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Synthesis, Characterization and Eco-friendly Applications of Biodegradable Polycaprolactone-Tapioca Starch Polymeric Composite Membrane

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In the pursuit of sustainable materials, this study on the synthesis and multifaceted characterization of a novel biodegradable polymeric composite membrane. The polymeric composite composed of polycaprolactone (PCL) and tapioca starch (TS) was meticulously prepared and it's properties were systematically investigated. FTIR was employed to elucidate the structure of the composite, while SEM facilitated the morphological examination. The biodegradability of the material was rigorously assessed through a burial method and a comparative analysis was also conducted against a commercially available facemask. The antimicrobial efficacy and the material's suitability for water purification were also evaluated. The versatile application potential of the polymeric composite was further demonstrated through packaging tests utilizing tomatoes. The comprehensive investigated presented in this study demonstrates the advantageous sustain-ability of the PCL-TS polymer composite, hence highlighting its potential for many environmental friendly applications.

Keywords: Biodegradable polymer, Polycaprolactone, Tapioca starch, Antimicrobial activity, Sodium rejection, Packing.

INTRODUCTION

Polymers are high molecular weight compounds made up of repeating smaller units of monomers. These useful materials have become an essential part of our lives due to their unique physical and chemical properties, such as high durability, light weight, chemical resistance, anti-corrosive and plasticity. From the clothes to automobiles, polymers have a substantial impact on various fields, including construction, medication, packaging and transportation, to name a few [1]. One of the crucial benefits of polymers is their contribution to sustainable development [2]. As the world endeavors to reduce its carbon footprint and create a more ecologically friendly future, polymers are emerging as a feasible solution [3]. Polymeric material offers several advantages over traditional materials, such as wood (which cannot be flexible), metal (can undergo corrosion) and glass (fragile). Polymers are more energy-efficient to produce and compared to numerous other materials, it can be producing less carbon footprint. Polymers also play a decisive role in reducing waste and improving reutilizing [4].

As polymers play a crucial role in numerous applications, however, due to its non-biodegradability nature, most of the polymers has raised significant environmental concerns. The presence of these polymers contributes to the escalating accumulation of plastic debris in both marine environments and landfills, so escalating an alarming situation [5].

Recently, polycaprolactone (PCL) and tapioca starch (TS) are the two biodegradable polymers that have gained significant attention in recent years due to their excellent biodegradability and low toxicity [6,7]. Polycaprolactone (PCL) is known for its excellent biocompatibility, biodegradability and low toxicity, making it an attractive option for different types of applications [8,9]. In environment, PCL breaks down into caproic acid and other biodegradable byproducts through hydrolysis of ester linkages. In general, PCL has a degradation time ranging from a few months to several years, which makes it suitable for long-term implantable devices/applications [10,11]. Similarly, tapioca starch, a natural polymer, is widely used in various applications, including food packaging, textiles and biodegradable plastics [12,13]. Tapioca starch degrades through hydrolysis of its α-1,4-glucosidic bonds, leading to the formation of glucose and other biodegradable products [14].

Thus, the objectives of this study were to (i) to prepare a novel biodegradable polymer composite membrane comprising polycaprolactone (PCL) and tapioca starch (TS); (ii) to elucidate the structural, mechanical and morphological properties of the films; (iii) to investigate the biodegradability of the films using soil burial method; and (iv) finally the applicability of the prepared films as water purification, packaging material and as the antimicrobial activity of the films against the growth of *Staphylococcus aureus* and *Escherichia coli*.

EXPERIMENTAL

Tapioca starch (TS) grains were purchased from the local grocery shop, polycaprolactone (PCL) having molecular weight of 14,000 g mol^{-1}, reagent grade carbon tetrachloride and non-woven porous fabric scrim (polyester along with basic weight 2-92 g, porosity 2000 at 200 Pa, thickness 0.13 mm) were obtained from Sigma-Aldrich, USA.

Characterization: Infrared analysis of the prepared membranes were carried out using Nicolet Avatar 330 FT-IR (Thermo corporation) spectrometer in the range of 4000-500 cm^{-1}. Jeol JSM-84 scanning electron microscope (SEM) in low vacuum mode at 10 kV was used to analyze morphology of the prepared membranes. Instron 5569 machine (Instron, USA) was used to measure Young's modulus and nominal elongation at break of the membranes. For the impact analysis, the computerized vertical drop weight impact tester (Glob tex industries) machine was used.

Preparation of biodegradable membranes: For the preparation of biodegradable membranes, except CCl_4 no other hazardous chemicals were used (Table-1). Finely powdered tapioca sago grain was kept in cold water containing 0.2 mL of vinegar for 24 h followed by drying in sunlight. To prepare the virgin TS membrane, a known quantity of TS was dissolved in a hot water and then the resulting solution was agitated at 30 ºC. Subsequently, the solution was filtered and the filtrate was cast into the desired form. Prior to casting, a specific quantity of CCl_4 was added to the solution at 30 ºC. The obtained film then was dried in natural condition for minimum 3 days followed by heat treatment at 25 ºC.

