

# EFFECT OF SURFACE MODIFICATION OF REGENERATED CELLULOSE FIBERS ON MOISTURE ABSORPTION AND FIBER/MATRIX ADHESION

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## Abstract

This paper describes the effect of surface modification of regenerated cellulose fibers by chemical treatment and deposition of cellulose nano-crystals onto fibers. The effect of this modification on the moisture absorption by fibers and interface properties with epoxy matrix has been studied. The preliminary results show positive trends in reducing moisture uptake by fibers and improving interfacial shear strength.

The deposition of cellulose nano-crystals at different concentrations onto regenerated cellulose fibers creates a network covering surface of fibers and interconnecting them. This resulted in rather significant reduction of the moisture absorption compared to untreated fibers (8% vs 12% respectively) and improving interfacial shear strength of regenerated cellulose fiber/epoxy system. The increase of the interfacial shear strength measured from bundle pull-out test on fibers conditioned at 64% relative humidity has been observed. Thus, the hierarchical structure created by grafting nano-crystals on micro-sized cellulose fibers resulted in improvement of fiber/matrix adhesion by reducing water absorption.

## 1. Introduction

Natural and manmade cellulosic fibers (flax, hemp, regenerated cellulose) exhibit good mechanical performance and they are more often considered as an alternative to synthetic reinforcement (e.g. glass fibers) in polymer composites. However, their inherent polar and hydrophilic character and the sensitivity to moisture remain a challenge and limit the use of these fibers as reinforcements for polymers. Therefore, surface modification is a way to overcome the mentioned drawbacks of lignocellulosic fibers.

In order to fully utilize properties of fibers in composite, good stress transfer from matrix to fiber is essential. The fiber/matrix interface can be realized either via molecular interactions such as covalent and hydrogen bonds [1-3] or through the mechanical interlocking at the fiber/matrix boundary. Even though the work to improve the fiber/matrix adhesion has been focus for number of studies for a long time [4-6], the research is still on-going and not all problems are resolved. This is especially true for

natural fibers where compatibility between cellulosic reinforcement and synthetic polymers is an issue. Throughout our previous studies [7], it was possible to show that chemical modifications improve the adhesion of regenerated cellulose fibers (RCF) to epoxy matrix. The current paper presents results of the study to reduce water uptake by fibers and enhance RCF/matrix adhesion by means of grafting cellulose nanocrystals (CNC) on fiber surface. The effect of the RCF treatment is evaluated by moisture absorption experiments and by pull-out test performed on fiber bundles. The typical synthetic epoxy resin is used as a matrix in this work.

## 2. Experimental

### 2.1. Materials

The regenerated cellulose fibers used in this work were commercial Cordenka 700 super 3 fiber bundles with high twist (Z100) [8]. The bundle consists of 1350 single filaments and the average fiber diameter is 12.5  $\mu\text{m}$ .

The fiber treatment was done by using the organo-functional trialkoxy silane  $\gamma$ -methacryloxypropyl trimethoxysilane (MPS) as coupling agent, purchased from Sigma Aldrich. Ceric Ammonium Nitrate (CAN) is a high purity product purchased from Fluka and used as initiator for the chemical reaction of MPS on RCF.

Cellulose nanocrystals (CNC) were chemically extracted from palm tree at the laboratory following the procedure described in details in our previous work [7].

The polymer used in bundle pull-out tests was two components epoxy resin Araldite LY5052 with Aradur Hardener CH5052 mixed in 80:20 weight ratio, respectively.

### 2.2. Fiber treatment

The MPS was employed as coupling agent to graft CNC to the fibers by utilizing CAN to initiate the copolymerization. The whole process of chemical grafting of CNC onto RCF consists of copolymerization of MPS with RCF followed by grafting CNC on MPS-modified fibers.

The first reaction is carried out by using blend of ethanol and deionized water 50/50 (v) as solvent for which the pH of a mixture (1600 mL) was adjusted to 7.0 at 65°C. The bundle of RCF (total mass of 32g) was wound on a metal holder and immersed in the solution. Then the CAN (4g) was added under inert atmosphere of N<sub>2</sub> gas and the reaction mixture was stirred for 30 minutes. It was followed by drop-wise addition of 4ml of MPS into the reactor and stirring for 5 hours at 65°C. At the end of the reaction the processed fibers were washed two times by ethanol and finally rinsed by deionized water.

