CELLULOSIC FIBER EXTRACTED FROM *ALSTONIA MACROPHYLLA* SEED PODS AS A POTENTIAL REINFORCEMENT FOR POLYMER COMPOSITES

ERUSAGOUNDER SAKTHIVELMURUGAN,* GANESAN SENTHILKUMAR,* SHETTAHALLI MANTAIAH VINU KUMAR* and HARWINDER SINGH**

^{*}Department of Mechanical Engineering, Bannari Amman Institute of Technology, Sathyamangalam, Erode-638401, Tamilnadu, India

**Department of Textile Technology, Bannari Amman Institute of Technology, Sathyamangalam, Erode-638401, Tamilnadu, India

Corresponding author: E. Sakthivelmurugan, sakthi.glen@gmail.com

Received December 6, 2022

The prime objective of the present work has been to investigate a novel natural fiber extracted from the seed pods of the *Alstonia macrophylla* (AM) tree. Chemical, physico-mechanical, and surface properties of untreated and alkali treated AM fibers were analysed. Chemical analysis confirmed that cellulose composition (78.31 wt%) of the AM treated fiber was improved as a result of alkali treatment, whereas other constituents, such as hemicelluloses, lignin and wax were decreased. This was supported by Fourier transform infrared (FTIR) analysis. Single fiber pull test showed that alkali treated AM fiber exhibited higher strength than untreated AM fiber. Scanning electron microscopy (SEM) studies revealed that surface roughness of the treated AM fiber was higher than in untreated AM fiber. Owing to an upsurge in the cellulose content, the tensile properties, crystallinity, and surface roughness of the AM treated fiber got enhanced, demonstrating that AM fiber could be potentially used as reinforcement for producing polymer composites for light weight applications.

Keywords: Alstonia macrophylla, alkali treatment, XRD, FTIR, SEM, Weibull distribution

INTRODUCTION

Currently, research efforts are dedicated to the exploration of new lignocellulosic materials from abundantly available natural resources. Natural fibers are composed of cellulose, hemicelluloses and lignin, and are the most abundant biomaterial on this planet.¹ There is a huge potential in natural fibres to cater the demands of the forthcoming generations in one or another way. The prime advantages of natural fibers are their low cost, light weight, high specific modulus, renewability and biodegradability.²

The major sector in which natural fibers are predominantly used as suitable alternatives for their synthetic counterparts is reinforced composites. As far as the comparison of the utility of natural fibers to that of synthetic fibers is concerned, no doubt the latter have gained more importance from the viewpoint of consistency in the fiber parameters, as well as overall properties of the composites. Despite the usefulness of synthetic fiber based composites, the main drawback is the difficulty of recycling at the end of the life cycle of the product.³ Meanwhile, composites fabricated by using natural fibers are environment-friendly to a large extent. The most challenging task for the researchers has been to improve the fiber matrix interphase, owing to the hydrophilic character of natural fibers. The most appropriate way to improve the interfacial adhesion between fibers and matrix is by subjecting the fibers to chemical treatments.

Lignocellulosic fibrous matter can be derived from bark, stem, flower, leaf, seed pods, fruit and roots of the plants and trees. The process of extraction of fibers from the fibrous assembly varies based upon the area from where it is to be extracted. The extraction of fibres from stem or bark is achieved by the retting process,^{4,5} whereas the extraction of fibers from leaves, stalk *etc.* can be done through alkali treatments⁶ or acid hydrolysis.⁷ Researchers have worked a lot globally to explore different lignocellulosic resources, which were never introduced before, and their findings helped the utilization of those natural fibers in various end uses like automobile parts, furniture, packaging, and construction.^{8,9} Still, there are numerous natural fibrous materials that are yet to be explored in order to utilize their potential to the full extent. *Alstonia macrophylla* (AM) tree is one of them, and it is majorly found in South East Asia. This tree is also referred to as hard alstonia, hard milkwood or big-leaved macrophyllum.¹⁰ To the best of the authors' knowledge, no work has been reported on the extraction of fibers, as well as on the physicochemical properties of fibers from *Alstonia macrophylla*, so far.

