

ENVIRONMENTALLY FRIENDLIER METHOD TO DEPOSIT CELLULOSE NANO-CRYSTALS ON REGENERATED CELLULOSE FILAMENTS AND EFFECT OF THE TREATMENT ON MECHANICAL PROPERTIES OF FIBERS

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Abstract

This paper presents environmentally friendlier technique for deposition of cellulose nano-whiskers onto the surface of regenerated cellulose fibres using γ -methacryloxypropyltrimethoxysilane as coupling agent. The result of this treatment is hierarchical reinforcement consisting of micro-scale fibres and nano-scale cellulose crystal network. In order to evaluate influence of treatment on fibre performance, tensile tests of fibre bundles were carried out. The results show that there is significant impact on stiffness of fibres only by first modification by silane, whereas grafting of cellulose nano-whiskers onto the surface of the fibre allowed recovery of initial properties. It is assumed that the treatment may have induced the misalignment of macromolecular chains and crystalline cellulose phase with respect to the fibre axis.

1. Introduction

Due to increasing interest of various industries and society in general in environmentally friendlier and sustainable structural materials, there is rather intensive on-going research in the area of natural cellulosic fibres for use in polymer composites [1]. Cellulose is an environmentally friendly material which is obtainable in vast quantities, since it is present in every plant. Cellulosic fibres are commercially found in two forms: natural (flax, hemp, cotton, sisal, wood, etc.) and regenerated cellulose fibres (RCF). Numbers of studies have been focused on regenerated cellulose fibres as polymer reinforcement [2-5]. The biodegradability, the morphological and mechanical properties make these fibres a good alternative to the synthetic reinforcement (e.g. glass fibres). However, as all other cellulosic fibres these materials also have similar drawbacks, such as sensitivity to moisture and poor adhesion with polymers. The present work was focused on improving fibre/matrix bonding through modification of Cordenka fibres by cellulose nano-whiskers (extracted from date palm tree) using environmentally friendlier chemical process.

2. Experimental

2.1. Materials

The RCF Cordenka 700 Super 3, 2440 dtex, Z100 (Z100 refers to twist, 100 rev/meter) were used as received. Fibres were supplied in spools of bundles, each fibre bundle contains 1350 filaments and average diameter of single fibre (assuming circular cross-section) is 12.5 microns.

The initiator Cerium ammonium Nitrate (CAN), nitric acid, NaOH, MPS and pure ethanol (99%) were used as received without purification. Distilled water was employed as co-solvent with ethanol for the grafting reaction. The cellulose nano-whiskers (CW) used in this study were extracted from date palm tree according to the procedure reported in [6].

2.2. Chemical modification of fibres

2.2.1. Silane treatment

A 1600ml mixture of ethanol and water (50/50 v%) was poured into a reactor and heated up to 65°C. After stabilizing the temperature, NaOH and Nitric acid solutions were utilized to adjust the pH to 7. When the pH was stabilized (takes approximately 2 hours), 16 grams of fibres previously wound on a holder and fixed on mechanical stirrer were introduced into the solution. The ratio fibres/solvent was adjusted to be 1% (w/v). The polymerisation (or co-polymerisation) of MPS was carried out by adding first Cerium Ammonium Nitrate (CAN) 10-3 molL⁻¹ in the reactor and stirred for 30 minutes. Meanwhile, the mixture was purged with Nitrogen gas for 15 minutes to remove any dissolved oxygen gas. At this stage, the free-radicals are supposed to be created at the surface of the cellulose backbone and ready to react with vinyl monomers (MPS). To initiate the graft copolymerisation, 10-3 mL of MPS was added to the reactor and the nitrogen gas flow was maintained until the end of the reaction (5 hours) while stirring at medium constant rate. Fibres were then washed two times by ethanol and once by water to remove unreacted products and other impurities trapped in the fibres.

