Journal of Natural Fibers

ISSN: 1544-0478 (Print) 1544-046X (Online) Journal homepage: https://www.tandfonline.com/loi/wjnf20

Studies on Ramie cellulose microfibrils reinforced cassava starch composite: influence of microfibrils loading

Edi Syafri, Anwar Kasim, Alfi Asben, P. Senthamaraikannan & M.R. Sanjay

To cite this article: Edi Syafri, Anwar Kasim, Alfi Asben, P. Senthamaraikannan & M.R. Sanjay (2020) Studies on Ramie cellulose microfibrils reinforced cassava starch composite: influence of microfibrils loading, Journal of Natural Fibers, 17:1, 122-131, DOI: 10.1080/15440478.2018.1470057

To link to this article: https://doi.org/10.1080/15440478.2018.1470057

JOURNAL OF NATURAL FIBERS
2020, VOL. 17, NO. 1, 122–131
https://doi.org/10.1080/15440478.2018.1470057

Taylor & Francis
Taylor & Francis Group

Studies on Ramie cellulose microfibrils reinforced cassava starch composite: influence of microfibrils loading

Edi Syafri [a], Anwar Kasim[b], Alfi Asben[c], P. Senthamaraikannan [d], and M.R. Sanjay [e]

[a]Department of Agricultural Technology, Agricultural Polytechnic, Payakumbuh, West Sumatra, Indonesia;
[b]Department of Agricultural Product Technology, Andalas University Kampus Limau Manis, West Sumatra, Indonesia;
[c]Department of Mechanical Engineering, Andalas University Kampus Limau Manis, West Sumatra, Indonesia;
[d]Department of Mechanical Engineering, Kamaraj College of Engineering and Technology, Virudhunagar, India;
[e]Department of Mechanical Engineering, Ramaiah Institute of Technology, Bengaluru, India

ABSTRACT

Composites were fabricated from Ramie cellulose microfibrils (RCMF) with cassava starch as matrix and glycerol as a plasticizer. Different composites were fabricated with microfibrils loadings of 0, 2, 4, 8, and 10 wt%. The Particle Size Analyzer results show the average size of RCMF as 1.573 µm. The addition of RCMF considerably influenced the physical, crystalline, thermal, and tensile properties of composites. The addition of RCMF enhanced the crystallinity index (CI) from 32% to 36.67%. Thermogravimetric analysis and tensile test results showed improvement in thermal stability and tensile strength of composite up to 6 wt% microfibrils addition.

摘要

以Ramie纤维素微纤维（RCMF）为原料，以木薯淀粉为基质，甘油为增塑剂，制备了复合材料。用微纤维负载量分别为0、2、4、8和10WT%制备不同的复合材料。粒度分析结果表明，Ramie纤维素微纤维的平均粒径为1.573µm。苎麻纤维素微纤维的加入显著影响了复合材料的物理、结晶、热、拉伸性能。苎麻纤维素微纤维的加入使结晶度指数（CI）从32%提高到36.67%。热重分析和拉伸试验结果表明，复合材料的热稳定性和拉伸强度提高到6重量%的微纤维。

KEYWORDS

Cassava starch; Ramie cellulose microfibrils; thermal stability; tensile strength

关键词

木薯淀粉; 纤维素微纤维; 热稳定性; 抗拉强度

Introduction

The inventions of biodegradable materials are necessary for overcoming today's environmental pollution. Thus, many of the researchers are focusing on natural-fiber-reinforced polymer composites instead of synthetic-fiber-reinforced composites (Senthamaraikannan et al. 2015; Rajesh Jesudoss Hyness et al. 2018). Moving toward natural fibers, most of the researchers are still using matrix material as synthetic resins. So, the resultant composites are partially biodegradable material. To make completely bio degradable material, we have to move toward the biodegradable matrix. Cassava (*Manihotesculenta*) starch is one of the commercially available biodegradable matrices throughout the world (Tongdeesoontorn et al. 2011). However, the cassava starch is brittle in nature which results in poor mechanical properties; to overcome this difficulty, plasticizers are added to the starch which may decrease the brittleness of the material and enhance the process ability. On the other hand, it may reduce the degradation temperature of starch (Chang et al. 2006). In addition to these, starch has higher water absorption nature. Reinforcement of natural fiber is one of the efficient

CONTACT P. Senthamaraikannan senthamaraikannan1991@gmail.com; senthamaraimech@kamarajengg.edu.in
Department of Mechanical Engineering, Kamaraj College of Engineering and Technology, Virudhunagar 626001, Tamilnadu, India.

