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Research Article

Preparation and characterization of Cassava starch/Polybutylene (adipate-co-terephthalate) biodegradable composite film

Samarakoon S. M. L. R.[2], Milani M. D. Y.[*1], Nayanajith L. D. C.[1], Arachchige R. C. W.[1], C. P. Abeyratne[2]

[1]*Materials Technology Section, Industrial Technology Institute, Colombo 07, Sri Lanka*

[2]*Department of Physics, University of Sri Jayewardenepura, Sri Lanka.*

Abstract

Extruded biodegradable films based on Poly (butylene adipate-co-terephthalate) (PBAT) and Cassava starch (CS) at varying weights were prepared, and their relevant properties for packaging applications are here reported. Neither the peak position nor the intensity of the film's distinctive infrared absorption peaks was altered by the addition of CS to PBAT. Therefore, adding CS to PBAT is solely a physical process. Experimental results show that the increase in CS content, the tensile strength, elongation at break, and the tear resistance of the composite are decreased. The "30% CS" included composite film was selected as the optimized composition since it is cost-effective while acquiring the required physical properties to be a better fit as a packaging material. However, the overall migration of residue on the surface of the "30% CS/PBAT" sample wasn't in the acceptable range (<10 mg/dm^2). Therefore, the developed product is suitable for use as a packaging material except for food packaging. Thus, the extrusion process needs to be further modified to be used as food packaging.

Keywords: Biodegradable composite; Mechanical Properties; PBAT; Cassava Starch; Extrusion.

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* Corresponding author: yoga@iti.lk

1. INTRODUCTION

Plastic products have the advantages of being lightweight, having beneficial mechanical properties, and having excellent water resistance. They are also relatively easy to recycle and, if made with bio-based materials, are suitable for the environment.

A composite material is made from two or more different materials and when combined, the resulting material acquires the best properties of those individual materials by itself. Generally, scientists expect many desirable properties from composites, such as higher strength, lower cost, higher efficiency, or durability[1,6,10].

Biodegradable plastic is a material that is engineered to degrade in a relatively short amount of time, typically in a few months or years, rather than the hundreds of years that conventional plastic takes to break down. Biodegradable materials have been widely used in the food packaging industry, pharmaceutical packaging, and others. These materials have been well accepted by consumers and have replaced the conventional materials in the market. Hence, the use of biodegradable materials has great potential for applications in packaging and other industries and has drawn many researchers' attention[3,4].

However, there are still many challenges that need to be addressed to make biodegradable products more sustainable and environmentally friendly. One of the major tradeoffs is that while biodegradable plastics are good for the environment, they may not be the best fit for the final product since they may not be fulfilling the requirements for the final product (Cost-effectiveness, mechanical properties, general use)[3,4]. Therefore, scientists are working on producing cost-effective biodegradable products by incorporating natural plant/animal materials as fillers. Then, they can be used both to resolve environmental pollution problems and to produce new products with various physical properties and several other effective functions[9,11,12].

The need for bio-degradable materials that are non-toxic to the human body and environment is ever-increasing due to the increasing levels of environmental pollution, large-scale waste generation, and lack of resources[12].

Thus, this study is proceeding to develop a biodegradable, eco-friendly composite using the most environmentally friendly, low-cost, bio-based material as a filler and thermoplastic polymer as a matrix. The convenience of this composite lies in the fact that the filler material is easily obtainable from natural wastes from domestic and industries. Therefore, the making process is relatively easy. They can be used both to resolve environmental pollution problems and to produce new products with various physical properties and several other effective functions.

PBAT is a thermoplastic, semi-aromatic, biodegradable ternary co-polyester and is easily moldable and thermoformed. PBAT polymer breaks completely, leaving no toxic residues behind when it is composting. This is one of the major reasons to use PBAT as an excellent alternative to toxic or harmful materials like non-biodegradable plastics. It has been widely used in various fields, such as food packaging bags, daily plastic bags, agricultural mulch films, garbage bags, greenhouse insulation films, etc[2,7,15].

The price of PBAT products may be relatively higher than the products made from Polyethylene (PE) and other polymer products. Therefore, the applications of PBAT are somewhat fewer. Therefore, scientists are practicing more effective methods to reduce the price of PBAT products. One of the main solutions is to use natural starch as a filler. It can help to improve the biodegradability of the PBAT product while reducing the cost and can make use of a wide range of applications[5,13,14,15].