The next stage of the process is carried out in an aqueous solution (1600mL) of deionized water at pH of 4.5. The 0.1wt% suspension of CNC was added on MPS-modified fibers in the reactor and the mixture was stirred for 4 hours at room temperature. In order to remove the unreacted products at the end of the process the treated fibers were washed twice by ethanol and rinsed by deionized water.

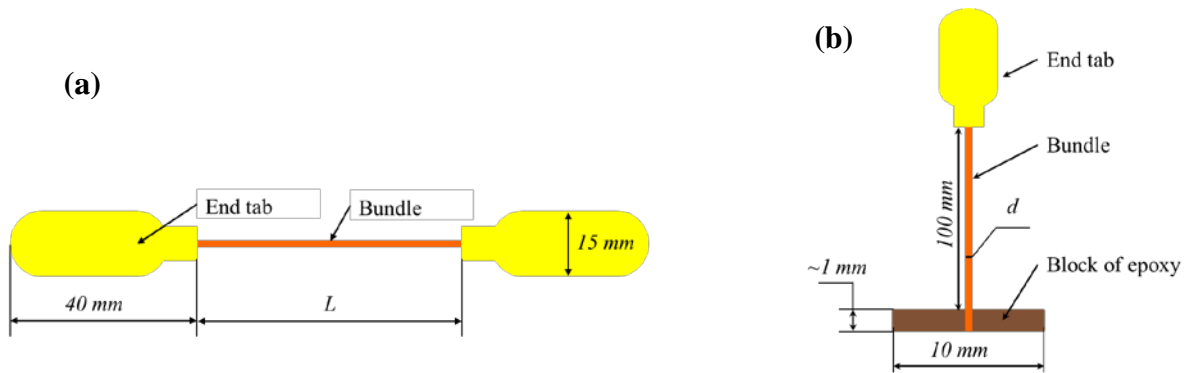
The notations MPSCNC1, MPSCNC2 and MPSCNC3 are introduced (and used throughout the paper) for fiber batches produced with CNC concentrations of 0.1, 0.2wt%, and 0.4wt% respectively.

### 2.3. Specimen preparation

The untreated and modified (different surface treatments) fibers were tested. Tensile tests were carried out on fiber bundles fitted with wooden tabs (glued by using Araldite 2011 epoxy adhesive). The gauge length of bundles (distance between tabs) was 100 mm.

Specimens for bundle pull-out tests were prepared by embedding fiber bundle in circular block of polymer with 10 mm in diameter and 1 mm thickness. This was done by using specially build mold

which allowed preparation of up to ten specimens at once. Fiber bundles were passed through hole in each individual cavity which then was filled with epoxy. After all cavities were filled with polymer the whole mold was placed in pre-heated oven at 80°C and left to cure for 8 hours. Then it was slowly cooled down and specimens were demolded. The free end of the bundle was also fitted with wooden tab, similarly to the specimens for tensile tests. The schematic drawings of ready-to-use tensile and pull-out specimens are shown in Fig. 1.



**Figure 1.** Specimen for tensile (a) and pull-out (b) tests.

## 2.4. Moisture uptake

The conditioning of untreated and treated fiber bundles was carried out in desiccators at two different relative humidity (RH) levels,  $RH^1 = 33\%$  and  $RH^2 = 64\%$ . Fibers were dried at 50°C to remove storage moisture before placing them into desiccators. During the moisture uptake experiment the mass of fibers was regularly measured to determine the kinetic of sorption as well as the saturation level. The saturation level (equilibrium) was reached when there is no more significant weight gain during time period of approximately 20h. The moisture content  $M$  was calculated as ratio between measured fiber weight gain and initial mass of the fibers after drying. It was presumed that transport of water molecules into fiber occurs only from their surfaces and therefore one-dimensional Fikian diffusion through the fiber diameter was assumed. The diffusion coefficient  $D$  was then calculated from the initial linear part of the absorption curves and moisture content at saturation  $M^\infty$  (see [9-10]). The specimens for tensile and pull-out tests were conditioned at  $RH = 64\%$  according to the procedure described above.