While preparing composite membranes of PCL-TS, two solutionswere prepared separately. The first known weight of PLC dissolved in CCl_4 and then stored at 40 ºC, while the second solution consisted of known amount of TS and hot water stirred for 24 h at 40 ºC, filtered the solution, to this added appropriate volume of CCl_4, sonicated the solution for 30 min followed by heating at 40 ºC for 30 min. Now both solutions were mixed, carefully by maintaining the temperature of 40 ºC. After quick sonication, membranes were obtained by dipping in cold water. Formed membranes were dried overnight followed by drying in hot air oven for 8 h at 25 ºC. Pure PLC membrane was synthesized by dissolving in CCl_4 followed by diffusion induced phase separation (DIPS) technique [15]. The physico-chemical characteristics of the prepared membranes are summarized in Table-1. The viscosity of the casting solution was analyzed at 25 ºC by L type, digital rotational viscometer, Viscotech.

RESULTS AND DISCUSSION

FTIR studies: Formation of the polymeric composite membrane was confirmed by IR spectrum (Fig. 1), which exhibited the characteristic functional groups present in pure and biodegradable polymeric composite membranes. Pure polycaprolactone membrane exihibited the chacteristic peaks at 2942, 1726 and 1290 cm^{-1} for C-H_2, C=O and C-C functional groups, respectively. Interestingly, the polymeric composite membranes prepared from TS and PCL, namely TP-1, TP-2 and TP-3 do not show any additional peak, which confirms there is neither chemical interaction nor new additional bond formed between TS and PCL. All the three TP membranes shows the IR stretching frequency at 3098, 1750 and 1200 cm^{-1} for O-H, C=O and C-O-H functional groups, respectively. Similar results are also reported in the literature [16].

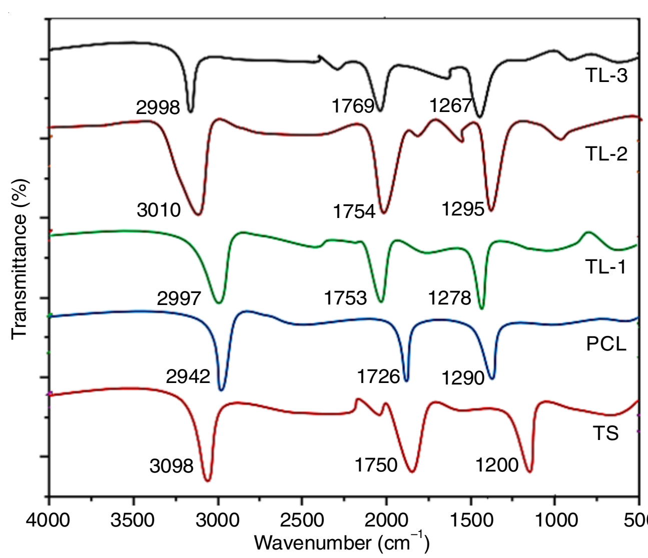

Fig. 1. FTIR spectra of the prepared membranes

Water uptake and contact angle analysis: The ability of the membrane to swell under the influence of water is measured by its water uptake capability. Dried membranes (5 mm × 5 mm) were weighed before dipped in the deionized water for 24 h and then the wet membranes were vacuum dried at

TABLE-1
PHYSICO-CHEMICAL CHARACTERISTIC OF PREPARED MEMBRANES

Code	Thickness (µm)	Composition		Pore size (µm)	Porosity	Viscosity (m Pa.s)
		Tapioca starch	Polycaprolactone			
TS	200 ± 24	100%	–	0.2-1.0	7O-80%	3460
PCL	200 ± 24	–	100%	0.4-1.2	60-70%	900
TL-1	200 ± 24	90%	10%	0.5-1.3	76-77%	2780
TL-2	200 ± 24	10%	90%	0.6-1.4	65-75%	1000
TL-3	200 ± 24	50%	50%	0.65-1.5	62-67%	2200

60-80 ºC and weighed again. The percentage of water uptake of the membranes sample was calculated by calculated using eqn. 1 [17]:

$$\text{Water uptake (WU, \%)} = \frac{m_{wet} - m_{dry}}{m_{dry}} \times 100 \quad (1)$$

where m_{wet} is the weight of wet membrane sample and m_{dry} is the weight of dry membrane sample. Contact angle indicates the wettability of the membrane.

Contact angles were measured by the sessile drop method, using a goniometer VCA-Optima (AST products Inc., USA). Clean and dried membrane films were cut into small pieces (8 mm × 8 mm) and mounted on a support followed by placing an approximately 2.0 µL droplet of double distilled water on the membrane surface and the contact angle was measured. Reported values were the averages of the contact angles (right and left) of 5 droplets.