CS is made by grating and drying the waste fibrous cassava root. CS is an abundant, renewable, and easy thermoplastic processing material. Since CS is a natural biodegradable material, it can be easily decomposed by microorganisms. However, usage in the application is limited because of its fragile nature and poor mechanical and barrier properties[12].

Considering the above facts, the fabrication of an economically feasible CS/PBAT composite with the required properties is feasible. In the present study, PBAT was used as the polymer matrix and the industrial waste CS was used as the filler material to prepare a bio-degradable composite to examine the possibility of using industrial-wastes as a filler material and to determine testing data for the physical properties of the resulting composite according to the filler content in respect to the thermoplastic polymer.

Therefore, this research was mainly focused on evaluating the effect of CS on the chemical and physical properties of CS/PBAT composite through the series of the CS/PBAT with various ratios to find an optimized composition.

2. METHODOLOGY

2.1. Materials

The main materials were CS (*Manihot esculenta*) (Food grade, Ranliya Products, No.188, Diganwela, Meewanapalana, Horana) and PBAT (Analytical grade, Natur-Tec Lanka (Pvt) Ltd, No. 10, Makola Road, Sapugaskanda). Except for these materials, all other chemicals were facilitated by the Industrial Technology Institute (ITI), 363 Bauddhaloka Mawatha, Colombo 00700.

2.2. Preparation of Materials

2.2.1. Determination of Moisture Content of CS

The moisture content was determined according to the Association of Analytical Communities (AOAC) official method 925.10.

2.2.2. Preparation of CS

The original CS was dried in an oven (BINDER – Chub1529) at 60 ˚C for 24 h and the oven-dried sample was stored in a desiccator.

2.2.3. Preparation of CS/PBAT Composite Films

A series of CS/PBAT was prepared for five levels of filler loading (10, 20, 30, 40, and 50 wt%) and sorbitol (4 wt%) was added to the above mixture. The total amount of CS, PBAT, and sorbitol was kept constant at 200 g. The three ingredients were mixed using an electronic mixer and, then the composite mixture was poured into the laboratory scale Brabender extruder machine (Gepruft); mesh to form a film, and the extruded film was passed on a conveyor belt.

2.3. Characterization

2.3.1. FTIR characterization of CS

The oven-dried CS powder sample (10 mg) was mixed with 300 mg of potassium bromide and formed into a pellet. The pellet was scanned using an FTIR-ATR spectrophotometer (Bruker – TENSOR 27), in the scanning range of 4000–400 cm^{-1} for chemical characterization by observing the characteristic IR absorption peaks.

2.3.2. Laser Diffraction - Particle size distribution analysis of CS

The oven-dried, CS was selected for this analysis. The particle size distribution of the dried cassava starch was analyzed using a Laser diffraction device and the dry powder technique was used[16,17,18].

2.3.3. SEM analysis of CS/PBAT composite films

The morphologies of CS/PBAT composite films were examined by SEM analysis (LEO – 1420VP).

2.3.4. FTIR characterization of CS/PBAT composite films

The CS/PBAT composite film samples were scanned using an FTIR spectrophotometer (Bruker – TENSOR 27), in the scanning range of 4000–400 cm^{-1} for chemical characterization by observing the characteristic IR absorption peaks.

2.3.5. Mechanical Properties of CS/PBAT composite films

The CS/PBAT films were cut into dumbbell-shaped strips using a specimen cutting press (Elastocon – EP 02) having a width of 4 cm and tested using an electronic universal material testing machine (Tinius Olsen – H10Ks) at a stretching speed of 50 mm/min. Each group of test specimens was tested three times to ensure consistency in results and the average of the three readings was taken for analysis.

2.3.6. Total migration of aqueous foods and fatty foods

All tests were run in triplicate to ensure consistency in results and the average of the three readings was taken for analysis.

2.3.6.1. Determination of aqueous foods – Stimulant A (Distilled water)

The test was conducted according to SLS 1718: 2021 – 70 ℃ (Materials and articles in contact with foodstuffs).

2.3.6.2. Determination of fatty foods – Stimulant D (95% Ethanol and Isooctane)

The test was conducted according to BSEN 1186-1:200 (Materials and articles in contact with foodstuffs).

