Characterization of New Natural Cellulosic Fabric *Grewia tilifolia*

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ABSTRACT

The new natural fabric *Grewia tiliflia* was extracted from its tree.This uniaxial fabric was analyzed by Chemical, Fourier transform infrared spectroscopy, Thermogravimetric analysis, X-ray diffraction, Scanning electron microscopy and Polarized optical microscopic techniques. The effect of alkali-treatment on the mechanical, morphological, and thermal properties of the fabric was examined. The tensile strength, modulus, and the thermal stability of the fabric were found to improve on alkali-treatment. From the mechanical and thermal degradation studies of this fabric, it was concluded that the fabric can be used as reinforcement in the preparation of green composites and for other high-value fabric applications.

Keywords: *Grewia tilifolia* fabric; biofabric materials; Infrared spectroscopy; X- ray diffraction; Mechanical properties, Thermal properties

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1. Introduction

The use of polymers in general and polymer composites in particular is increasing ever day due to their unique properties and as a consequence, the environmental problems posed by them are also simultaneously increasing. In order to address this problem, efforts are being made to make green composites that are environment friendly. In this direction, some green composites were developed using some natural fibres/fabrics (Avérous, & LeDigabel, 2006; Jayaramudu, Guduri, & Rajulu, 2009a; Reddy, & Yang, 2007; Varada Rajulu et al., 2003; Varada Rajulu, Venu Nadhan, & Rama Devi, 2006; Uma Maheswari, Guduri, & Varada Rajulu, 2008). The natural fibers and fabrics have certain advantages over the conventional glass gibers such as environmental friendly nature, low cost, low density, non-toxicity, lower abrasion of equipment during processing and recycling. The properties of the reinforcement and the matrix and the strength of their interfacial bonding determine the quality of a composite. So, for developing green composites, one must have an idea about the properties of the reinforcement also. The properties of some natural fibres/fabrics are reported in the literature (Prasad, Pavithram, & Rohatgi, 1983; Jayaramudu, Guduri, & Varada Rajulu, 2009b; Li, Tabil, & Panigrahi, 2007; Li et al., 2004). In the present work, we identified and extracted a new natural fabric *Grewia tilifolia* from the tree and studied its properties using chemical analysis, Fourier transform infrared spectroscopy (FTIR), Thermogravimetric analysis (TGA), X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Polarized optical microscopic (POM) techniques. We also examined the effect of alkali-treatment on the properties of this fabric. The selection of

the fabric for the study is mainly due to its uniaxial nature of the fabrics. Usually it is rare to observe uniaxial orientation in natural fabrics.

2. Materials and methods

2.1. Materials

The fabric exracted from the branches of the tree *Grewia tilifolia*, Sodium Hydroxide pellets purified(Merk specialities private limited, Mumbai, India) Benzene, Sodium Chlorite, Acetic acid, Sodium bisulphate and Ethnol S.d.fine-Chem Limited, Mumbai, India were the materials used in the present work.

2.2. Extraction of the fabric from the tree

The fabric samples of *Grewia tilifolia* were extracted from the bark of the tree. They were kept in water for a week to remove the dirt and other foreign material. They were then thoroughly washed and dried in the sun for a week. Some of the samples were treated with 5% NaOH solution (by weight) at a maximum temperature of 30 ºC and a hold time of 45 min and after treatment, the fabrics were thoroughly washed and then dried at 80 ºC for 24 h and stored. The samples were also redried before analysis.

2.3. FT-IR Spectral Analysis

Some of the samples were cryogenically cooled and powdered. This powder was diluted to 1% using KBr and pellets were prepared employing a hydraulic press. The FT-IR spectra of the untreated and the alkali-treated samples were recorded in the 4000 – 500 cm^{-1} region on a Perkin Elmer 16PC FT-IR instrument with 32 scans in each case at a resolution of 4 cm^{-1}.

2.4. Chemical Analysis

The *Grewia tilifolia* fabrics (untreated and alkali-treated) were preconditioned before cellulose extraction took place. The fabrics were washed with distilled water several times and dried in an oven at 80 °C for 24 h. Then they were chopped to an approximate length of 5–10 mm. Finally a de-waxing step was carried out: boiling in a mixture toluene/ethanol (2:1 volume/volume) in a sachet for 6 h. The de-waxed fabrics were then filtered, washed with ethanol for 30 min and dried.

In order to find out the lignin content, the de-waxed preweighed samples were treated with 0.7 w/v % sodium chlorite at pH 4 maintaining a fabric to liquor ratio of 1:50 and boiling for 2h. Later, it was treated with sodium bisulphate solution (5 w/v %). In this way, the lignin was removed so that the lignin and holocellulose contents were calculated. From the isolated holocellulose, hemi-cellulose was removed by treating it with 17.5 w/v % aq.NaOH solution. The insoluble α-cellulose was filtered, washed thoroughly with distilled water and dried at 60 ºC in a vacuum oven. In this way, the components of the fabric were estimated. This procedure was adopted from the earlier works (Chattopadhyay, & Sarkar, 1946; Sarkar, Mazumdar, & Pal, 1948). In each case, five samples were analyzed and the average values are reported.

2.5. Thermogravimetric Analysis

The thermograms of the untreated and the alkali-treated fabrics were recorded on a Perkin Elmer TGA-7 instrument in nitrogen atmosphere at a heating rate of 10 ºC/min.

2.6. X-Ray Analysis

The X-ray diffractograms of the untreated and the alkali-treated fabrics were recorded on a Rigaku Dmax 2500 diffractometer (Tokyo, Japan).The system has a rotating anode

generator with a copper target and a wide-angle powder goniometer. The generator was operated at 40 kV and 150 mA. All the experiments were conducted in the reflection mode at a scan speed of 4º /min in steps of 0.05º. All samples were scanned in 2θ range varying from 5º to 50º. The crystallinity index (I_c) of the fabric was calculated using the formula (Mwaikambo, & Ansell, 2002).

$$I_c = \frac{(I_{(002)} - I_{(am)})}{I_{(002)}} \times 100 \quad \ldots\ldots\ldots \quad (1)$$

Where $I_{(002)}$ ($2\theta=23.71^o$) represents the intensity of crystalline peak while $I_{(am)}$ ($2\theta=14.28^o$) denotes intensity of the amorphous peak in the diffractograms.

