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CHARACTERIZATION OF CHEMICALS FROM PROSOPIS JULIFLORA (PJ) – A POTENTIAL ENHANCER FOR LIGHTWEIGHT POLYMER APPLICATIONS

KARAKTERIZACIJA KEMIKALIJ IZ MEHIŠKEGA MESKITA – POTENCIALNO UPORABNIH ZA IZDELAVO LAHKIH POLIMEROV

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The latest research is about ProsopisJuliflora's mining and characterization officers. The fibres were cut, chemically treated using sodium and hydrochloric acid (alkali) solutions. Chemically modified and non-modified fibres have been analysed for their thermal, chemical, crystalline, electrical, morphological and tensile characteristics. The findings showed that a cellulose content was increased by 59.8 % with a reduction of amorphous content and humidity by chemical treatment with alkali. However, due to its acid-plus attacks whose values were lower than untreated, the treatment for hydrochloric acid reduced cellulosis material. There were four hundred and seventeen nm of crystalline fibre of alkaline therapy, less than one 68.01 nm. Thus the ProsopisJuliflora can be suggested for lightweight polymer applications as a possible reinforcement.

Keywords: characterization, Prosopis juliflora, lightweight, polymer, reinforcement

V pričujočem članku avtorji opisujejo najnovejše raziskave na področju izkoriščanja in karakterizacije za Slovenijo sicer tujerodne invazivne rastline, imenovane mehiški meskit (bot. Prosopis Juliflora). Avtorji so posekali vzorce rastline in njena vlakna kemično obdelali v raztopinah NaOH in HCl. Nato so jih termično, kemijsko, kristalografsko, električno, morfološko in mehansko okarakterizirali ter med seboj primerjali modificirana in nemodificirana vlakna. Na osnovi analiz so ugotovili, da je po alkalni kemijski obdelavi vlaken vsebnost celuloze narasla za 59,8 % zaradi zmanjšanja vsebnosti amorfne faze in vlage. Kemijska obdelava vlaken s solno kislino, pa je po drugi strani zmanjšala vsebnost celuloznega materiala v njih. Po alkalni terapiji je bilo 417 nanometerskih kristaliničnih vlaken manjših od 68,01 nm. Avtorji na osnovi analiz ugotovljajo in priporočajo, da bi bil lahko mehiški meskit uporaben kot ojačitvena faza v izdelavi lahkih polimernih kompozitov.

Ključne besede: karakterizacija, mehiški meskit (Prosopis Juliflora), lahki polimeri, ojačitev

1 INTRODUCTION

Natural fibers have been used for a number of synthetic fibers including carbon fiber, Kevlar, glass, etc., because of their fascinating properties such as low density, reduced weight, substantial costs, bio-degradability and availability.[1] They are also used in the aerospace industry. In particular, plant parts such as the stem, the leaf, the radius of the bark, etc., are affected by the quality and strength of these fibers.[2] They are also used for filling and upgrading the composites of natural fibers. Furthermore, the location of the plant helps to determine the properties of manufactured composites. These are also affected by the type of orientation, size factor and chemical fibre components.[3]

For the current work, fibers were collected from the plants cultivated in tropical areas. A good knowledge of the fibers that can help us produce an eco-friendly composite has to be sought. The characteristics that we have to examine include chemical, physical, mechanical and binding ones. A variety of plant fibers, including hemp, linen, coir, kenaf and jute have been researched and used for a variety of purposes.[4] Many new fiber products were reported as new cellulose fibers, acting as possible reinforcements of polymer composites, e.g., Prosopis juliflora, Tridax procumbent, Acacia, Azadirachta indica, Ceiba pentandra, Heteropogon contortus, Aureum, Calotropis gigantea and so on.[5] Most plants are only native to a specific region; it is necessary that new fibers are discovered so that they can be used as vital reinforcements for polymer matrices. It was found that the fiber movement in a matrix increases the mechanical resistance of composites. By means of a chemical treatment or surface modification, fiber wettability can be improved. Various attempts have been made to improve the nature of the fiber-matrix binding that can improve the properties of the newly formed composites.[6] Attempts have been made to improve the surface properties of Prosopis juliflora fibers, using various chemical modifications such as NaOH, $KMnO_4$ (Potassium permanganate), $C_{17}H_{35}COOH$ (stearic acid) and