All the 5 membranes water uptake and contact angle values are summarized in Fig. 2, tapioca starch (TS) exhibit larger WU (%), this may be larger pores and surface area, but its contact angle value indicates it has hydrophilic surface than hydrophobic. Pure polycaprolactone membrane (PCL) has high hydrophobic with contact angle approximately 72º and also shows least water uptake percentage among all the prepared membranes. Interestingly, PCL demonstrated improved activity of water uptake and decrease in contact angle with addition of tapioca starch. Such a decrease in contact angle was also observed in earlier reports [18,19]. With 50% tapioca starch composition, water uptake percentage of PCL increase to 54% from 42%. It reported that improved hydrophilicity helps in better biodegradability.

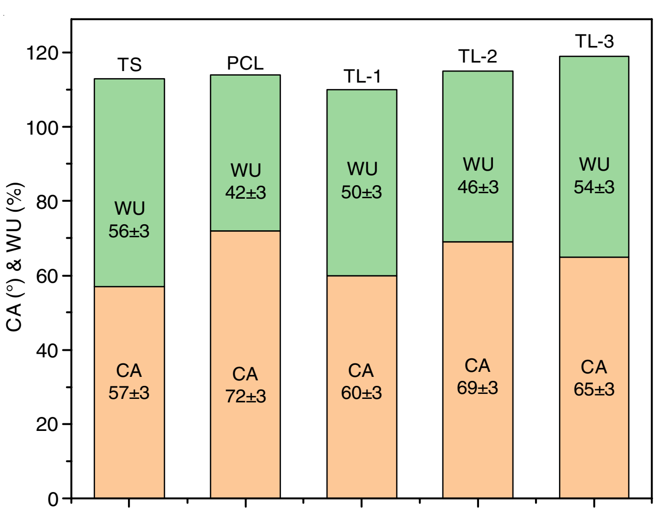

Fig. 2. Contact angle and water uptake values of the membranes

SEM study: The surface morphology of biodegradable membrane films gives the following important information on the surface appearance. Fig. 3a displays a surface which is rough and lacks visible pore openings, whereas Fig. 3b exhibits a fibrous appearance with a higher quantity of pores. This difference in pore structure could be one of the factors contributing to the higher water uptake % observed in tapioca starch.

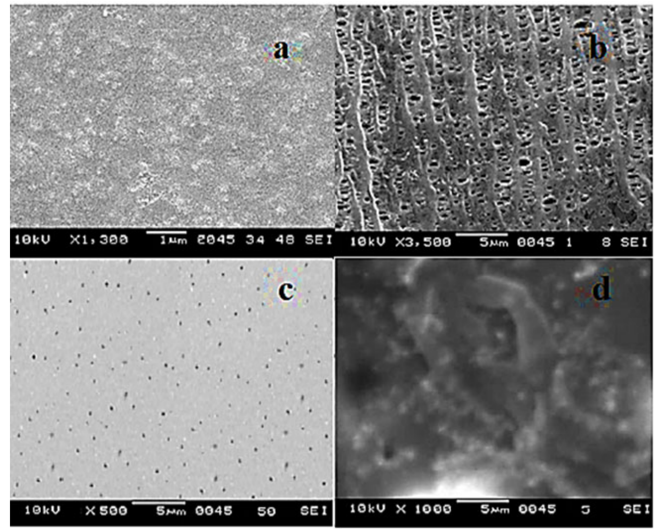

Fig. 3. SEM images of the prepared membranes

With 10% TS has smooth surface with increased number of pores opening as compared to PCL (Fig. 3c), while with 50% addition of TS, there is occurrence of agglomeration (Fig. 3d) [20].

Mechanical stability: In this study, the prepared membrane film were examined for mechanical stability using Young's modulus, elongation at break and weight drop impact method. The percentage of nominal elongation break is given by:

$$\frac{\text{Elongation of the membrane after7 days burriel}}{\text{Virgin membrane}} \times 100$$

For impact analysis, the specimen cut into 8 cm circular diameter and placed bottom of the machine stage. An object weighing 6.30 kg was released from a height of 0.20 m in order to strike the center of the specimen during impact analysis. Energy absorbed at fracture was calculated using eqn. 2:

$$\text{Energy absorbed at fracture (J)} = \text{Impact force (F)} \times \text{displacement (d)} \quad (2)$$

Figs. 4 and 5 show the mechanical stability of the prepared membranes films under stress. Tapioca sago exhibits the lowest values for Young's modulus, elongation at break percentage, and energy absorption before brakage since tapioca sago being more brittle in nature has less mechanical strength. Incorporation of PCL to tapioca sago increases mechanical property, for example with 10% PCL composition, TL-1 shows increased tensile strength. TL-3 being of the highest mechanical strength suggests there is strong cohesion between tapioca sago starch and polycaprolactone polymer as reported by Odusanya *et al.* [21]. Impact analysis test conducted with weight drop equipment also shows the consistent pattern with increase in percentage of PCL. Thus, TL-3 sample having 50-50% TS and PCL give higher absorption energy before failure.