2.7. Microscopic Analysis

The scanning electron micrographs of the untreated and the alkali-treated fabrics were recorded on a JOEL JSM 820 microscope (Akishima, Japan). The micrographs of the cross section of the fibres were also recorded. The samples were coated with gold and their micrographs were recorded. The optical micrographs were recorded using an Olympus Bx 50 Polarized optical microscope.

2.8. Tensile properties

The tensile properties such as maximum stress, Young's modulus, and % elongation at break were determined using an INSTRON 3369 Universal Testing Machine(Norwood, Massachusetts, U.S.A) at a crosshead speed of 3mm/min maintaining a gauge length of 50mm. In each case, ten samples were tested and the average values are reported.

3. Results and discussion

The tree *Grewia tilifolia* from which the fabric was extracted belongs to the tiliaceae family. The scanning electron micrograms of the untreated and the alkali-treated fabrics are shown in Fig. 1 (a), and (b) and Fig. 1 (c), and (d) respectively at different magnifications. From these micrographs, it is evident that the fabric is made up of uniaxial roughly parallel fibers. Further, at higher magnification, the void regions present in the fabric are visible. The micrographs also reveal a white layer on the untreated fabric which may be the hemicellulose component. Upon alkali-treatment, the white layer content is found to decrease. This is attributed to the reduction in the hemicellulose content on alkali-treatment. Further, in the case of the alkali-treated fabric, the common parenchyma cells (Van Soest, 1963; Rowland, & Roberts, 1994) are clearly visible at higher magnification.

The Polarized optical micrographs of the fabric before and after alkali-treatment are shown in Fig. 2. It is evident from the figure that the intensity of the pattern of the micrograms increased on alkali-treatment. This further indicates the elimination of amorphous hemicellulose layer on alkali-treatment as a result the birefringence increases (Guduri, Rajulu, & Luyt, 2006). The FT-IR spectra of the untreated and the alkali-treated fabric are presented in Figure 3. The band positions and possible assignments are given in Table 1. From Figure 3, it can be observed that there are well-defined bands around 3400, 2900, 1630, 1300 and 1030 cm^{-1} present in the spectra. Further, there is another band at around 1738 cm^{-1} corresponding to the hemicellulose content. On alkali-treatment, the intensity of this band is found to decrease, indicating a reduction in the hemicellulose content (Pandey, 1999). From Table 1, it can be seen that the bands around

3400 cm^{-1} and 2930 cm^{-1} correspond to α-cellulose whereas the remaining bands correspond to lignin. Further, for the alkali-treated fabrics, the intensity of the bands corresponding to α-cellulose increased.

The chemical analysis of the untreated and the alkali-treated fabrics is presented in Table 2. From this table, it is evident that on alkali-treatment, the percentage of α-cellulose increased whereas that of hemicellulose decreased. This is in conformity with the observations made in the FT-IR analysis.

The X-ray diffractograms of untreated and alkali- treated *Grewia tilifolia* fabric can be seen in Fig. 4. It can be observed that the major crystalline peak on each pattern occurred at around $2\theta = 23.71^{o}$, which represents the cellulose crystallographic plane (002). The X-ray diffractograms show that the intensity of the (002) crystallographic plane was increased significantly on alkali treatment of the *Grewia tilifolia* fabric. The crystallinity index of the treated and untreated *Grewia tilifolia* fabric samples was calculated using Eq. (1) which is described in the experimental section and the results are summarized in Table 3. It can be seen in Table 3 that the crystallinity index of the *Grewia tilifolia* fabric increased with alkali- treatment. This is thought to be due to better packing and stress relaxation of cellulose chains as a result of the removal of amorphous constituents and pectin from the fabric (Ouajai, & Shanks, 2005; Roncero et al., 2005; Tserki et al., 2005). The increase in crystallinity by alkali- treatment might be the main contributing factor for the increase in fabric tensile properties as seen in Table 4.

Other well-defined peak present on the X-ray diffractograms is at $2\theta = 14.28^{o}$, and this reflection corresponds to the (110) crystallographic plane. When the crystalline cellulose content is high, this peak is more pronounced, and when the fabric contains

large amounts of amorphous material (such as lignin, hemicelluloses, pectins and amorphous cellulose), this peak is smeared and appears with lower intensity (Mwaikambo, & Ansell, 2002). It can be seen in Fig. 4 that the peak at 14.28^{o} is more defined for the alkali- treated *Grewia tilifolia* fabric, therefore suggesting that the alkali-treatment removed some of the amorphous materials from the fabric.

The primary thermograms of the untreated and the alkali-treated fabrics are presented in Fig. 5. From these thermograms, it is evident that the thermal stability of the alkali-treated fabric is greater than that of the untreated fabric. The decrease in the amorphous hemicellulose content of the fabric on alkali-treatment may be the reason for this behavior (Doyle, 1985).

The tensile properties of the untreated and the alkali-treated fabric are presented in Table 4. It is evident that the maximum stress and the modulus of the alkali-treated fabric are higher than those of the untreated fabric. The decrease in the amorphous hemicellulose content on alkali-treatment might have increased the tensile properties. The chemical composition, moisture content, and the tensile properties of the fabric Grewia Tilifolia are compared with those of some reinforcing natural fibers and the values are presented in Table 5. Of these, jute, flax, hemp, ramie, sisal, and coir are fibers whereas *Hildegardia populifolia* and *Grewia Tilifolia* exist in fabric form. The chemical composition of fabric is compared with that of *Hildegardia*. As both the natural fabrics listed in the table have many void regions, their real area may be lower than the values used in the calculation of tensile strength and modulus. As such, the actual tensile properties may be higher for the fabric under study than calculated. The elongation at break for the fabric under consideration is 2% which is comparable with that of all the

fibers listed in the Table except coir. This indicates that the fabric is rigid. The moisture content of the fabric Grewia Tilifolia is found to be only 2.3% and such low moisture content is expected to facilitate good bonding of the fabric with the matrix in the preparation of composites and other high-value fabric applications. Further, the uniaxial nature of the fibers in the fabric can be exploited to control the mechanical propertied of the composites with proper orientation towards stress direction (Bledzki, Reihmane, & Gassan, 1996; Varada Rajulu et al., 2003). As the fabric of the *Grewia tilifolia* has sufficient modulus and thermal stability, it can be used as reinforcement in the development of green composites and for other high-value fabric applications.