The present research work has been carried out to gain in depth knowledge about the physicomechanical and chemical properties of novel AM fiber. The fiber was subjected to alkali treatment, followed bv characterization bv various X-ray diffraction, techniques, viz. Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and tensile testing. The characteristics of the AM fibers were compared with those of other natural fibers.

EXPERIMENTAL

Materials

Fibers were extracted from the seed pods of Alstonia macrophylla (AM) tree. Sodium hydroxide

granules (98% purity) and acetic acid (98% purity and 98% concentration) were supplied from Sigma Aldrich Pvt Ltd., India.

Fiber extraction

Alstonia macrophylla tree grown to a height of 30meters and found in the region of Sathyamangalam Taluk, Erode district, Tamilnadu, India, was selected for the present investigation. Dry seed pods of *Alstonia macrophylla* were collected and cleaned with regular water to remove any dust present in them. Dry seed pods were soaked in a water basin for 2 weeks for removal of the hard skin of the seed pods via biological retting.^{4,11} After two weeks of biological degradation, fibers were manually extracted, followed by cleaning with water and were subjected to drying in sunlight at room temperature for removing excess moisture from their surfaces. Stepwise extraction of fibers from the seed pods of *Alstonia macrophylla* tree is presented in Figure 1.

Alkali treatment of AM fiber

Raw AM fibers were soaked in 5% (w/v) aqueous solution for 60 minutes at room temperature (29 °C).¹² Afterwards, these fibers were subjected to a neutralization process, where fibers were allowed to soak in water containing 1% (w/v) acetic acid for eliminating any traces of NaOH present on the fiber surface.^{13,14} Alkali treated AM fibers were kept in air oven at 65 °C for 120 minutes. Finally, untreated and treated AM fibers were sealed in air-tight polyethylene covers until further studies were performed.



Figure 1: Extraction process of Alstonia macrophylla fiber

Analysis of chemical composition

Chemical constituents of both untreated and alkali treated AM fibers were computed in accordance with

the standard procedures. The cellulose and lignin weight fractions of the AM fibers were determined as per Kurschner and Hoffer method, and Klason method, respectively.^{12,15} The hemicellulose weight fraction was found by employing the neutral detergent fiber technique.¹⁴ The wax content of the AM fiber was measured by Conrad's approach, whereas the ash content as per ASTM E1775-61 standard.¹⁶ The density of the AM fiber was determined using the pycnometer procedure in distilled water as an immersion medium.¹⁷ An electronic moisture analyser device was employed to quantify the moisture content in the AM fiber.

X-ray diffraction (XRD) analysis

An XPERT³ powder diffractometer (Panalytical) was employed to measure the crystalline index (CI) and crystallite size (CS) of the untreated and alkali treated AM fiber. Diffractograms for the AM fiber samples were recorded in the 2θ range 10° to 80° in the continuous scanning mode, with a step of 0.05 degrees. CI and CS were determined using Segal^{18,19} and Scherrer's equations,^{20,21} respectively, as presented in Equations (1) and (2):

$$C = \frac{I_{2 \ 0 \ \overline{0}} \ I_{a \ m}}{I_{2 \ 0 \ 0}} \times 1 \ 0 \tag{1}$$

where I_{200} and I_{am} represent the intensity of the peaks of the crystalline and amorphous region, respectively.

$$C = \frac{S K\lambda}{\beta C \theta o}$$
(2)

where K is the Scherrer's constant (0.89), λ is the wave length of the radiation (0.154 nm) and β indicates the peak's full width at half-maximum.

Fourier transform infrared spectroscopy (FTIR) analysis

Untreated and alkali treated AM fiber was subjected to FTIR to analyse the functional groups and types of bonding existing in them.^{12,22} The infrared spectra on the fiber specimens were recorded with an ABB Bomem MB3000 (Canada), with a capture rate of 16 scans per minute, covering the scan range from 4000 to 400 cm⁻¹.

