MISSISSIPPI STATE UNIVERSITY

UNIVERSITY of NORTH TEXAS

Effect of Impregnated Inorganic Nanoparticles on the Properties of the Kenaf Bast Fibers

Presented by

Dr. Sheldon Q. Shi

Department of Mechanical and Energy Engineering

University of North Texas

Denton, Texas 76207, USA

Authors: Kaiwen Liang, Sheldon Q. Shi

NSF

National Science Foundation (NSF)

Grant No. CMMI 0928641

NSF CMMI: IMPREGNATED INORGANIC NANOPARTICLES AT THE NATURAL FIBER - THERMOPLASTIC POLYMER INTERFACE

Objective: *prove the hypotheses of using inorganic nanoparticle impregnation (INI) technology to improve the interfacial compatibility for natural fiber polymer composites.*

1) Void space measurement in the fiber
2) Surface characteristics of the fiber
3) Crystalline formation of the polymer
4) Molecular dynamic simulation

- DOE under funding no. 362000-060803 through Center for Advanced Vehicular System (CAVS) at Mississippi State University (Dr. Mark Horstemeyer)
- ICBR, Beijing, China (Dr. Ge Wang)
- NEFU, Harbin, China (Dr. Jun Cao)

Acknowledgement

- Dr. Jinshu Shi, former Ph.D. student
- Dr. Kaiwen Liang, Research Assistant Professor
- Dr. Jinwu Wang, former Post-doc/research scientist
- Dr. Sangyeob Lee, former Post-doc

kenaf fibers (*Hibiscus cannabinus*, L.)

Retting

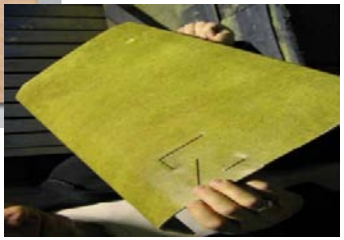
Yarns

Fiber felts

Kenaf

- ❖Fast growing
- ❖High fiber yield
- ❖High cellulose content
- ❖Good mechanical properties

Biodegradable Composites for Automobile Component Designs



Advantages

- ❖ Light weight
- ❖ Low cost
- ❖ Less reliance on petroleum resource
- ❖ Environmental friendly

Sisal

Bagasse

Bamboo

Kenaf

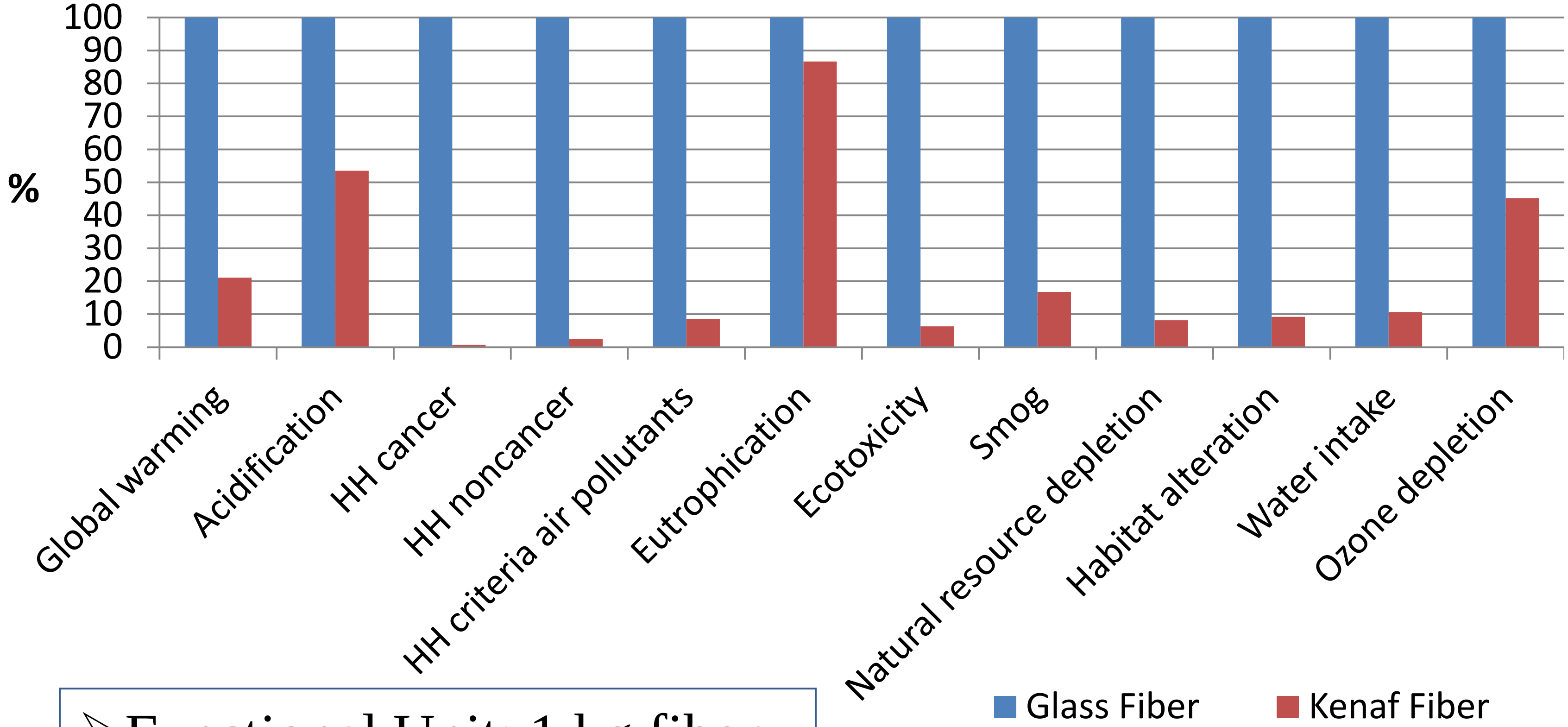
Woody Materials

Other Annual Crops

About 50% of vehicle internals are made of polymeric materials. According to the American Plastics Council, the vehicles contain an average of 250 pounds of plastics, which accounts for 12% of their weight.

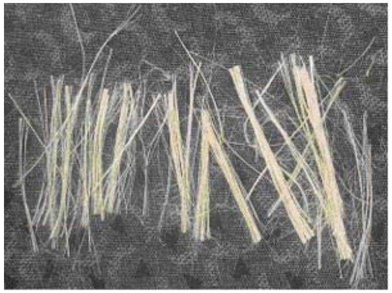
Manufacturer	Parts	Fiber Source
Chrysler	Door cladding, seatback lining, package shelves, seat bottoms	Flax, hemp, sisal, coconut
Ford	Door trim, trunk liner	Kenaf
Toyota	Door trim	Kenaf
Volvo	Dashboards, ceilings, seat filling, cargo floor tray	Hemp, jute, rapeseed