## 2.5. Mechanical tests

Tensile and pull-out tests of treated/untreated fiber bundles unconditioned (notation “UC” is used further in the text; these fibers were stored in the lab at  $T=23^\circ\text{C}$  and  $RH \sim 12\text{-}16\%$ ) and conditioned at  $RH=64\%$  were performed. Ten batches in total were tested with at least five specimens in each batch. Tensile tests were performed on INSTRON 4411 machine in displacement controlled mode at constant cross-head speed of 10 mm/min (corresponding to strain rate of 10%/min) using 500N load-cell and mechanical grips. The stress was calculated from load registered during the test and cross-section area of the bundle was calculated from multiplication of number of fibers in the bundle by the cross-section of single fiber (assuming circular shape of the fiber). The strain was calculated from the initial bundle length and displacement obtained from the movement of the machine cross-head (compliance of the test system is taken into account).

The pull-out tests were carried out on INSTRON 4411 machine in displacement controlled mode at constant cross-head speed of 5 mm/min using 500N load-cell and mechanical grips. The load and displacement was registered during the test. The interfacial shear strength (IFSS) is then calculated from the maximum load achieved during the test to pull out the bundle from the block of matrix. The simple force balance consideration is employed: at the moment of the pull-out the axial stress in the bundle (force  $F_{max}$  over the cross-section area of the bundle  $\pi \cdot d_b^2/4$ , where  $d_b$  is the diameter of the

bundle) is equal to the shear stress acting on the bundle surface embedded into the polymer ( $\pi \cdot d_b \cdot L_e$ , where  $L_e$  is the length of the embedded bundle, equal to approximately 1mm). When the pull-out occurs the shear stress acting on the embedded bundle surface is equal to IFSS and similarly to the Kelly-Tyson model for single fiber [11] the IFSS is calculated from the following equation:

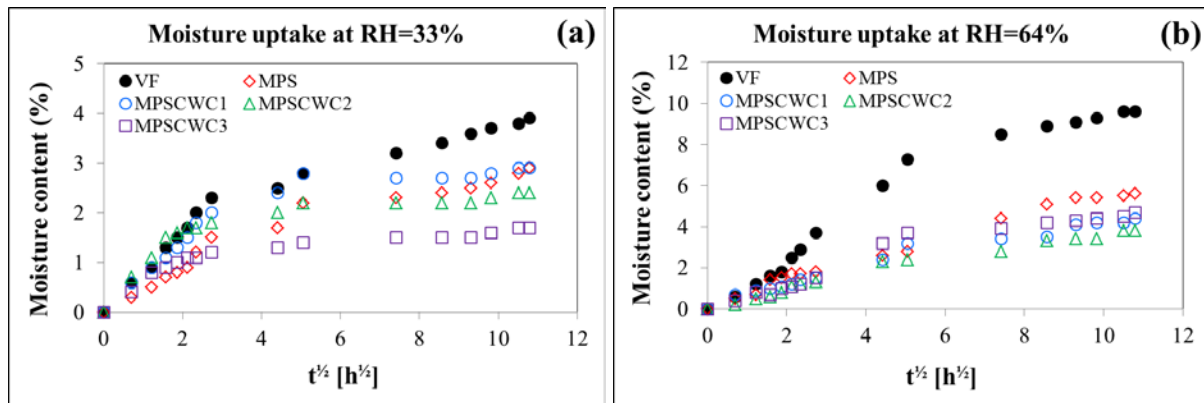
$$IFSS = F_{max}/(\pi \cdot d_b \cdot L_e) \quad (1)$$

The  $d_b$  was calculated from the area of the hole in the polymer block after the pull-out.