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/wjnf.

methods to improve the performance of the starch-based composite. The hydrophilic character of natural fiber may disturb the bonding between fiber and matrix which may be considerably reduced by surface modification of fibers (Saravanakumar et al. 2014). The fiber size also plays an important role in the composite properties (Kathiresan. and Sivaraj 2015; Sanjay et al. 2018). In this study, we have characterized the Ramie cellulose microfibrils (CMF)-reinforced cassava starch composites through TGA, FTIR, XRD, SEM, tensile testing and water absorption test for checking the effect of microfibrils loading on the physical, chemical, thermal, and tensile properties.

Materials and methods

Materials

Cassava starch (Cap Tani, Indonesia), Glycerol (PT Cisadane Raya Chemicals, Tangerang Indonesia), and CMF were used to manufacture the composite. NaOH, KOH, $NaClO_2$ were utilized for the preparation of CMF.

Preparation of Ramie cellulose microfibrils

Various processes involved in preparation of CMF are illustrated in Figures 1 and 2 which presents different forms of Ramie.

Composite preparation

The procedure followed by the Tongdeesoontorn et al. was adopted with some modification for preparation of thermoplastic starch (TPS) composites (Figure 3) (Tongdeesoontorn et al. 2011). Cassava starch of 10 g and glycerol of 2.5 g (plasticizer) were dissolved in 140 ml of water and then 0, 0.2, 0.4, 0.6, 0.8, 1 g of Ramie CMF were mixed with this solution for making different composite varieties as noted in Table 1. The (Cassava starch/glycerol/CMF) solutions were heated up to 100°C with continuous stirring (350 rpm) to gelatinization and then poured into a glass mould ($20 \times 20 \times 0.5$ cm^3). The mould setup is placed in ultrasonic bath for removing voids from composite and then is positioned in an oven at 40°C for 5 h.

Particle size analyzer

The particle sizes of CMF were finalized by Particle Size Analyzer (DelsaNano C) with the capacity to measure 0.6 nm to 30 mm. The samples were mixed with deminaralized water and then laser light was passed through this solution and the scattering angle was measured to find the particle size. Experiments were done at 25°C and Delsa Nano software was used for data processing.

Thermogravimetric analysis (TGA)

The thermal stability of composites was measured by the TGA 4000 (Perkin Elmer) instrument. The samples were heated from room temperature to 400°C with the heating rate of 10°C/min. Nitrogen gas was passed with the mass flow rate of 40 ml/min during the experimentation (Prithiviraj et al. 2016).

Fourier transformed infrared spectroscopy (FTIR)

The FTIR (Perkin Elmer) spectrums of composites were documented to find the structural difference between composites. The spectrums were recorded from 4000 to 600 cm^{-1} wave number range at room temperature with the resolution of 4 cm^{-1}(Kathiresan et al. 2016).

