The Potential of Beeswax Colloidal Emulsion/Films for Hydrophobization of Natural Fibers Prior to NTRM Manufacturing

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Abstract. Despite all the advantages of applying natural fibers in structural composites, their expected short life span constitutes a challenge due to their hydrophilicity and deterioration in alkaline lime or cement matrices. The present paper proposes eco-friendly hydrophobic coatings to protect natural fibers in lime mortars resorting to polymers reinforced with hydrophobic beeswax micro colloids. The physical, mechanical and chemical characterization suggest the potential of the coated fibers for NTRM casting and further investigation of their interface and bond behavior with the mortar.

Introduction

Natural fibers present an appealing solution to substitute synthetic fibers as possible reinforcements for external strengthening techniques. Owing to their green character, economic viability, and their mechanical compatibility to historical masonry, they present a great potential for sustainable applications at the largescale construction industry. However, when embedded within lime or cement mortars, the degradation kinetics of natural fibers appear as a serious limitation [1]. The alkalinity of such media as well as fibrils dimensions instability upon alkaline-water uptake reveal the necessity to adopt surface modification aiming at delivering reinforcements with enhanced durability [2]. In the literature, different chemical treatments (e.g., maleic anhydride and acetylation) as well as coatings were reported to achieve natural fibers with higher durability [2]. However, the harsh environmental impact of these treatments does not preserve the overall environmental objectives of using natural fibers. Therefore, a need to adopt environmentally friendly methods to improve the long term-serviceability of natural fiber composites is crucial to conserve the green trait of natural fibers application. Hence, the engagement of eco-friendly coatings fabricated from latexes loaded with lipid-based hydrophobic substances suggest a promising approach in this regard.

Natural waxes such as beeswax and carnauba wax present significant hydrophobicity due to the abundancy of hydrocarbon aliphatic products and fatty acids in their composition [3]. In the literature, the adsorption of natural waxes onto different surfaces has proven to be a good candidate to reduce their water affinity [4] [5]. Lozhechnikova et al. investigated carnauba wax coatings to hydrophobize wood surface in two forms, as continuous melted-dried films and as colloidal wax dispersion in water [6]. They reported interesting water repellent characteristics in the latter case as compared to the continuous melting-wax coating, as it showed a decrease in hydrophobicity to a negligible level along time. It is held that natural waxes suffer from brittleness and lack of homogeneity [5]. Thus, films cast from continuous pure wax might be subjected to microcracking of its structure and, consequently, faster moisture penetration to the substrate beneath may occur. The latter highlight demonstrates the

preference of waxes adsorption onto surfaces as micro colloidal emulsions and adhering to the lignocellulosic surface via a polymeric matrix. Therefore, the choice of the polymeric phase is crucial, and a thorough selection should be carried out.

Polyurethane is one of the most versatile polymers, with high mechanical properties, that is used in various fields of engineering and has been used for adhesives, foams and coatings. However, given the rising environmental concrens, efforts have been made to synthesis polyurthenes relying upon eco-friendly resources [7].

Chitosan, a natural biopolymer, is a linear polysaccharide obtained from the exoskeleton of crustaceans and has been used in many fields as an appealing coating, such as in food packaging and paper industry [8] [9] [10] [11]. Chitosan is the N-deacetylated derivative of chitin (the second most abundant polysaccharide after cellulose) and it is insoluble in alkaline media, while solubilizing in acidic aqueous solutions.

In this paper, the authors considered the potential of chitosan as a coating to be used in highly alkaline environment (i.e., lime mortar), due to its resistance to alkaline media. Furthermore, chitosan polycationic nature is promising to engage as a polymer phase to envelop natural fibers [12], and may be as efficient as many polymers widely used such as polyurethane [13], that is also investigated in this work.

Thus, a dip-dry coating resorting to chitosan and to bio-based hydrophobic lipids (i.e., beeswax) at micro scale in the form of colloidal emulsions, prepared in different polymeric gels/latexes, is presented. To the best of the authors' knowledge such environmentally friendly coatings have not been used yet as possible surface durability enhancers of natural fibers reinforcements for structural composites application. Thus, the key objective is to investigate on the efficiency of these latexes to endow promising hydrophobic and mechanical improvements upon incorporation onto lignocellulosic reinforcements.