### 3. Results and discussion

#### 3.1. Moisture uptake

The moisture uptake curves are presented in the Fig. 2. It is assumed that the saturation is achieved after approximately 100h (plateau of sorption curves in Fig. 2), although the water uptake did not completely stopped for untreated fibers and it is still continued at a very slow rate. It should be noted that while the shape of the sorption curves differ considerably for different relative humidity levels, the time to reach saturation is almost independent on RH. It is also evident that the moisture content in fibers significantly increases with increasing the relative humidity. The moisture content at saturation  $M^\infty$  along with diffusion coefficient  $D$  are presented in Table 1. The Table 1 contains diffusivity coefficient only at RH = 64% because no significant difference between untreated and treated fiber behavior at the initial sorption stage has been observed (see Fig. 2a).



**Figure 2.** Moisture uptake by RCF bundles as a function of square root of time (time in hours) at RH = 33 % (a) and RH = 64% (b).

**Table 1.** Summary of the results of water uptake experiments.

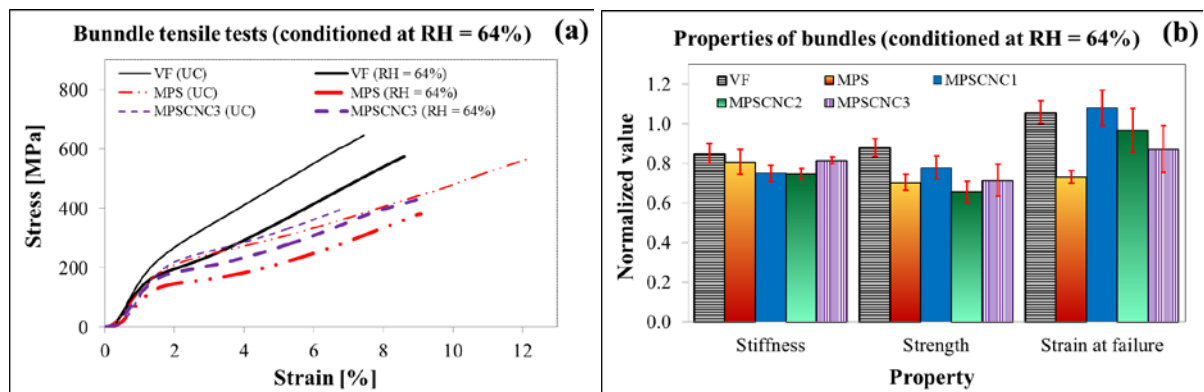
	Batch				
	VF	MPS	MPSCNC1	MPSCNC2	MPSCNC3
$M^\infty$ [%] (RH = 33%)	3.6	2.3	2.2	2.5	2.7
$M^\infty$ [%] (RH = 64%)	9.1	4.1	5.7	5.4	4.1
$D$ [mm <sup>2</sup> /s] (RH = 64%)	$4.5 \cdot 10^{-11}$	$2.8 \cdot 10^{-11}$	$4.5 \cdot 10^{-11}$	$4.3 \cdot 10^{-11}$	$4.9 \cdot 10^{-11}$

The results show that at RH = 33% the water uptake is only slightly higher for untreated fibers (VF) than for treated, while at RH = 64% treated fibers show significantly better resistance to water absorption compared to untreated fibers ( $M^\infty$  is almost two times lower). These observations reveal that the chemical treatments had considerably reduced the polarity of RCF. The values of diffusion coefficient  $D$  for untreated fibers and CNC-grafted bundles are very similar,

while  $D$  for MPS-treated fibers is almost two times lower than the rest of fibers. Most likely it is because MPS polymerized on the surface of fiber bundles hides the trimethoxysilane groups which are highly hydrophobic compared to Hydroxyl groups present on the surface of the untreated fibers. The rate of penetration by water molecules into the fibers can be delayed due to the hydrophobic character of the trimethoxysilane groups and the carbon backbone of the poly-MPS, thus fibers become more resistant to water diffusion/adsorption. However, after CNC are grafted on MPS-treated bundles, the fiber is covered with hydroxyl groups which increase its hydrophilic nature and the water absorption rate increases so the diffusion coefficient becomes comparable to untreated fibers. Based on these considerations it can be stated that the water uptake in CNC-grafted fibers is combination of adsorption on grafted nanocrystals and absorption by fibers.

