Effect of glycerol on the properties of coconut oil cake reinforced poly(lactic acid)

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Abstract: The effect of the addition of 10–25 wt% coconut oil cake (COC) on the properties of poly(lactic acid) (PLA) was studied. PLA/COC (80/20) composite showed better mechanical properties and higher thermal stability than PLA. Glycerol used as a plasticizer further improved tensile and flexural mechanical properties, as well as the impact strength and the ability to suppress noise.

Keywords: poly(lactic acid), copra, glycerol, mechanical properties, thermal properties, noise damping properties.

Wpływ glicerolu na właściwości poli(kwasu mlekowego) wzmocnionego makuchami z oleju kokosowego

Streszczenie: Zbadano wpływ dodatku 10–25% mas. makuchów z oleju kokosowego (COC) na właściwości poli(kwasu mlekowego) (PLA). Kompozyt PLA/COC (80/20) wykazywał lepsze właściwości mechaniczne i wyższą stabilność termiczną niż PLA. Glicerol zastosowany jako plastyfikator dodatkowo poprawił właściwości mechaniczne przy rozciąganiu i zginaniu, a także udarność i zdolność do tłumienia hałasu.

Słowa kluczowe: poli(kwas mlekowy), makuchy oleju kokosowego, glicerol, właściwości mechaniczne, właściwości termiczne, właściwości tłumiące hałas.

India is one of the largest producers of coconut in the world. The residue left behind after the extraction of coconut oil from dried coconuts is called coconut oil cake (COC), natively known as copra (dried coconut kernels, from which oil is obtained) [1]. The annual average production of COC currently used as a meal for farm animals and poultry feed throughout the country is approximately up to 17,000 million tons. It contains 72% fat, 8% protein, 7% fiber, and negligible amounts of carbohydrate, ash, and moisture [2]. During further drying the COC, its gross weight is reduced resulting in a very light weighing material. This product is considered as the polymer reinforcement providing a light weight composite material.

Poly(lactic acid) (PLA) is another derivative of vegetable starch that is developed through the polymerization process of carbohydrates from plants like tapioca, potato, *etc*. This biopolymer is known for its excellent inherent mechanical properties in comparison with other biopolymers [3, 4]. PLA composites reinforced with long and short natural fibers and the molecular form of reinforcements showed positive mechanical properties described in most of the literature [5]. Currently developed PLA/natural fibers composites like, *e.g.*, PLA/maple wood flour for industrial bioplastics [6], PLA/poplar wood flour used as 3D printing materials [7], PLA/paddy straw powder as a food packaging material [8], PLA/Prosopis juliflora and PLA/Azadirachta indica as structural materials [9, 10], PLA/Tamarindus indica as biomedical material [11], and numerous other versatile applications are widely studied. Recent research focuses on such a novel combination of PLA/COC and its use in automobile floor mat applications.

EXPERIMENTAL PART

Materials

Poly(lactic acid) of grade 3052D was sourced from NatureTec industries Chennai, India. The material had melting temperature of 170°C, glass transition temperature of 55–60°C, and crystallization temperature of 150–155°C. It was in a form of granules with a density of 1.24 kg/m^3. Coconut oil cake was obtained from V.K.T. Ginning mills Chennai, India. It was sun dried in the shape of flat biscuits. The plasticizer used in this research, glycerol having a density of 1.13 kg/m^3, was sourced from Sri Sakthi enterprises Chennai, India.

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Preprocessing

The sun dried COC was subjected to drying in order to retain the fiber content and maximum reduce the amount of oil content that may decrease the bonding of the matrix and fiber during processing. This was achieved by heating the raw COC in an induction furnace at 180°C for 48 hours [10]. During the heating process the oil present in the raw COC turned volatile, evaporated and left the remains of dry coconut cake residue. The COC residue was then ground using a food blender at 1000 rpm for 2 minutes to obtain fine powdered COC [9], which was subsequently sieved using a #400 mesh to obtain reinforcement material, having a maximum particle size of 30 μm.