Materials and Methods

Two types of natural fibers were investigated in this work, namely hemp and flax. Hemp yarns formed by two twisted cords with nominal linear density of 2×400 Tex were purchased from Italy, and flax meshes with yarn-linear density of 1500 Tex were purchased from Switzerland, and used as-received. Chitosan (CS) with medium molecular weight in the range of 190,000-310,000 Da and a degree of de-acetylation of 75%-85%, Polyethylene glycol (PEG 400), and acetic acid (99% analytical grade) were purchased from Merck Life Science, Portugal. Water-based polyurethane (PU) is Takelac WS 4022- grade with water content of 70 % was purchased from Mitsui Chemicals Europe GmbH, Germany. Glycerol plasticizer (Gl) and beeswax (BW) were obtained from local suppliers. All tests were conducted at room temperature conditions.

Coating of flax and hemp fibers

In this paper, three approaches of fiber coating resorting to beeswax colloidal emulsification in different latexes were investigated, as described below:

i) Beeswax colloids self-emulsified in alcohol

The self-emulsification (SE) of waxes in alcohol has been studied as a versatile coating to award barrier effects to different surfaces without including any emulsifiers in the protocols [3] [14]. In this work, the preparation of beeswax-self emulsification in alcohol was carried out according to Bayer et al. [14]. Briefly, 1% (w/v) of beeswax in isopropanol were brought to beeswax melting point and mechanically stirred on a IKA RCT basic stirrer (at 550-600 rpm) until homogenous pale-yellow suspension of wax-alcohol was obtained. Afterwards, the cooling process was carried out at room temperature to attain a clear and dense emulsion. The designation of the resulting coating is SEBW.

ii) Beeswax-chitosan-glycerol emulsions

This emulsion preparation protocol was adapted from Zhang et al. [15] with optimized formulations for NTRM application as follows: in 100 ml of 2% aqueous acetic acid solution, 4% (w/v) of CS+ Gl was dissolved (0.4g of CS+ 3.6g Gl in 100 ml of the acidic solution). The ratio of

CS: Gl is 1:9 (w/w) as recommended by Cui et al [16] aiming at fostering glycerol plasticizing effect, enhance hydrophobicity and flexibility of the resultant film. The mixture was magnetically stirred for two hours without heat until complete solubility was achieved. Afterwards, two different loadings of BW were added to the CS-Gl solutions (100% and 200% w/w of CS) and magnetically stirred in tandem with heating the solution to the melting point of beeswax until the complete emulsification. Finally, vigorous homogenizing at 15000 rpm for 15 minutes was conducted to apply homogenizing shear and avoid coalescence. The terminologies of the resultant coatings are CSBW4100 and CSBW4200 where (4) refers to the concentration of (CS+ Gl), (100) and (200) refer to beeswax loadings respectively.

iii) Beeswax-PEG- glycerol emulsified in water-based polyurethane

To prepare this latex, the as-received PU solution was diluted so that the final weight fractions of urethane resin and water are 10% and 90 % respectively. This dilution aims at limiting the urethane resin content in the films, thus delivering more flexible coating with less environmental impact. In 100 ml of this solution, 4% PEG 400 (v/v), and 4% Gl (w/v) were added and magnetically stirred without heat for a few minutes up to total solubility. Afterwards, BW was added to the mixture (30 % w/v of urethane resin) and magnetically stirred with heat until full emulsification was reached; then the emulsion was stirred overnight at room temperature to inhibit coalescence. The resultant coating is designated PUBW. To the best of the authors' knowledge, this protocol has not been reported yet in the literature.

To cast the coatings onto flax and hemp fibers, a one-layer dip-coating followed by annealing treatment was carried out at 100 °C in a convection oven for one hour, then cooled slowly overnight inside the oven. The coating was also conducted on 2D fabrics.

Contact angle tests

Contact angle measurements were carried out on an OCA 20 equipment from Dataphysics, capturing the image/video optical contact angle established with a distilled water droplet of 8 µL, to investigate the wettability of the fibers before and after coating via static sessile drop contact angle measurements (CA). Due to the irregular morphology of the hemp fabric, contact angle was measured only for flax fabrics. The fabrics had an area of 2×5 cm^2 and were non-coated and coated with the abovementioned coatings. Contact angles were measured on ≥ 10 different samples for each coating scenario.