### 3.2. Tensile properties

The typical stress-strain curves for treated/untreated fiber bundles conditioned at RH = 64% and unconditioned are presented in Fig. 3a. The summary of average values of stiffness, strength and strain at failure obtained from tensile tests are shown in Table 2. The same results in normalized form are plotted in Fig. 3b (values are normalized with results for unconditioned fibers for more convenient comparison).



**Figure 3.** Typical stress-strain curves from tensile tests of bundles (a) and normalized values of mechanical properties of fiber bundled conditioned at RH=64% (b). Values are normalized to the data of unconditioned bundles.

**Table 2.** The average mechanical properties of unconditioned and conditioned at RH=64% RCF.

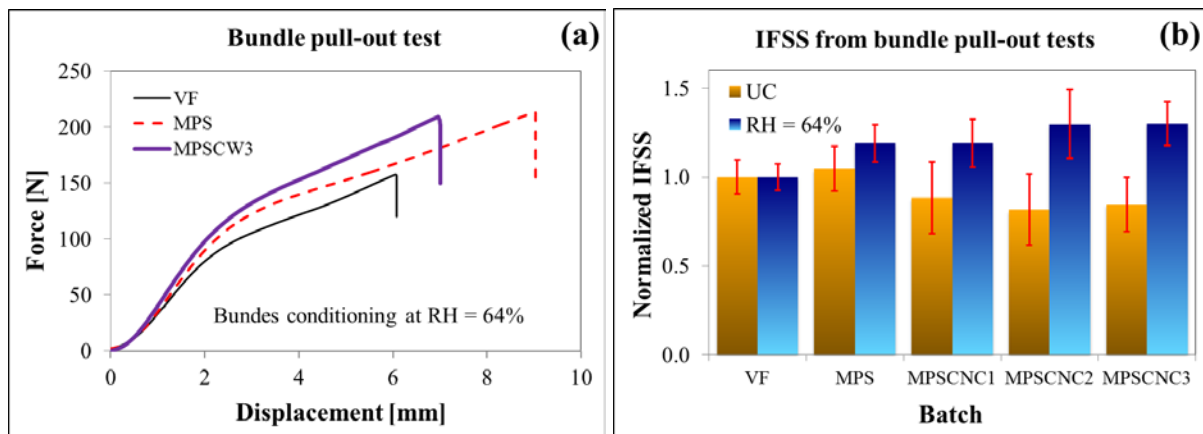
Batch	Stiffness [GPa]		Strength [MPa]		Strain at failure [%]	
	UC	RH=64%	UC	RH=64%	UC	RH=64%
VF	22.9 ± 0.8	17.3 ± 0.8	618 ± 20	575 ± 26	7.6 ± 0.6	8.4 ± 0.5
MPS	15.4 ± 0.4	13.0 ± 1.0	519 ± 5	414 ± 23	12.0 ± 0.3	9.4 ± 0.3
MPSCNC1	18.7 ± 1.0	14.4 ± 0.7	455 ± 13	424 ± 33	8.2 ± 0.3	9.2 ± 0.7
MPSCNC2	18.0 ± 0.8	14.8 ± 0.5	408 ± 60	345 ± 31	7.2 ± 1.4	7.3 ± 1.0
MPSCNC3	17.8 ± 0.7	15.7 ± 0.3	384 ± 23	384 ± 46	6.8 ± 0.2	7.8 ± 1.0

The results show that strength and stiffness of all materials are degraded by moisture whereas strain at failure shows increase (except for MPS treated bundles). It should be noted that fiber treatment itself significantly affects stiffness and strength of fibers with no significant effect on strain at failure (see detailed discussed in [12]).

The most affected by moisture is stiffness of untreated fibers (decrease by almost 25%) while stiffness of MPS, MPSCNC1, MPSCNC2 and MPSCNC3-treated fibers exhibited 15, 23, 18, and 12% reduction, respectively. The strength is most notably affected for MPS-treated fibers (decrease by 20%) with second largest decrease for MPSCNC2 fibers (approximately 16%) followed by VF and MPSCNC1 (decrease by 7%), while MPSCNC3 are not affected. The largest strength decrease for MPS-treated fibers is probably due to the irregularities (defects) induced by the treatment whereas grafting of CNC may have shadowed these defects and reduced their effect (see [12]). The increase of failure strain for RCF is rather expected, since it is well known that water plays a role of plasticizer for cellulosic fibers.