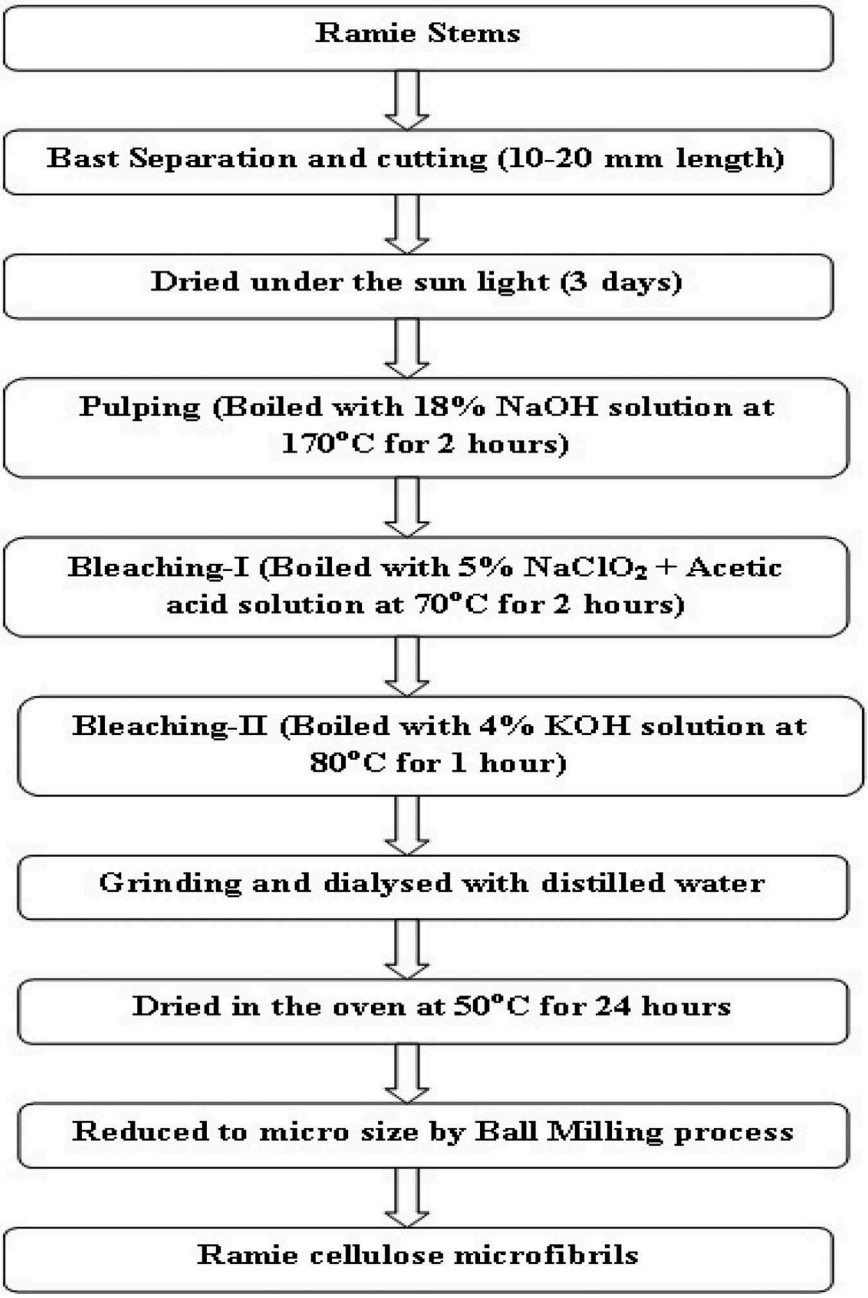


Figure 1. Preparation of Ramie cellulose microfibrils.

X-ray diffraction (XRD) analysis

Crystallinity index (CI) is the important parameter which influences the tensile properties of the composites. In order to investigate the effect of microfibrils loading on the CI of the composites, the X-ray diffractograms of composite were recorded by PANalytical's X-ray diffractometer in the 2θ range of 10.0181° to 99.9781°. The experimentation conditions were: Generator Settings (30 mA, 40 kV), continuous scanning with the step size of 2θ = 0.001°, and measurement temperature (25°C).

Figure 2. (a) Chopped Ramie fibers, (b) pulped Ramie powder, (c) bleached Ramie powder.

The CI was assessed through the following equation (Manimaran et al. 2018):

$$I_c = \left(1 - \frac{I_{am}}{I_{002}}\right) \times 100\,\% \tag{1}$$

where I_{002} is the intensity of crystalline peak, and I_{am} is the intensity of amorphous peak in the XRD spectrum.

Tensile testing

The tensile strength, young's modulus, and strain (%) of composite were measured by a Com-Ten of 95T Series tensile testing machine. The tests were conducted as per the guidelines of ASTM D 638-1 (Tongdeesoontorn et al. 2011). All the trials were carried out at crosshead speed of 2 mm/min in the ambient temperature.

Results and discussion

Particle size analyzer

The combined pulping, bleaching, and grinding processes converted Ramie cellulose fiber into CMF with an average size of 1.573 µm which is used as reinforcement in composites. Figure 4(a) shows the size distribution of microfibrils.

Thermogravimetric analysis (TGA)

The TGA curves of the composites were presented (Figure 4(b)) to understand the effect of CMF on the thermal stability of composites. From Table 2 it was established that the initial degradation temperature (IDT), final degradation temperature (FDT), and inflection point of composites increased up to 6 wt% on microfibrils addition and after that, it decreased. The first phase happened between 90 and 115°C, which is related to the loss of moisture and related impurities in the composites (Sadanand et al. 2017). The second phase of mass loss occurred between 280°C and 345°C which may be due to the decomposition of cellulose, hemicellulose, and lignin in the composite (Alireza Ashori & Reza Bahrami 2014) The final, tailing phase from 345°C to 500°C indicated the degradation of the charred residue.