Attenuated Total Reflectance–Fourier Transform Infrared Spectroscopy

The attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) was used to investigate the chemical modifications of the surface before and after flax fiber coating as well as to verify the coating adsorption onto the fiber surface. The acquisition of the spectra was carried out using a single reflection diamond ATR System in the range from 4000 cm^{-1} to 600 cm^{-1} over 64 scans with a resolution of 8 cm^{-1}.

Tensile tests

For tensile behavior characterization, a total of 8 replicates of hemp and flax yarns before and after coating were tested under uniaxial direct tensile tests using H100KS testing equipment, equipped with a load cell of 5 kN. The tensile specimens had a 250 mm-gauge length, and displacement rate of 250 mm/min was applied monotonically until reaching the total rupture, in accordance with EN ISO 2062-2009. Prior to each test, preloads of 5 N for hemp and 7.5 N for flax were applied. The results are extracted from stress-strain graphs and Young's modulus was calculated as the slope of the elastic part between 30–70% of the tensile strength in stress-strain graphs (further illustrated in the result section). The cross-section area was calculated depending on yarn´s linear density (Tex) and density (g/cm^3) according to the authors´ previous work [17], see Eq. 1. Furthermore, as the structural tensile strength is mainly provided by the fibers, the dry fibers´ cross-section area was considered for tensile stress calculations before and after coating.

$$A_{Yarn} = \frac{Linear\ density\ (Tex)}{Density\ (g/cm^3) * 1000} \qquad (1)$$

Results and Discussion

The emulsions obtained in polyurethane and chitosan revealed a relative stability, Figure 1 (b.1 and b.2 respectively). According to Jumaa et al [18] and Zhang et al [15], the significant emulsification capacity of the polycationic chitosan achieved with beeswax, rich with negatively charged-free fatty acids, can be attributed to their electrostatic interaction. SEBW alcoholic emulsions also showed significant stability. Moreover, fabrics coated with SEBW promoted good hydrophobicity, however, given the brittle resultant film, this coating protocol was excluded from the study.

Contact angle

Contact angle measurements were recorded for flax fabrics after coating. Non-coated flax had a superhydrophilic surface (0° CA). Hemp fabrics possess an irregular surface morphology as depicted in Figure 1e, hindering the measurement of meaningful contact angle values, therefore CA was not recorded for hemp. The CA was measured along 15 minutes, after 1 minute of droplet deposition for stabilization onto the fabric surface, and the results are depicted in Figure 2. It is possible to see that CSBW4200 coating has resulted in near superhydrophobic behavior with a significant stability of droplet shape observed even after 15 minutes. Similarly, PUBW-coated flax showed a consistent hydrophobic trait with CA around 140-130°. Fabrics coated with the latter two protocols have endowed less variations in CA readings as compared to CSBW4100 coated ones. Furthermore, it was evident that the increase of BW loading in CSBW4200 emulsion led to more water-resistant surfaces; it was also noticed that several samples coated with CSBW4100 decreased the hydrophobic response after 13 minutes, characterized by partial wetting at the droplet location, as observed in Figure 2. It is important to highlight that film production via solution casting, water in this case, employing the annealing treatment is a key factor for the reformation of wax microparticles and their redistribution along the polymer's surface, Figure 1c and Figure 1d. Besides, after heat treatment, the long aliphatic tails present in the free fatty acids of the waxes redirect outwards the surface of lignocellulosic substrate and convey greater water resistance [19], Figure 1d, Figure 1e and Figure 1f.

(a) Superhydrophilic flax fabric

(b) Fibers & fabrics dip-coating

(b.1) (b.2)