Processing Technology

Phase I

Measured quantities of PLA and COC were initially formed into composite pellets using a mini twin screw extruder (Rheomix, model S1000) at 180°C and 100 rpm screw speed [9]. The pellets were then formed into a composite slab using compression moulding machine (JRRD, model CE-15) under a pressure of 6 bar for 12 hours at 180°C [12]. The test specimens were then cut to dimensions according to ASTM standard using wire cut EDM. The ratio of composite components and specimen codes used in both phase I and phase II are summarized in Table 1.

T a b l e 1. Content of the composites

Specimen Code	PLA, wt%	COC, wt%	Glycerol, wt%
Phase I			
P	100	0	0
PC1	90	10	0
PC2	85	15	0
PC3	80	20	0
PC4	75	25	0
Phase II			
PCG1	79	19	2
PCG2	78	18	4
PCG3	77	17	6

Since strong evidence from many previous studies stated that reinforcement of polymers with natural fibers below 5 wt% does not show any significant change in the properties, the initial COC filler content was considered not lower than 10 wt% [5, 9, 10].

Phase II

In the second phase of the research, the best performing specimen during the first phase was selected for further studies. Due to high stiffness of the PLA/COC composites it was decided to improve the material's flexibility, taking into consideration the application that the composite was developed for. In this study, PC3 composite with PLA:COC ratio of 80:20 showed the best performance in phase I. It was treated with glycerol as an additive to improve plasticity [13]. For the preparation of the PLA/COC/glycerol composites, 80 wt% of PLA and 20 wt% of COC were thoroughly melt mixed using stir casting technique. This method had been proven successful for processing PLA-based composites with powdered reinforcements in previous research carried out by the author [14]. The stir casting parameters were adapted to 200°C and 50 rpm stirrer speed. After 7 minutes of melt mixing and assured homogeneity the furnace temperature was switched off and measured quantity of glycerol was added and stirred again thoroughly with stirrer speed increased to 100 rpm. When the composite still remained in its molten state, it was poured onto the platform of the compression molding machine and processed into test specimens in similar method as performed in phase I.

Methods

Mechanical characterization of all the composites was done according to ASTM standards [15]. Tensile test was performed according to ASTM D638 using Universal Testing Machine (UTM) (INSTRON, model 3365) at a load of 10 kN and cross head speed of 5 mm/min. Three-point bending flexural test was performed according to ASTM D790 using the same UTM by changing the fixtures while maintaining similar testing parameters [16]. Izod impact test was performed according to ASTM D256 with an impact load of 25 J. Water absorption test was performed according to ASTM D570. Noise damping test was performed using tunnel testing method [17], similarly to other studies on composites used in noise reduction in automotive exhausts [18]. Composites PC3 and PCG2 were compared with plain rubber mats that are currently used as automobile floor mats. Test specimens were cut into circular discs of 5 inch diameter and 3.2 mm thickness and placed in the middle part of the tunnel tube. The noise emitted from the source at one end was measured in decibels at the receiving end using a sound level meter (Figure 1).