After copolymerisation of MPS with fibres, different concentrations of cellulose nano-whiskers were prepared in order to create hierarchical structure combining the micro-sized fibres and cellulose nano-whiskers. The CW were prepared according to the method described in [6].

2.2.2. Grafting of CW

The grafting process of the nano-whiskers was performed by adding three different concentrations of CW; 0.1, 0.2 and 0.4 wt% (further in the text, MPSCWC1, MPSCWC2 and MPSCWC3), respectively. First, distilled water (1600 ml) was poured in the reactor and the pH was adjusted to be between 4 and 5. When the pH was stabilised, the MPS-modified fibres were re-placed in the reactor and a specific concentration of nano-whiskers was added. Prior to sonication, a solution of NaOH (0.1 M) was added to cellulose nano-whiskers to reduce the amount of sulfonate groups and release the hydroxyl (or alcoholate) groups of CW. The CW suspensions were then sonicated for 5 minutes and added into the reactor.

The reaction was maintained at medium stirring rate at room temperature for 5 hours. Afterwards, the fibres were washed three times by distilled water and dried at 110°C for 4 hours under vacuum.

Final product was stored in desiccator to protect the fibres from dust.

2.3. Characterisation

2.3.1. Microstructure

The chemical treatments of fibres were followed by Fourier Transform Infrared spectroscopy (FTIR). The FTIR analysis was performed using a Perkin-Elmer Paragon 1000 FTIR spectrometer. The fibre

bundles were put directly into the spectrometer without using KBr. A Scanning Electron Microscopy (SEM) was used to observe the surface of fibres before and after the chemical treatments. The SEM images were obtained using a JEOL JSM 5200 SEM Microscope after the conventional vacuum coating of the fibres with gold.

2.3.2. Tensile test

Tensile tests were performed on fibre bundles using Instron 4411 machine with 500 N load cell. Tensile specimens were prepared by gluing bundles between wooden tabs using two components epoxy Araldite 2011, the final fibre length between the tabs was 100 mm. At least 5 successful tests (specimen loaded until the failure) from each fibre batch were performed. In order to obtain comparative results, all tests were run at the same strain rate of 10% min⁻¹ and at 23°C while the relative humidity was around 14%. Additionally to the 100 mm long specimens three different bundle lengths (50, 150, and 200 mm) were tested in order to determine the machine compliance which should be accounted for measurements of strain (similarly as described in standard ASTM D 3379-75 for single fibre tensile tests).

The stress was obtained by dividing the applied force by the total cross section area of fibre bundle (combined cross-sections area of 1350 single fibres). Strain was obtained from the displacement of cross-head of machine (system compliance was accounted for). Stiffness was determined from the linear part of the stress-strain curve within strain interval of 0.4 and 0.9%. Strength and strain at failure were obtained from the stress-strain curve at the point of bundle failure.

3. Results and discussion

3.1. Infrared spectroscopy

The grafting of the coupling agents was evaluated by infrared analysis to show the corresponding bands characterizing the chemical modification. The infrared spectrum of the modified and unmodified fibres is presented in Fig. 1. After the chemical treatment by MPS, a peak located at 1718 cm⁻¹ appeared. This peak corresponds to the stretching vibration of the carbonyl group of the MPS coupling agent. However, the peaks corresponding to the Si-OH and Si-O-Si resulting from the reactions are hidden by the large band between 1000 and 1100 cm⁻¹.