2.3.7. Heavy metal analysis of 30% CS/PBAT composite film

The heavy metals of 30% CS/PBAT composite film were analyzed according to Food packaging material and article regulation 2010 (Government gazette notification 1660-30 issued on 2010/06/29)

3. RESULTS AND DISCUSSION

3.1. Characterization of CS

3.1.1. Moisture Content

Table 1. Moisture Content of CS

Sample no:	Moisture %
1	5.87
2	5.79
3	5.81
Average Moisture %	**5.82**

3.1.2. FTIR Spectroscopy

Figure 1 illustrates the FTIR spectrum of CS. The spectrum shows characteristic peaks at 1643, 2930, and 3247 cm^{-1} which may be attributed to the stretching vibration peak of symmetric bending vibration of the C=C double bond, -CH$_2$ stretching vibration, and O–H under the molecular association, respectively.

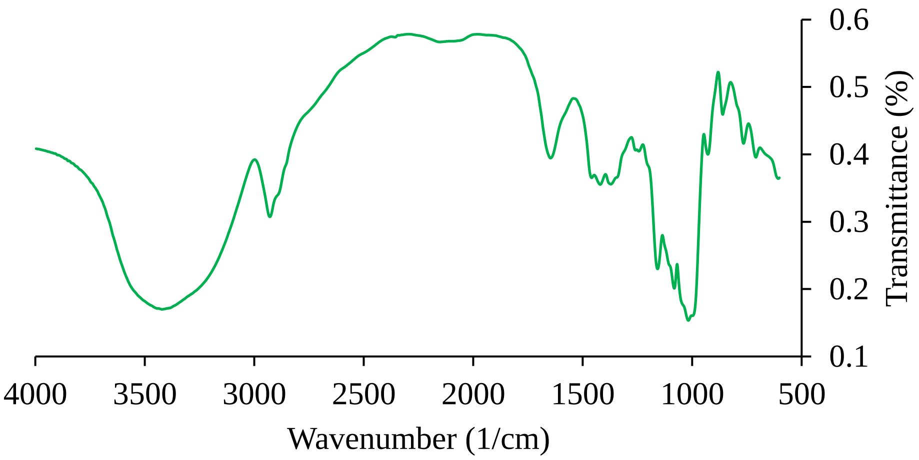


Figure 1. FTIR spectra of CS

The absorption peaks that appear at 1018, 1083, and 1158 cm^{-1} may be identified as the C–O stretching vibration of a primary alcohol, secondary alcohol, and tertiary alcohol, respectively. The vibration peak of primary alcohol represents the anti-symmetric stretching vibration of C–O–C.

3.1.3. Laser Light Diffraction – particle size analysis

Figure 2 illustrates the particle size distribution analysis result of the CS.

