0.9	9.6±0.4	11.18±0.45
Crimp (weft) [%]	4.1±0.4	4.2±0.2	6.5±0.5
Linear density (warp) [tex]	45.1±4.6	30.9±2.2	14.6±1.2
Linear density (weft) [tex]	41.3±5.0	60.8±1.5	14.8±0.8
Thickness [mm]	0.37±0.02	0.47±0.01	0.27±0.01
Breaking Force (warp) [N]	390.6	164.1	233.3
Elongation (warp) [%]	24.05	11.17	24.05
Pilling resistance	5	4-5	4-5

Table 4 Characterization of woven composite of flax & cotton

	Control	A	B	C	D
Thickness [mm]	0.46±0.02	0.55±0.03	0.52±0.02	0.53±0.04	0.50±0.03
Breaking Force (warp) [N]	371.6	295.2	339.6	348.4	352.4
Elongation (warp) [%]	9.33	8.13	8.93	9.55	8.60
Peel Strength [N]	0.18	0.18	0.18	0.08	0.08
Pilling resistance	4	5	4	4	5

Table 5 Characterization of woven composite of flax & viscose

	Control	E	F	G	H
Thickness [mm]	0.40±0.02	0.45±0.02	0.44±0.02	0.44±0.03	0.42±0.04
Breaking Force (warp) [N]	372.8	395.6	424.0	474.0	372.4
Elongation (warp) [%]	8.48	10.27	9.60	10.33	9.20
Peel Strength [N]	1.325	0.825	1.175	0.925	1.075
Pilling resistance	4-5	5	5	5	5

Table 6 Characterization of woven composite of cotton & viscose

	Control	I	J	K	L
Thickness [mm]	0.35±0.04	0.45±0.02	0.43±0.02	0.46±0.03	0.40±0.02
Breaking Force (warp) [N]	248.0	281.6	275.6	287.2	274.4
Elongation (warp) [%]	19.93	22.65	22.35	23.25	22.33
Peel Strength [N]	0.675	1.000	1.075	1.000	1.25
Pilling resistance	5	5	5	5	5

On the flax & viscose composite it can be seen that, based on the result of Breaking Force and Elongation of Textile Fabrics (Strip Method) test, there is some improvement in the end product, where the breaking force increased up to the maximum of ≈12% (Table 5). However, on the essay of the Determination of Peel or Stripping Strength of Adhesive Bonds, the outcomes are worse than in the control composite, which can perhaps be explained by induced adherence due to the enzymes which restricts the elongation of composite material.

The cotton & viscose composite presented the best behaviour of all combinations - the Breaking Force increased by 11 to 15%, depending on base materials, and the peel adhesion was also slightly higher than composite control (Table 6). It can also be noted that the abrasion resistance was slightly improved, based on the results of the Evaluation of Pilling Resistance; nevertheless, the results in this essay were already good in the composite control. Another aspect that can be very interesting is the fact that the thickness of all composites was significantly smaller than the sum of the two individual materials, which can perhaps be explained by the absence of the usual polymeric matrix which can eventually reduce the entanglement of the fibres resulting in a thicker end product.

4 CONCLUSIONS

The purpose of this work was to study the possibility of making composites from cellulosic textile materials by enzymatic surface modification

of materials as an alternative to conventional polymeric matrices. The combination cotton & flax did not work probably due to the relatively greater linear density of the yarns that may restrict the entanglement of the fibres and minimize the adhesion between components. The flax & viscose combination did not show peel strength improvement, however for Dyadic® Xylanase PLUS it exhibited a remarkable effect on elongation and breaking force at the 0.5% dosage. The cotton & viscose composite appears to be the best combination, exhibiting improved breaking force (0.5% of Xylanase PLUS™) and percentage of elongation at maximum force (0.1% of Xylanase PLUS™), as well as better results in the peel adhesion test (0.5% of AlternaFuel® MAX™). The abrasion resistance has also been slightly improved, based on the results of the evaluation of pilling resistance, despite of the good results on the control composites. Due to the small dosages that had been used, it is very difficult to assess the influence of the enzyme concentration on the obtained results, however higher enzymatic concentrations should be studied to clarify the contribution of this parameter on the surface modification and adhesion promotion.