4. Conclusions

The properties of the uniaxial natural fabric *Grewia tilifolia* were studied. The SEM analysis showed the morphology of the fabric as containing uniaxial roughly parallel fibers. The FT-IR and chemical analyses indicated a decrease in the hemicellulose content on alkali-treatment. The XRD and POM analyses revealed an increase in the crystallinity of the fabric on alkali-treatment. The thermal stability and tensile properties of this fabric increased on alkali-treatment. Because of its higher modulus, the alkali-treated natural fabric can be utilized as reinforcement in the making of green composites and for other high-value fabrics applications. .

Acknowledgements

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Captions for the figures

Fig.1. Scanning electron micrograms of *Grewia Tilifolia* fabric – (*a*) and (b) for untreated and (c)and (d) for 5% NaOH -treated fabrics at different magnifications

Fig.2. Polarized optical micrograms of (a) untreated and (b) 5% NaOH -treated *Grewia Tilifolia* fabrics.

Fig.3. FT-IR spectra of untreated and 5% NaOH -treated *Grewia Tilifolia* fabrics

Fig.4.X-ray diffractograms of untreated and 5% NaOH -treated *Grewia Tilifolia* fabric.

Fig.5. Thermograms of untreated and 5% NaOH -treated *Grewia Tilifolia* fabrics.

Figure 1(a)

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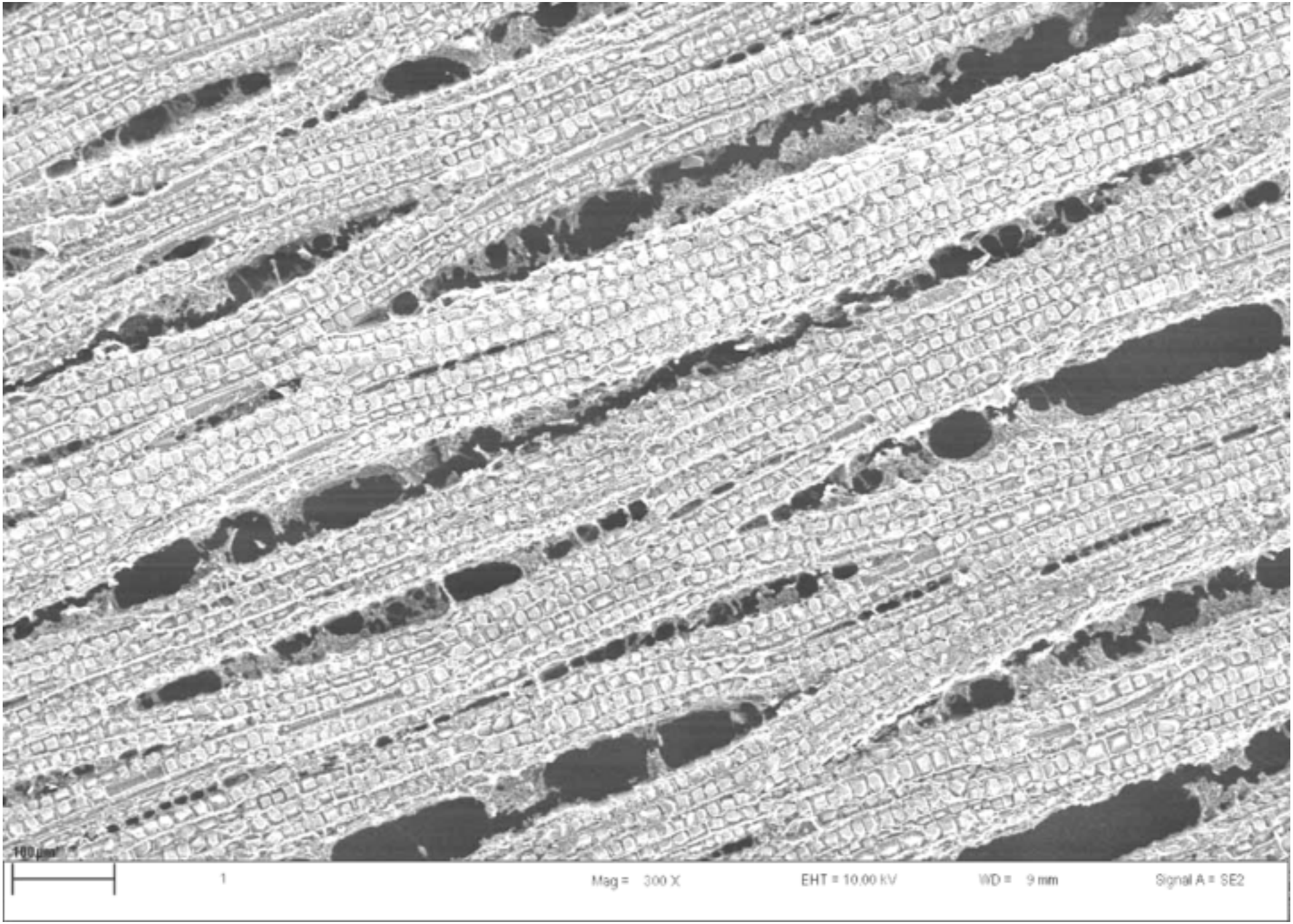

Figure 1(b)