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benzoyl peroxide. The treatments improved the fiber chemical properties, ensuring that the hydrophobic aspect of the matrix was closely observed. Overall, the findings show that Prosopis fibers were improved by 1 % through the $C_{17}H_{35}COOH$ treatment.[7]

A manual for removing Agave americana was done. Its fibers were treated with an alkaline solution (5 *w*/% NaOH) for an hour. The chemical, mechanical and physical properties of the fibers were studied and compared with the untreated ones. Results showed that the surface ruggedness and crystallinity improved due to the NaOH treatment as it reduced its diameter due to the removal of excess amorphous constituents.[8] In the case of Tridax procumbens, the treatment with NaOH improved the physical and chemical properties of fibers. The same phenomenon was observed. It was shown that the surface roughness was increased so that the matrix could be measured better. The reference literature indicates that the chemical treatment eliminates amorphous contents to increase the wettability of the surface, causing a firm attachment to the matrix of the composite. Prosopis juliflora (PJ) is identified as a new cellulose fiber, meeting the requirements for natural fibers in the international market. The Eastern Fountain grass, also known as the PJ plant, belongs to the Poaceae grass family of flowering plants. This plant comes from the north-western Asia and northern Africa. It grows to a height of 60 cm and forms panicles with several tufts of 14 cm. PJ fibers were extracted, using a manual machine for removing these fibers. A 5 % alkaline and a 5 % HCl solution were then used for the recovered fibers. Diverse experiments were performed to evaluate different properties of chemically treated and untreatable PJ fibers and the findings were recorded.

2 MATERIALS AND PROCEDURES

2.1 Surface processing and fiber extraction

The collected PJ was plunged into water for 8 h to simplify the biodegradation. The grass was then fed manually between the two rollers of a retting system. The resulting fibers had a length of 10–12 cm. The recirculated fibers were dehydrated in a hot-air oven for 24 h and kept at 80 °C. In order to allow the fiber-surface alteration, chemical treatment was used. First of all, for the HCl treatment, the re-used PJ fiber of 250 g was not considered. The HCl solution corresponding to 1:20 *w*/% was mixed into 5 L in the amount of 5 *w*/% for 2 h at room temperature. Similarly, 250 g of retted PJ fibers in 5 L were treated with the NaOH solution of 5 *w*/%, which was equal to 1:20 *w*/%, at room temperature for 2 h. These chemical processes paved the way for the excess amorphous components of the PJ fibers to be dissolved. The chemical traces of the treatment were removed by rinsing them in distilled water from the treated PJ fibers. The processed PJ fibers were then dried for 48 h in a heated oven, at 80 °C.

2.2 PJ-fiber SEM studies (untreated, HCl- and NaOH-treated)

SEM was used to examine the morphology of the untreated PJ fibers as well as those treated with HCl and NaOH in order to detect the chemical-treatment effects that can remove impurities from the PJ fibers treated chemically by reducing their hydrophilicity. **Figure 1** shows SEM images of the longitudinal surfaces of the untreated PJ fibers. These fibers were formed cylindrically with parallel microfibrils, as seen in the photos. Furthermore, as shown in **Figure 2**, the surface of the fibre was polluted with waxes and oils as a result of the HCl treatment of the PJ fibers. The surface pores increased with unclean surfaces. It can be seen that waxes, oils and other impurities were also removed by the NaOH treatment as shown in **Figure 3**. Furthermore, the treatment with HCl caused some harm to the surface, having been as rough as the fiber surface, and it might have caused some obstacle, decreasing the composite resistance when the HCl-treated PJ fibers were used to strengthen the fiber. But NaOH exhibited several perfor-