Environmental Performances: glass fiber vs. kenaf fiber



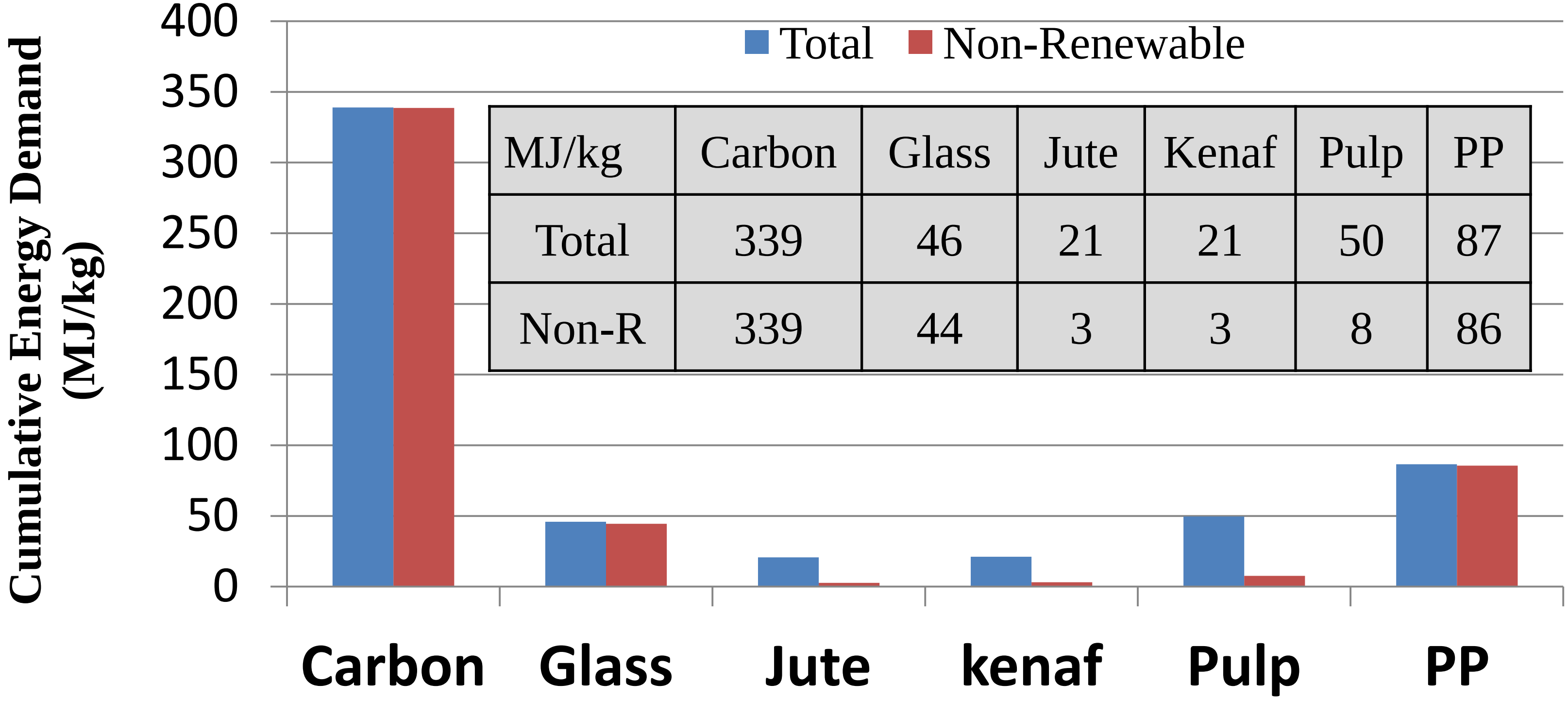
- ➢Functional Unit: 1 kg fiber,
- ➢Cradle to gate.
- ➢Data: Kenaf Fiber, India; Glass Fiber, Europe;
- ➢SigmaPro Version 7.3

Glass Fiber



Kenaf Fiber

Environmental Performance: Energy consumption

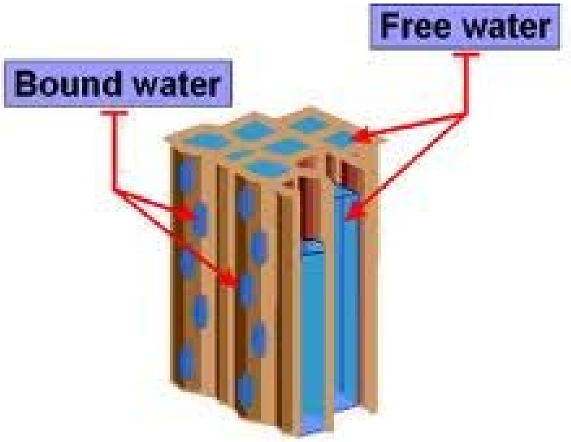


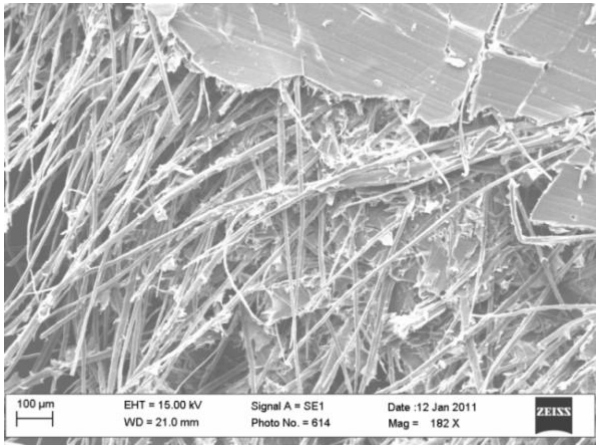
MJ/kg	Carbon	Glass	Jute	Kenaf	Pulp	PP
Total	339	46	21	21	50	87
Non-R	339	44	3	3	8	86

- Bast fibers consume less energy than other fibers
- Wood pulp and bast fibers consume less non-renewable energy
- Method to calculate Cumulative Energy Demand (CED), based on the method published by ecoinvent version 2.0 and expanded by PRé Consultants for raw materials available in the SimaPro 7 database.

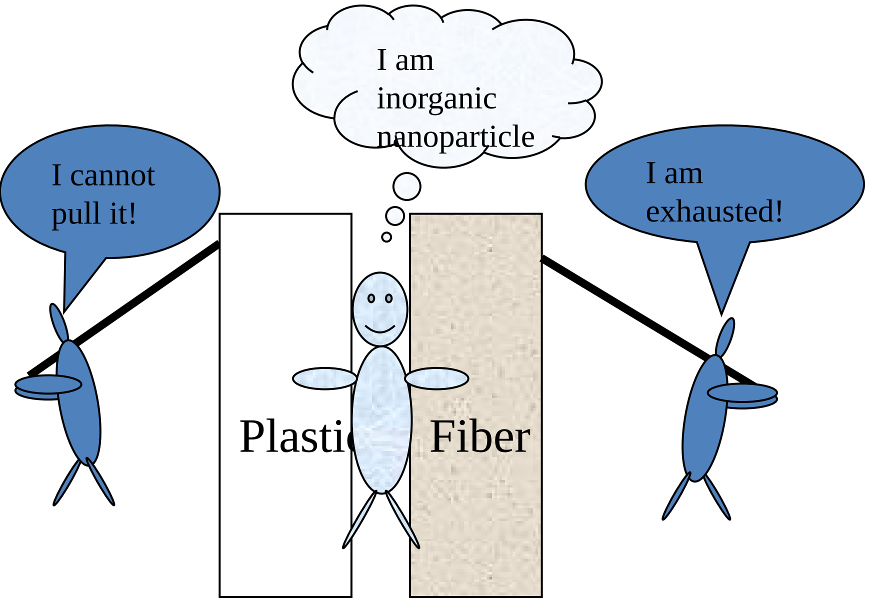
Issues: Nature Fiber Polymer Composites

- ➢Homogenization of the fiber distribution in polymer matrix
- ➢Surface compatibility between fiber and matrix (hydrophilic vs. hydrophobic)
- ➢Moisture repellence