Chemical resistance: The chemical stability of the polycaprolactone-tapioca starch (PCL-TS) polymeric composite membranes was further indicated by filtration performance after soaking the membranes in organic solvent (ethanol) as well in acid and alkali for 120 h. The membranes were kept at

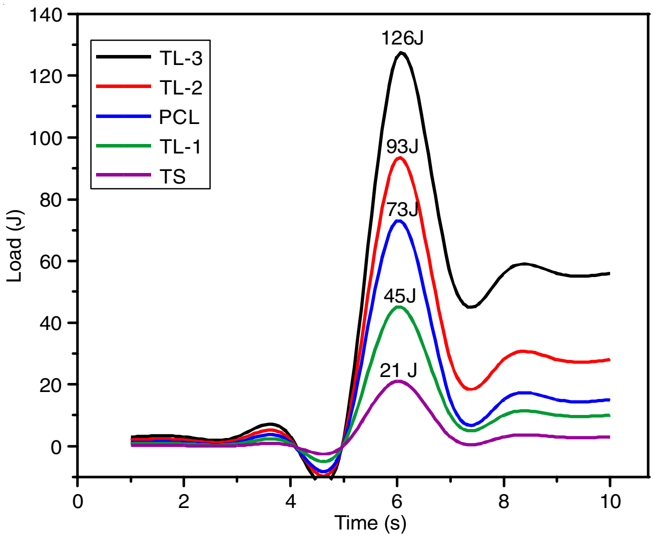

Fig. 4. Impact analysis test variation

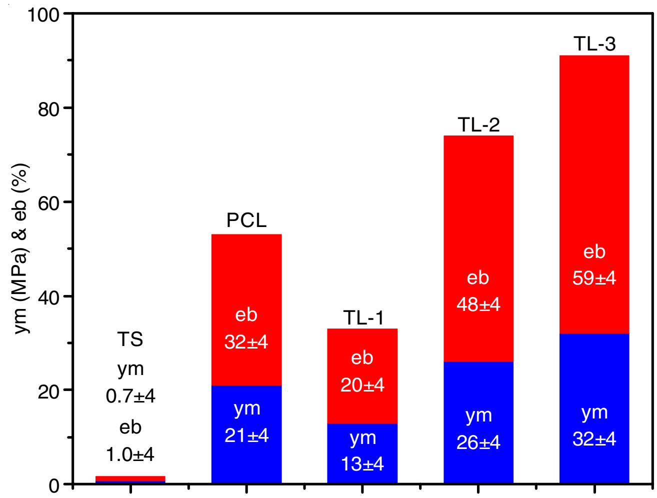

Fig. 5. Young's modulus (ym), elongation at break (eb) value of the membranes

a constant temperature of 27 ± 2 °C. Both acid and alkali have an impact on all the membranes. Biodegradable films are known to absorb solvents and soften as a result (Table-2), which may attributed due to the modifications of layer or the accumulation of polymer chains under strong solvent medium.

Antimicrobial activity: Using broth micro-dilution method, the prepared polymeric composite membranes were tested against the two food pathogens *viz. Staphylococcus aureus* (ATCC 25923) and *Escherichia coli* (ATCC 25922). Lysogeny broth (LB) was used to cultivate *E. coli* and *S. aureus* strains at 370 and 300 °C, respectively. By placing 3 cm diameter sample in a sterile micro test tube with 300 µL of deionized water and 100 µL of bacterial broth solution, the antimicrobial activity was assessed. The test tube was then shaken for 24 h at 37 °C to evaluate the antimicrobial activity. Then, 120 µL of each sample set's solution was distributed uniformly across the agar plates. Finally, after each plate had been incubated for 24 h at 30 °C and 37 °C for *S. aureus* and *E. coli*, respectively, bacterial growth was evaluated. For *E. coli*, there was no significant visible activity observed with the prepared membrane films at any concentration (Fig. 6). With pathogen *S. aureus*, the biodegradable membrane films exhibit a range of antibacterial efficacy.

TABLE-2
CHEMICAL RESISTANCE STUDY OF THE PREPARED MEMBRANES

Solvent	Reaction of biodegradable film*				
	TS	PCL	TL-1	TL-2	TL-3
0.1 N HCl	a, b, f, g	a, b, d, f,	a, b, d, f, g	a, b, d, e, f	a, b, d, e, f, g
0.1 M NaOH	a, b, d, f, g	a, b, d, f, g	a, b, d, e, f	a, b, d, e, f	a, b, d, e, f, g
Sat. NaCl	a, b, d, f, g	a, b, d, f,	a, b, d, f,	a, b, d, f,	a, b, d, f, g
Ethanol (50%)	b, d, f, g	b, d, f, g	b, d, f	b, d, f, e	b, d, f, g

*a = change in dimension; b = weight change; c = no solubility; d = liquid absorbance; e = wrinkle; f = softened; g = brittle