Single fiber tensile test

The tensile strength of the untreated and treated AM fiber was determined using a Zwick Roell universal testing machine (ASTM D3822-07), which was operated at a crosshead speed of 5 mm/min for the constant fiber gauge length of 50 mm. Twenty-five samples were tested for each untreated and treated AM fiber, and their average value was considered. Furthermore, Weibull analysis was performed for the fiber properties, namely: tensile strength, tensile modulus, and elongation at break.^{12,23,24}

Fiber length distribution (FLD)

The fiber length distribution of the AM fiber was achieved by adopting a manual technique. Around 280 fiber samples were considered for the analysis, and obtained FLD data were fitted in the histogram using SigmaPlot software V12.0.

SEM analysis

The microstructure of the untreated and alkali treated AM fiber was examined under a scanning electron microscope (SEM) (Hitachi S-3400N), with different magnifications (x350, x500, and x700). Furthermore, the diameter of the AM fiber was also measured using SEM.

RESULTS AND DISCUSSION Chemical analysis

The chemical properties of untreated and alkali treated AM fibers were determined and compared with those of other natural fibers, as shown in Table 1. It can be observed from the findings that the cellulose content of untreated and treated AM fiber is 72.59% and 78.31%, respectively. This improvement of 5.72% in the cellulose content as a result of the reduction in amorphous region may contribute to an enhancement of tensile strength, thermal stability and crystallinity properties of the fiber.¹⁴ These afore-said findings are in line with the results of the single fiber tensile test, XRD and TGA, which are described in the subsequent sections. Besides, alkali treated AM fiber exhibited lower content of lignin, wax, moisture and ash, in contrast with raw fiber, as detailed in Table 1. Higher wax content imparts poor interfacial strength between fiber and matrix.^{25,26} Meanwhile, the treatment reduces the wax content by 28.72%, which is favourable for the use of AM fiber as reinforcement in polymer composites. The ash content of the treated fiber decreased from 1.28% to 0.55%, which is far better than in any other natural fiber compared in Table 1. The density of the untreated fiber is 1.52 g/cc and that of the treated AM fiber is 1.32 g/cc. After the alkali treatment, density reduced by 13.16%, which is favourable for the fabrication of materials for light weight applications.^{25,27}

XRD analysis

X-ray diffractograms of the untreated and alkali treated AM fibers are presented in Figure 2. In this XRD plot, the untreated AM fiber exhibited two intense peaks in the 2θ range between 18.54° and 22.63° , whereas alkali treated AM fiber – at 18.15° and 22.48° , and these peaks mainly represent the existence of amorphous components and cellulose, respectively.²¹ The crystalline index (CI) of the untreated and alkali treated AM fiber was computed using Equation

and values of 35.87% and 40.54%, (1),¹⁹ respectively, were obtained. This marginal improvement in CI implies that chemical treatment has reduced the amorphous constituents.¹³ Hence, there is an increment in the ratio of crystalline constituents.³⁰ Fibers with higher CI tend to be brittle, but, at the same time, they possess higher tensile strength,³¹ and this has been confirmed in the subsequent section on tensile testing. Crystallite size (CS) of the untreated and treated AM fibers is 3.04 nm and 2.00 nm, respectively, which was determined by

employing Equation (2). The significant reduction of 34.21% in the CS of the treated AM fiber is mainly attributed to the alkali treatment. This reduction in the CS effects the close packing of the crystals and improves the resistance to moisture penetration, in contrast to the untreated AM fiber, which has higher CS.¹² Thus, the hydrophilic characteristics of the AM fiber are decreased. The obtained CI and CS of the AM fiber are compared with those of other natural fibers, as shown in Table 2.