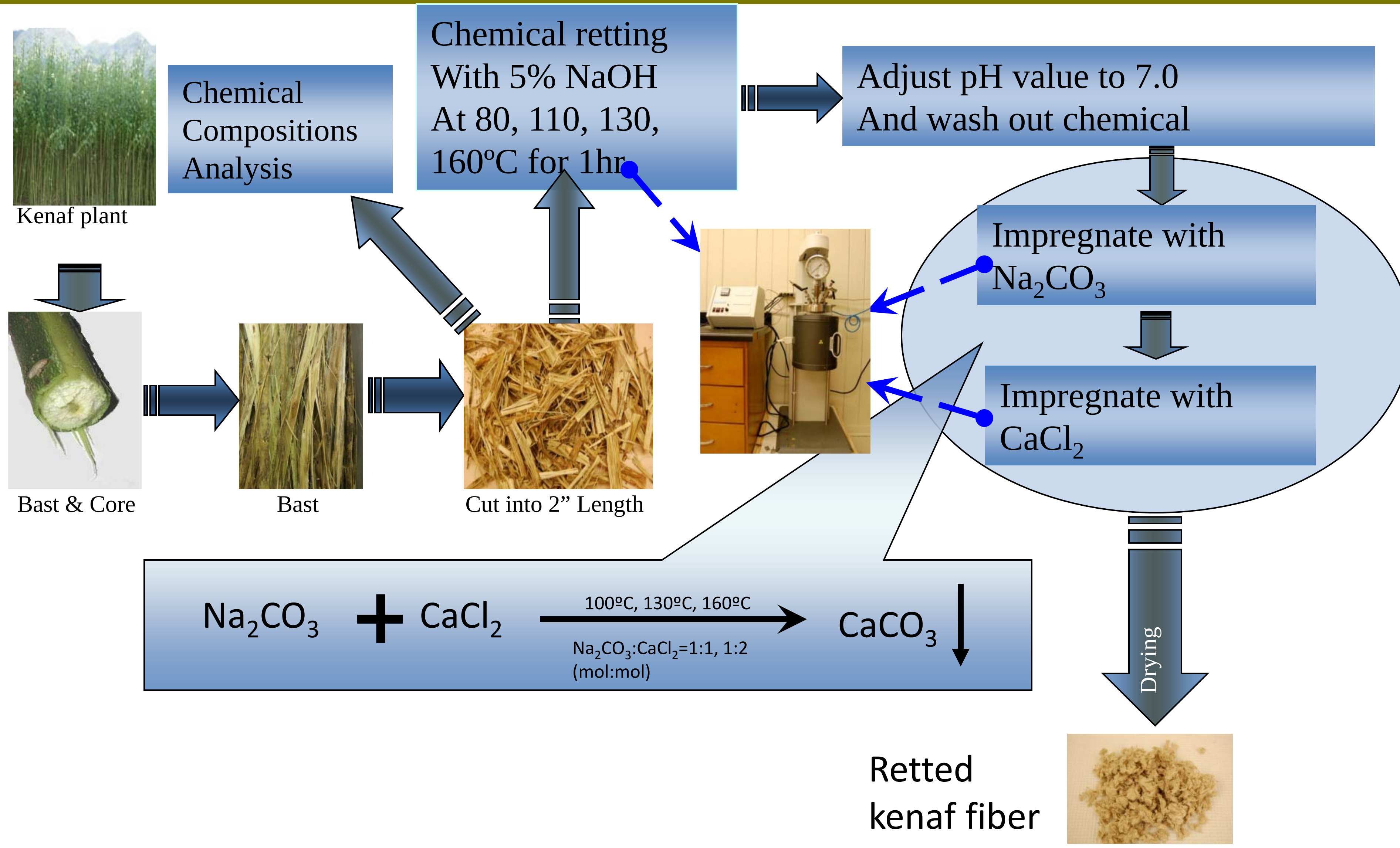


Inorganic Nanoparticle Impregnation of the Kenaf Fibers

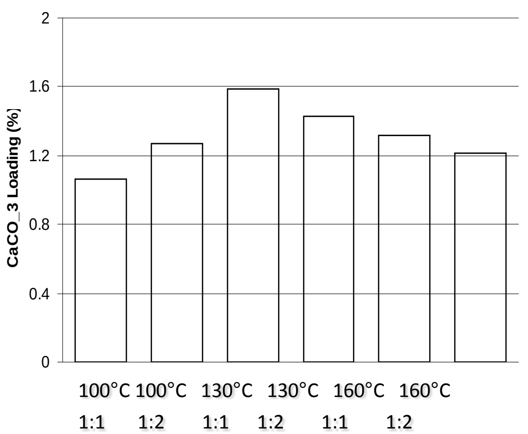


- The impregnated inorganic nanoparticles will serve as fillers in the micropores of fibers and to improve the hydrophobicity of the fiber
- The nanoparticles on the fiber surface could potentially provide the nucleation sites in the polymer matrix to improve the crystallization of the polymers, which will improve the overall properties of the composites

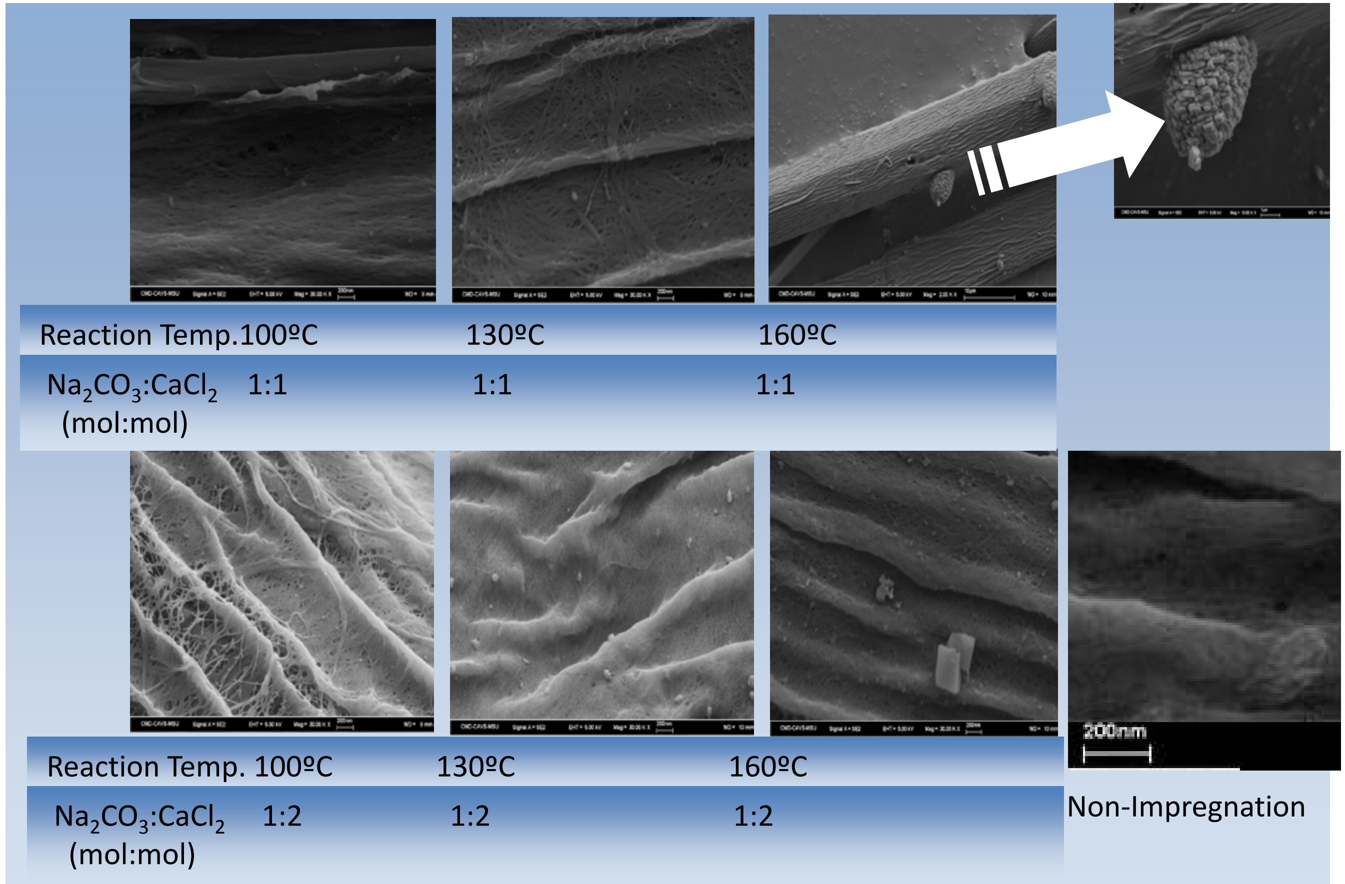
Inorganic Nanoparticle Impregnation



Morphology of Impregnated Fibers



The highest $CaCO_3$ loading was found at the condition of 130 °C .

