Effect of Potassium Permanganate treatment on physico-Chemical and mechanical properties of extracted Pine Needle Fiber

Rajesh Kumar[1*], *Pawan* Kumar Rakesh[1], *Dungali* Sreehari[1]

[1]Department of Mechanical Engineering & Design Innovation Center, National Institute of Technology Uttarakhand, Srinagar, Pauri (Garhwal), Uttarakhand, India

Abstract. This study investigates the potential of extracted pine needle fiber (PNF) to substitute synthetic fibers in biopolymer composites as a reinforcing material. The study is focused on the surface modification and characterizing of the extracted PNF. Water retting method was used to extract the PNF before being subjected to potassium permanganate treatment. The surface treatment with potassium permanganate resulted in higher density (1058 kg/m^3) compared to the untreated fibers (1017 kg/m^3). X-ray Diffraction (XRD) analysis shows the surface treatments positively impacted the natural fiber's crystallinity index (CI). Additionally, the tensile strength of PNF were found to be enhanced on potassium permanganate treatment from 49.67 ± 9.6 MPa (untreated PNF) to 56.75 ± 16.54 MPa (treated PNF). Based on the findings, it can be concluded that the potassium permanganate treated PNF will be suitable to be used as reinforcement in fabricating the ecologically friendly composites.

1 Introduction

The utilization of natural fibers (NFs) in composites has gained significant attention in recent years, as it provides a sustainable and eco-friendly alternative to synthetic fibers. NFs are materials derived from plants, animals, or minerals used for various applications for thousands of years [1]. Cellulosic fiber can be sourced from different plant parts, like its bark, root, seed, or leaf. Incorporating these fibers has become a significant consideration in the design and manufacturing of sustainable products [2]. Lignocellulosic NFs like coir, sisal, jute and kenaf have been recognized as potential alternatives to glass reinforcement materials in polymeric composites [3]. Natural cellulosic fibers are becoming popular composite reinforcing phases due to their renewable, biodegradable, inexpensive, excellent physical qualities, and low density, these fibers have been effectively employed in composite reinforcement in recent years [4]. The properties of NFs are significantly affected by the growth environment, temperature, and soil conditions, which impact fiber strength and density.

*Corresponding author : rajeshkumaruit1@gmail.com

NFs reinforced polymer composites have been extensively demonstrated to have the potential for use in numerous industries, including aerospace, construction, sports equipment and automotive [1-5]. Proper use and management of potassium permanganate are crucial to minimize its environmental impact. Avoid overuse and inappropriate disposal to protect the environment. Use wisely and dispose properly for environmental protection. [6]. The method used for extracting fibers, whether water retting, chemical retting or mechanical technique, can also result in distinct properties [7]. The moisture absorption capacity of a material can varies from 5% to 20% by its dry weight, depending on the environmental conditions. Therefore, one of the major concerns for composites that use cellulosic fibers as reinforcement is the fiber-matrix interaction, which can be negatively impacted by the dimensional changes that the fibers undergo due to the absorption of water [8]. Research suggests that the use of $KMnO_4$ treatment can effectively lower the water absorption of natural fiber [9]. Pine needles, which are abundantly available and widely considered waste materials, have the potential to be utilized as a source of NFs. Pine trees grow in Uttarakhand's forests, with elevations from 500 to 2,000 meters above sea level, and they are abundant in the area. When the pine needles fall, they form a dense layer on the forest floor, which can stop other plants from growing and make forest fires more likely, especially when it's dry. To address this issue, the local people of Uttarakhand burn pine needles to clean the forest floor [10]. Burning pine needles emits air pollutants, harming the environment and health. Hence, by utilizing the pine needles in composite fabrication, instead of burning them, the demand for wood and synthetic fibers can be reduced, which would effectively prevent the unnecessary burning of pine needles and minimize its adverse effects. The current study involved the extraction of PNFs from pine needles and subsequent treatment of the fibers with potassium permanganate solution. The physical, chemical, and mechanical properties of the treated fibers were investigated.

2 Materials and method

2.1 Materials

Pine needle tree also known as chir tree is commonly found in the Himalayan region of India up to a height of 50 meters. The needle-shaped leaves of the pine tree are commonly referred to as "pine needles". This is because the leaves have a needle-like structure. Potassium permanganate ($KMnO_4$) for extracted fiber treatment was procured from the local market of Pauri Garhwal, Uttarakhand.