Table 1	
---------	--

Physical and chemical properties of AM fiber and those of other cellulosic fibers reported in the literature

Fiber	Cellulose	Hemicell.	Lignin	Wax	Moisture	Ash	Density	Refs.	
	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(g/cc)		
Acacia nilotica L.	56.46	14.14	8.33	0.85	-	4.93	1.16	25	
Common reed fiber	64.56	12.57	10.84	-	-	-	-	11	
Piliostigma racemosa	60.3	0.27	30.76	-	-	-	-	24	
Shwetark	69.65	0.2	16.82	-	-	-	-	27	
Sida rhombifolia	75.09	15.43	7.48	0.49	12.02	4.07	1.32	28	
Acacia leucophloea	68.09	13.60	17.73	0.55	8.83	0.08	1.38	28	
Cyperus pangorei	68.50	-	17.88	0.17	9.19	-	1.10	28	
Saharan aloe vera	67.4	8.2	13.7	0.24	5.8	-	1.32	29	
Heteropogon contortus	64.87	19.34	13.56	0.22	7.4	-	0.602	28	
Furcraea foetida	68.35	11.46	12.32	0.24	5.43	6.53	0.77	29	
Coccinia grandis L.	62.35	13.42	15.61	0.79	5.64	4.38	1.24	29	
Ficus religiosa	55.58	13.86	10.13	0.72	9.33	4.86	-	14	
Dichrostachys cinerea	72.4	13.08	16.89	0.57	9.82	3.97	-	14	
Ziziphus mauritiana	43	10.2	5.1	-	7.9	-	1.132	12	
Phaseolus vulgaris	62.17	7.04	9.13	-	6.1	-	0.854	12	
Untreated Alstonia	72.50	28.95	12.78	3.62	8.14	1.28	1.52	This	
macrophylla fiber	12.39							work	
5% Alkali treated Alstonia	78 31	11 78	10.55	2 58	6.88	0.55	1 32	This	
macrophylla fiber	/ 0.31	/0.51	11./0	10.55	2.38	0.00	0.55	1.32	work



Figure 2: XRD results of untreated and alkali treated AM fiber

FTIR analysis

The FTIR spectra of untreated and alkali treated AM fiber are shown in Figure 3, revealing the changes in the various functional groups, as well as the reduction in the transmittance intensities after the treatment of the AM fibers. The untreated AM fiber shows a high intensity peak at 3425 cm⁻¹, unlike that of the alkali treated AM fiber. In the case of the alkali treated AM fiber, the reduction in intensity of the peaks

corresponding to 2860 cm⁻¹ and 2924 cm⁻¹ is attributed to the partial removal of the CH₂ vibration band in hemicellulosic components and CH band for cellulose.³⁹ The peak at 2360 cm⁻¹ is assigned to the streching of the C=O of lignin and hemicellulose amide groups.⁴⁰ The peak of untreated AM fiber at 1727 cm⁻¹, representing the acetyl or ester groups of hemicelluloses, is missing in the spectra of alkali treated AM fiber, owing to the removal of hemicelluloses to a great extent after the alkali treatment.¹ In the case of untreated AM fiber, higher intensity characteristic peaks corresponding to lignin are observed at 1027 cm⁻¹ (ether linkage), 1288 cm⁻¹ (C–O stretching vibration of acetyl groups), 1350 (phenolic-OH stretching) and 1543–1620 cm⁻¹ (aromatic skeletal vibration) respectively.^{41,42} The decrease in the intensity of all the peaks corresponding to lignin in the spectrum of the alkali treated AM fiber is attributed to the delignification of fibers due to chemical treatment.⁴⁴

Ta	ble	2

Thermal and crystalline characteristics of AM fiber and those of other cellulosic fibers reported in the literature