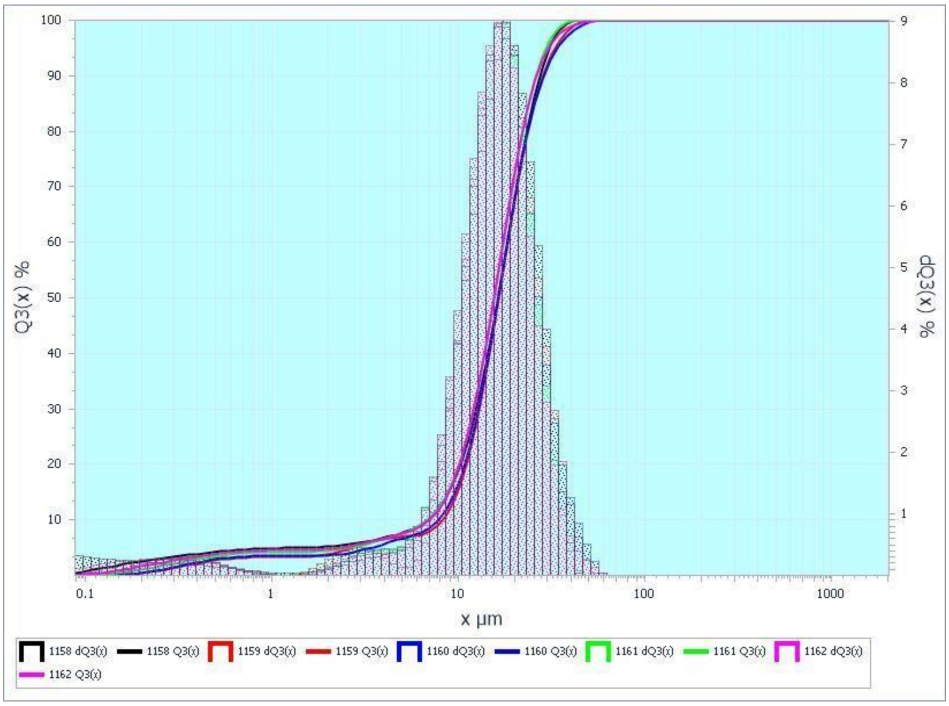


Figure 2. Particle size distribution of CS

3.2. Characterization of CS/PBAT composite film

3.2.1. FTIR Spectroscopy Analysis

Figure 3 shows the FTIR spectra of the pure PBAT film and 10% CS/PBAT composite film. Compared with the pure PBAT film, the composite film shows a broad peak at 3400 cm^{-1}, which may be attributed to the stretching vibration of –OH due to the presence of a large number of hydroxyl groups in the CS. The peak at 2953 cm^{-1} may be ascribed to the stretching vibration of $–CH_3$ and $–CH_2$. The strong absorption peaks in 1720 and 1722 cm^{-1} may be corresponded to the carbonyl group in PBAT, whereas weak absorption peaks may be corresponded to $–CH_2OH$ and $–CH_2$ appear at 1251 cm^{-1}. The asymmetric C–O–C stretching vibration and C–O stretching, and skeleton vibration may be attributed to an absorption peak at 723 cm^{-1}.

The addition of CS to PBAT changed neither the position nor the intensity of the characteristic infrared absorption peaks of the film. Therefore, the mixing of CS with PBAT was a purely physical process.