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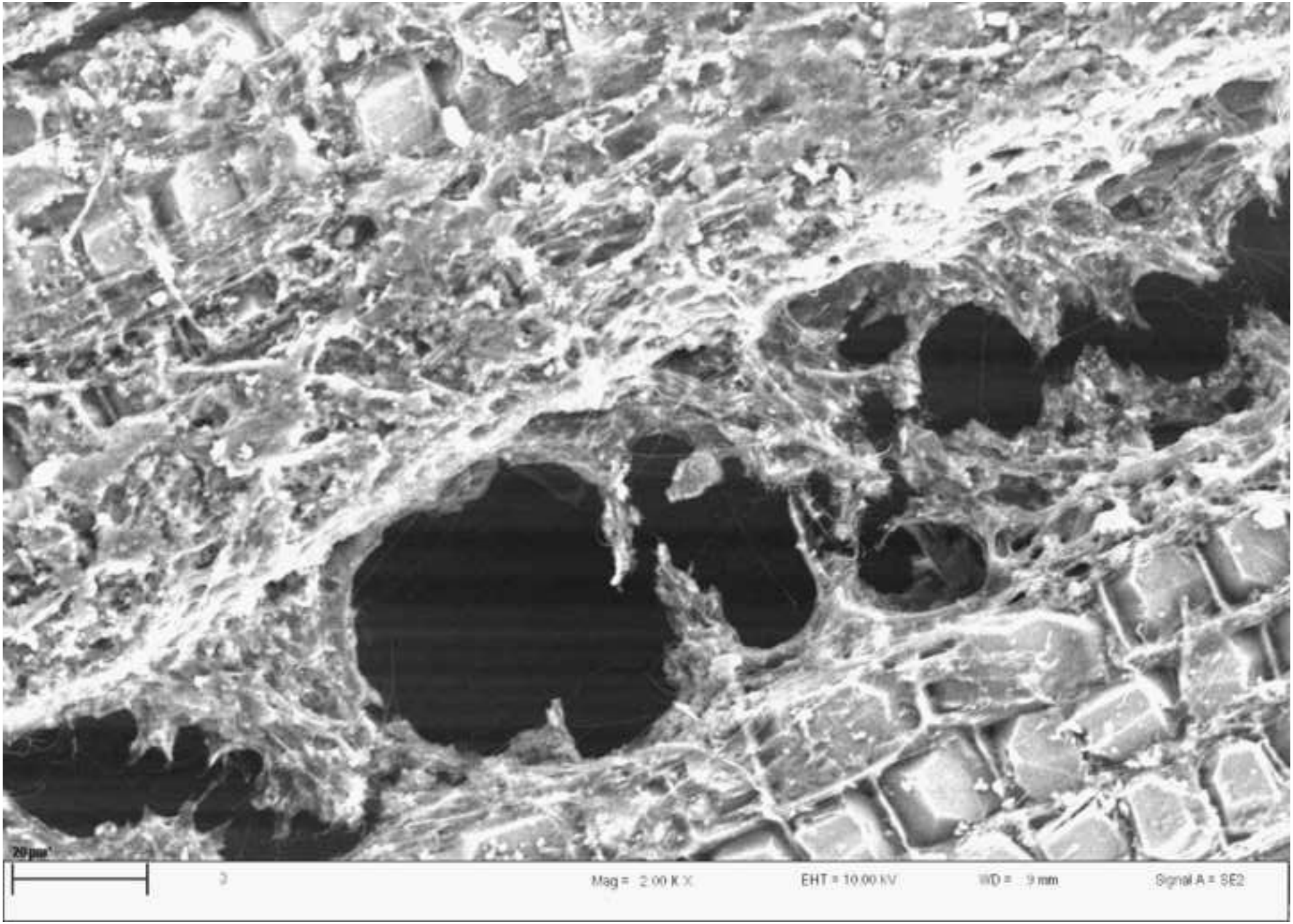

Figure 1 (c)

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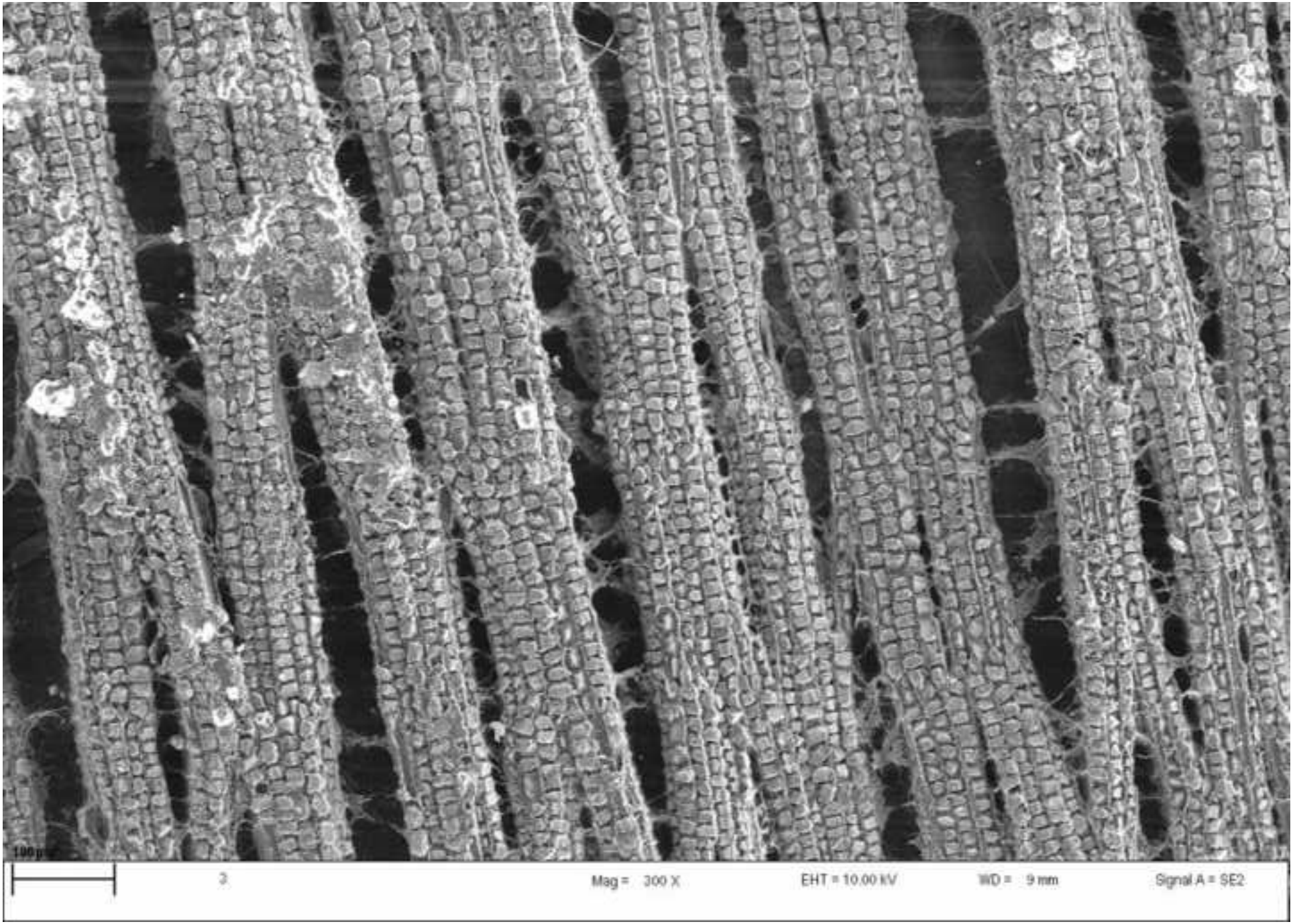

Figure 1(d)