(c) Emulsified beeswax colloids in the polymer

Polymer

Natural fiber surface

(f) Hydrophobic flax fabrics

(e) Hydrophobic hemp fabrics

(d) Outwards surface-aliphatic tails after water casting via annealing treatment (100 °C for 1 hour then cooled down overnight slowly)
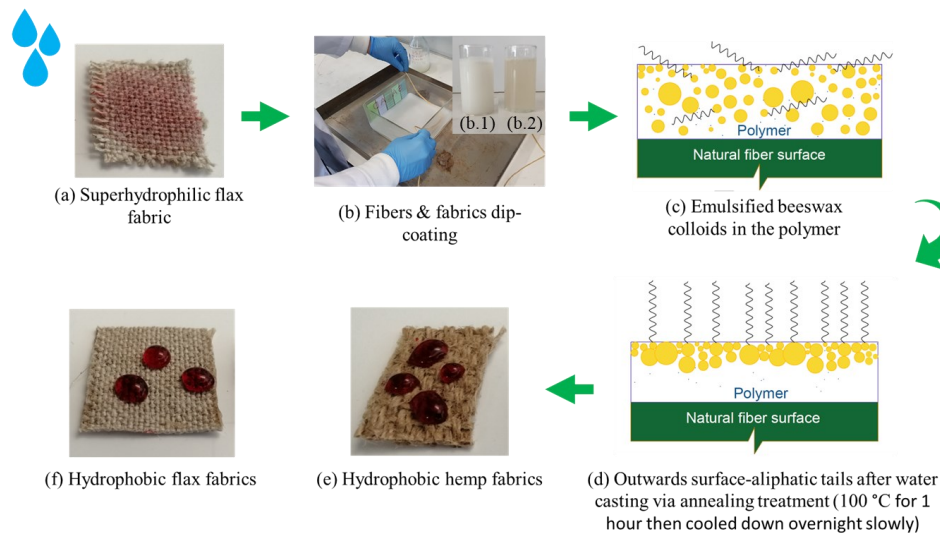
Polymer

Natural fiber surface

Figure 1- Schematic illustration of the coating process (red coloring pigment was used with water in this scheme to display water droplet and/or propagation through the fabrics).
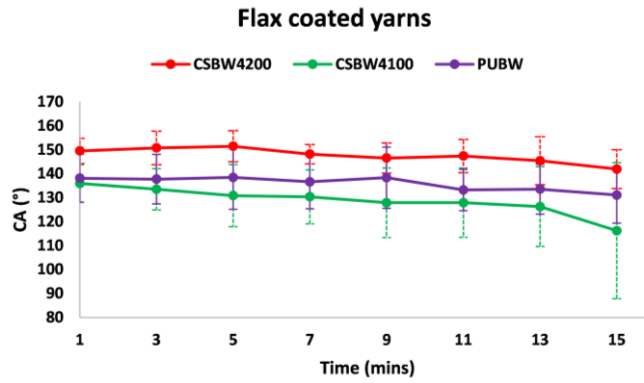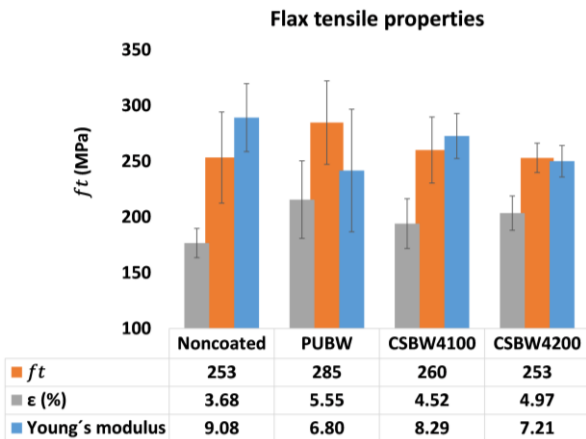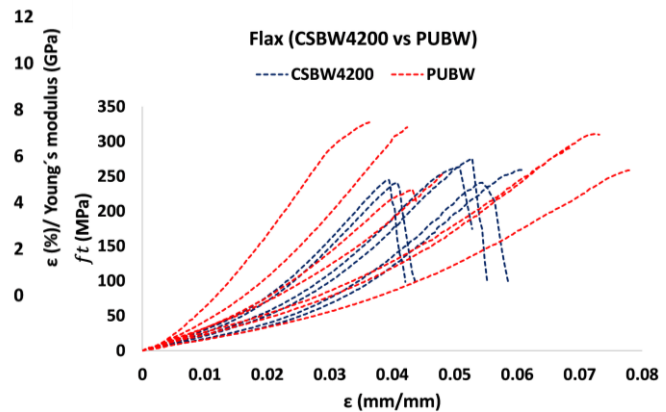
Figure 2- CA of flax fabric after coating (with standards deviations).