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5 REFERENCES

1. Porras A., Maranon A., Quijano A.: Development and Characterization of a Laminated Composite Material from Polylactic Acid (PLA) and Woven Bamboo Fabric. In: Binetruy C, Boussu B, editors. *Advances in Textile Composites*, Lancaster: DEStech Publications, Inc, 546-554, 2010
2. Mobasher B.: *Mechanics of fiber and textile reinforced cement composites*. Boca Raton: Taylor & Francis Group, LLC; 2012
3. Biron M.: *Thermosets and Composites-Material Selection, Applications, Manufacturing and Cost Analysis*, 2nd ed. Oxford: Elsevier Ltd, 2014
4. Ageorges C., Ye L.: *Fusion Bonding of Polymer Composites*, London: Springer-Verlag, 2002
5. Plackett D.: *Biodegradable polymer composites from natural fibres*, In: Smith R, editor. *Biodegradable polymers for industrial applications*, Boca Raton: CRC Press LLC, 189-218, 2005
6. Soykeabkaew N., Sian C., Gea S., Nishino T., Peijs T.: *Cellulose* 16, 2009, pp. 435-444
7. Huber T., Mussig J., Curnow O., Pang S., Bickerton S., Staiger M.P.: *J Mater Sci* 47, 1171-1186, 2012
8. Fedorak P.M.: *Microbial processes in the degradation of fibers*, In: Blackburn RS, editor, *Biodegradable and sustainable fibres*, Cambridge: Woodhead Publishing Limited, 1-35, 2005
9. Thomas S., Paul S.A., Pothan L.A., Deepa B.: *Natural Fibres: Structure, Properties and Applications*, In: *Cellulose Fibers: Bio- and Nano-Polymer Composites – Green Chemistry and Technology*, Kalia S, Kaith BS, Kaur I, editors, Berlin: Springer-Verlag, 3-42, 2011
10. Keenan T.M., Tanenbaum S.W., Nakas J.P.: *Biodegradable polymers from renewable forest resources*, In: Smith R, editor, *Biodegradable polymers for industrial applications*, Boca Raton: CRC Press LLC, 219-250, 2005
11. Asunción J.: *The Complete Book of Papermaking*. New York: Lark Books; 2003
12. Strezov V., Evans T.J., Nelson P.F.: *Carbonization of Biomass Fuels*, In Michael D. Brenes, editor, *Biomass and Bioenergy: New Research*, New York: Nova Science Publishers, Inc., 91-123, 2006
13. Murphy J.F.: *Safety Considerations in the Chemical Process Industries*, In: Kent J.A., editor, *Handbook of Industrial Chemistry and Biotechnology Vol. 1, 2, 12th ed.* New York: Springer Science + Business Media, 46-105, 2012
14. Nierstrasz V.A.: *Enzyme surface modification of textiles*, In: Wei Q, editor, *Surface Modification of Textiles*, Cambridge: Woodhead Publishing in Textiles: Number 97, 2009
15. Nierstrasz V., Cavaco-Paulo A.: *Preface*. In: Nierstrasz V., Cavaco-Paulo A., editors, *Advances in Textile Biotechnology*, Cambridge: Woodhead Publishing Series in Textiles: Number 107, 139-163, 2010
16. Kubicek C.P.: *Fungi and Lignocellulosic Biomass*, Ames: John Wiley & Sons, Inc, 2013
17. McKelvey S.M., Murphy R.: *Biotechnological Use of Fungal Enzymes*, In: Kavanagh K., editor, *Fungi Biology and Applications*, 2nd ed. Oxford: John Wiley & Sons, Ltd., 2011
18. Miettinen-Oinonen A.: *Cellulases in the Textile Industry*, In: Polaina J., MacCabe .AP., editors, *Industrial Enzymes Structure, Function and Applications*, Dordrecht: Springer, 51-63, 2007
19. Bajpai P.: *Environmentally Benign Approaches for Pulp Bleaching*, 2nd ed, Oxford: Elsevier, 2012
20. Pickering K.L., Aruan Efendy M.G., Le T.M.: *Composites: Part A* 83, 98-112, 2016
21. Hu J.: *Introduction to fabric testing*, In: Hu J., editor, *Fabric Testing*, Cambridge: Woodhead Publishing Limitedp., 1-27, 2008