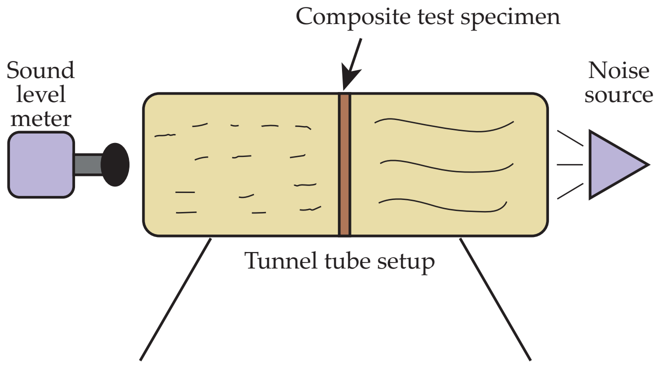

Fig. 1. Sound test impedance tube

RESULTS AND DISCUSSION

The addition of COC to PLA matrix resulted in marginal increment in tensile strength. At 10 wt% reinforcement of COC, the tensile strength did not show any significant change while higher COC content resulted in an increase of tensile strength of PLA from 58 MPa to 60.5 MPa for PC1, 66 MPa for the PC2, and 71 MPa for the PC3, and 68 MPa for the PC4 specimen. The tensile modulus showed increasing trend with addition of COC as depicted in Figure 2. The increment in tensile properties might be due to the good adhesion of the COC with PLA. The decrement of tensile properties of PC4 was due to internally blowhole defects caused by the dominating COC content in the matrix [10]. Flexural strength and modulus of PLA increased with addition of COC as shown in Figure 3. The flexural properties were the best for PC3, which exhibited flexural strength and flexural modulus increased by 38% and 44% respectively when compared to P. The increase in flexural properties was due to the increased stiffness attained by PLA due to the addition of COC. The impact strength of the COC reinforced composites was higher than that for plain PLA as shown in Figure 4, and it was the best in case of PC3. The COC had provided better absorption of the impact energy than the plain PLA specimen thereby resulting in better toughness. At 25 wt% reinforcement the larger content of COC resulted in quicker and sudden fracture of the specimen due to blowholes and lower stress transfer ability within the matrix and reinforcement [9]. Water absorption test showed increased water uptake with increasing of COC content. The inherent tendency of the natural fiber to absorb moisture revealed in the following data [5] depicted in Figure 5. Thermogravimetric analysis (TGA) was performed with 50 mg of sample powders under the nitrogen atmosphere using SDT Q600 TGA equipment. The temperature range varied from 20°C to 500°C with the rate of 20°C/min. TGA of the composites in comparison with plain PLA showed increasing trend with increasing of COC content as depicted in Figure 6. It was due to the better thermal stability of COC. The thermal stability of PLA increased from 210°C to 260°C for PC3. PLA had no remains while the composites showed very small quantities of residue in the form of ash.

Phase II of the study was continued using previously selected 20 wt% reinforced PLA/COC composite. Since PC3 showed the best performance in mechanical tests, it was considered to be further treated with glycerol and the effect of its addition on composite mechanical properties was studied. Glycerol was added to PC3 in three amounts: 2, 4, and 6 (wt% glycerol). The effect of glycerol on PC3 composite is comparatively tabulated in Table 2.

The addition of glycerol in general improved the mechanical properties of the PC3 composite. This phenomenon was similar to the results obtained in related studies in which glycerol was used to improve the physical properties of polymer composites [19]. The morpho-