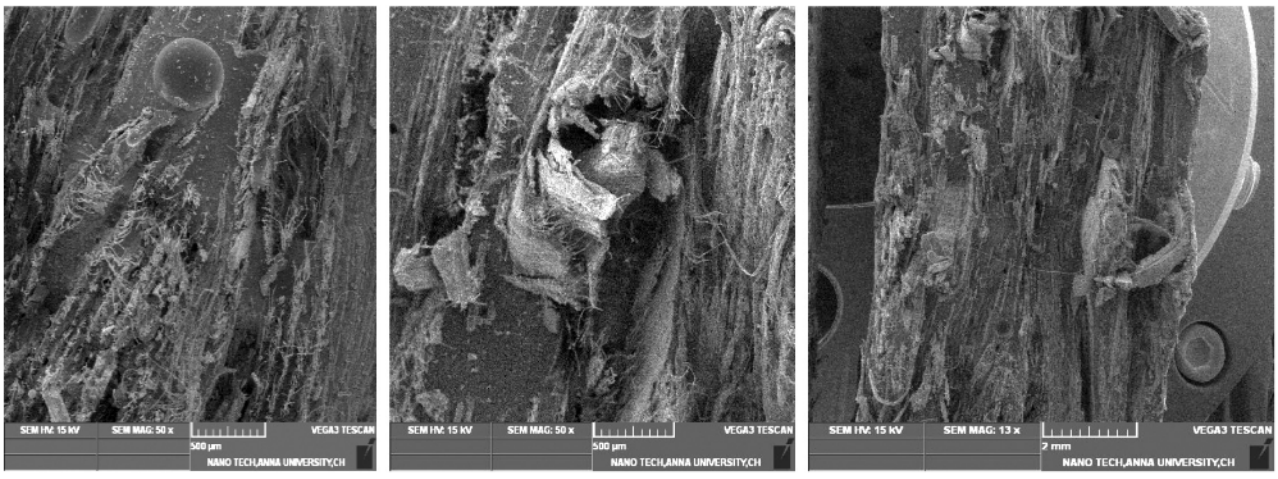

Figure 1: Untreated PJ fibers

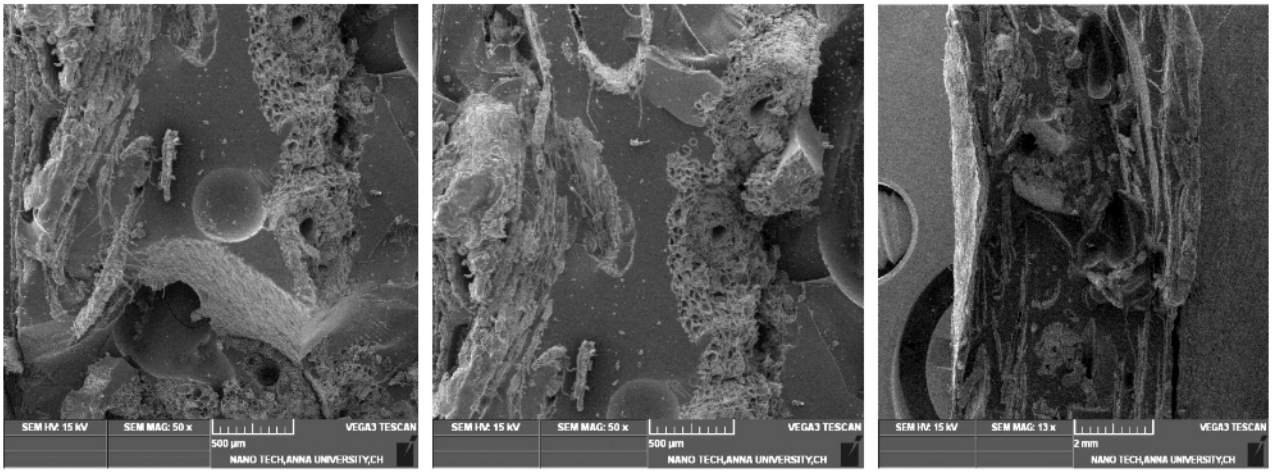

Figure 2: HCL-treated PJ fibers

mance benefits, which could be applied by using the PJ fibers as the reinforcement for the composite output.