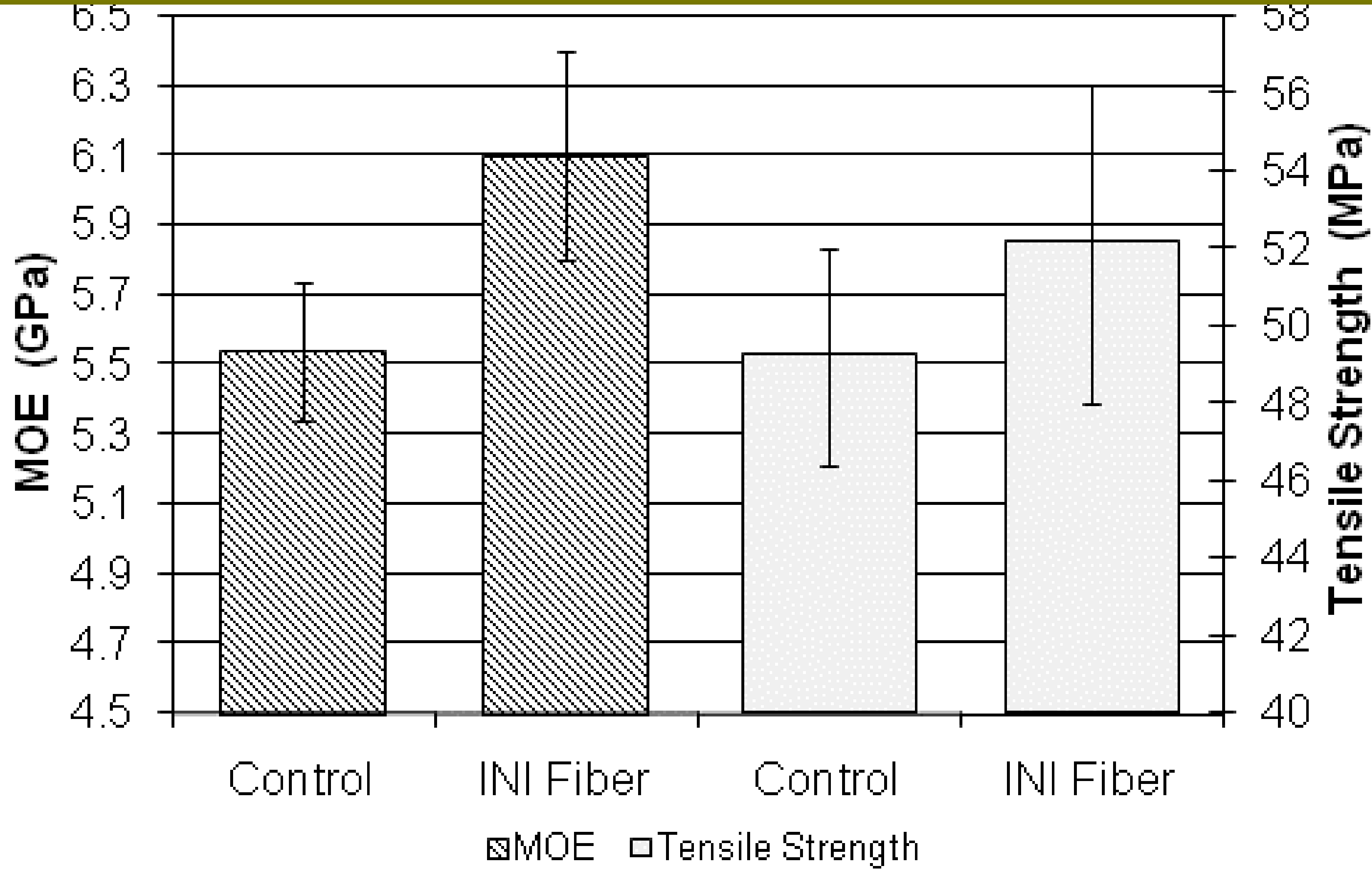


At 100ºC: Less $CaCO_3$ Nanoparticles can be found.

$CaCO_3$ nanoparticles generated from inner cell wall and grow to the fiber surface.

S.Q. Shi, S. Lee, J. Shi and M.F. Horstemeyer, 07-09

Mechanical Properties of Composites



- **MOE was improved by 8~10 %**
- **Tensile strength was improved by about 12%**

S.Q. Shi, S. Lee, J. Shi and M.F. Horstemeyer, 07-09

Objectives

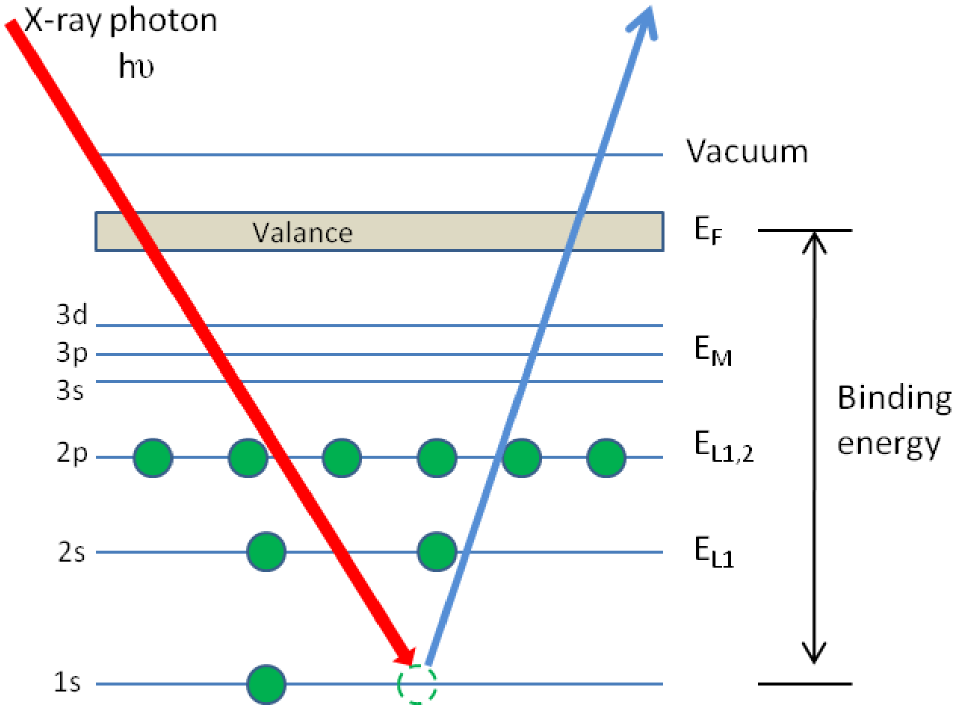
To investigate the effect of impregnated inorganic nanoparticles in the kenaf bast fibers on the fiber properties, such as chemical components, morphology, surface roughness and modulus.

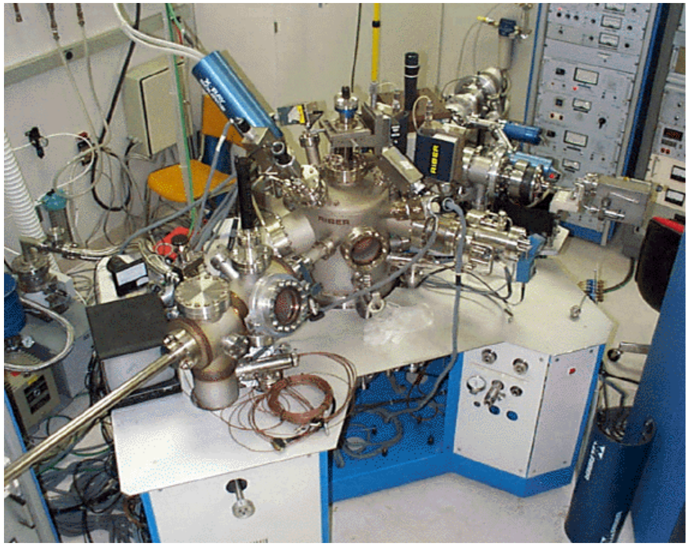
Characterization Techniques

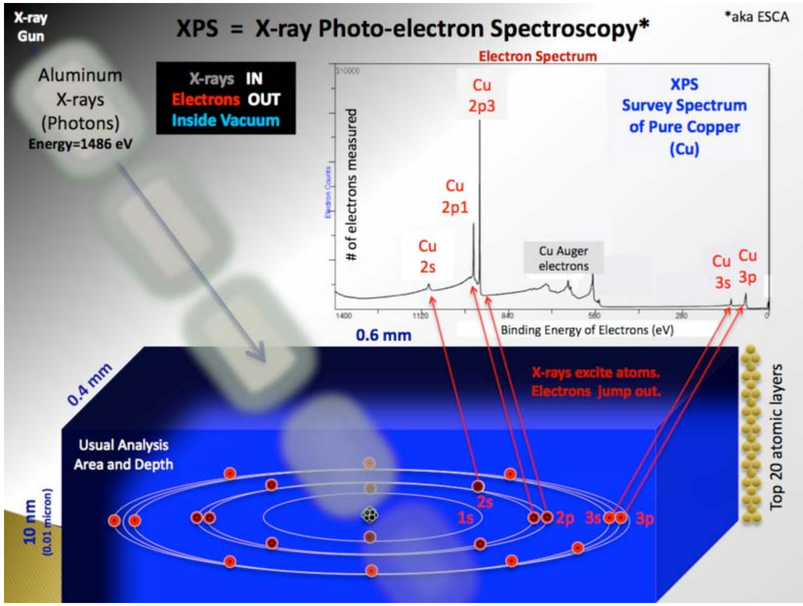
- ✓X-ray Photoelectron Spectroscopy (XPS)
- ✓Scanning Electron Microscopy (SEM)
- ✓Atomic Force Microscopy (AFM)
- ✓Contact Angle Measurement

X-ray Photoelectron Spectroscopy

Model: PHI 1600 XPS from Physical Electronics
Mg K_alpha X-Ray source was operated at 300 W and 15 kV
High resolution scans were energy referenced to C 1s CHx environment at 285 eV







$$E_{binding} = E_{photon} - (E_{kinetic} + f)$$

$E_{binding}$ = Binding energy (BE) of the electron

E_{photon} = The energy of the X-ray photons being used

$E_{kinetic}$ =The kinetic energy of the electron as measured by the instrument

f =The work function of the spectrometer (not the material).

http://wiki.utep.edu/display/~mnooraalam/X-ray+Photoelectron+Spectroscopy+%28XPS%29

http://en.wikipedia.org/wiki/File:XPS_PHYSICS.png

X-ray Photoelectron Spectroscopy (XPS)

Table. Surface Composition of Inorganic Nanoparticle Impregnated (INI) Kenaf Bast Fibers with Chemical Retted Fibers Used as Control.