Fiber	Thermal	Max. thermal	Crystallinity		Kinetic activation	Refs.
Fiber	stability (°C)	degradation (°C)	CI, %	CS, nm	energy (kJ/mol)	
Common reed	230	370	49.02	-	-	11
Heteropogon contortus	220	337.7	54.1	-	-	28
Shwetark	225	350	72.81	3.00	-	27
Acacia nilotica L.	210	339	44.82	3.21	69.73	25
Cissus quadrangularis	270	342.1	47.15	3.91	74.18	32
stem						
Sansevieria ehrenbergii	223	232	52.27	-	-	33
Ficus religiosa	325	400	42.92	5.18	68.02	14
Prosopis juliflora bark	217	331	46	15	76.72	34
Lygeum spartum L.	220	338	46.19	-	68.77	17
Juncus effuses L.	200	300	33.4	3.6	-	35
Napier grass strands	220	383	62.4	2.83	-	36
Piliostigma racemosa	244	327	56.69	5.25	67.91	24
Phaseolus vulgaris	250	328	43.01	4.0	-	22
Catharanthus roseus	203	296	25.9	-	-	37
Cereus hildmannianus	285	356.7	40.19	28.27	-	38
Untreated Alstonia	274	373	35.87	3.04	62.79	This
macrophylla fiber						work
5% Alkali treated Alstonia	269	375	40.54	2.00	73.48	This
macrophylla fiber						work



Figure 3: FTIR spectra of untreated and alkali treated AM fiber

Single fiber tensile test

Figure 4 depicts the tensile stress-strain curves for untreated and alkali treated AM fibers. The determination of the tensile strength of fiber plays a very important role, as it provides an insight into crack propagation and failure of composites reinforced with such fibers. From the plot, it can be seen that the maximum tensile strength of the untreated and alkali treated AM fibers is 239.45 <u>+12.89 MPa and 324.89 + 29.41 MPa,</u> respectively. As far as the tensile modulus of the AM fiber is concerned, untreated fiber displays 2.07 GPa, whereas for the treated one, it is 2.43 GPa. This deviation in the tensile strength of AM fiber is due to its non-uniform inherited characteristics.^{27,44} A nearly 35.68% increment in the tensile strength and a 17.39% increment in tensile modulus of the treated AM fiber over those of the raw AM fiber are mainly due to the elimination of the amorphous constituents by the chemical treatment.^{12,45} During the tensile testing of the alkali treated AM fiber, few of the specimens endured a lower strain rate than untreated AM fiber, which may be attributed to the improvement in the stiffness of the AM fiber as its crystallinity content is increased due to the alkali treatment, which has been supported by the XRD analysis.⁴⁶ Weibull distribution plots of the

tensile properties for both untreated and treated AM fiber specimens are presented in Figure 5. As can be observed from the plot, all aforementioned parameters have followed the Weibull distribution pattern, with the Weibull slope being higher than 1 (β >1).²⁴

Fiber length distribution (FLD)

Mechanical properties of the fiber reinforced polymer (FRP) composites, such as strength, Young's modulus and fracture toughness, depend on the fiber length distribution.47 It is clearly evident from the literature survey47-49 that the inclusion of short fibers into a polymer matrix may not ensure an improvement in mechanical properties. This may be explained by a decline in the reinforcement efficiency when the fiber content in composites is increased beyond its optimal level, resulting in a FLD increment due to intense fiber-fiber interaction. In this work, the FLD of the Alstonia macrophylla fiber is depicted in Figure 6. It is clearly seen that maximum number of fibers were in the ranges of 28-32 mm and 37-41 mm. In contrast, the minimum number of fibers were in the ranges of 18-23 mm and 41-46 mm, and thus it can be deduced that the novel AM fiber would be suitable for the fabrication of continuous fiber reinforced polymer composites.



Figure 4: Single fiber tensile strength of untreated and alkali treated AM fiber

SEM analysis

In order to study the effect of chemical (alkali) treatment on AM fiber morphology, untreated and alkali treated AM fibers were observed by SEM under different magnifications (x350, x500, and x700) and the respective images are shown in

Figure 7. The diameter of the AM fiber was measured using SEM and its value was found in the range of 78.2 μ m to 111.5 μ m. SEM images of the untreated AM fiber revealed its smoothness and shiny surface characteristics, as compared to



that of treated AM fiber. This may be owing to

the presence of wax and to its lignin content.