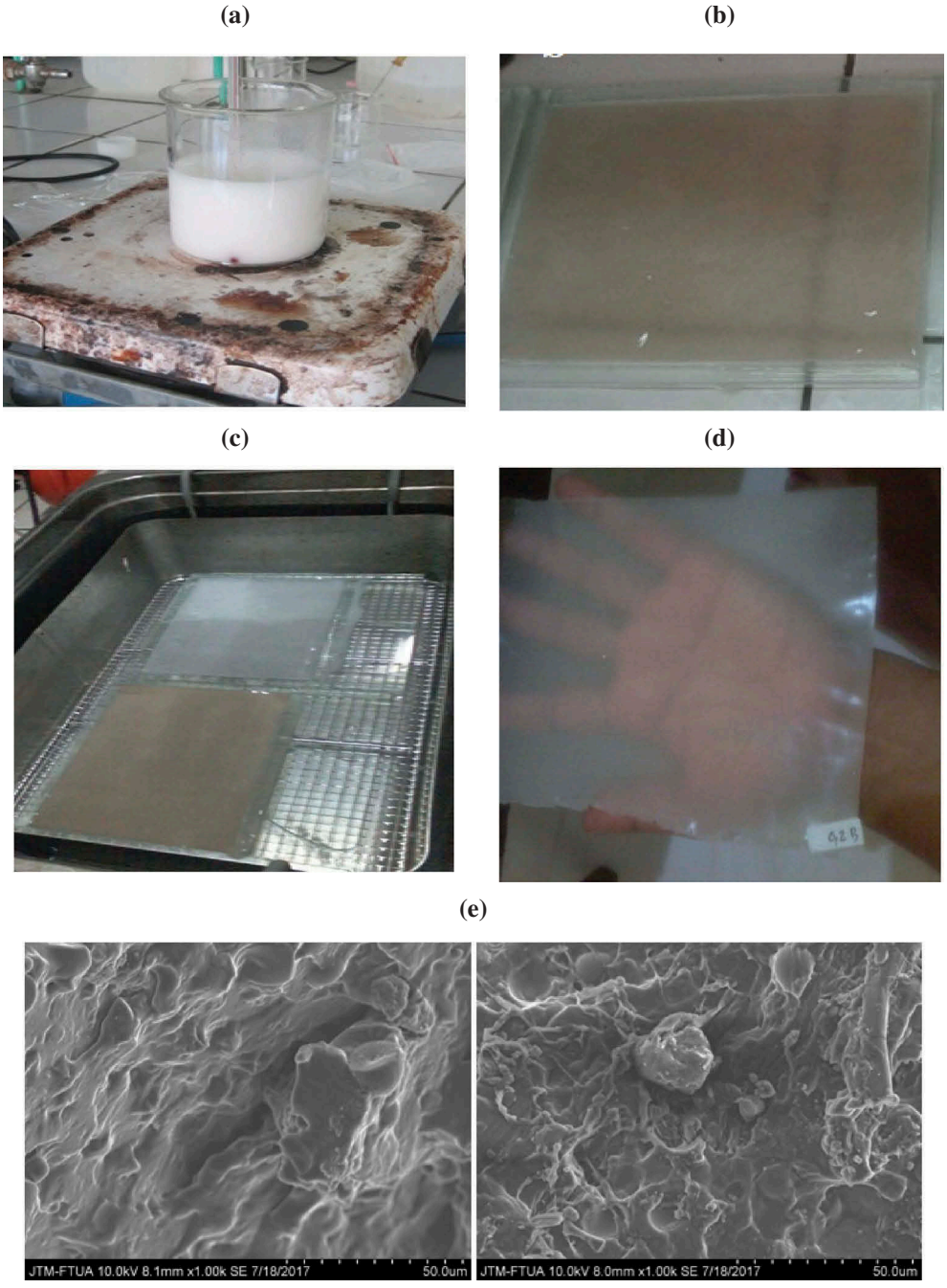


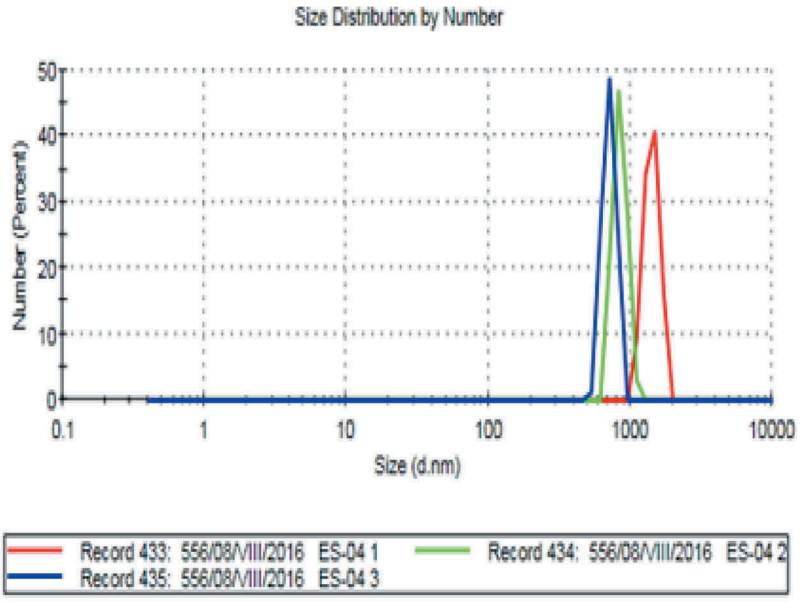
Figure 3. (a) Cassava starch/glycerol/CMF solution (before gelatinization), (b) poured into the mould, (c) mould placed in the ultrasonic bath, (d) composite (after removed from mould), and (e) SEM images of Ramie cellulose microfibrils-reinforced cassava starch composites.

Fourier transformed infrared spectroscopy (FT-IR)

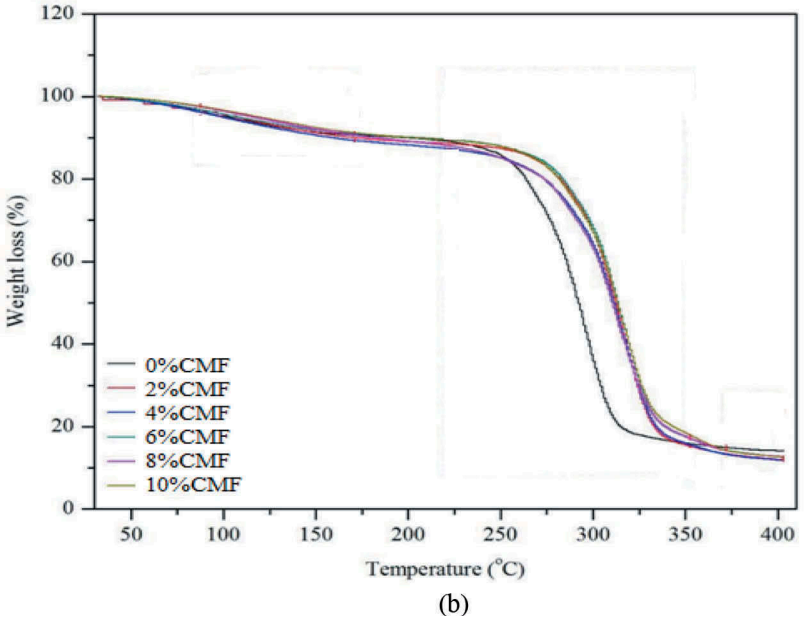
The chemical functional groups existing in the CMF-reinforced cassava starch composites were investigated by FT-IR (Figure 5(a)). FT-IR spectra of all the specimens have similar bands which show that cassava starch is not chemically affected or modified by the glycerol or the fiber loading

Table 1. Composition of Ramie cellulose microfibrils-reinforced cassava starch composites.

	Composition (g/140 ml distilled water)		
Composite	Cassava starch (g)	Glycerol (g)	Ramie CMF (g)
TPS + 0% CMF	10	2.5	0
TPS + 2% CMF	10	2.5	0.2
TPS + 4% CMF	10	2.5	0.4
TPS + 6% CMF	10	2.5	0.6
TPS + 8% CMF	10	2.5	0.8
TPS + 10% CMF	10	2.5	1



(a)