Sample	Surface composition (%)				
	O	C	N	Ca	O/C
Retted fiber	27.72	64.79	7.47	0.22	0.43
Impregnated fiber	33.73	57.37	7.49	1.41	0.59

- Carbon and oxygen were the main elements detected in the fibers in the XPS survey scan. Carbon was the dominant element at the surface of these two fibers
- The content of calcium increased after the INI treatment
- The O/C ratio for the components of the surface increased from 0.43 to 0.53 (the O/C for the pure cellulose is reported as 0.8): after the INI treatment, some lignin-based component was further removed after the INI treatment.

X-ray Photoelectron Spectroscopy

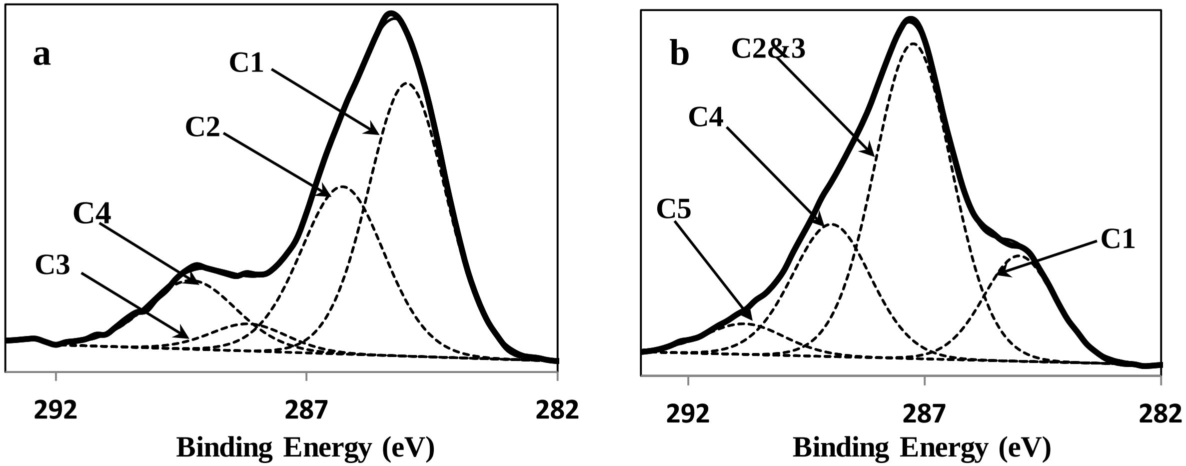


Figure. Deconvoluted C 1s XPS high resolution spectra of (a) chemical retted and (b) inorganic nanoparticle impregnated kenaf bast fibers.

Table. C 1s Component Intensities of Inorganic Nanoparticle Impregnated (INI) Kenaf Bast Fibers with Chemical Retted Fibers used as control.

	C1 (C-C, C-H)	C2 (C-O)	C3 (O-C-O)	C4 (O-C=O)	C5 CO_3^{2-}
Binding energy (eV)	285	286.5	288.1	289	290.8
Retted fiber	49.7 %	32.4 %	4.8 %	14.1 %	0
Impregnated fiber	16.7 %	54.6 %		23.3 %	5.5 %

Scanning Electron Microscopy

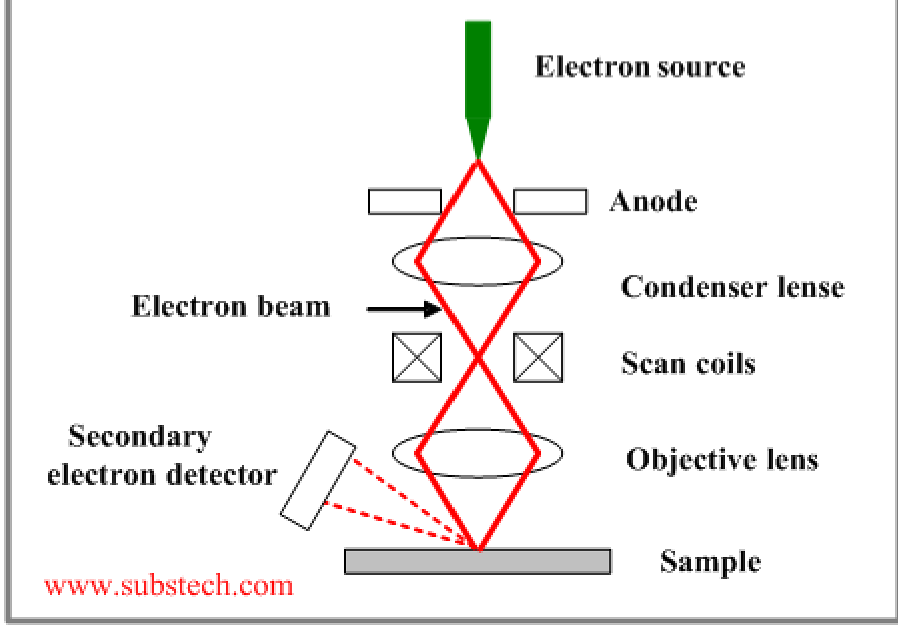
Model: JSM-6500F field emission scanning electron microscope (FESEM) (JEOL USA Inc., Peabody, MA)

An attached X-ray energy dispersive spectrometer (X-EDS) was used to obtain elemental compositions of $CaCO_3$ nanoparticles in the composites.

SEM samples were coated with gold before SEM measurements.

The electron beam spot size used in X-EDS is about 5 nm in diameter.

The resolution of SEM is about 1 – 20 nm.



Scanning Electron Microscopy

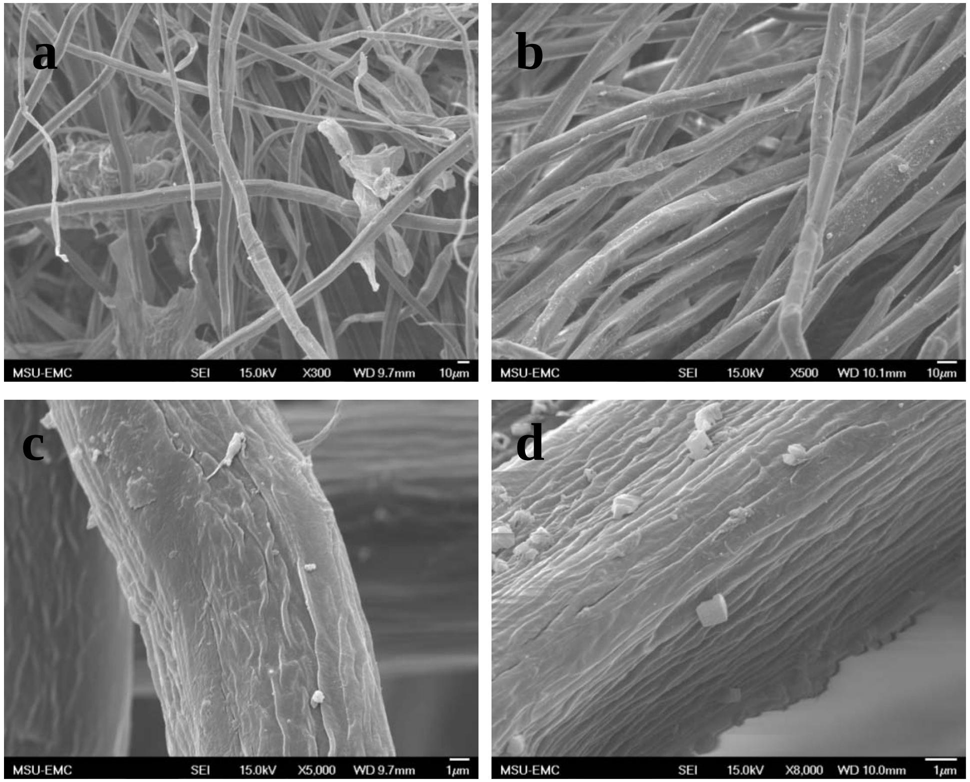


Figure. Scanning electron micrographs (SEMs) of the [a (X300) & c (x5000)] chemical retted and [b (X500) & d (x8000)] inorganic nanoparticle impregnated kenaf bast fibers.