Tensile tests

Figure 3a and Figure 3c summarize fibers mechanical properties as tensile strength (f_t), elongation at break ε (%) and Young´s modulus (E) for flax and hemp yarns. Yarns´ cross-section areas are presented in in Table 1. In terms of failure mechanisms, the abrupt-brittle failure dictated the rupture mechanism of the yarns, observing a gradual decrease in fiber cross-section as the load increased. For the tensile properties, is its clear that the coatings did not induce any drop of the tensile strengths of hemp and flax yarns, Figure 3a and Figure 3c. By contrast, 12% and 55% higher tensile strength was observed in case of PUBW-coated flax and hemp yarns respectively when compared with their corresponding non-coated yarns. CSBW4200-coated flax and hemp yarns also presented promising tensile strength values. These observations suggest that the acidity of the coatings and treatment conditions were not aggressive to the fibers´ structure, and hence, did not damage the yarns, Table 1. Furthermore, the higher strain values achieved in flax and hemp yarns after casting all coating scenarios, compared to the non-coated yarns, support this hypothesis too, Figure 3a and Figure 3c. It is important to stress that the high strain scores observed by the coatings are a key factor to ensure that the coating deforms as the yarns elongates, thus, avoid the cracking and water propagation to fiber's surface. Young´s modulus was calculated as the slope of the elastic phase in the stress-strain graphs between 30% and 70% of the (f_t) as the coated fibers exhibited low initial yet increasing stiffness up to 25% of yarn load carrying capacity (specially PUBW-samples), Figure 3b and Figure 3d. All the coated fibers presented lower Young´s modulus when compared with non-coated yarns, still, CSBW4200- coated samples outperformed in this regard the other two coatings in both flax and hemp yarns; CSBW4200-coated samples were also characterized by low standard deviation of Young´s modulus values. The drop of Young´s modulus might be an effect of the thermal treatment conducted to cast the water and form the films. Overall, reinforcing polyurethane or chitosan with increased content of beeswax lead to the best mechanical properties for the surface treated yarns.

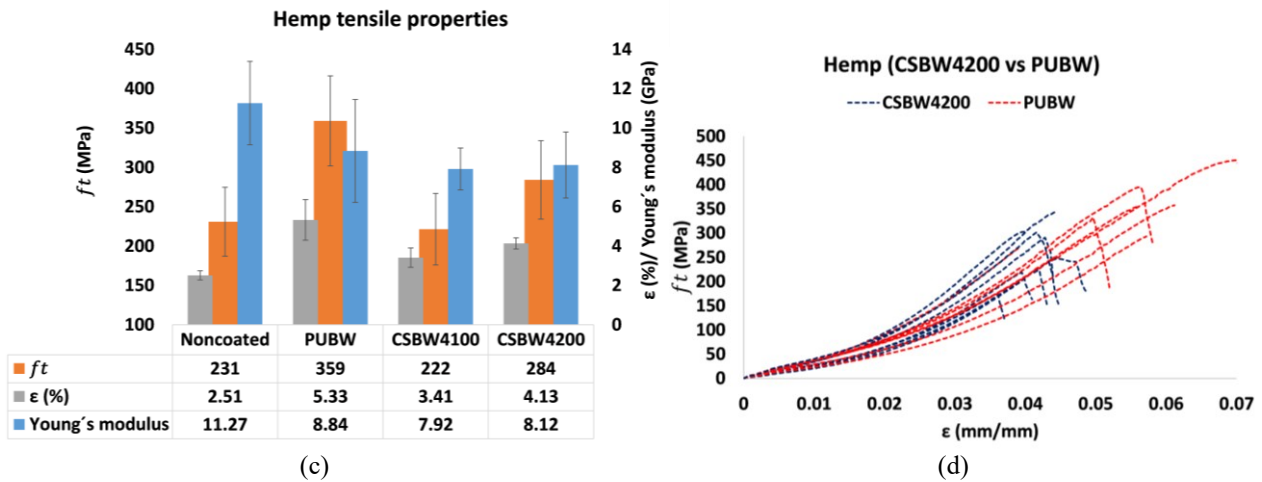|	Noncoated	PUBW	CSBW4100	CSBW4200
f_t	253	285	260	253
ε (%)	3.68	5.55	4.52	4.97
Young´s modulus	9.08	6.80	8.29	7.21

(a)

(b)

(c)   (d)

Figure 3-Tensile properties of (a) flax and (c) hemp with corresponding standard deviations as well as stress-strain graphs of (b) flax and (d) hemp