Figure 5: Weibull plots of single fiber (a) tensile strength, (b) Young's modulus, and (c) elongation at break (%)



Figure 6: Fiber length distribution

More importantly, micrographs exposed the presence of pores in the untreated AM fiber, but after the chemical treatment, the pores were significantly reduced – this may be the reason for the lower density property of the fiber.

Moreover, the alkali treatment of AM fiber has promoted a rougher surface due to the elimination

of amorphous constituents, such as wax and others. Hence, treated AM fiber could be a good choice as a reinforcement element in producing polymer matrix composites for structural applications, as interfacial adhesion between fiber and matrix would increase due to the high cellulose content and high surface roughness.



Figure 7: SEM images of untreated and alkali treated AM fibers at various magnifications

CONCLUSION

In the present study, natural fibers were successfully extracted from a new source - the seed pods of Alstonia macrophylla, and their physico-mechanical, chemical, and surface roughness characteristics are reported. Chemical analysis results confirmed that alkali treated AM fiber has higher cellulose content than the raw AM fiber. The density of fibers was reduced by 13.16% after the alkali treatment. XRD results conveyed that the crystallinity index (CI) and crystal size (CS) of the alkali treated AM fiber were improved from 40.26% to 48.86%, and from 5.25 nm to 3.09 nm, respectively. Furthermore, this improvement in the crystallinity of the AM fiber was supported by FTIR. Tensile strength and tensile modulus of the alkali treated AM fiber increased from 239.45 + 12.89 MPa to 324.89 + 29.41 MPa, and from 2.09 GPa to 2.43 GPa, respectively. SEM morphology analysis revealed an improvement in the roughness characteristics of AM fiber. Finally, it can be concluded that alkali treated AM fiber is a promising fiber to be potentially applied as reinforcement in continuous manufacturing fiber reinforced polymer composites, exclusively for light weight applications.

REFERENCES

¹ M. G. Thomas, E. Abraham and P. Jyotishkumar, *Int. J. Biol. Macromol.*, **81**, 768 (2015), https://doi.org/10.1016/j.ijbiomac.2015.08.053

A. K. Mohanty, M. A. Khan and G. Hinrichsen,

Compos. Sci. Technol., **60**, 1115 (2000), https://doi.org/10.1016/S0266-3538(00)00012-9

³ L. Yan, N. Chouw and K. Jayaraman, *Compos. B. Eng.*, **56**, 296 (2014), https://doi.org/10.1016/j.compositesb.2013.08.014

⁴ N. Kulandaivel, R. Muralikannan and S. Kalyana Sundaram, *J. Nat. Fibers*, **17**, 769 (2020), https://doi.org/10.1080/15440478.2018.1534184

⁵ R. Dalmis, G. B. Kilic and Y. Seki, *Cellulose*, 27, 8621 (2020), https://doi.org/10.1007/s10570-020-03385-2

⁶ N. F. Jasmi, J. Kasim, N. F. Yusoff, M. C. Hussin and I. I. Maidin, *Int. J. Lastest Res. Sci. Technol.*, **3**, 150 (2014)

 ⁷ C. J. Chirayil, C. George, M. Hosur and S. Thomas, "Unsaturated Polyester Resins", Elsevier, 2019, p. 257
 ⁸ P. G. Baskaran, M. Kathiresan, P. Senthamaraikannan and S. S. Saravanakumar, *J. Nat. Fibers*, **15**, 62 (2018), https://doi.org/10.1080/15440478.2017.1304314

⁹ O. Y. Keskin, R. Dalmis and G. Balci Kilic, *Cellulose*, **27**, 9963 (2020), https://doi.org/10.1007/s10570-020-03498-8

¹⁰ M. S. Khyade, D. M. Kasote and N. P. Vaikos, *J. Ethnopharmacol.*, **153**, 1 (2014), https://doi.org/10.1016/j.jep.2014.01.025

¹¹ P. Pandiarajan and M. Kathiresan, *Int. J. Polym.* Anal. Charact., **23**, 442 (2018)

¹² A. Vinod, R. Vijay and D. Lenin Singaravelu, *J. Ind. Text.*, **51**, 2444S (2022), https://doi.org/10.1177/152808372094261