- INI treatment further removed some residues between the fibers (Figure 2a)
- Large amount of inorganic particles at the surface of the impregnated fiber (Figure 2b) and many particles grow from inside of the fibers onto outer surface (Figure 2d)
- Different shapes (square, sphere) and sizes (80 nm - 6 um) of inorganic nanoparticles $CaCO_3$ were observed
- INI treatment increased the surface roughness

Scanning Electron Microscopy

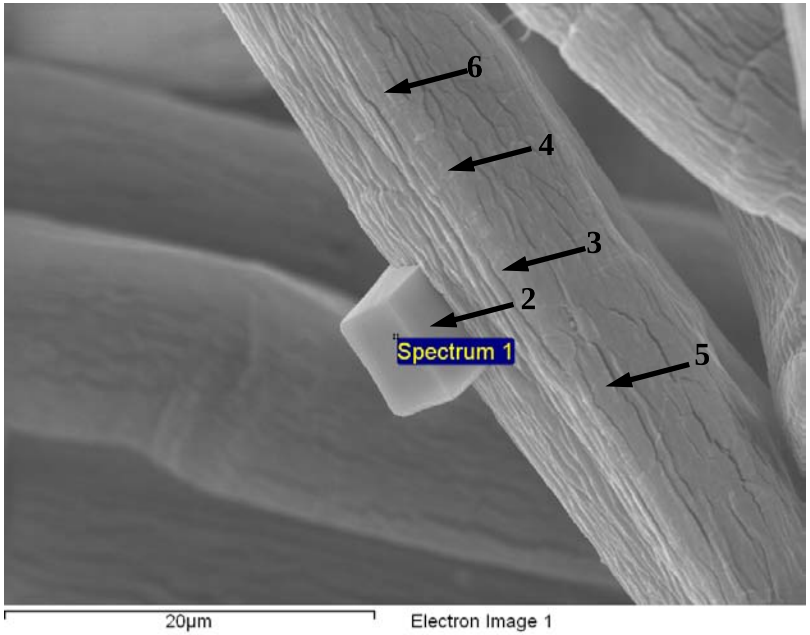


Figure 3. Scanning electron micrograph (SEM) of the inorganic nanoparticle impregnated kenaf fibers at 6 different locations.

Table 3. X-ray EDS Spectra Data of Inorganic Nanoparticle Impregnated (INI) Kenaf Bast Fibers

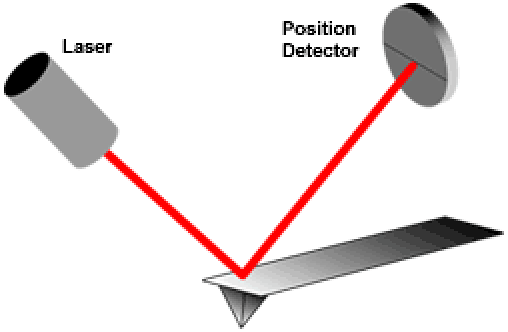
spectrum	element	weight %	atomic %	$CaCO_3$ weight %
1	O	36.81	33.72	
	C	42.50	51.86	
	N	10.02	10.48	
	Ca	10.52	3.85	26.27
2	O	56.57	62.48	
	C	17.74	26.11	
	N			
	Ca	**25.41**	**11.21**	63.46
3	O	34.07	29.50	
	C	51.33	59.22	
	N	9.56	9.46	
	Ca	4.65	1.61	11.61
4	O	25.46	20.95	
	C	62.26	68.24	
	N	11.09	10.42	
	Ca	1.19	0.39	2.97
5	O	26.08	21.87	
	C	58.58	65.42	
	N	11.83	11.33	
	Ca	2.28	0.76	5.69
6	O	26.39	22.18	
	C	58.43	65.41	
	N	11.61	11.15	
	Ca	3.26	1.09	8.14

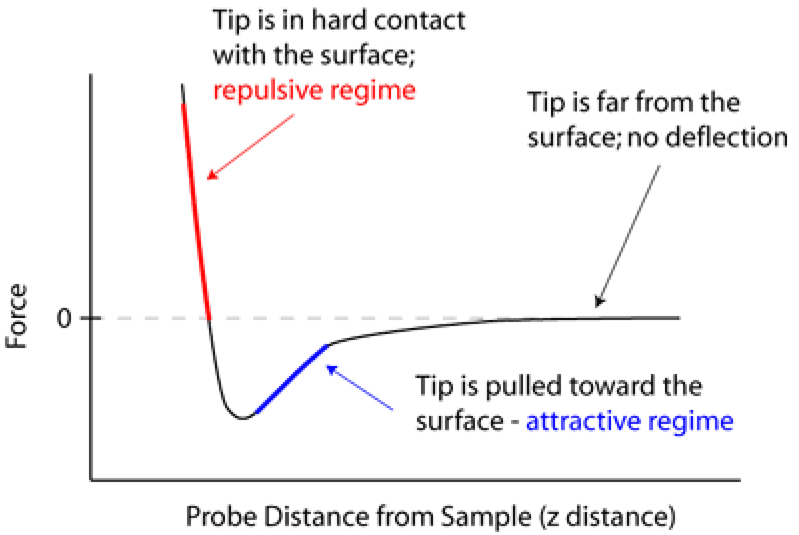
Atomic Force Microscopy

Model: Bruker Dimension Icon

Mode: PeakForce QNM (Quantitative NanoMechanics) - an extension of Peak Force Tapping^{TM} mode

Tip: Tap525A, P/N MPP-13120-10





http://www.nanoscience.com/education/afm.html

Atomic Force Microscopy

Table. Root Mean Square Surface Roughness, Image Mean Average Adhesion and DMT Young's modulus of Inorganic Nanoparticle Impregnated (INI) Kenaf Bast Fibers with Chemical Retted Fibers Used as Control.

Sample	Root mean square surface roughness nm	Image mean average	
		Adhesion nN	DMT modulus GPa
Retted fiber	155	387	27
Impregnated fiber	164	157	120

- Impregnated fiber presented a higher surface roughness (improved surface area for adhesion)
- Impregnated fiber presented a higher modulus
- Impregnated inorganic particles decreased adhesion force between the fiber and the hydrophilic silicon nitride AFM tips, from which the present of CaCO3 nanoparticles at the fiber surface somewhat decreased the hydrophilic nature of the fiber