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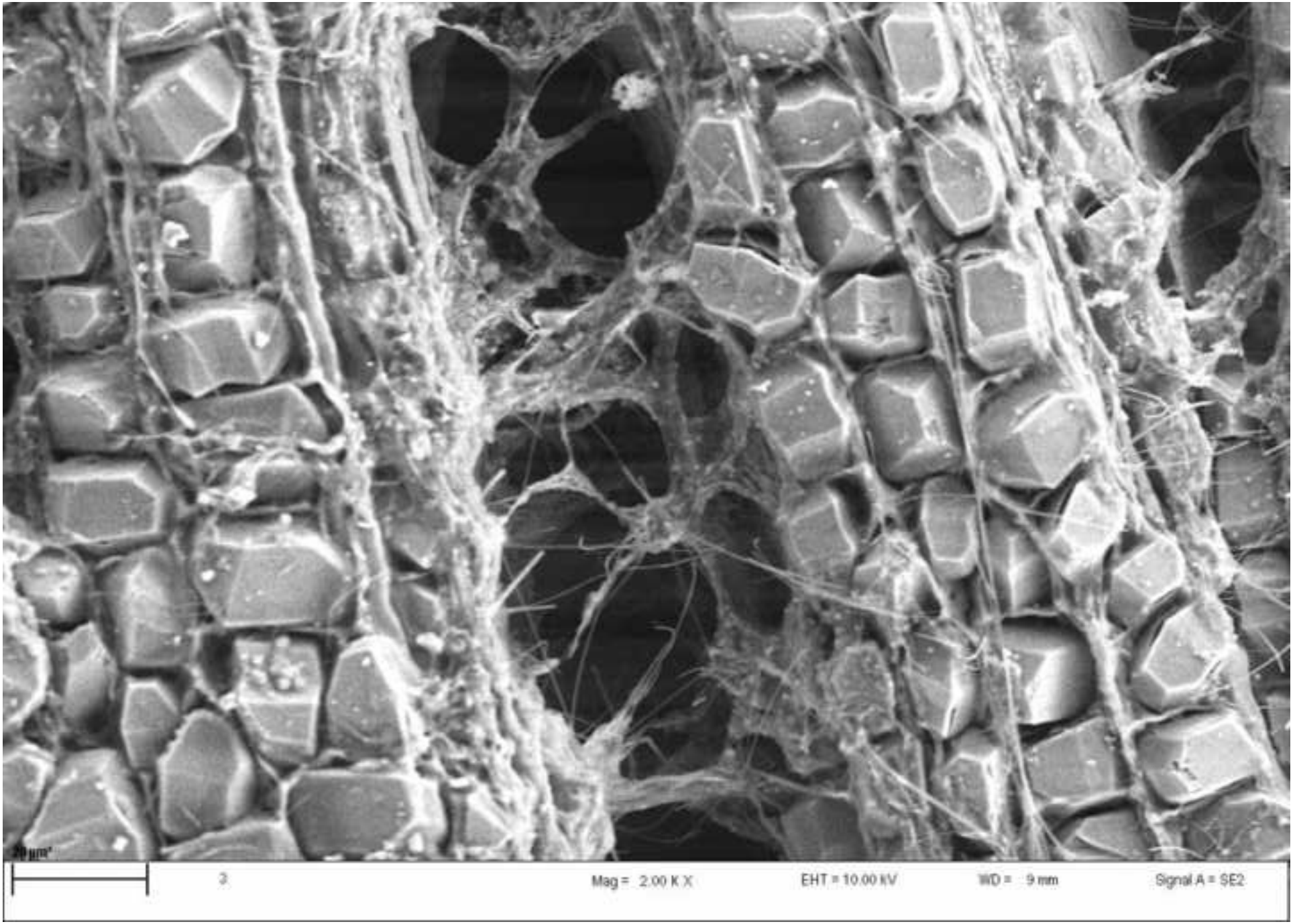

Figure 2(a)

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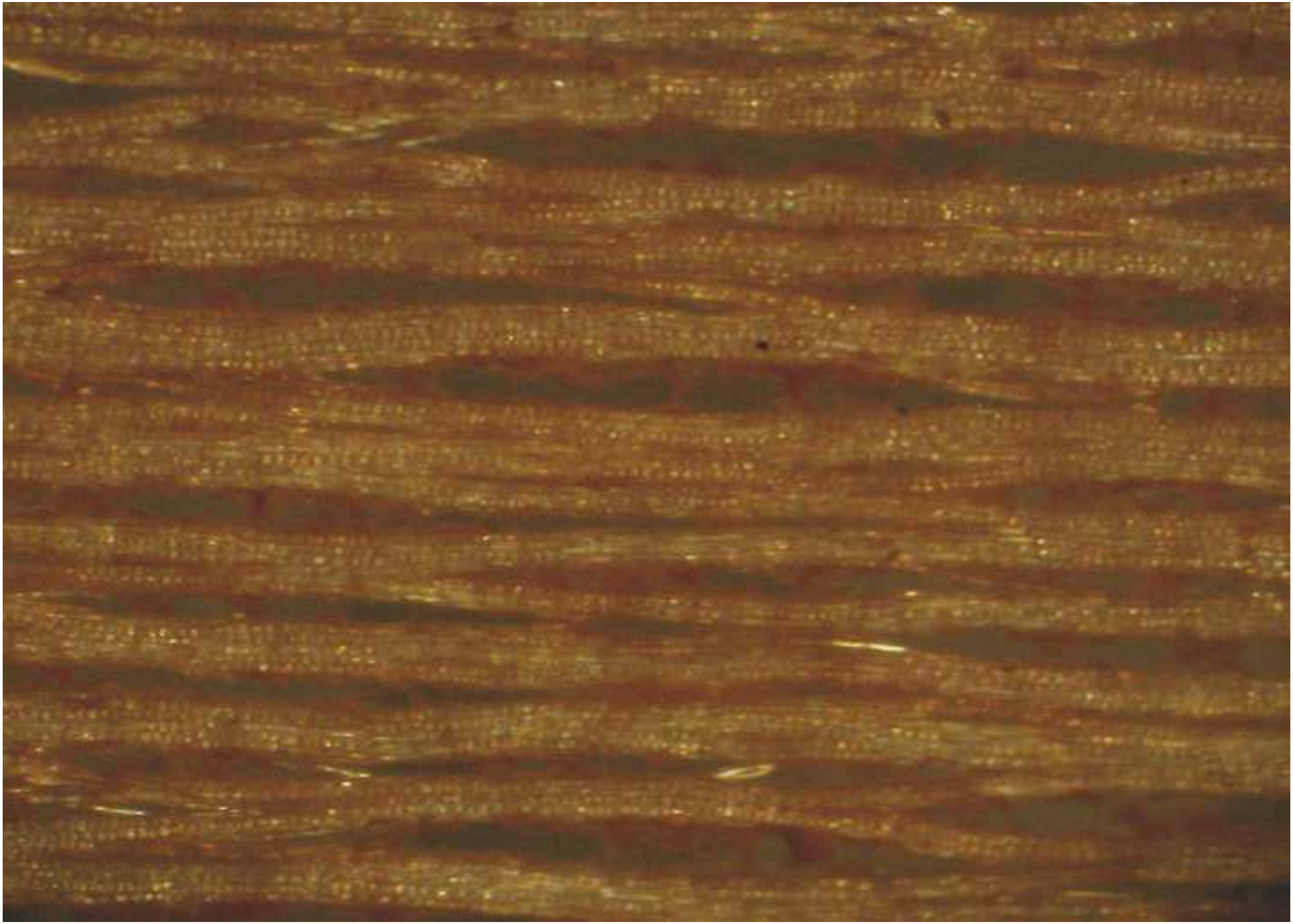