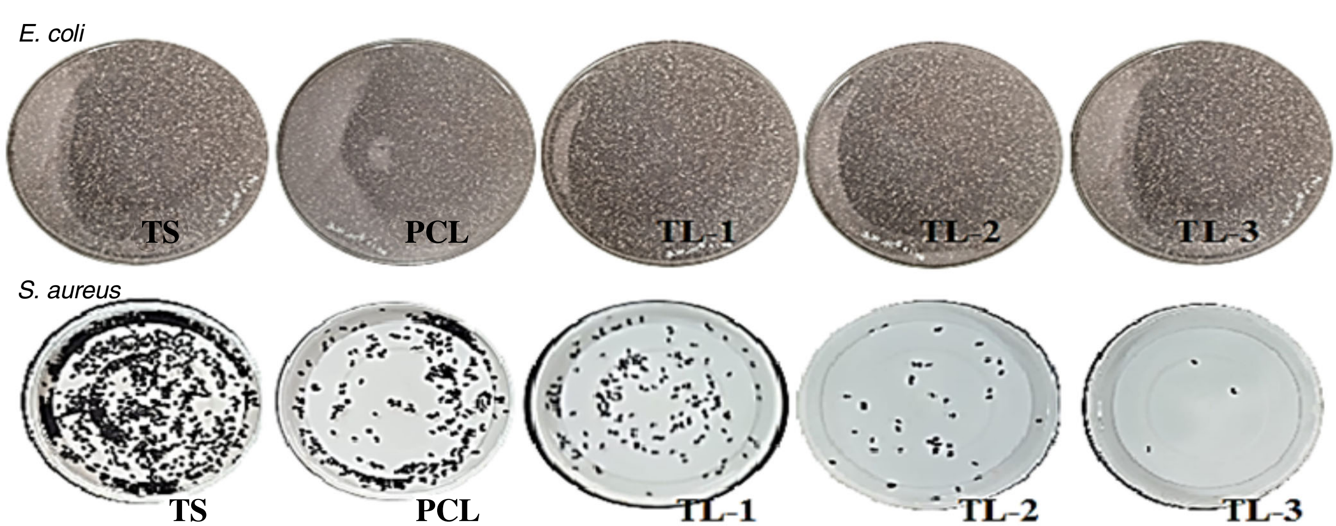

Fig. 6. Antimicrobial activity of the prepared membranes

An increased in PCL % can be considered as effective resistance to *S. aureus*.

Water purification study: A water purification study focused on the salt removal (R) efficiency using custom-made lab equipment (Fig. 7). The procedure involved passing a saline solution through a membrane module of specific dimensions, aiming to calculate flux (F) and removal efficiency (%) as per eqns. 3 and 4 respectively.

$$\text{Flux (F)} = \frac{W}{A} \times t \quad (3)$$

where W is the permeated water volume; A is the membrane area and t represents the operation time. The removal efficiency (%) was calculated using the following formula:

$$R\ (\%) = \frac{\text{Concentrate of feed} - \text{Concentrate of permeate}}{\text{Concentrate of feed}} \times 100 \quad (4)$$

The experiment encompassed varying pressure levels (1 to 8 Bar) and utilized membranes pure PLC membrane (PCL), TL-2 and TL-3 due to their compatibility with the applied pressure. To bolster membrane strength at high pressure, non-woven porous scrim support was introduced. From trials, PCL, TL-2 and TL-3 membranes exhibited the commendable water purification performance, while TS and TL-1 membranes suffered the fractures under pressure [22]. All the membranes were cast on non-woven porous synthetic scrim to enhance reliability at applied pressure. Notably, PCL membrane demonstrated a flux rate of 4.4 L/m^2 h and 69% sodium rejection at 8 bar pressure. TL-2 exhibited improved performance with higher rejection and flux at the same pressure, whereas TL-3 slightly outperformed PCL, albeit hindered by agglomeration resulting in the reduced filtration and performance compared to TL-2 (Fig. 8).

Biodegradability test: Biodegradability of the prepared membrane films studied in real time environment. The membrane film of size 6 cm × 6 cm was completely buried at a depth of 15 cm in soil for 50 days. This experiment was conducted at room temperature and humidity was maintained by smattering water every day. Before weighing, the samples were dried in oven at 35 ºC. To check the possibility of biodegradable mask making, TL-3 cut in the size of face mask (17 cm length and 8.5 cm width) and its biodegradability compared with commercially available face mask. The degrading behaviour of prepared polymeric composite membrane is depicted in Fig. 9. With the increase in starch load, it is observed that biodegradability enhanced. This fairly agrees with reference to work conducted by Nevoralová *et al*. [23]. Table-3 shows the samples' % weight loss from their starting weight prior to burial. Thus, it is clear that sample TL-3 has shown greater biodegradability than the commercially available face mask.