3 EXPERIMENTAL PART

A Carl Zeiss optical microscope allowed us to measure the physical characteristics, such as the diameter and fiber density with a pycnometer (toluene). A chemical analysis was used to identify cellulose, hemicellulose and lignin in the chemically treated and untreated PJ fibers. The Kushner and Hoffer methods helped us calculate the proportion of the cellulose present. The NFT 120-008 and APPITA P11s-78 standards were used for hemicellulose and lignin. To measure the crystallinity index and the crystal size of the specimens, we used an X-Pert Pro diffractometer. A Fourier analysis was used for the examination of the components of the PJ fibers, using infrared spectroscopy (FTIR) (Diamond UTAR). With a thermographic analysis (TGA), the thermal stability of the PJ fibers was determined, using 5 mg of nitrogen at a speed of 20 mL/min. The physical qualities, such as the diameter, were measured with Carl software. The test was conducted at a heating rate of 600 °C/min starting at room temperature. An INSTRON universal testing machine (5500R) was used to calculate the tensile properties of the PJ fibers according to ASTM D3822-07. The surface morphology of the PJ fibers including surface roughness, porosity and cell wall was examined using a scanning electron microscope (SEM).

4 RESULTS AND DISCUSSION

4.1 Untreated, HCl- and NaOH-treated PJ-fiber physical/chemical characterization

The density of the treated PJ fibers was higher than that of the untreated ones. PJ fibers were treated with alkaline and HCl solutions due to the surface pores having been packed with graft molecules, as seen in **Table 1**. Another potential reason for it is the increased weight of the molecular cellulose as compared with the other components.[9] A treated PJ fiber was relatively smaller in diameter than an untreated PJ fiber, as microfibril bundles disintegrated after the chemical treatment, which led to

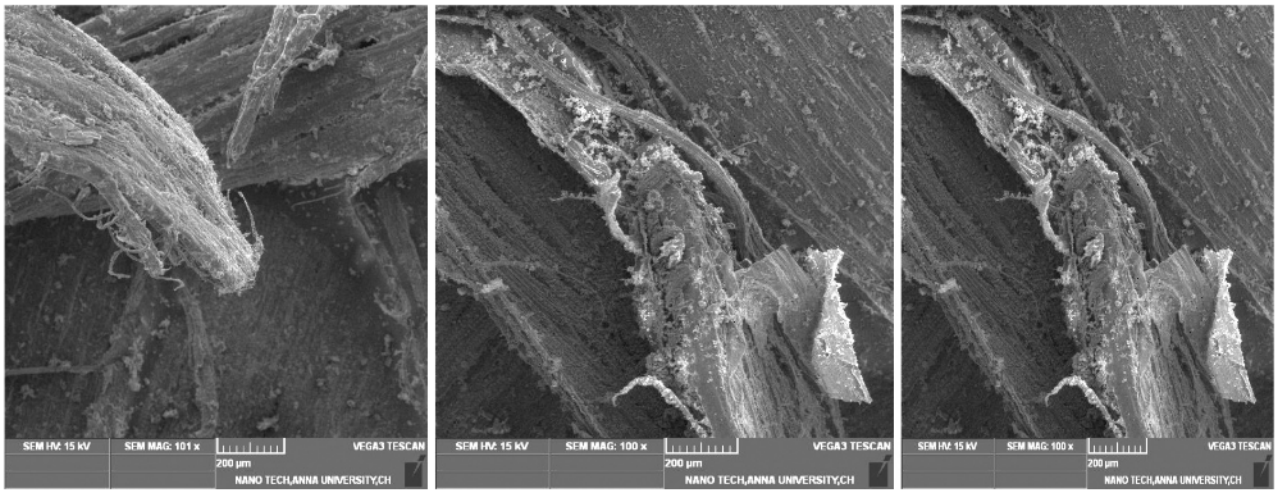

Figure 3: NaOH-treated PJ fibers

lignin and hemicellulose reductions. The percentage of the PJ fibers treated with NaOH increased in comparison with the others, up to 66.7 %. This activity was largely due to the unwanted cellulose; hemicellulose and lignin were chemically treated because they bear the least molecular weight and are thus vulnerable to chemical reactions. In the case of HCl, the chemical reaction would have been more extreme since it is an acidic medium and thus all the components would have been significantly reduced. Thus, we found that alkali processing improves the chemical properties to an acceptable extent, which is consistent with the findings from the literature.[10]