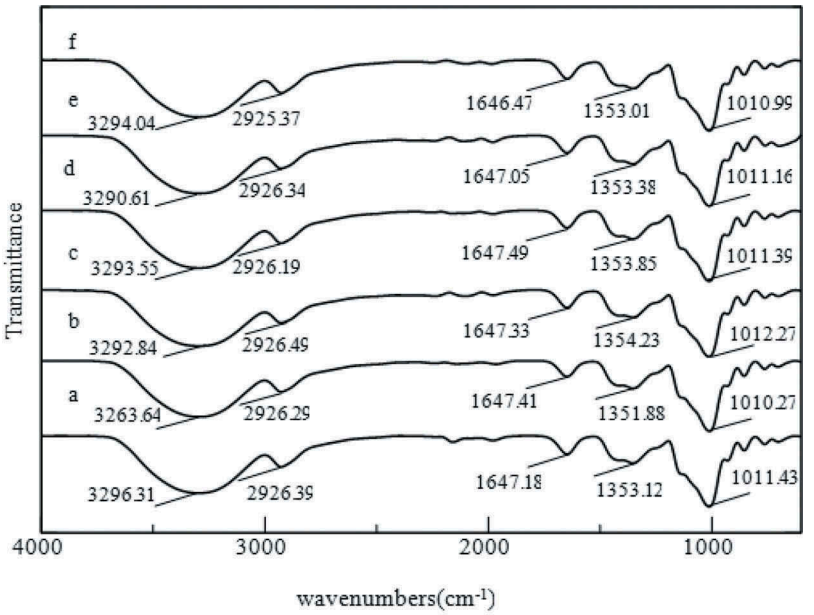


(b)

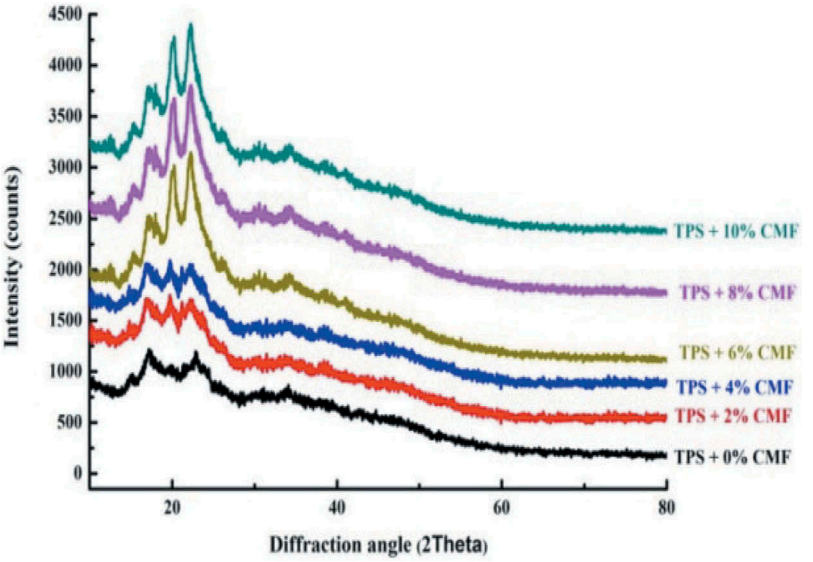
Figure 4. (a) Distribution of size CMF Ramiemicrofibrils, (b) TGA of RCMF reinforced cassava starch composites.

Table 2. Thermal degradation parameters of RCMF-reinforced cassava starch composites.

Composite	IDT (°C)	FDT (°C)	Inflection point (°C)	Char content (%)	Moisture content (%)
TPS + 0% CMF	281.46	336.61	310.62	11.56	9.42
TPS + 2% CMF	285.29	338.71	316.67	12.15	10.71
TPS + 4% CMF	286.87	340.14	316.92	11.99	11.27
TPS + 6% CMF	291.41	342.42	318.98	12.63	9.72
TPS + 8% CMF	288.78	338.77	316.42	12.56	10.31
TPS + 10% CMF	271.71	339.78	313.82	12.67	10.73



(a)



(b)

Figure 5. (a) FTIR analysis of Ramie cellulose microfibrils reinforced cassava starch, (b) XRD analysis of Ramie cellulose microfibrils reinforced cassava starch.

during the composite manufacturing (Edi Syafri et al. 2017). From Figure 5(a) it can be detected that five distinct bands were existing in all the samples nearby 3296, 2926, 1647, 1353, and 1011 cm^{-1} (Senthamaraikannan et al. 2015). The band around 3296 cm^{-1} specify the occurrence of O–H groups in cassava starch and microfibrils which illustrate that composites are reactive to water molecules because of the existence of hydroxyl groups (Kishanji et al. 2017). The band raised nearby 2926 cm^{-1} belongs to the C–H stretching vibrations. The band around 1647 cm^{-1} validates the occurrence of water in the composites. The bands formed between 1353 cm^{-1} and 1647 cm^{-1} are an indication of the occurrence of strong and broad –C–O stretching, which is the alcohol groups of cellulose (Syafri et al. 2017). The bands around 1353 cm^{-1} and 1010 cm^{-1} are corresponding to the C–OH bending vibrations. Table 3 presents the band positions and assignments of chemical groups in the CMF-reinforced cassava starch composites.