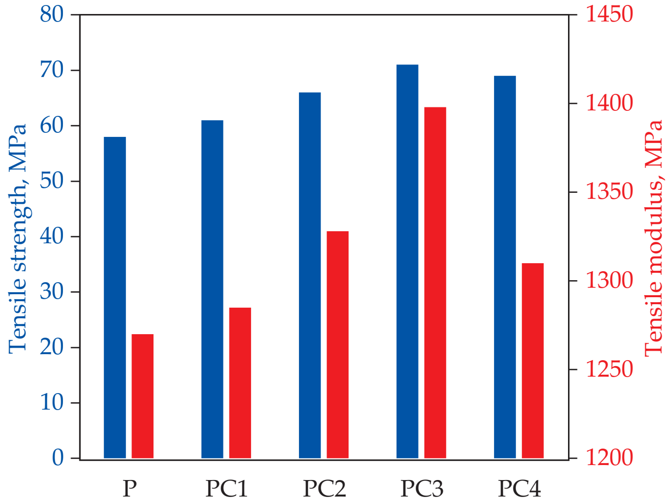

Fig. 2. Tensile strength and modulus of PLA biocomposites

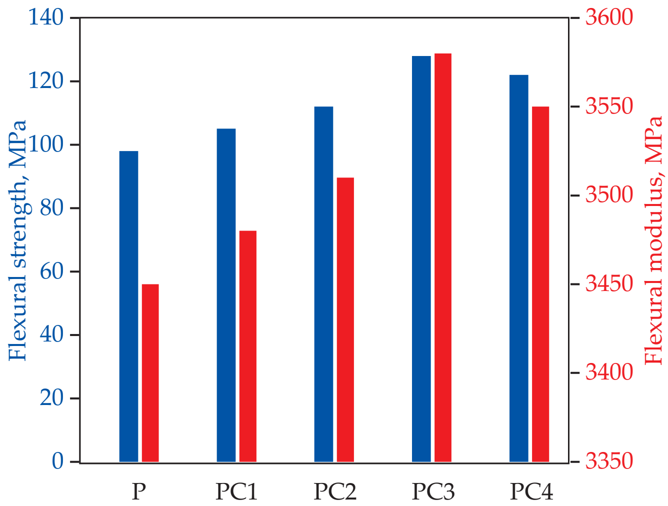

Fig. 3. Flexural strength and modulus of PLA biocomposites

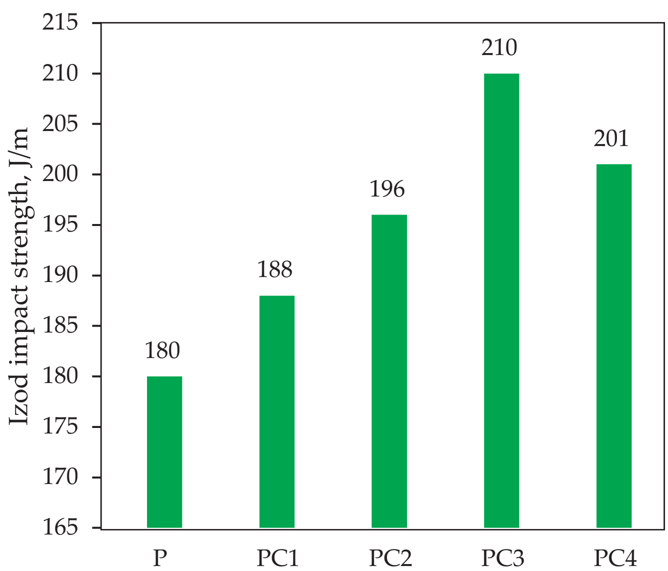

Fig. 4. Impact strength of PLA biocomposites

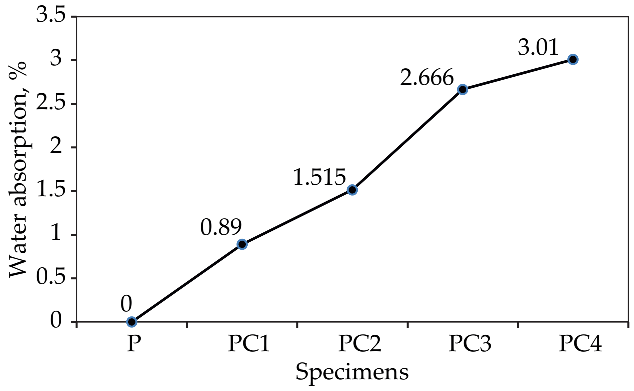

Fig. 5. Water absorption of PLA biocomposites

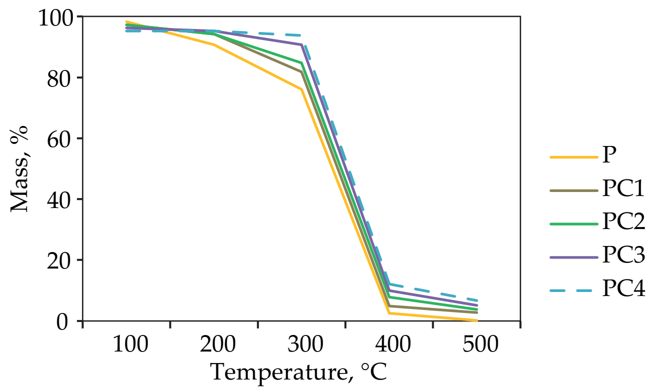

Fig. 6. TGA curves of PLA biocomposites

T a b l e 2. Mechanical properties of glycol reinforced PC3 composite

Property	P	PC3	PCG1	PCG2	PCG3
Tensile strength, MPa	58	71	75	79	76
Tensile modulus, GPa	1.270	1.328	1.357	1.401	1.388
Elongation at break, %	7	7.5	8.5	10	13.5
Flexural strength, MPa	98	128	130	134	132
Flexural modulus, GPa	3.450	3.580	3.818	4.250	4.066
Impact strength, J/m	180	210	295	338	341
Water absorption, %	0	2.66	2.55	2.49	2.40