2.2 Water retting

Various methods have been utilized for fiber extraction from plant stems, with retting being the predominant technique. Retting involves controlled degradation of the stem to separate the fibers from the woody core [3]. Retting is a biological process that depends on moisture and warm temperatures to enable microbial action. The collected leaves were soaked in water at ambient temperature for a period of 14 days. The microorganisms in the water broke down the non-fiber material, which caused the fibers to loosen and separate during the process [11]. After 14 days, a fine long metal wire brush was used to assist in the traditional combing process for separating the fibers.

2.3 Surface Modification of PNF

The extracted PNF was submerged in 0.05% $KMnO_4$ solution at 25 °C for fifteen minutes [9]. After that PNF was washed repeatedly with deionized water to remove any trace of potassium permanganate. Subsequently, the solution was poured off and the fibers were rinsed with acetone to eliminate any remaining solution on the fibers. Finally, the treated PNF was dried in a oven at 80°C for six hours.

2.4 Determination of physical properties

2.4.1 Diameter measurement

The diameter of the PNF was estimated by analyzing 25 fiber samples using an optical microscope. The analysis was conducted by examining longitudinal microscope images of the fibers [11]. The diameter of both untreated and treated PNF was measured at four randomly locations.

2.4.2 Density measurement

Measuring the density of NFs is typically done through the standard procedure of utilizing the pycnometer setup. This involves analyzing the fibers with a liquid of known density, such as toluene (toluene = 866 kg/m^3 at room temperature), for the density analysis [12]. PNF's density was calculated using Eq. 1.

$$\rho_{PNF} = \frac{(m_2 - m_1)}{(m_3 - m_1) - (m_4 - m_2)} \times \rho_{toluene} \quad (1)$$

Where, m_1 weight of empty pycnometer, m_2 weight of pycnometer filled with PNF, m_3 weight of toluene in pycnometer, and m_4 weight of pycnometer filled with both toluene and PNF.

2.5 Chemical composition analysis

Several distinct methods were utilized to determine the percentage of chemical components present in PNF, specifically cellulose, hemicellulose, and lignin. To determine the cellulose content weight fraction, the Krushner and Hoffer method was utilized [13]. Hemicellulose was assessed using the neutral detergent fiber technique [12], while lignin was estimated using the APPITA P11s-78 method [14]. PNF moisture content was measured using the starting and oven-dry weights of the fibers. Eq. 2 was used for moisture calculation and the mean value was reported after five repetitions to assure data accuracy [15].

$$\%\ \text{of moisture in PNF} = \frac{(W_1 - W_2)}{W_1} \times 100 \quad (2)$$

The fiber's weight before drying is W_1, and after drying in a hot air oven is W_2.

2.6 XRD analysis of PNF

XRD was utilized to predict the CI and CS of the PNF, which indicates the extent of structural arrangement. A Bruker D8 XRD equipment was used at room temperature [13]. The measurements were performed within a range of 10° to 35°, employing a scanning rate of 4°

per minute. This measurement is crucial as it has a direct effect on the mechanical behaviour of the material. Using Eq. 3, the CI of PNF was calculated.

$$CI = \left\{1 - \frac{I_{amorphous}}{I_{crystalline}}\right\} \quad (3)$$

Where "*Iamorphous*" denotes the peak's amorphous intensity and "*Icrystalline*," the peak's crystalline intensity in the diffractogram. Scherrer's equation (Eq. 4) is a useful formula for estimating the size of cellulose crystals within a fibrous structure [11].

$$CS = \frac{K\lambda}{\beta cos\theta} \quad (4)$$

Scherrer's constant, denoted as K = 0.89, is used in the formula, β represents the full width at half-maximum of the peak, and λ signifies the wavelength of radiation.

2.7 Single fiber tensile test

Tensile properties of a material, including its tensile strength and modulus are critical factors in assessing the suitability of a fiber for a specific application. The mechanical properties of plant-based fiber can vary and affected by several factors including retting duration, extraction method and plant age. To analyze the tensile properties of PNF, a tensile test was conducted using an INSTRON (5982) machine, with sample dimensions and testing parameters according to ASTM D3822-07 [16]. Untreated and treated groups were tested, with twenty-five specimens in each group, and the results were recorded. A setup consisting of a paper frame was used to carry out the tensile test (Fig. 1).