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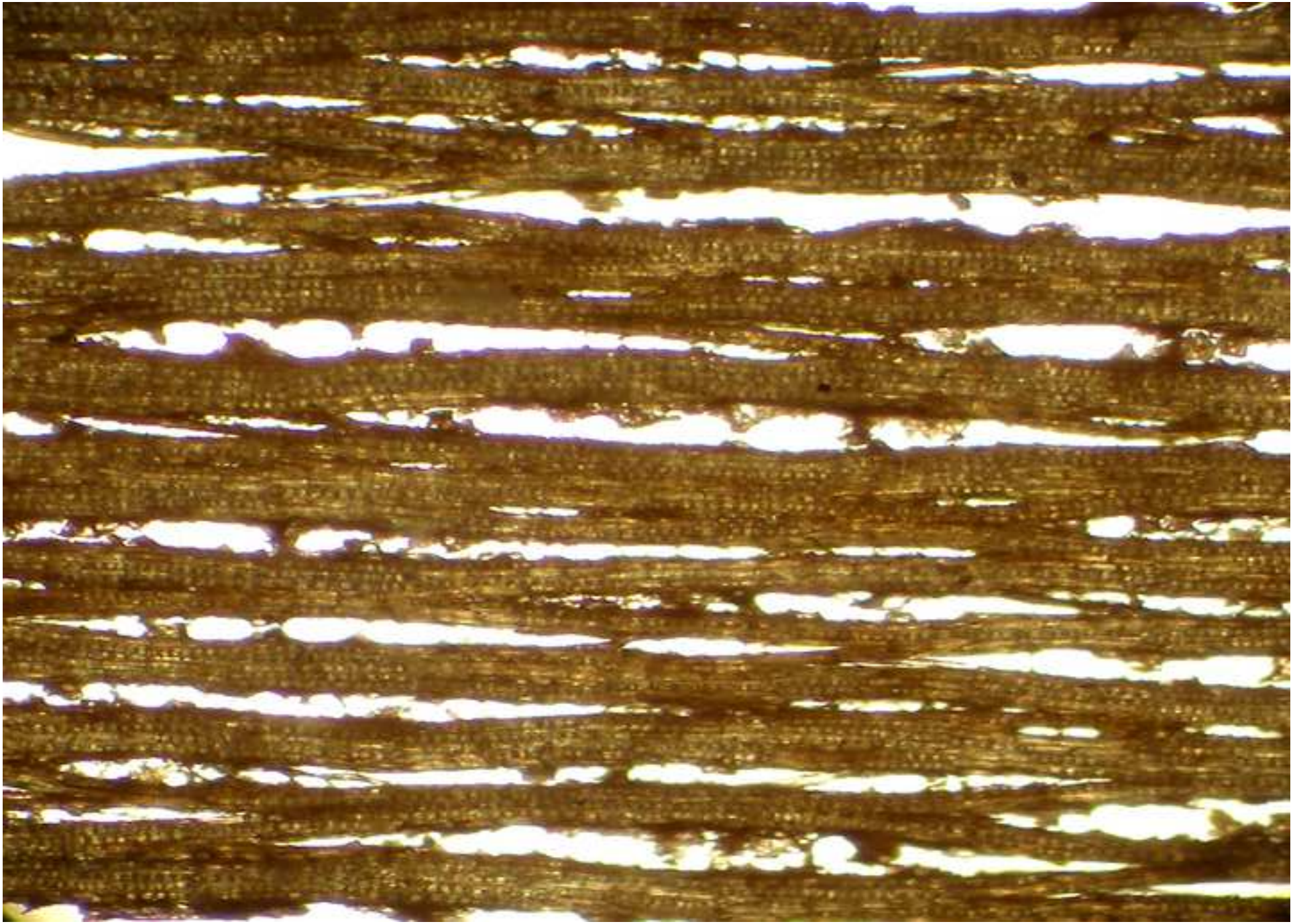