Table 1: Prosopis juliflora's physical properties and chemical composition (PJ)

Chemical composition (*w*/%)		Physical properties	
Cellulose	53.92	Thickness (mm)	0.30–1.58
Hemicellulose	22.68	Length (mm)	12–32
Lignin	17.503	Density (g/cm^3)	0.5–0.85
Moisture content	1.80	Ultimate stress (MPa)	114.7–528.1
Ash content	2.09	Strain rate (%)	1.5–4.76

4.2 PJ-fiber thermal-stability features (untreated, HCl- and NaOH-treated fibers)

Figure 4 shows the TGA curves of the PJ fibers, treated with HCl or NaOH and untreated ones. During the moisture removal from the structure of the fibers, i.e., structurally incorporated molecules of water, the temperature ranged from 40–100 °C. Hydrophilic contents were also removed from these components. The PJ fibers that were not treated exhibited an 8.3 % reduction in weight; the PJ fibers treated with HCl reached 5.3 %, while the PJ fibers treated with NaOH reached 4.15 %. The second step then involved lignin, hemicellulose and cellulose degradation. For the untreated PJ fibers, this degradation occurred between 197–243 °C, exhibiting a 7.5 % weight loss; the HCl-treated PJ fiber exhibited an 8.6 % weight loss in a range of 203–237 °C; and the NaOH-treated fibers exhibited a 5.1 % weight loss in a range of 207–252 °C. In the next step, the cellulose degradation was completed. This was accomplished with a weight loss of 50 % exhibited by the untreated PJ fibers in a 251–379 °C range, while the PJ fibers treated with HCl exhibited a 57 % weight loss in a 245–369 °C range. In the NaOH-treated PJ fibers, a weight loss of 45 % occurred between 255–393 °C. Carbohydrate residuals at 600 °C amounted to 37 %, 24 % and 19 %, respectively, for the PJ fibers treated with NaOH, untreated and treated with HCl.

The results of the TGA showed that the NaOH-treated PJ fibers exhibited an improved thermal stability compared to the untreated PJ fibers and HCl-treated fibres because amorphous substances were extracted during the treatment with NaOH. However, the percentage of weight loss for the PJ fibers treated with HCl was increased as amorphous and cellulose fibers were excessively removed, achieving the minimum thermal stability.[11] When comparing the degradation of Sahara aloe vera leaves and Prosopis juliflora stem fibers treated with the alkaline solurion, the weight-loss percentage for the NaOH-treated PJ fibres increased.

4.3 PJ-fiber XRD review (untreated, HCl- and NaOH-treated fibers)

Figure 5 displays NaOH- and HCl-treated and untreated PJ-fiber X-ray diffractograms. Crystallinity index determines and strongly affects a material's degree of long-range order. The more crystalline a fiber is, the more its chains align and its crystalline strength and density increase. Two distinct peaks that are often observed in most natural fibers can be observed in **Figure 2**. The first peak indicates the amorphous material, as in the cases of pectin, lignin, hemicellulose and cellulose. The NaOH- and HCl-treated PJ fibers are located at 2q1/416.58, 16.54 and 16.84, respectively.[12] The second highest point indicates cellulose and plane 002. For the untreated, HCL-treated and NaOH-treated PJ fibers,[13] the values were 21.30, 21.74, and 21.72, respectively. The crystallinity index (CI) and crystal size (CS) of the PJ fi-