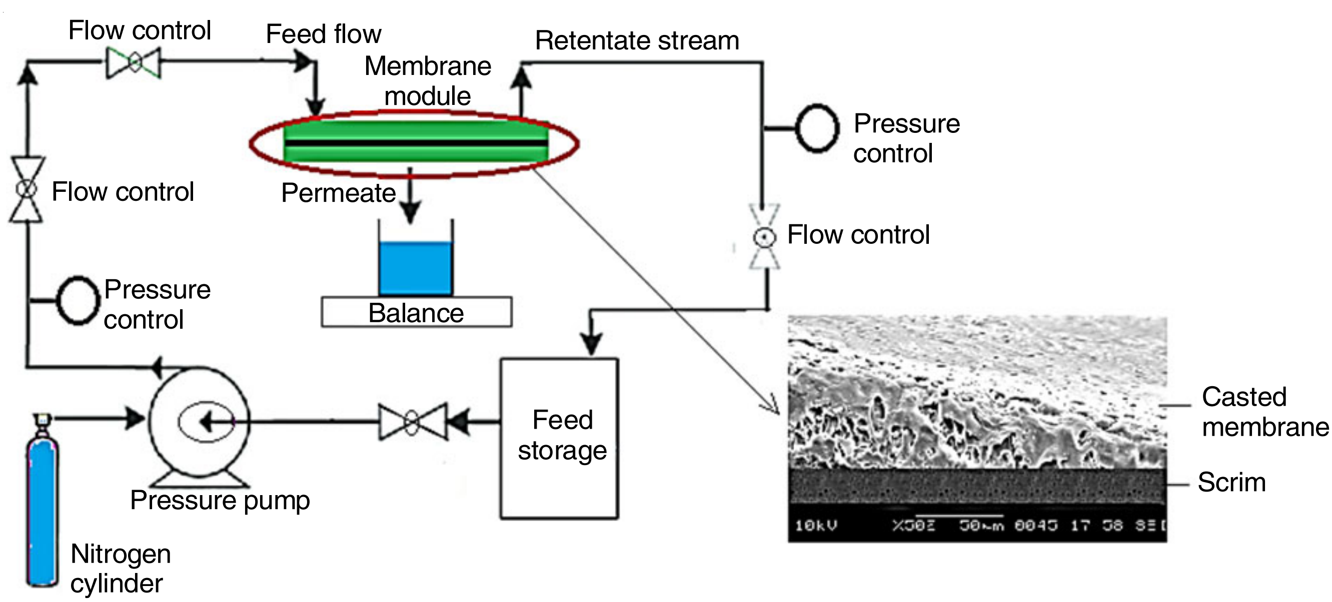

Fig. 7. Water purification experimental schematic set up

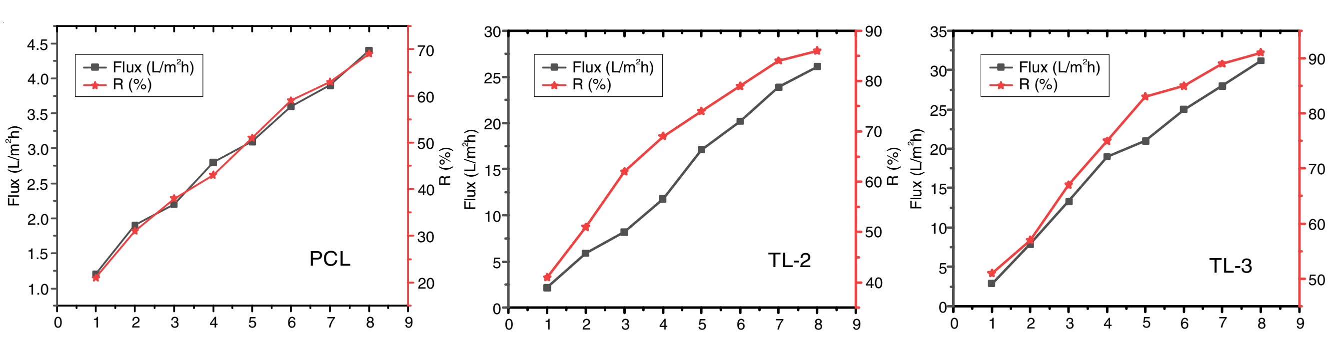

Fig. 8. Water flux and sodium rejection of the prepared polymeric membranes

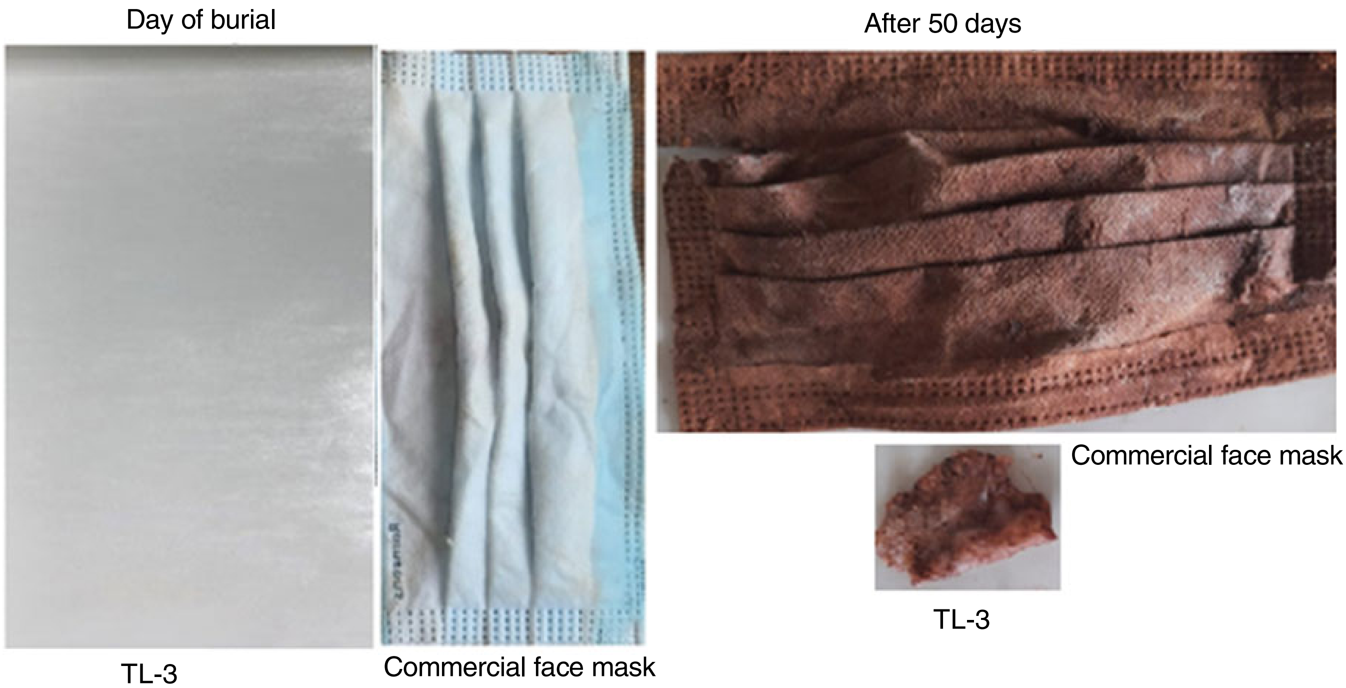

Fig. 9. Photograph of the biodegradability of the prepared membrane film

TABLE-3
WEIGHT LOSS COMPARISON OF COMMERCIAL FACE MASK AND TL-3

Sample	Weight loss after 50 days (%)
Commercial face mask	0.67
TL-3	84.31

Packaging experiment: Packaging property of the prepared samples were carried out by covering fresh tomatoes (*Solanum lycopersicon*) purchased from the local fruit market, Bangalore in pouches made from membrane sheets. The packed pouches containing three tomatoes were stored at room temperature and after 7 days of storage, the firmness and weight loss of the tomatoes compared with unpacked tomatoes. Firmness was measured using a hand pressure gauge and weight loss determined using digital electronic balance. For the study, the weight loss of tomato was measured using the following formula:

$$\text{Weight loss (\%)} = \frac{W_o - W_t}{W_o} \times 100$$

where W_o = weight of the tomatoes at day 0; W_t = weight of the tomatoes after storage.