Figure 3

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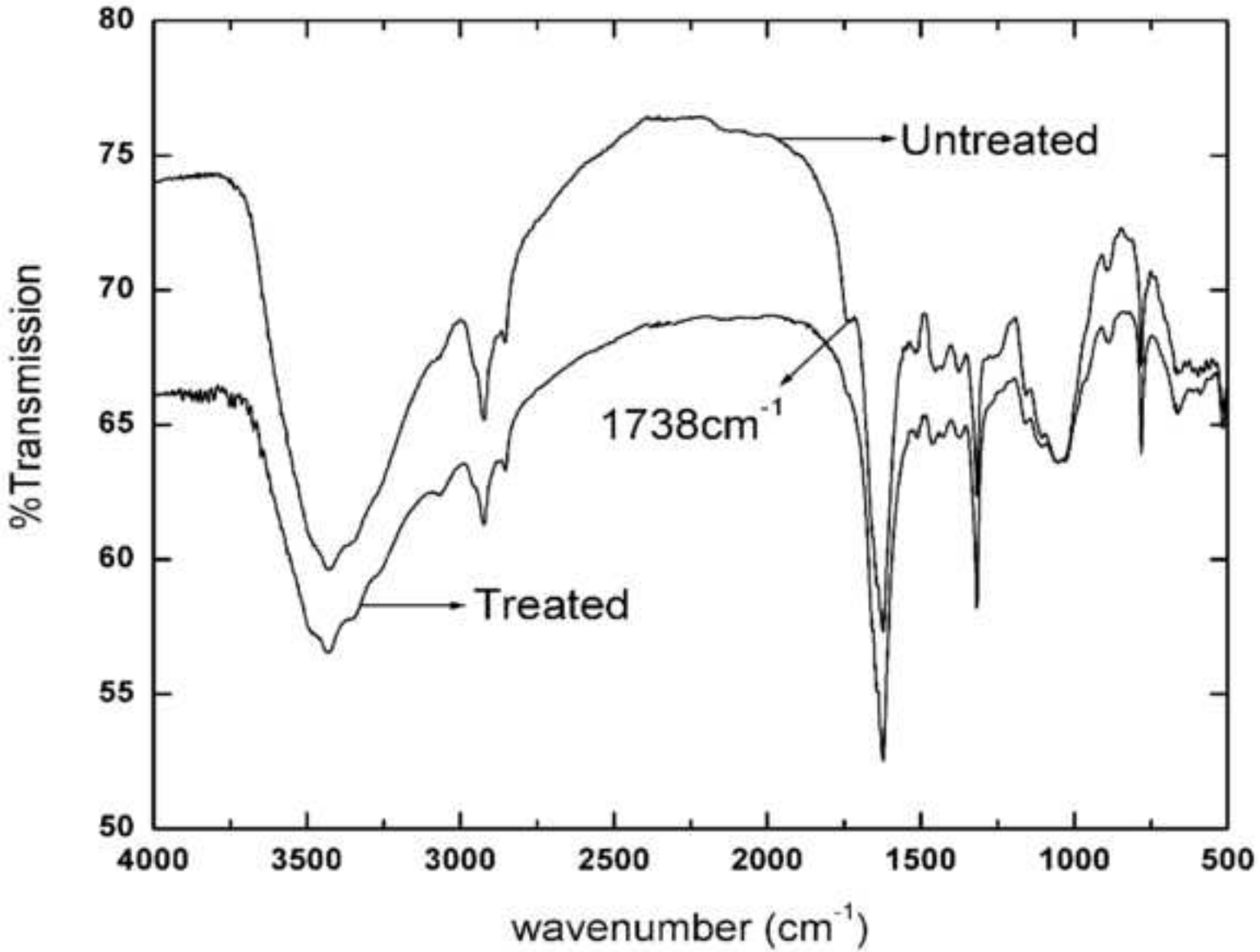

Figure 4

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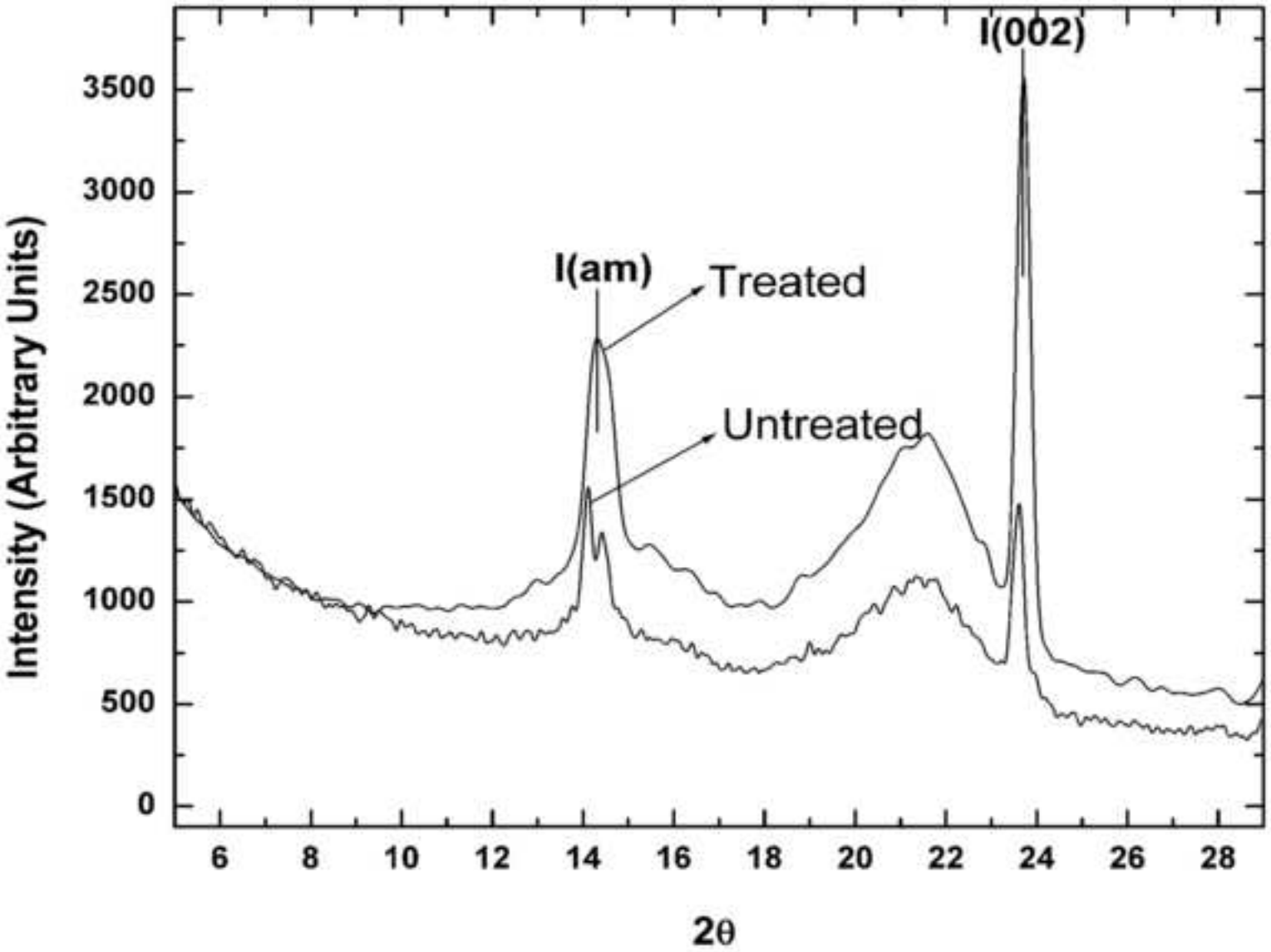