Atomic Force Microscopy

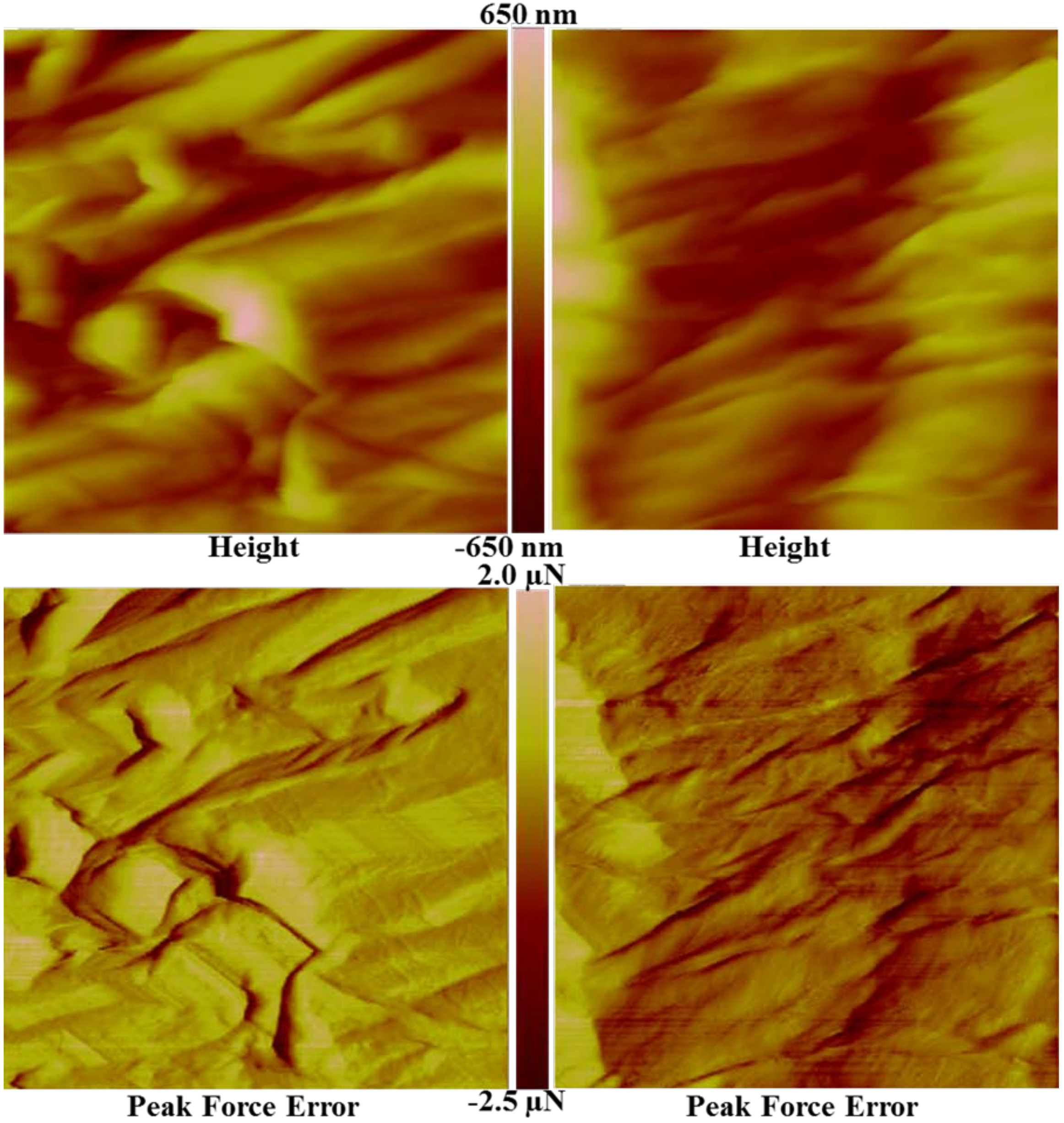


Figure 4. AFM height and peak force error images (25 μm^2) of (a & c) chemical retted and (b & d) inorganic nanoparticle impregnated kenaf fibers.

- The RMS surface roughness of the chemical retted and inorganic nanoparticle impregnated kenaf fibers were 155 and 164 nm, respectively.
- The roughness of the impregnated fiber was higher than that of retted fiber. This may be due to a large amount of nano and micro size $CaCO_3$ inorganic particles generated at the surface of the impregnated fiber.
- The increased fiber surface roughness would be favorable for the improvement of fiber surface specific area, interfiber friction and bonding.

Atomic Force Microscopy

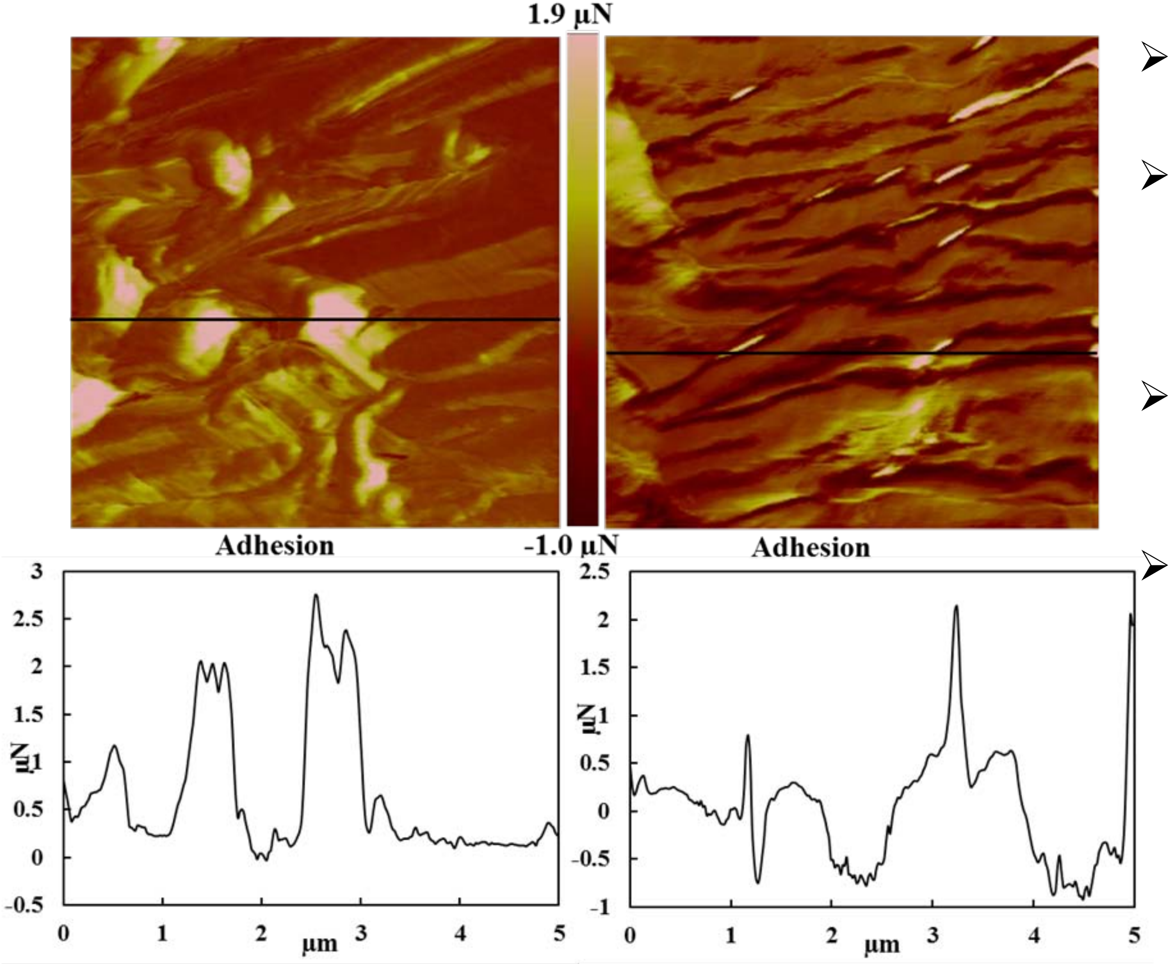


Figure 5. AFM adhesion images (25 µm^2) of (a) chemical retted and (b) inorganic nanoparticle impregnated kenaf fibers. Numerical values in each image across the sections indicated by the line in (a) and (b) are given below the images.

- Bright area corresponds to the higher adhesion forces
- The image mean average adhesion of the chemical retted and inorganic nanoparticle impregnated kenaf fibers were 387 and 157 nN, respectively.
- The adhesion force between the fiber and AFM tip decreased after inorganic nanoparticle impregnation treatment.
- The adhesion of the impregnated fiber decreased by 146 %. Thus the presence of $CaCO_3$ nanoparticles at the fiber surface decreased the affinity between the fiber and hydrophilic silicon nitride AFM tip. This indicated that the presence of $CaCO_3$ inorganic nanoparticles at the fiber surface somewhat decreased the hydrophilic nature of the fiber.