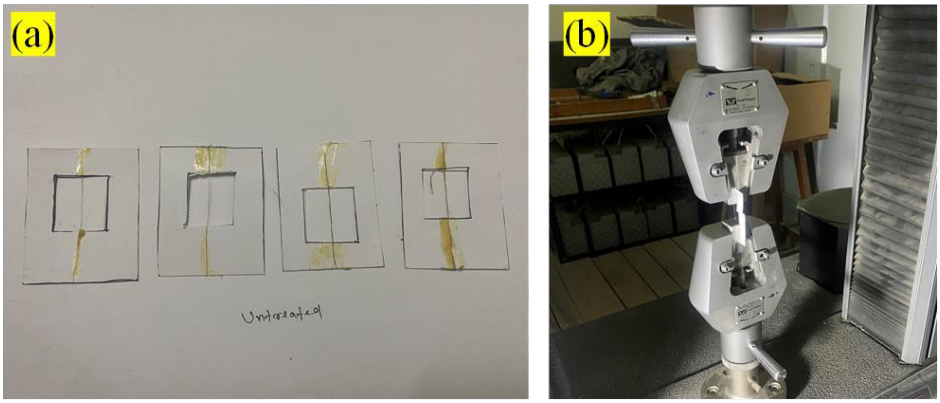

Fig. 1 (a) Paper frame designed for tensile tests on individual fibers. (b) Sample set into Instron machine

3 Results and discussion

3.1 Physical analysis of the fibers

The diameter of a NFs is a critical factor in determining its usability. Fig. 2 displays the optical microscope image of diameter measurements of the extracted fibers, indicating that the treated fiber had a smaller diameter of 131 ± 20 μm compared to the raw fibers 150 ± 17

μm. Table 1 compares the Physical, Mechanical and crystallinity properties of PNF with other NFs.

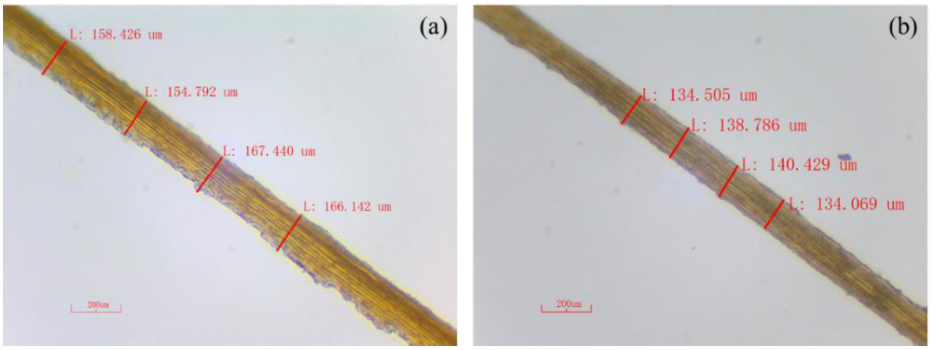

Fig. 2 Diameter Measurement of (a) Untreated and (b) Potassium Permanente treated PNF

There are various factors that can impact the density of fibers, which include soil, weather conditions, moisture levels, extraction methods. PNF has a lower density than manmade fibers like E-glass (2500 kg/m^3) and S-glass (2500 kg/m^3), making it a viable lightweight replacement [13].

Table 1 Physical, Mechanical, and Crystallinity Properties of PNF and few other NFs.

Fiber	Diameter (μm)	Density (kg/m^3)	Tensile strength (MPa)	Young's Modulus (GPa)	Crystallinity Index (CI)	Ref.
PNF	150 ± 17	1017	49.67 ± 9.6	1.43 ± .13	43.62	Current work
Treated PNF	131 ± 20	1058	56.75 ± 16.54	1.77 ± .37	47.26	Current work
Areca palm leaf	285-330	1090	364.66 ± 21.46	9.39 ± 1.1	-	[2]
Banyan root fiber	0.09 - 0.14	1234	19.37 ± 7.72	1.8 ± .40	72.47	[17]
Coccinia grandis L.	27.33 ± 0.3	1243	273 ± 27.74	10.17 ±1.2	46.09	[18]
Cymbopogon flexuosus	118.00	1270	431.1 ± 23.9	53.88	46.02	[13]
Ficus religiosa	25.62 ± 0.9	1246	421.25 ± 18	5.11 ± 1.4	42.92	[12]
Furcraea foetida	12.80	778	623.52 ± 45	6.52 ± 1.9	52.60	[19]
Tridax procumbens	233.1 ± 9.9	1160	25.75 ± 2.45	0.94	34.46	[16]