X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) analyses were executed to find out the influence of microfibrils content on the CI of the composites. The XRD spectrums of the CMF-reinforced cassava starch composites are shown in Figure 5(b). Two important peaks were detected at $2\theta = 16.6°$ (amorphous phase) and $2\theta = 22.3°$ (crystalline phase) indicating the presence of cellulose type-I which signifies its semi crystalline nature. The minor peak at $2\theta = 16.6°$ is attributed to (2 0 0) crystallographic plane contributing toward amorphous fraction and the major peak at $2\theta = 22.3°$ is ascribed to (0 0 2) crystallographic plane showing the occurrence of both amorphous and crystalline fractions. From Table 4 it was recognized that the composite with a higher microfibrils content have a higher CI. CMF are orientated materials than cassava starch, which influenced the crystallinity of the composites (Edi Syafri et al. 2017).

Tensile testing

The tensile behavior of CMF-reinforced cassava starch composites are shown in Table 5. It is detected that the tensile strength and young's modulus of composites enhanced with addition of microfibrils content up to 6 wt%; after that, it decreased which may be due to the lack of interfacial bonding between the microfibrils and cassava starch above 6 wt% microfibrils addition (Tongdeesoontorn et al. 2011). If the microfibrils content is more than 6 wt%, the cassava starch matrix will not be sufficient to dissolve the microfibrils and so tensile strength and young's modulus of composites were reduced. However, strain rate of composites decreased with addition of microfibrils content. The 6 wt% microfibrils added composite delivered favorable properties than other composites which directs enhanced stress transfer between the microfibrils to the matrix and interfacial bonding in this composite (Sanjay et al. 2018)

Table 3. Peak positions and assignments of chemical groups in the Ramie cellulose microfibrils-reinforced cassava starch composites.

Peak positions (Wavenumber (cm^{-1}))							
Ideal FTIR peak position	TPS + 0% CMF (a)	TPS + 2% CMF (b)	TPS + 4% CMF (c)	TPS + 6% CMF (d)	TPS + 8% CMF (e)	TPS + 10% CMF (f)	Allocations
3600–3100	3296.31	3263.64	3292.84	3293.55	3290.61	3294.04	O–H stretching vibration of cellulose molecules
2960–2850	2926.35	2926.29	2926.49	2926.19	2926.34	2925.37	C–H stretching vibrations
1740–1600	1647.18	1647.41	1647.33	1647.49	1647.05	1646.47	Presence of water
1320	1353.12	1353.88	1353.23	1353.85	1353.38	1353.01	C–OH bending vibrations
1050–1020	1011.43	1010.27	1012.27	1011.39	1011.16	1010.99	C–OH stretching

Table 4. The crystallinity index of RCMF-reinforced cassava starch composites.

Composite	Crystallinity index (%)
TPS + 0% CMF	23.91
TPS + 2% CMF	26.24
TPS + 4% CMF	28.46
TPS + 6% CMF	34.56
TPS + 8% CMF	35.72
TPS + 10% CMF	36.67

Table 5. Mechanical properties of the Ramie cellulose microfibrils-reinforced cassava starch composites.

CMF Ramie contents	Tensile strength (MPa)	Tensile modulus (MPa)
TPS + 2% CMF	5.65	188.45
TPS + 4% CMF	6.37	235.31
TPS + 6% CMF	7.41	261.22
TPS + 8% CMF	5.25	234.82
TPS + 10% CMF	4.88	181.81

Conclusion

CMF-reinforced composites were produced with the main aim to create completely biodegradable composites with better performance. The addition of CMF considerably improved the performances such as thermal stability, tensile strength, and CI of the composites. However, no noteworthy chemical functional group modification was found on the FTIR spectrums. The tensile strength of the composites was improved from 1.65 ± 0.21 MPa to 7.41 ± 1.63 MPa (6 wt%) and tensile stability was enhanced from 281.46°C to 291.41°C (6 wt%).

ORCID

Edi Syafri http://orcid.org/0000-0002-5784-6694
P. Senthamaraikannan http://orcid.org/0000-0002-5136-2269
M.R. Sanjay http://orcid.org/0000-0001-8745-9532

References

Ashori, A., and R. Bahrami. 2014. Modification of physico-mechanical properties of chitosan-tapioca starch blend films using nano graphene. *Polymer-Plastics Technology and Engineering* 53:312–18. doi:10.1080/03602559.2013.866246.