Fruit firmness was determined using a hand pressure gauge by pressing the probe of gauge against the fruits. Each side of the fruits had their circumference measured using the pressure gauge. Firmness was determined using the scale 0-20 (very soft), 20-30 (soft), 30-40, (flexible) and > 50 (very firm) [24]. Change in the morphological characteristics of the tomatoes is shown in Fig. 10 and the average weight loss and firmness are summarized in Table-4.

Conclusion

This research has effectively demonstrated the remarkable potential of the biodegradable polycaprolactone-tapioca starch (PCL-TS) polymeric composite membrane for a wide range of eco-friendly applications. The synthesized polymeric composite materials were characterized using FTIR and SEM techniques. The biodegradability assessment, carried out through the burial method, not only highlighted the environmentally friendly nature of the polymeric composite material but also

Fig. 10. Variation of quality with packing (b) and without packing (a)

TABLE-4
PACKAGING CHARACTERISTIC OF THE COMPOSITES

Packaging	Day	Visual colour	Weight loss (%)	Firmness (N)
Open	D0	Bright red	0.00	44.25 ± 5.62
	D10	Reddish with black spot	8.34 ± 0.21	27.56 ± 9.63
Packed	D0	Bright red	0.00	44.25 ± 5.62
	D10	Red	1.01 ± 0.38	41.14 ± 2.51