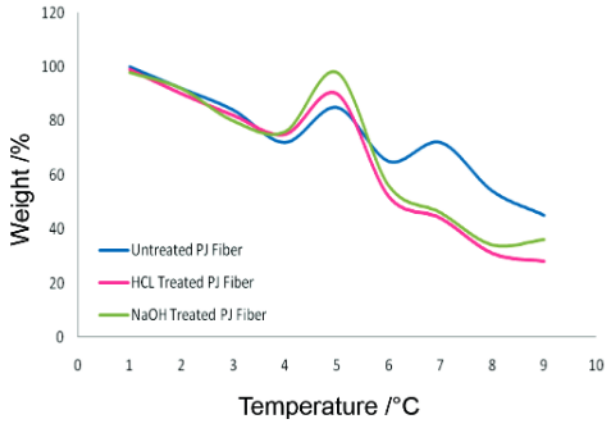

Figure 4: TGA curves of PJ fibers (untreated, HCl- and NaOH-treated)

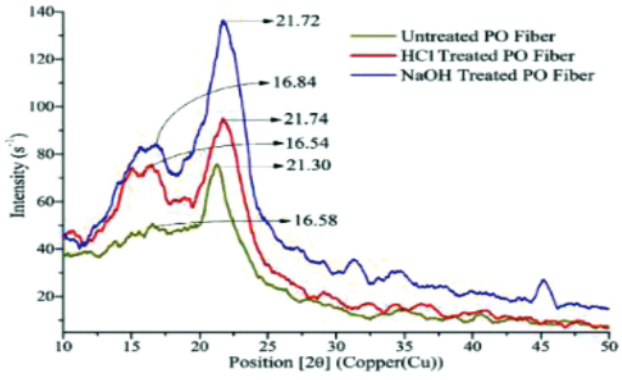

Figure 5: X-ray diffractograms for PJ fibers (untreated, HCl- and NaOH-treated)

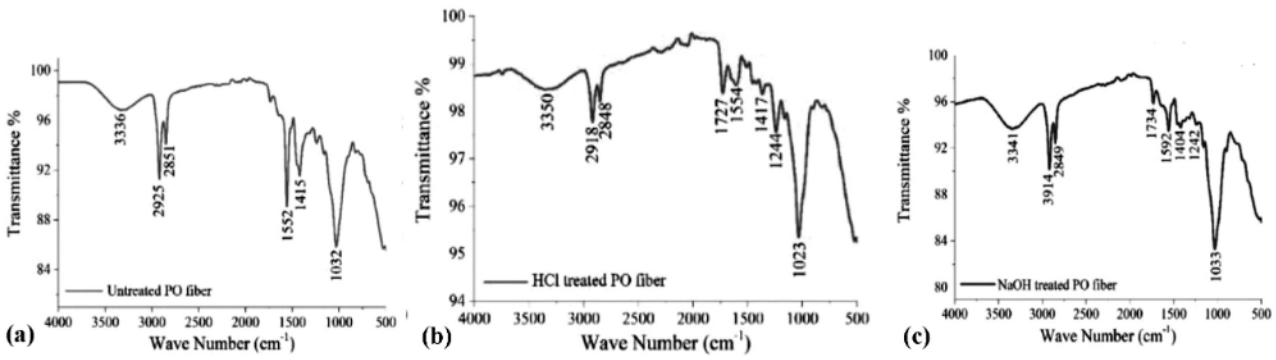

Figure 6: FTIR spectrograms of PJ fibers: a) untreated, b) HCl-treated, c) NaOH-treated

bers were calculated using the formulas from the literature. **Table 2** shows that the CI increased during the alkaline treatment in comparison with the HCl treatment since the NaOH (alkali) treatment dissolved and eliminated excess concentration of the amorphous material. In contrast to the NaOH-treated and untreated PJ fibres, HCl is an acid that deteriorated the cellulose present in the constituents, resulting in a low CI.[14] The crystal size for the NaOH-treated and HCl-treated PJ fibers was reduced compared to the untreated PJ fibers; water absorption was also reduced by this phenomenon. The crystal size of the PJ fibers treated with HCl was as low as 37.24 nm, causing a very low water absorption.