3.2 Chemical composition analysis

The chemical composition of NFs depends on various factors, including extraction methods, climate, and soil conditions. This analysis shows that the cellulose content increased after the treatment which led to rise in tensile strength and Young's modulus. Table 2 confirms that the chemical treatment of PNF increased the cellulose wt.% compared to raw fibers. The chemical treatment decreases the hydrophilic characteristic of PNF by decreasing

hemicellulose and lignin weight %. Furthermore, the lowered moisture and wax content in the chemically modified PNF suggests that the bonding between the fiber and matrix in composite applications may be improved [20]. Table 2 presents a comparison between the chemical composition of PNF and a few other NFs.

Table 2 Chemical composition of PNF and other NFs.

Fiber	Cellulose (Wt.%)	Hemicellulose (Wt.%)	Lignin (Wt.%)	Wax (Wt.%)	Moisture (Wt.%)	References
PNF	53.67	19.14	21.39	1.13	11.67	Current work
Treated PNF	61.51	11.29	15.17	0.66	6.71	Current work
Areca palm leaf	57.49	8.34	7.26	0.71	9.35	[2]
Banyan root fiber	67.32	13.46	15.62	0.81	10.21	[17]
Coccinia grandis	63.22	–	24.42	0.32	9.14	[18]
Cymbopogon flexuosus	68.13	11.56	23.9	0.53	9.17	[13]
Ficus religiosa root	55.58	13.68	10.13	0.72	9.3	[12]
Furcraea foetida	68.35	11.46	12.32	0.24	5.43	[19]
Tridax procumbens	32.00	6.80	3.0	0.71	11.2	[16]

3.3 Crystallinity analysis of the fibers

Fig. 3 shows two prominent peaks are observed at approximately 2θ = 15° and 23°, corresponding to the lattice numbers (1 1 0) and (2 0 0), respectively. These peaks are indicative of cellulose I and IV, respectively. These two peaks are commonly found in NFs [17]. The untreated PNF has a crystallinity index (CI) of 43.62%, but the alkali treatment results in an improved CI of 47.26%. The fibers' improved CI was due to the removal of non-crystalline substances, which was supported by chemical analysis.

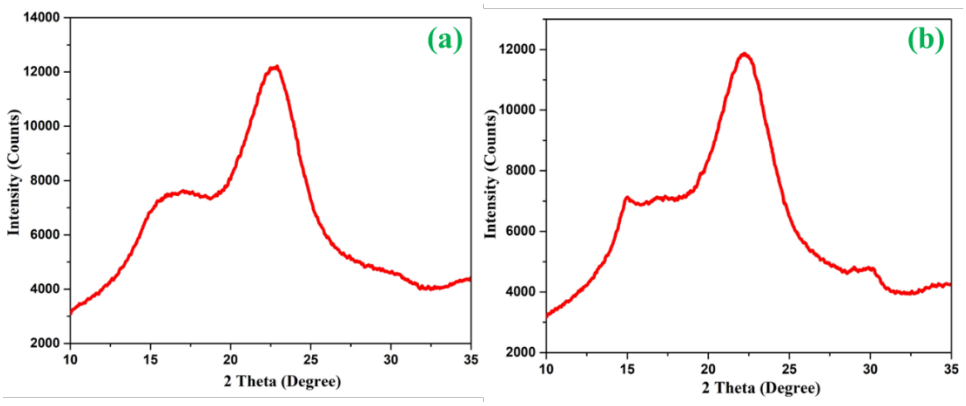

Fig. 3 XRD of (a) Untreated and (b) Treated PNF

The untreated PNF exhibit a calculated CS of 4.03 nm, whereas the treated PNF show an increased crystal size estimated at 5.61 nm. The enlargement in crystallite size promotes the fiber's resistance to moisture absorption and chemical reactivity [21].

3.4 Mechanical Properties of PNF

The Mechanical properties of NFs is influenced by the existence of cellulose, hemicellulose, and lignin, as well as the method of extraction and chemical treatment applied [1]. The tensile test showed that the treatment improved PNF tensile strength. The chemically treated PNF exhibited a higher tensile strength (56.75 ± 16.54 MPa) compared to the untreated PNF (49.67 ± 9.6 MPa). The untreated PNF has a Young's modulus of 1.43 ± .13 GPa, while the treated PNF has a Young's modulus of 1.77 ± .37 GPa.