Figure 5
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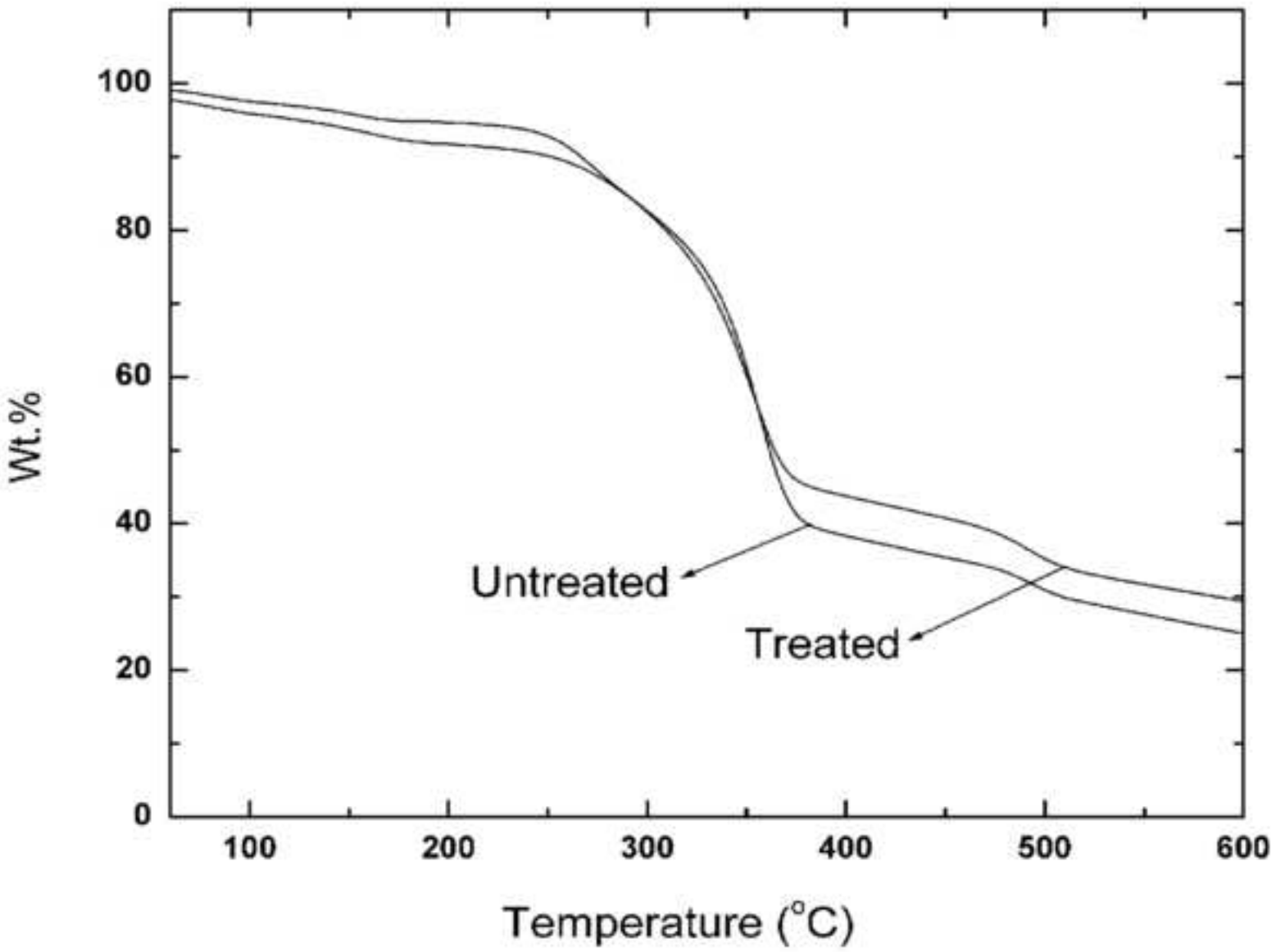

Table1. Peak positions and assignments of chemical groups in the untreated and the 5% NaOH-treated *Grewia Tilifolia* fabrics.

Wavenumber (cm^{-1})		Assignments
Untreated	5% NaOH treated	
3432	3432	OH-stretching of α –cellulose
2928	2928	Alkyl CH stretching
1738	----	CO stretching of hemi cellulose
1615	1627	CO stretching of lignin
1308	1324	Asymmetric C-O-C stretching of lignin
1036	1036	Symmetric CO stretching of lignin

Table 2. Chemical analysis of the untreated and the 5% NaOH -treated *Grewia Tilifolia* fabrics.

Component	Untreated	5% NaOH -treated
α – Cellulose	62.8%	67.9%
Hemicellulose	21.2%	15.0%
Lignin	14.9%	17.0%

Table 3

Table 3. Crystallinity index of untreated and 5% NaOH -treated Grewia *tilifolia* fabrics.

	I_{am} ($2\theta=14.28^{\circ}$)	I_{002} ($2\theta=23.71^{\circ}$)	*Crystallinity index (%)*
NaOH (5%) treated *Grewia tilifolia*	2474.5	4244.8	41.7
Untreated *Grewia tilifolia*	1329.3	1457.3	8.8

Table 4

Table 4. Tensile Properties of the Untreated and the 5% NaOH -treated *Grewia Tilifolia* fabrics.

Parameter	Untreated	5% NaOH -treated
Maximum Stress (MPa)	65.2	75.3
Young's Modulus (MPa)	4567.1	4986.7
% Elongation at Break	1.6	2.1

Table 5. Chemical Composition, Comparative Values of Cellulose and with Conventional Reinforcing fibers.

Fibres	Cellulose (%)	Hemi-cellulose (%)	Lignin (%)	Moisture Content (%)	Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation to Break (%)
Jute	61.0	20.4	13.0	12.6	550	13	1.5
Flax	71.0	18.6	2.2	10.0	1100	100	2.4
Hemp	74.4	17.9	3.7	10.8	690	----	1.6
Ramie	68.6	13.1	0.6	8.0	870	128	1.2
Sisal	78.0	10.0	8.0	11.0	640	15	2.5
Coir	43.0	0.3	45.0	8.0	140	5	15.0
Hildegardia populifolia	69.0	17.2	14.0	9.2	80.1	2.7	3.52
Grewia Tilifolia*	67.9	17.0	15.0	2.3	75.3	5	2.0

*Present Work