¹³ V. P. Arthanarieswaran, A. Kumaravel and S. S. Saravanakumar, *Int. J. Polym. Anal. Charact.*, **20**, 704 (2015),

https://doi.org/10.1080/1023666X.2015.1081133

¹⁴ A. A. M. Moshi, D. Ravindran, S. R. Sundara Bharathi, S. Indran and G. Suganya Priyadharshini, *Int. J. Biol. Macromol.*, **156**, 997 (2020), https://doi.org/10.1016/j.ijbiomac.2020.04.117

¹⁵ A. N. Balaji, M. K. V. Karthikeyan and V. Vignesh, *Int. J. Polym. Anal. Charact.*, **21**, 599 (2016), https://doi.org/10.1080/1023666X.2016.1192324

¹⁶ A. Saravanakumaar, A. Senthilkumar and S. S. Saravanakumar, *Int. J. Polym. Anal. Charact.*, **23**, 529 (2018),

https://doi.org/10.1080/1023666X.2018.1501931

¹⁷ Z. Belouadah, A. Ati and M. Rokbi, *Carbohyd. Polym.*, **134**, 429 (2015), https://doi.org/10.1016/j.carbpol.2015.08.024

¹⁸ A. Thygesen, J. Oddershede, H. Lilholt, A. B. Thomsen and K. Stahl, *Cellulose*, **12**, 563 (2005), https://doi.org/10.1007/s10570-005-9001-8

¹⁹ A. D. French, *Cellulose*, **21**, 885 (2014), https://doi.org/10.1007/s10570-013-0030-4

²⁰ M. Wada and T. Okano, *Cellulose*, **8**, 183 (2001)

²¹ A. D. French and M. Santiago, *Cellulose*, **20**, 583 (2013), https://doi.org/10.1007/s10570-012-9833-y

²² B. Gurukarthik Babu, D. Princewinston, S. S. Saravanakumar, P. V. Anish Khan, A. Bhaskar *et al.*,

J. Nat. Fibers, **19**, 770 (2022), https://doi.org/10.1080/15440478.2020.1761930

²³ R. Vijay, D. Lenin Singaravelu, A. Vinod, M. R. Sanjay, S. Siengchin *et al.*, *Int. J. Biol. Macromol.*, **125**, 99 (2019),

https://doi.org/10.1016/j.ijbiomac.2018.12.056

²⁴ R. Ramkumar and P. Saravanan, *J. Nat. Fibers*, **19**, 5101 (2022),

https://doi.org/10.1080/15440478.2021.1875356

²⁵ R. Kumar, S. Sivaganesan, P. Senthamaraikannan,
 S. S. Saravanakumar, A. Khan *et al.*, *J. Nat. Fibers*, 19, 199 (2022),

https://doi.org/10.1080/15440478.2020.1738305

²⁶ Y. Zhou, M. Fan and L. Chen, *Compos. Part B. Eng.*, **101**, 31 (2016),

https://doi.org/10.1016/j.compositesb.2016.06.055 ²⁷ K. Raja, B. Prabu and P. Ganeshan, *J. Nat. Fibers*,

18, 1934 (2021), https://doi.org/10.1080/15440478.2019.1710650

²⁸ N. R. J. Hyness, N. J. Vignesh and P. Senthamaraikannan, *J. Nat. Fibers*, **15**, 146 (2018), https://doi.org/10.1080/15440478.2017.1321516

²⁹ P. Senthamaraikannan and M. Kathiresan, *Carbohyd. Polym.*, **186**, 332 (2018), https://doi.org/10.1016/j.carbpol.2018.01.072

³⁰ A. D. French, *Cellulose*, **27**, 5445 (2020), https://doi.org/10.1007/s10570-020-03377-2

³¹ P. Manimaran, M. R. Sanjay and P. Senthamaraikannan, J. Nat. Fibers, **17**, 359 (2020), https://doi.org/10.1080/15440478.2018.1492491