4 Conclusion

The investigation of the chemical composition showed that the treatment of PNF with potassium permanganate led to a substantial enhance in cellulose content, while simultaneously causing a reduction in components such as hemicellulose, lignin, and wax. The density of PNF increased slightly to 1058 kg/m^3 after chemical treatment, but it remains significantly lower than that of synthetic fibers. XRD analysis confirmed that the CS enhanced from 4.03 nm to 5.61 nm as a result of chemically treatment. The single fiber tensile test indicated that the treatment had a positive impact on the tensile strength of PNF, with the chemically treated PNF exhibiting a strength of 56.75 ± 16.54 MPa compared to 49.67 ± 9.6 MPa for the untreated PNF. The results indicated that treated PNF are highly suitable for reinforcement in composite fabrication.

References

1. O. Faruk, A. K. Bledzki, H. P. Fink, M. Sain. Prog Polym Sci. **37**, 1552–1596 (2012)
2. N. Shanmugasundaram, I. Rajendran, T. Ramkumar. Carbohydr Polym. **195**, 566–575 (2018)
3. K. Shaker, R. M. W. U. Khan, M. Jabbar, M. Umair, A. Tariq, M. Kashif, Y. Nawab. Ind Crops Prod. **152**, 112518 (2020)
4. D. Kumar, A. Mandal. Constr Build Mater. **348**, 128691 (2022)
5. P. Manimaran, S. P. Saravanan, M. R Sanjay, J. Mohammad, S. Suchart, F. Fiore. J. Polym. Environ. **28**, 803–811 (2020)
6. S. Lin, X. Yu, J. Fang, J. Fan Water Research, **177**, 115786 (2020)
7. N. Moussaoui, M. Rokbi, H. Osmani, M. Jawaid, A. Atiqah, M. Asim, L. Benhamadouche. J Polym Environ. **29,** 3779–3793 (2021)
8. H. Ventura, J. Claramunt, A. Navarro, M. A. Rodriguez-Perez, M. Ardanuy. Materials. **92**, 93 (2016)
9. L. He, W. Li, D. Chen, G. Lu, L. Chen, D. Zhou, J. Yuan. Polym. Compos. **39** (9), 3353-3362 (2018)
10. M. Nand, P. Maiti, H. C. Joshi. ENVIS Bulletin Himalayan Ecology. **28**, 86 (2020)
11. R. Kumar, P. K. Rakesh, D. Sreehari. J Nat Fibers. **20** (1), 2157924 (2023)
12. A. A. M. Moshi, D. Ravindran, S. S. Bharathi, S. Indran, S. S. Saravanakumar, Y. Liu. Int J Biol Macromol. **142**, 212-221 (2020)
13. S. Raja, R. Rajesh, S. Indran, D. Divya, G. S. Priyadharshini. J Ind Text. **51**, 1207S-1234S (2022)
14. M. Pokhriyal, P. K. Rakesh, S. M. Rangappa, S. Siengchin. Biomass Convers. Biorefinery. **1**-17, (2023)

15. B. NagarajaGanesh, P. Ganeshan, P. Ramshankar, K. Raja. Ind Crops Prod. **139**, 111546 (2019)
16. R. Vijay, D. L. Singaravelu, A. Vinod, M. R. Sanjay, S. Siengchin, M. Jawaid, J. Parameswaranpillai. Int J Biol Macromol. **125**, 99-108 (2019)
17. T. Ganapathy, R. Sathiskumar, P. Senthamaraikannan, S. S. Saravanakumar, A. Khan. Int J Biol Macromol. **138**, 573-581 (2019)
18. P. Senthamaraikannan, M. Kathiresan. Carbohydr Polym. **186**, 332-343 (2018)
19. A. S. Madival, S. Maddasani, R., Shetty, D. Doreswamy. J Nat Fibers. **20** (1), 2136816 (2023)
20. P. Madhu, M. R. Sanjay, S. Pradeep, K. S. Bhat, B. Yogesha, S. Siengchin. J Mater Res Technol. **8**, (3) 2597-2604 (2019)
21. M. Kathirselvam, A. Kumaravel, V. P. Arthanarieswaran, S. S. Saravanakumar. Carbohydr Polym. **217**, 178-189 (2019)