Table 2: PJ-fibre crystalline index and crystal size (untreated, HCl- and NaOH-treated)

Fiber	Chemical concentration	CS (nm)	CI (%)
Untreated PJ fibers	–	65.08	32.40
HCl-treated PJ fibers	4 % (HCl)	38.29	25.61
NaOH-treated PJ fibers	4 % (NaOH)	45.62	34.94

4.4 PJ-fiber FTIR analysis (untreated, HCl- and NaOH-treated fibers)

Figure 6 shows FTIR spectrograms for the untreated PJ fibers, and those treated with HCl and NaOH. The first U form, which corresponds to the vibration of OH, indicates the hydrogen bonding for a hydroxyl group from 3336–3350 cm^{-1}; it was confirmed by the existence of Cellulose I. The next two U-shaped peaks are located in the cellulose and hemicellulose range of 2925–2848 cm^{-1}, due to the CH vibration of CH and CH_2.[15] At 1727 and 1734 cm^{-1}, the next peaks are observed because the C=O vibration and stretching are attributable to the carboxylic acid in lignin. For the non-treated PJ fibers, no blocking of the penetration of IR rays by the amorphous material was observed as shown in **Figure 6a**. On the other hand, carboxylic acid was dissolved and the fiber strength was weakened by HCl. The next peak, which is due to the aromatic presence and bending of C, is observed between 1552 cm^{-1} and 1592 cm^{-1}.[16] For the non-treated PJ fibers and those treated with HCl, the next stretch is found to be between 1404 cm^{-1} and 1417 cm^{-1}. It occurred due to xylene, wax and hemicellulose impurities.

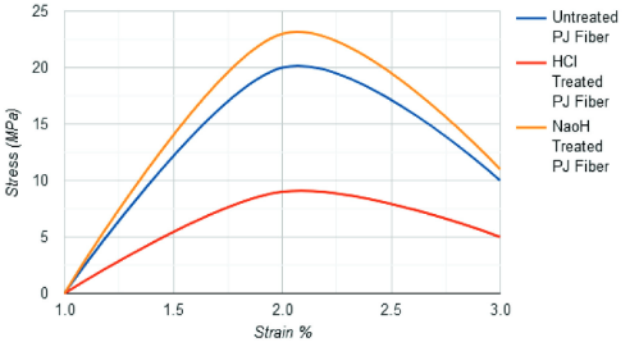

Figure 7: Tensile-tested single-PJ-fibre stress-strain graphs (untreated, HCl- and NaOH-treated)

4.5 PJ-fiber tensile properties (untreated, HCl- and NaOH-treated fibers)

Figure 7 depicts the stress-strain conduct of the single tensile fibers tested. Importantly, during the chemical treatment with the required chemical, the concentration increases the interlocking characteristics, i.e., the mechanical rigidity of the surface.[17] The NaOH-treated PJ fibers displayed similar behavior when the stress was lower than that of the other fibers and due to the higher cellulose content, they also had high strength. Owing to the increased cellulose removal, both the structure and components were degraded when the PJ fibers were treated with HCl. However, the strain was lower than the strain of the untreated fibers due to the removal of hemicellulose and lignin. Untreated PJ fibers had a slightly higher strength and stress than the HCl-treated PJ fibers, as shown in **Figure 7**. This is due to the presence of more non-cellulose material, which contributes to higher pressures. This behavior is consistent with the report from publication.[18]

5 CONCLUSIONS

The following conclusions were reached for the untreated, HCl-treated and NaOH-treated PJ fibers with re-

spect to their chemical, tensile, morphological, physical and thermal characteristics.

The NaOH-treated PJ fibers showed a density increase and a reduced diameter compared to the untreated and HCl-treated PJ fibers.

The alkali treatment removed the amorphous content such as excess lignin, pectin, hemicellulose, wax and cellulose as shown with the chemical analysis, FTIR and XRD.

The SEM studies showed that the surface roughness improves with the NaOH and HCl treatments. However, HCl also caused more surface damage, which was confirmed by the tensile strength.

The thermal stability of the PJ fibers treated with NaOH was 36 % higher than those of the unprocessed PJ fibers or HCl-treated fibers.

Thus, the test results show that Prosopis juliflora fibers can be used as a reinforcement in light-weight composites.

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