Chang, Y. P., A. Abd Karim, and C. Seow. 2006. Interactive plasticizing antiplasticizing effects of water and glycerol on the tensile properties of tapioca starch films. *Food Hydrocolloids* 20 (1):1–8. doi:10.1016/j.foodhyd.2005.02.004.

Kathiresan, M., P. Pandiarajan, P. Senthamaraikannan, and S. S. Saravanakumar. 2016. Physicochemical properties of new cellulosic *Artisditahystrix* leaf fiber. *International Journal of Polymer Analysis and Characterization* 21 (8):663–68. doi:10.1080/1023666X.2016.1194636.

Kathiresan., M., and P. Sivaraj. 2015. Preparation and characterization of biodegradable sugarcane bagasse nano reinforcement for polymer composites using ball milling operation. *International Journal of Polymer Analysis and Characterization* 21 (5):428–35. doi:10.1080/1023666X.2016.1168061.

Kishanji, M., G. Mamatha, K. Obi Reddy, A. VaradaRajuluand, and K. Madhukar. 2017. In situ generation of silver nanoparticles in cellulose matrix using *Azadirachtaindica* leaf extract as a reducing agent. *International Journal of Polymer Analysis and Characterization* 22 (8):734–40. doi:10.1080/1023666X.2017.1369612.

Manimaran, P., P. Senthamaraikannan, K. Murugananthan, and M. R. Sanjay. 2018. Physicochemical properties of new cellulosic fibers from Azadirachtaindica plant. *Journal of Natural Fibers* 15 (1):29–38. doi:10.1080/15440478.2017.1302388.

Prithiviraj, M., R. Muralikannan, P. Senthamaraikannan, and S. S. Saravanakumar. 2016. Characterization of new natural cellulosic fiber from *PerotisIndica* plant. *International Journal of Polymer Analysis and Characterization* 21 (6):669–74. doi:10.1080/1023666X.2016.1202466.

Rajesh JesudossHyness, N., N. J. Vignesh, P. Senthamaraikannan,S.S.Saravanakumar, and M. R. Sanjay. 2018. Characterization of new natural cellulosic fiber from *Heteropogoncontortus* plant. *Journal of Natural Fibers* 15 (1):146–53. doi:10.1080/15440478.2017.1321516.

Sadanand, V., F. A. Tia Hua, V. Rajulu, and B. Satyanarayana. 2017. Preparation and properties of low cost cotton nanocomposite fabrics with in situ generated copper nanoparticles by simple hydrothermal method. *International Journal of Polymer Analysis and Characterization* 22 (7):587–94. doi:10.1080/1023666X.2017.1344916.

Sanjay, M. R., P. Madhu, M. Jawaid, P. Senthamaraikannan, S. Senthil, and S. Pradeep. 2018. Characterization and properties of natural fiber polymer composites: a comprehensive review. *Journal of Cleaner Production* 172:566–81. doi:10.1016/j.jclepro.2017.10.101.

Saravanakumar, S. S., A. Kumaravel, T. Nagarajan, and I. Ganesh Moorthy. 2014. Investigation of physico-chemical properties of alkali-treated prosopis juliflora fibers. *International Journal of Polymer Analysis and Characterization* 19:309–17. doi:10.1080/1023666X.2014.902527.

Senthamaraikannan, P., S. S. Saravanakumar, V. P. Arthanarieswaran, and P. Sugumaran. 2015. Physicochemical properties of new cellulosic fibers from bark of *acacia planifrons*. *International Journal of Polymer Analysis and Characterization* 21 (3):207–13. doi:10.1080/1023666X.2016.1133138.

Syafri, E., A. Kasim, H. Abral, and A. Asben. 2017. Effect of precipitated calcium carbonate on physical, mechanical and thermal properties of cassava starch bioplastic composites. *International Journal on Advanced Science, Engineering and Information Technology* 7 (5):1950–54. doi:10.18517/ijaseit.7.5.1292.

Tongdeesoontorn, W., L. J. Mauer, S. Wongruong, P. Sriburi, and P. Rachtanapun. 2011. Mechanical and physical properties of cassava starch-gelatin composite films. *International Journal of Polymeric Materials and Polymeric Biomaterials* 61:778–92. doi:10.1080/00914037.2011.610049.