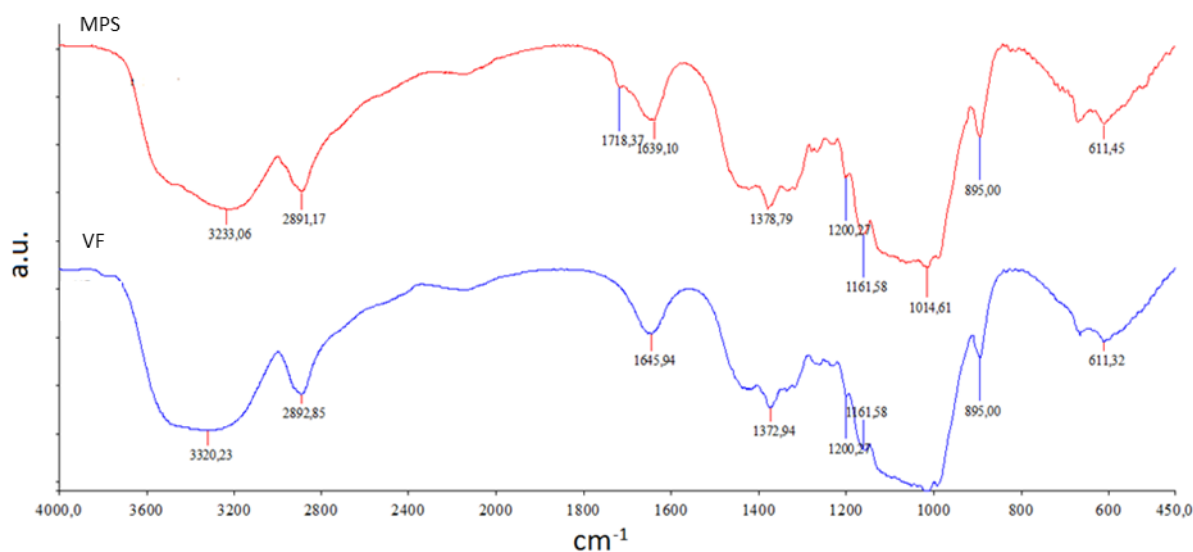


Figure.1. Infrared spectra of unmodified fibres (VF) and RCF modified by methacrylopropyl trimethoxysilane (MPS).

The SEM micrographs of treated and untreated fibres are presented in Fig. 2. The untreated fibres have smooth surface topography. However, when fibres were treated by MPS (Fig.2b), the particles are clearly visible at the surface of fibres which can be related the grafting of MPS. SEM micrographs of CW-modified fibres (for all concentrations, see Fig. 2 c,d and e) show networks of CW deposited at the surface of RCF and between single fibres. These cellulose nanofibrils were randomly oriented and formed a network by the so called percolation phenomenon.