emphasized its sustainable attributes. Additionally, the comparative study of biodegradability with a commercially available facemask underscored the polymeric composite's significance in addressing critical global issues, such as the reduction of environmental impact from single-use products. The antimicrobial analysis further revealed the inherent capacity of the composite material to hinder the microbial growth. The sodium rejection capacity in particular was the focus of this investigation into its water purification capabilities, which revealed its future potential for solving water quality issues. The practical viability of the PCL-TS composite was vividly illustrated through its successful application in packaging tests involving tomatoes, thereby indicating its aptness for food pre-servation purposes. This study shows the synergistic sustaina-bility of PCL-TS polymeric composite material, demonstrating its adaptability and potential to greatly contribute to a more sustainable future.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. E. Balla, V. Daniilidis, G. Karlioti, T. Kalamas, M. Stefanidou, N.D. Bikiaris, A. Vlachopoulos, I. Koumentakou and D.N. Bikiaris, *Polymers*, **13**, 1822 (2021); https://doi.org/10.3390/polym13111822
2. P. Rai, S. Mehrotra, S. Priya, E. Gnansounou and S.K. Sharma, *Bioresour. Technol.*, **325**, 124739 (2021); https://doi.org/10.1016/j.biortech.2021.124739
3. K. Amulya, R. Katakojwala, S. Ramakrishna and S.V. Mohan, *Composites Part C: Open Access*, **4**, 100111 (2021); https://doi.org/10.1016/j.jcomc.2021.100111
4. S.A. Miller, *ACS Macro Lett.*, **2**, 550 (2013); https://doi.org/10.1021/mz400207g
5. T.A. Hottle, M.M. Bilec and A.E. Landis, *Polym. Degrad. Stab.*, **98**, 1898 (2013); https://doi.org/10.1016/j.polymdegradstab.2013.06.016.
6. S.A.A Ghavimi, M. H. Ebrahimzadeh, M. Solati-Hashjin, and N.A.A. Osman, *J. Biomed. Mater. Res. A*, **103**, 2482 (2015); https://doi.org/10.1002/jbm.a.35371
7. P. Matzinos, V. Tserki, A. Kontoyiannis and C. Panayiotou, *Polym. Degrad. Stab.*, **77**, 17 (2002); https://doi.org/10.1016/S0141-3910(02)00072-1
8. A.L. Sisson, D. Ekinci and A. Lendlein, *Polymer*, **54**, 4333 (2013); https://doi.org/10.1016/j.polymer.2013.04.045
9. R.M. Mohamed and K.A. Yusoh, *Adv. Mater. Res.*, **1134**, 249 (2015); https://doi.org/10.4028/www.scientific.net/AMR.1134.249
10. M. Bartnikowski, T.R. Dargaville, S. Ivanovski and D.W. Hutmacher, *Prog. Polym. Sci.*, **96**, 1 (2019); https://doi.org/10.1016/j.progpolymsci.2019.05.004
11. Y. Fan, X. Miao, C. Hou, J. Wang, J. Lin and F. Bian, *Polymer*, **270**, 125778 (2023); https://doi.org/10.1016/j.polymer.2023.125778
12. W. Qing, Z. Liu, S. Yang, L. Tan, Y. Yang, D. Zhang and J. Li, *RSC Adv.*, **5**, 55619 (2015); https://doi.org/10.1039/C5RA08723F.
13. S. Flores, L. Famá, A.M. Rojas, S. Goyanes and L. Gerschenson, *Food Res. Int.*, **40**, 257 (2007); https://doi.org/10.1016/j.foodres.2006.02.004
14. E. Hernandez-García, M. Vargas, C. Gonzalez-Martínez and A. Chiralt, *Foods*, **10**, 1256 (2021); https://doi.org/10.3390/foods10061256
15. C. Hegde, A.M. Isloor, M. Padaki, P. Wanichapichart and Y. Liangdeng, *Desalination*, **265**, 153 (2011); https://doi.org/10.1016/j.desal.2010.07.046
16. F.M. Nor, H.Y. Lee, J.Y. Lim and D. Kurniawan, *E-Polymers*, **16**, 217 (2016); https://doi.org/10.1515/epoly-2015-0261
17. C. Hegde, S. Rao and J. D'Souza, *Desalination Water Treat.*, **57**, 3827 (2016); https://doi.org/10.1080/19443994.2014.988652
18. H. Li, *Biomaterials*, **25**, 5473 (2004); https://doi.org/10.1016/j.biomaterials.2003.12.052
19. G.K. Arbade, J. Srivastava, V. Tripathi, N. Lenka and T.U. Patro, *J. Biomater. Sci. Polym. Ed.*, **31**, 1648 (2020); https://doi.org/10.1080/09205063.2020.1769799.
20. S.A. Varghese, H. Pulikkalparambil, S.M. Rangappa, S. Siengchin and J. Parameswaranpillai, *Food Packag. Shelf Life*, **25**, 100538 (2020); https://doi.org/10.1016/j.fpsl.2020.100538
21. O.S. Odusanya, U.S. Ishiaku, B.M.N. Azemi, B.D.M. Manan and H.W. Kammer, *Polym. Eng. Sci.*, **40**, 1298 (2000); https://doi.org/10.1002/pen.11258
22. M. Qasim, D.D. Duong, J.Y. Lee and N.Y. Lee, *J. Appl. Polym. Sci.*, **137**, 49207 (2020); https://doi.org/10.1002/app.49207
23. M. Nevoralová, M. Koutný, A. Ujcic, Z. Starý, J. Šerá, H. Vlková, M. Šlouf, I. Fortelný and Z. Kruliš, *Front. Mater.*, **7**, 141 (2020); https://doi.org/10.3389/fmats.2020.00141
24. J. Pinheiro, C. Alegria, M. Abreu, E.M. Gonçalves and C.L.M. Silva, *J. Food Eng.*, **114**, 338 (2013); https://doi.org/10.1016/j.jfoodeng.2012.08.024