Atomic Force Microscopy

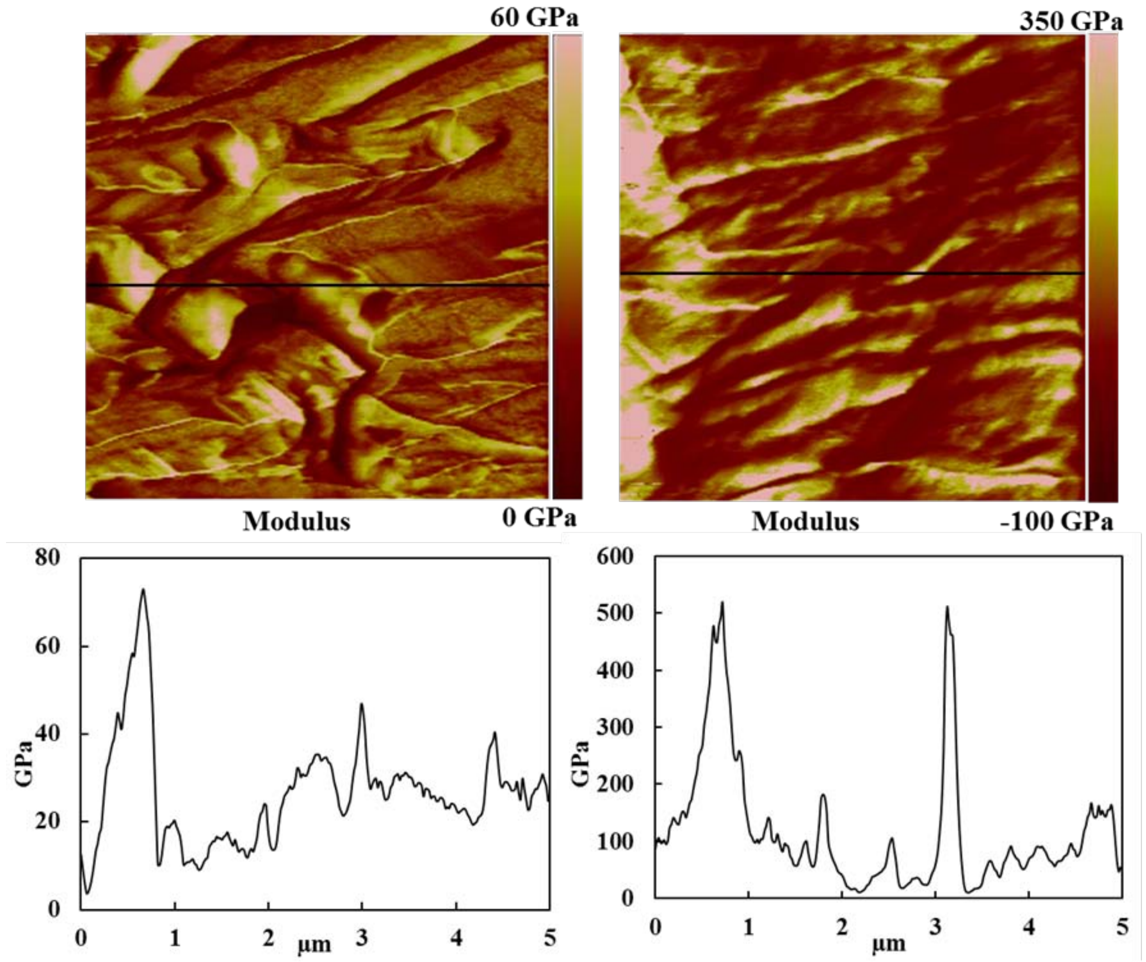
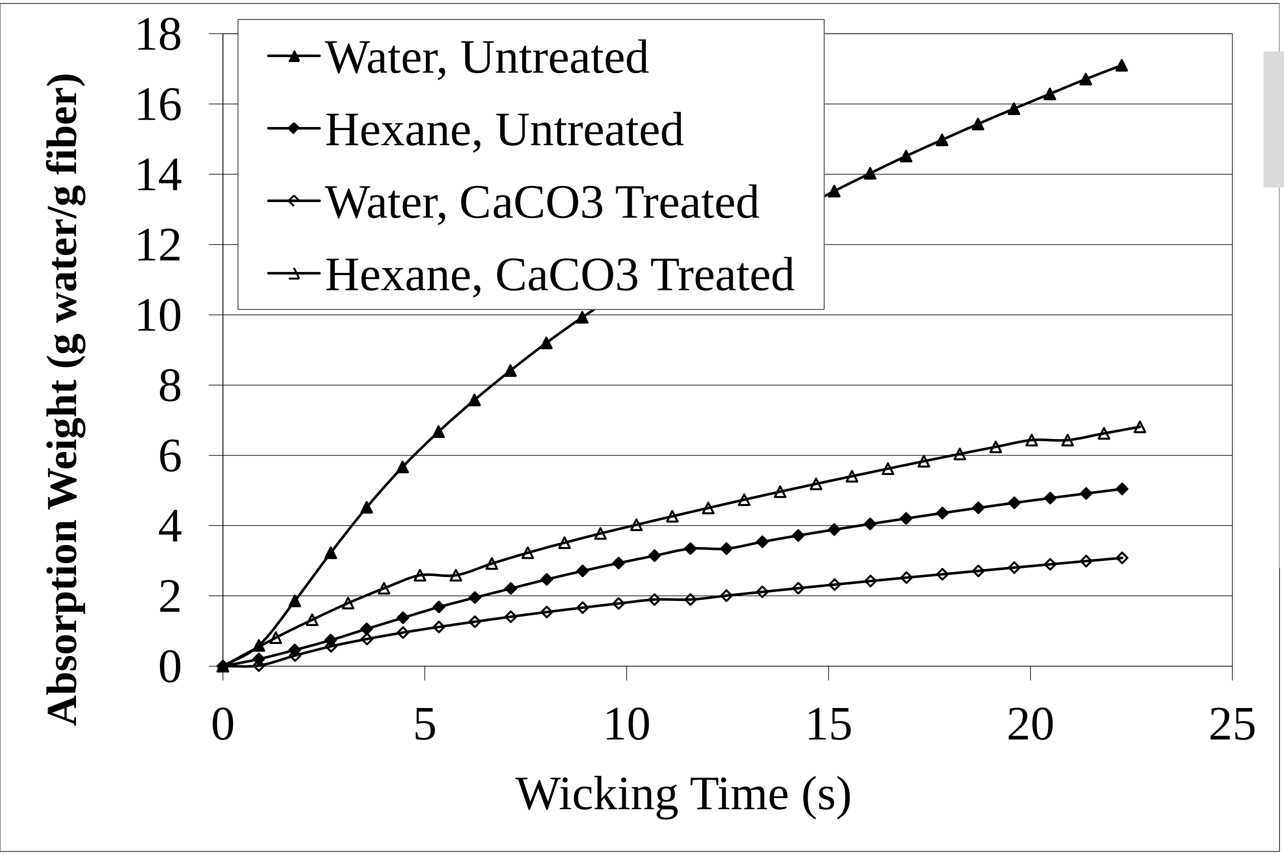
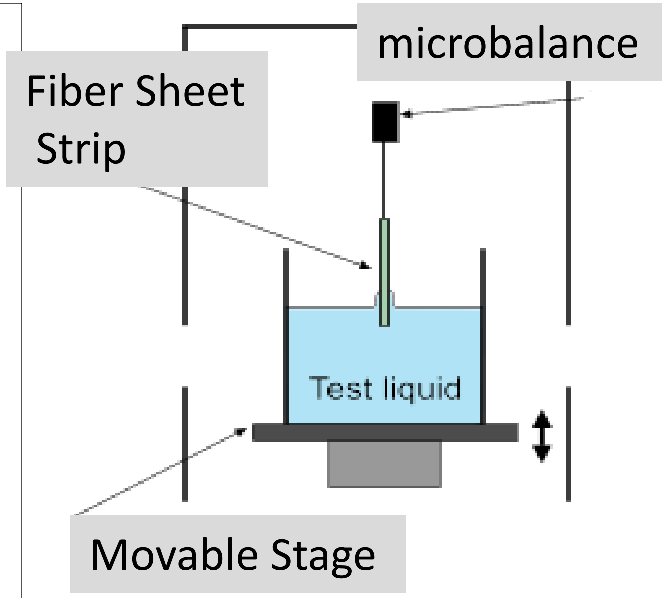


Figure 6. AFM modulus images (25 µm^2) of (a) chemical retted and (b) inorganic nanoparticle impregnated kenaf fibers. Numerical values in each image across the sections indicated by the line in (a) and (b) are given below the images.

- The image mean average modulus of the chemical retted and inorganic nanoparticle impregnated kenaf fibers were 27 and 120 GPa, respectively.
- The modulus of fiber increased 344 % by incorporating $CaCO_3$ inorganic nanoparticles into the fiber.
- Removal lignin-based components from retted fiber, the successful incorporation of inorganic nanoparticles $CaCO_3$ into the cell wall of the fiber during the inorganic nanoparticle impregnation treatment, and synergistic effect of the fiber and $CaCO_3$ inorganic nanoparticles contributed to the dramatic increase in the modulus of the impregnated fiber.

Contact Angles with Water





	θ (°)
Untreated fiber sheet	30
INI Treated Fiber sheet	55

The INI treatment decreased fiber water affinity

Conclusions

- C/O ratio on the fiber surface was affected by the INI treatment.
- Various $CaCO_3$ particle shapes was observed on the impregnated fiber surface.
- Heterogeneous $CaCO_3$ particle size distributed was observed on the impregnated fiber surface.
- The presence of $CaCO_3$ inorganic nanoparticles at the fiber surface increased root mean square (RMS) surface roughness by 5.8 %.
- INI treatment decreased the hydrophilic nature of the fiber as evidenced by 146 % decrease in adhesion force between the fiber and the hydrophilic ATM tip.
- The successful incorporation of inorganic nanoparticles $CaCO_3$ into the cell wall of the fiber during the inorganic nanoparticle impregnation treatment dramatically increased the Young's modulus of the fiber by 344 %.

Contact:

Dr. Sheldon Q. Shi
University of North Texas

Sheldon.shi@unt.edu
940-369-5930