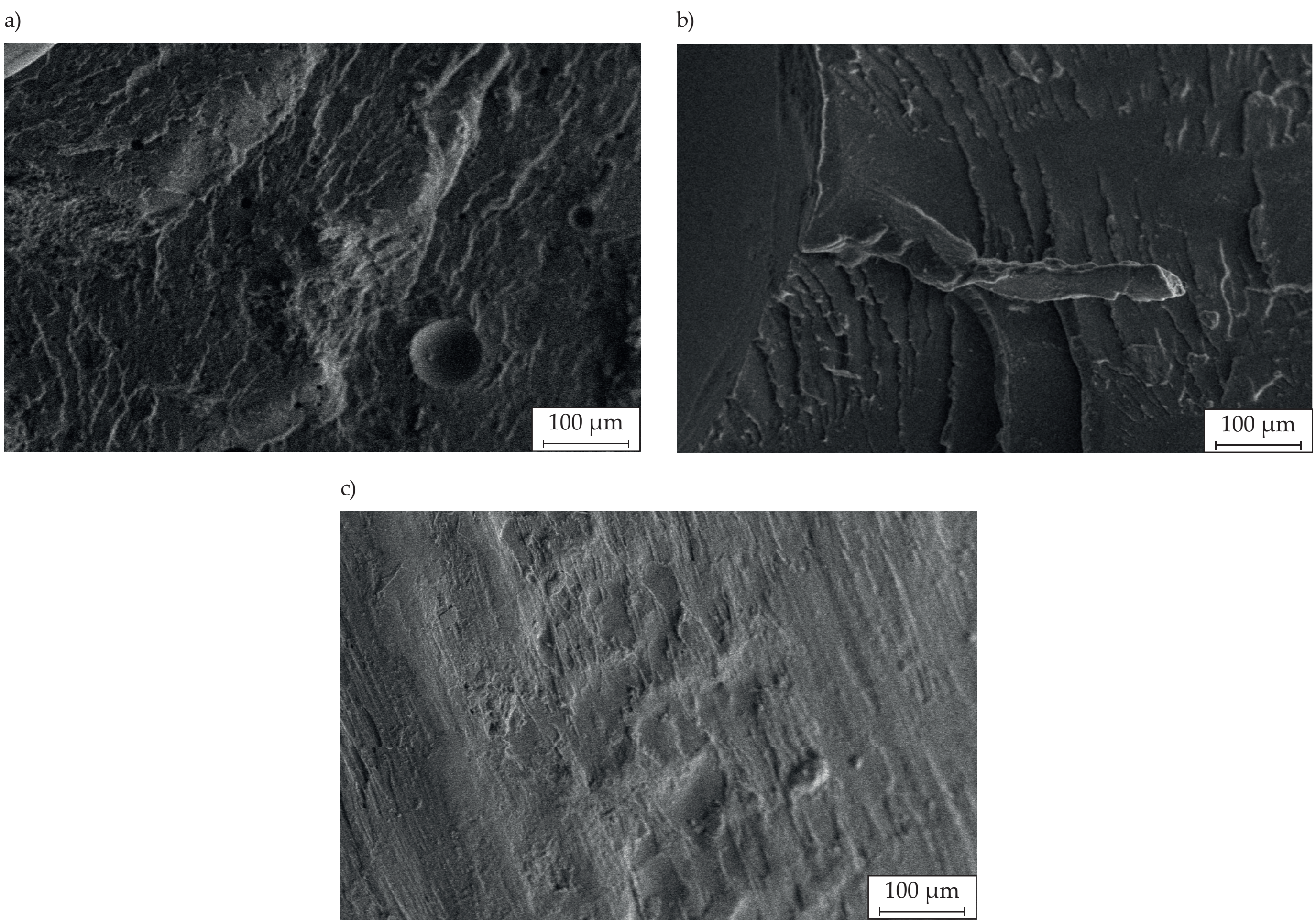

Fig. 7. SEM images of: a) PC4, b) PC3, c) PCG2

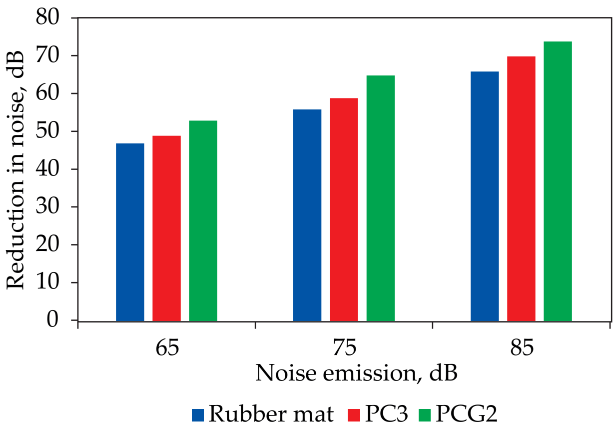

Fig. 8. Noise damping test analysis of rubber mat, PC3, and PCG2 biocomposites

logical images showed that the bonding density of the PCG composites were more compact than in case of PC3. Among the different ratios of glycerol added, PCG2 reinforced with 2 wt% of glycerol resulted in the best mechanical properties. Elongation of the composites with added glycerol was found to be greater than PC3, which was related to the improved toughness of the material. PCG3 showed worse mechanical properties than PCG2 since 4 wt% of glycerol reinforcement resulted in increasing the ductility of the composite above the optimal level. Moreover, water resistance of composites increased with increasing glycerol content. Comparing the best performing composites without and with glycerol addition, respectively, PC3 and PCG2, the PCG2 composite showed increase in tensile strength by 36.8%, tensile modulus by 14%, flexural strength by 26.7%, flexural modulus by 30.8%, and impact strength by 78.3%. Morphological images of the notable specimens are shown in Figure 7: PC4 with blowhole defects in Figure 7a, PC3 having delamination thereby representing good mechanical resistance towards the forces during testing in Figure 7b, and PCG2 displaying a densely packed appearance due to the effect of glycerol impregnating in between the interfacial spaces of PLA and COC materials in Figure 7c.

Figure 8 illustrates that the composites developed in this research provided better noise damping than the conventional rubber material. Since PC3 consisted of COC natural fibers having an inherent tendency to absorb vibrations, it showed better noise reduction. The denser molecular packing of the PCG2 composite, as shown in morphological study, reduced the noise levels comparing with the rubber mat and the PC3 composite. During the tests carried out at 85 dB, which is considered as the common maximum loudness for the human ear, the PCG2 composite showed a damping efficiency of 11% comparing with the currently used rubber mats.