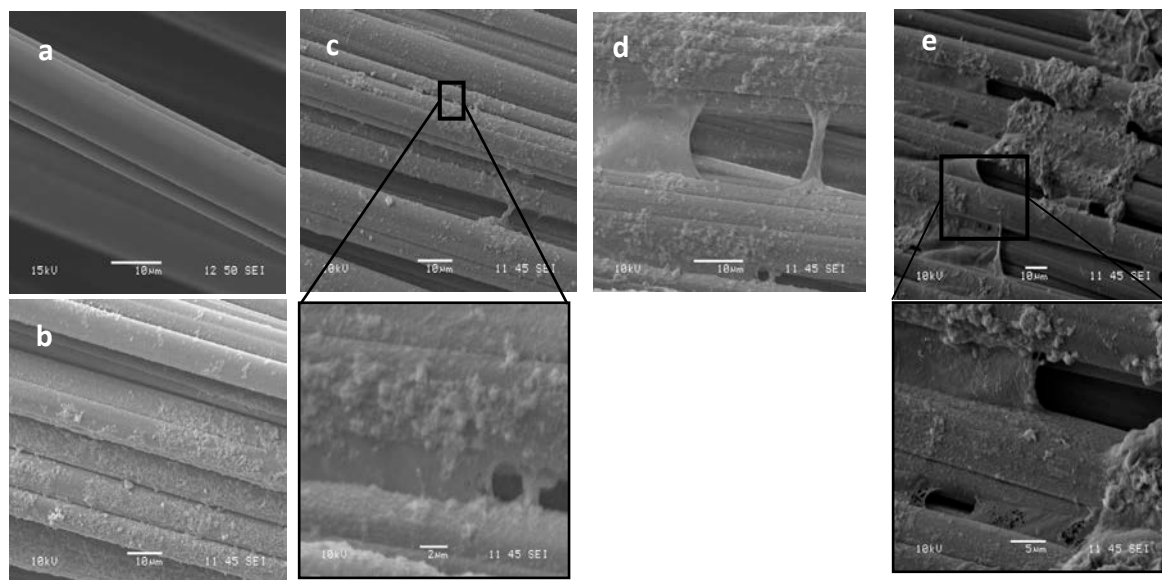


Figure 2. SEM micrographs of VF (a), MPS (b) and grafted CW 0.1w% (c), 0.2wt% (d),0.4 wt% (e).

3.2. Mechanical properties of fibres

In order to evaluate influence of treatment on fibre performance, tensile tests of fibre bundles were carried out. Typical stress-strain curves from tensile tests of fibre bundles (reference and treated) are presented in the Fig. 3 and average values for mechanical properties are summarised in Table 1.

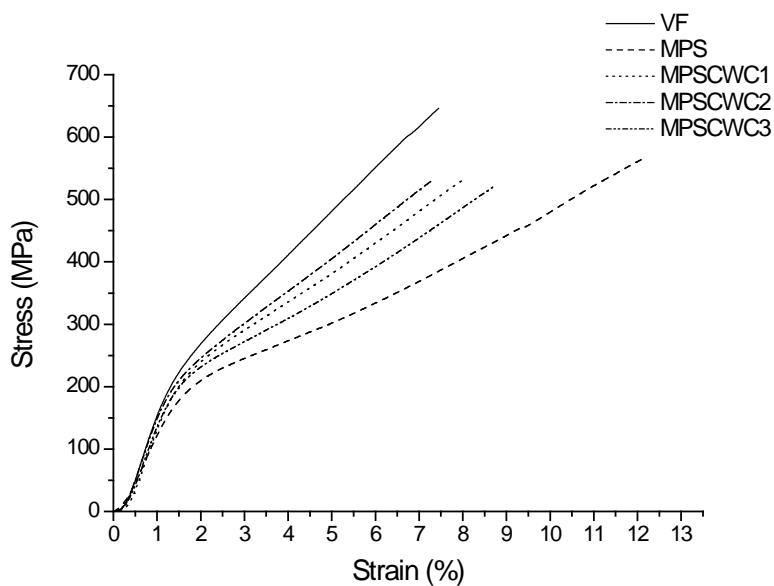


Figure 3. Typical fibre bundle stress-strain curves for fibres with different treatments.

Table 1. Summary results of mechanical properties for bundles with different fibre treatment.

	Stiffness (GPa)	Strength (MPa)	Strain (%)
VF	20.3±0.8	654±42	8.0±0.8
MPS	16.1±0.6	590±42	13.0±1
MPSCWC1	19.3±0.3	545±13	8.5±0.7
MPSCWC2	20.0±0.6	526±7	7.5±0.2
MPSCWC3	19.3±0.5	537±11	9.0±0.4

The results show that there is significant impact on stiffness of fibres only by first modification by silane, whereas grafting of cellulose nano-whiskers onto the surface of the fibre allowed recovery of initial properties. It is assumed that the treatment may have induced in the fibre the misalignment of cellulose molecular chains and crystalline cellulose phase with respect to the fibre axis.

4. Conclusions and perspectives

Cellulose nano-whiskers were successfully grafted onto the surface of Cordenka 700 Super 3 fibres using MPS as coupling agent. An environmentally friendlier method was developed to polymerise the coupling agent by creating free radicals on cellulose backbone. It was possible to retain fibre length (continuous filaments) in order to be used in composites for high performance applications. The nano-whiskers network was created and deposited on fibre surface along with poly-MPS particles as validated by SEM.

It is expected that presented fibre treatment will improve fibre/matrix adhesion and increase resistance of fibres to moisture. Consequently, obtained hierarchical reinforcement containing micro-/nano- scale cellulose can be used to design structural bio-based composites with enhanced durability.

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