### 3.2. Moisture effect on IFSS

A typical curves obtained from bundle pull-out test are presented in Fig. 4a. The results from the bundle pull-out tests are summarized in Table 3. The same results in normalized form are plotted in Fig. 4b (values are normalized with results for untreated fibers for more convenient comparison).



**Figure 4.** Typical load-displacement curves from fibers pull-out tests (a) and normalized values of IFSS for different batches of unconditioned bundles and conditioned at RH = 64% (b). Values are normalized with respect to the data of untreated (VF) bundles.

**Table 3.** Summary of IFSS from pull-out tests for conditioned/unconditioned fiber bundles with different treatments embedded in epoxy resin.

Batch	IFSS [MPa]	
	UC	RH=64%
VF	32.2 ± 3.1	24.9 ± 1.9
MPS	33.7 ± 4.0	29.7 ± 2.6
MPSCNC1	28.4 ± 6.5	29.6 ± 3.3
MPSCNC2	26.3 ± 6.5	32.3 ± 4.8
MPSCNC3	27.2 ± 5.0	32.4 ± 3.0

In case of unconditioned fibers the IFSS of MPS-treated bundles is slightly higher than that of VF fibers (~5%) and by 18-28% higher than for fibers treated with CNC. It is evident that MPS-treated unconditioned fibers have better adhesion to epoxy which is possibly achieved by one of these mechanisms: a) the moisture adsorption on surface of fiber is reduced (water molecules penetrating in between fiber and resin will degrade the interface strength); b) the roughness of fiber surface is increased (see [12]) and it improves mechanical interlocking between fiber and resin.

The decrease of the IFSS for unconditioned fibers after CNC-grafting may be explained by the hydrophilic nature of cellulose nanocrystals which adsorbs water (as stated in the section 3.1) thus

degrading interfacial strength.

The conditioning of RCF at RH = 64% results in decrease of IFSS for VF and MPS fibers by 22.5% and 12% respectively. It is likely that at higher humidity water molecules diffuse into fiber/matrix interface causing degradation of interfacial strength. In contrary, CNC-treated fibers show higher IFSS after conditioning even when compared to the unconditioned fibers (the effect is more pronounced for higher concentrations of CNC). This improvement may be due to mechanical interlocking (the epoxy penetrates into the network of nanocrystals and the contact surface between fibers and epoxy is increased) as well as because of swelling of fibers (the diameter of fibers increases and it results in higher friction at the fiber/matrix interface).

#### 4. Summary

This study showed effect of chemical modification of RCF on moisture uptake by fibers and on interfacial adhesion with epoxy matrix. Unconditioned fibers and bundles conditioned at two relative humidity levels (RH=33% and RH=64%) were studied. Moisture uptake experiments along with mechanical characterization of fiber bundles (tensile and pull-out tests) were carried out. The data for unconditioned RCF bundles were used as reference for benchmark.

Only higher humidity level (64%) had any significant impact on moisture uptake behavior for untreated and treated fibers while at lower humidity level (33%) all fibers performed fairly similar. Moreover, at RH=64% the CNC-treatment decreased water uptake by factor of two compare to untreated fibers. The diffusion coefficient is the same for all fibers, except MPS-treated bundles which had much lower diffusion coefficient because MPS is shielding cellulose on the fiber surface and decreases probability for water molecules to penetrate fiber.

The mechanical properties of RCF are degraded by moisture but the effect of conditioning at RH = 64% is not as severe for CNC-treated fibers as it is for VF and MPS-treated bundles.

The addition of CNC on the RCF surface decreases IFSS if unconditioned fibers are tested, however experiments on bundles conditioned at RH = 64% showed that IFSS of CNC-treated bundles/epoxy not only retained the same values but even exhibited some increase. The IFSS of untreated and MPS-treated fibers is greatly affected by moisture (decrease by 14-29%).

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