Table 1-pH values and yarns areas

Coating ID	Coating pH	Area (mm^2)	
		Flax	Hemp
Noncoated	-		
CSBW4100	3.48	0.985	0.752
CSBW4200	3.44	(0.049)	(0.004)
PUBW	6.57		

*Values in brackets correspond to standard deviation

FTIR

Non-coated fibers and fibers coated with chitosan-based protocols present a broad band near 3336 cm^{-1} characteristic of hydroxyl groups present in polysaccharides of the lignocellulosic materials and chitosan [8], Figure 4. It should be noted that the depth of the IR analysis is typically greater than the thickness of the coating, thus resulting in overlapping with the spectrum of the fiber beneath. Thus, for PUBW-coated samples, it is possible that band corresponding to the polyurethane NH–stretching mode may overlap with that of OH– stretching mode of the lignocellulosic surface. The bands in the range 2800-2950 cm^{-1} correspond to C–H group of methyl and methylene present in polysaccharides as well as fatty acids of beeswax. The increase of BW content in the coating is harmonized with the increase of these peaks' intensity observed in CSBW4200-samples (as compared with CSBW4100 and non-coated samples, Figure 4). The dominant band near 1729 cm^{-1} in PUBW-coated samples corresponds to carbonyl groups in urethanes; bands near the range 1581-1533 cm^{-1} correlate to NH– bending deformation vibration [20] [21] [22]. The latter two bands confirm the effective incorporation of polyurethane onto samples' surfaces. Other characteristic band of urethanes (in case of PUBW) is near 1245 cm^{-1} and corresponds to –C–N deformation [13] [23].
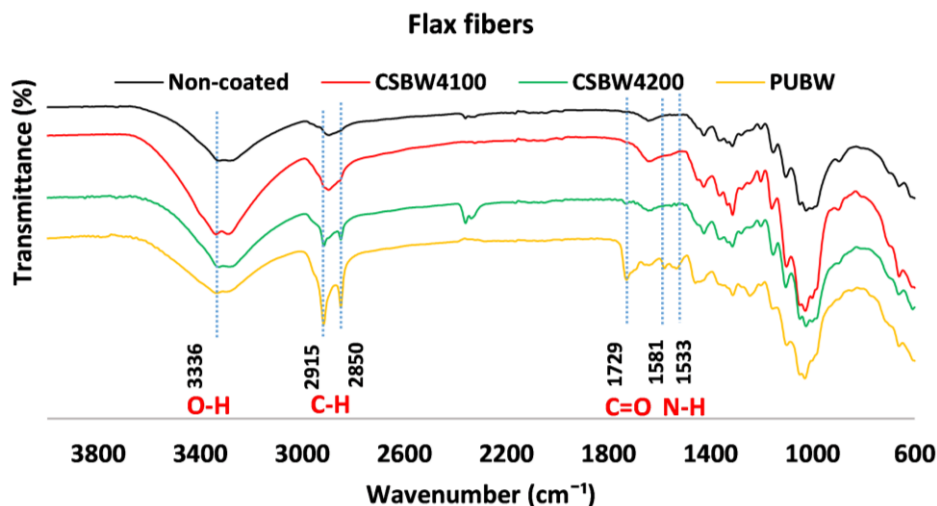
Figure 4- FTIR spectra of flax fibers coated and non-coated

Conclusion

The degradation and aging mechanisms of natural fibers when embedded in highly alkaline media (i.e., lime or cement mortars) draw the attention to the necessity of protecting their lignocellulosic surfaces, thus keeping their long-term structural characteristics. In this paper, the authors present a set of environmentally friendly coatings based on beeswax emulsions formed in aqueous solutions of different polymers. Chitosan polymer reinforced with lipids seems to have the potential to ensure a green and sustainable film with water resistant characteristics, leading to the formation of coatings with near superhydrophobicity. Polyurethane-beeswax films also present an appealing solution to hydrophobize and improve the mechanical properties of the natural fibers. However, polyurethane manufactured from eco-friendly constituent materials is recommended to be investigated as in similar coatings to comply with the environmental requirements. The incorporation of beeswax (rich in free fatty acids) onto fibers surfaces not only increase fibers´ water repellency but also sustain their mechanical properties. The redirection of coating engineering towards green methodology is a promising aspect, in particular when the green coatings can deliver relevant enhancements comparable to those of the synthetic ones.

Acknowledgement

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