³² S. Indran, R. E. Raj and V. S. Sreenivasan, *Carbohyd. Polym.*, **110**, 423 (2014), https://doi.org/10.1016/j.carbpol.2014.04.051

³³ T. P. Sathishkumar, P. Navaneethakrishnan, S. Shankar and R. Rajasekar, *Compos. Interfaces*, 20, 575 (2013), https://doi.org/10.1080/15685543.2013.816652
 ³⁴ S. S. Saravanakumar, A. Kumaravel, T. Nagarajan and I. Ganesh Moorthy, *Int. J. Polym. Anal. Charact.*, 19, 309 (2014),

https://doi.org/10.1080/1023666X.2014.902527

 ³⁵ M. Maache, A. Bezazi and S. Amroune, *Carbohyd. Polym.*, **171**, 163 (2017), https://doi.org/10.1016/j.carbpol.2017.04.096

 ³⁶ V. P. Kommula, K. O. Reddy and M. Shukla, *Int. J. Polym. Anal. Charact.*, **21**, 18 (2016), https://doi.org/10.1080/1023666X.2015.1089650

³⁷ A. Vinod, R. Vijay and D. Lenin Singaravelu, *Mater. Res. Express.*, **6**, 085406 (2019), https://doi.org/10.1088/2053-1591/ab22d9

³⁸ S. G. Subramanian, R. Rajkumar and T. Ramkumar, *J. Nat. Fibers*, **18**, 343 (2021), https://doi.org/10.1080/15440478.2019.1623744

³⁹ N. Kulandaivel, R. Muralikannan and S. Kalyana Sundaram, *J. Nat. Fibers*, **17**, 769 (2020), https://doi.org/10.1080/15440478.2018.1534184

 40
 M. Ramesh, L. Rajeshkumar and C. Deepa, J. Nat.

 Fibers,
 19,
 5888
 (2022),

 https://doi.org/10.1080/15440478.2021.1902896

⁴¹ H. Singh and A. Chatterjee, Cellulose, 27, 2555

(2020), https://doi.org/10.1007/s10570-019-02917-9
⁴² L. A. Costa, A. F. Fonseca, F. V. Pereira and J. I. Druzian, *Cellulose Chem. Technol.*, 49, 127 (2015), https://www.cellulosechemtechnol.ro/pdf/CCT2(2015)/p.127-133.pdf
⁴³ K. Zhang, F. Wang and W. Liang, *Polymers*

⁴³ K. Zhang, F. Wang and W. Liang, *Polymers* (*Basel*)., 10, 608 (2018), https://doi.org/10.3390/polym10060608

⁴⁴ K. O. Reddy, B. R. Guduri and A. V. Rajulu, *J. Appl. Polym. Sci.*, **114**, 603 (2009), https://doi.org/10.1002/app.30584

⁴⁵ D. B. Dittenber and H. V. S. Gangarao, *Compos. Part A. Appl. Sci. Manuf.*, **43**, 1419 (2012), https://doi.org/10.1016/j.compositesa.2011.11.019

⁴⁶ J. Jayaramudu, B. R. Guduri and A. Varada Rajulu, *Carbohyd. Polym.*, **79**, 847 (2010), https://doi.org/10.1016/j.carbpol.2009.10.046

⁴⁷ F. Asoodeh, M. Aghvami-Panah, S. Salimian, M. Naeimirad, H. Khoshnevis *et al.*, *J. Ind. Text.*, **51**, 8452S (2022),

https://doi.org/10.1177/15280837211043254

⁴⁸ S. Y. Fu, Y. W. Mai, E. C. Ching and R. K. Li, *Compos. Part A. Appl. Sci. Manuf.*, **33**, 1549 (2002), https://doi.org/10.1016/S1359-835X(02)00114-8

 ⁴⁹ R. M. Bajracharya, A. C. Manalo, W. Karunasena and K. T. Lau, *Compos. Part A. Appl. Sci. Manuf.*, 84, 405 (2016),

https://doi.org/10.1016/j.compositesa.2016.02.025