CONCLUSION

The addition of COC improved the physical properties of PLA and 20 wt% reinforcement of COC into the PLA matrix showed best characteristics (PC3). The addition of glycerol further improved the mechanical properties of the PLA/COC composite resulting in the 4 wt% glycerol reinforced hybrid composite exhibiting the maximum optimal outcomes (PCG2). The additive improved the elongation and toughness of the raw composite and provided better resistance towards moisture as well. Noise damping property of the PLA/COC composite was enhanced by addition of glycerol. Comparing with the rubber mats conventionally used for automobile floor applications, the PCG2 hybrid composite provided a significant improvement in mechanical properties and a considerable reduction in road rubber tire noise entering into the automobiles cabin. This research concludes that the developed composite can be successfully utilized for automobile floor mats.

REFERENCES

[1] Probir K.G., Paramita B., Souvik M. *et al.*: *International Journal of Food Science* **2014**, 310852. https://doi.org/10.1155/2014/310852
[2] Ashika D., Siaka D.: *Proceedings* **2019**, *36*, 198. https://doi.org/10.3390/proceedings2019036198
[3] Garlotta D.: *Journal of Polymers and the Environment* **2001,** *9*, 63. https://doi.org/10.1023/A:1020200822435
[4] Farah S., Anderson D.G., Langer R.: *Advanced Drug Delivery Reviews* **2016**, *107*, 367. https://doi.org/10.1016/j.addr.2016.06.012
[5] Raj S.S., Kannan T.K., Babu M. *et al.*: *International Journal of Mechanical and Production Engineering Research and Development* **2019**, *9(2)*, 933.
[6] Huda M.S., Drzal L.T., Misra M. *et al.*: *Journal of Applied Polymer Science* **2006,** *102*, 4856. https://doi.org/10.1002/app.24829
[7] Guo R., Ren Z., Bi H. *et al.*: *European Polymer Journal* **2018,** *107*, 34. https://doi.org/10.1016/j.eurpolymj.2018.07.035
[8] Yaacob N.D., Ismail H., Ting S.S.: *BioResources* **2016,** *11*, 1255. https://doi.org/10.15376/biores.11.1.1255-1269
[9] Raj S.S., Kannan T.K., Rajasekar R.: *Polimeros* **2020**, *30*, e2020012. https://doi.org/10.1590/0104-1428.00120
[10] Sachin S.R., Kannan T.K., Rajasekar R.: *Pigment & Resin Technology* **2019**, *49*, 465. https://doi.org/10.1108/PRT-12-2019-0117
[11] Sachin S.R., Kuzmin A.M., Thiruvasagam C.: *Journal of Optoelectronic and Biomedical Materials* **2020**, *12(4)*, 121.
[12] Sudhagar M., Kannan T.K., Benjamin L.S. *et al.*: *Proceedings of the Institution of Mechanical Engineers, Part C: Journal of Mechanical Engineering Science* **2021**. https://doi.org/10.1177/09544062211035796
[13] Muller J., González-Martínez Ch., Chiralt A.: *Materials* **2017,** *10*, 952.

https://doi.org/10.3390/ma10080952
[14] Sachin S.R., Kannan T.K., Kathiresan M. *et al*.: *MaterialsToday Proceedings* **2021,** *45*, 862. https://doi.org/10.1016/j.matpr.2020.02.926
[15] Sachin S.R., Kuzmin M.A., Krishnakumar S. *et al*.: *Materiale Plastice* **2021,** *58*, 247. https://doi.org/10.37358/MP.21.3.5523
[16] Manickam S., Kannan T.K., Simon B.L. *et al*.: *Polimeros* **2020**, *30*, e2020038. https://doi.org/10.1590/0104-1428.08520
[17] Arunkumar B., Jeyanthi S.: *ARPN Journal of Engineering and Applied Sciences* **2017**, *12(5)*, 1400.
[18] Chowdavaram S.P., Babu M., Sachin S.R.: *International Research Journal of Automotive Technology* **2018,** *1(6)*, 18.
[19] Tarique J., Sapuan S.M., Khalina A. *et al*.: "Effect of glycerol concentration on the physical properties of arrowroot starch (maranta arundinacea) biopolymer film", 7th Postgraduate Seminar on Natural Fibre Reinforced Polymer Composites, 2020.

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