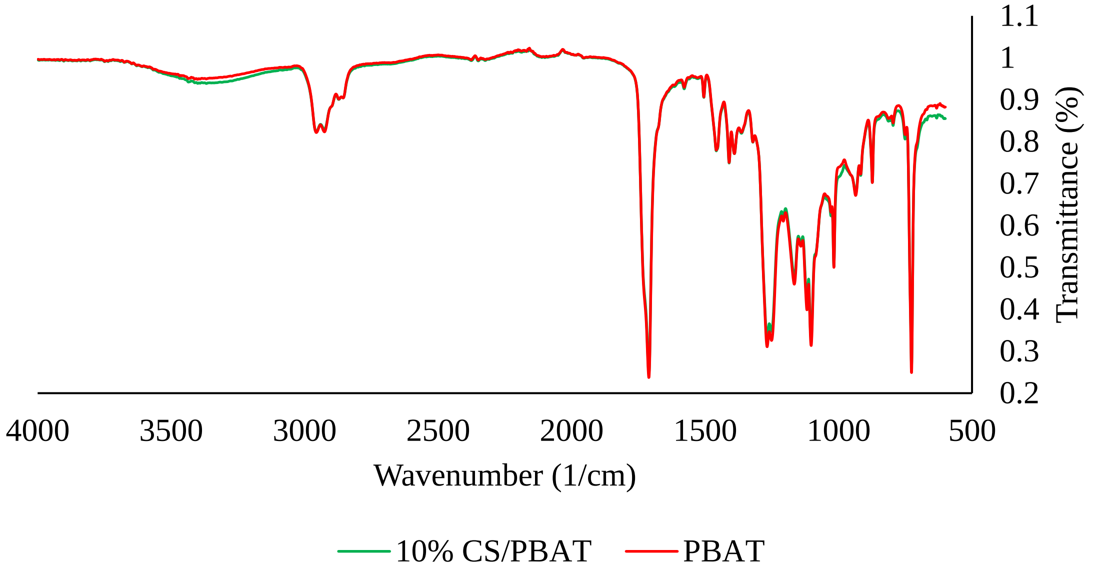


Figure 3. FTIR spectra of PBAT and 10% CS/PBAT

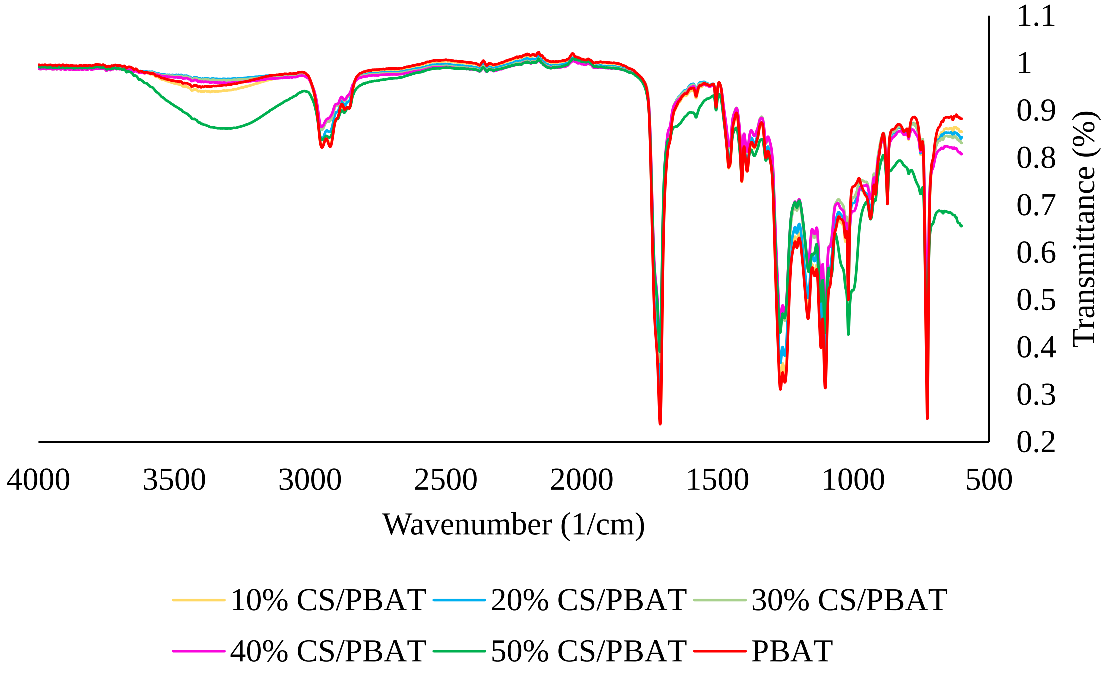


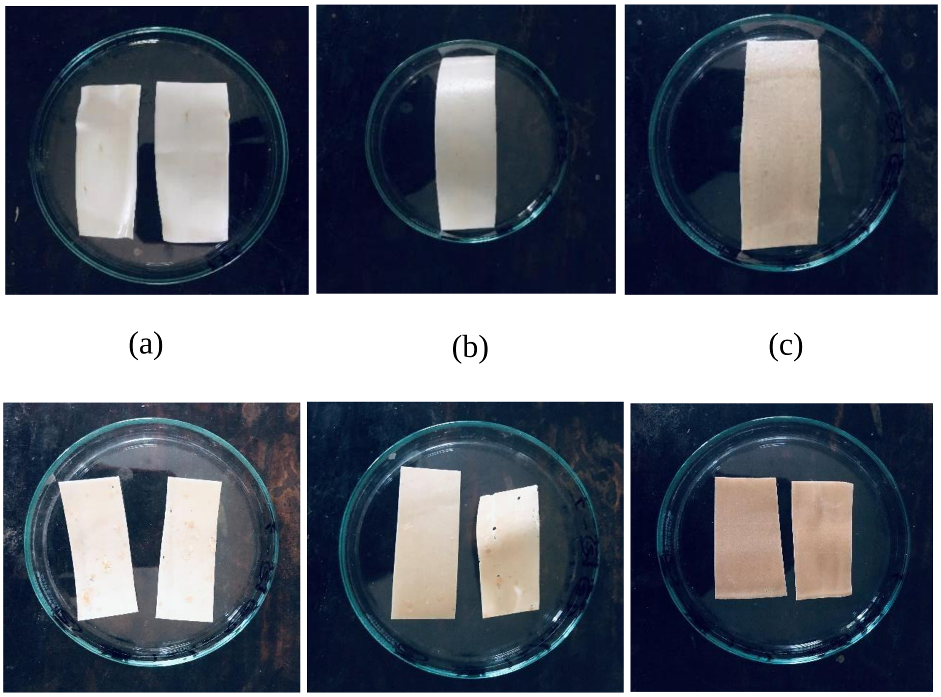
Figure 4. FTIR spectra of PBAT and 10%, 20%, 30%, 40% and 50% CS/ PBAT

3.2.2. Mechanical Properties

The tensile strength, elongation at break, and tear resistance for CS/PBAT composite sheets are provided in Table 2.

Table 2. The tensile strength, elongation at break and tear resistance for CS/PBAT composite films

% CS in CS/PBAT composite film	**Average tensile strength (MPa)**	**Average elongation at break %**	**Average tear resistance (N/mm)**
0	8.28	1192.0	59.11
10	6.46	800.0	52.58
20	6.03	730.0	28.90
30	4.59	275.4	20.85
40	4.23	207.3	19.95
50	2.90	135.7	12.71



(a) (b) (c)

(d) (e) (f)

Figure 5. Extruded films - PBAT (a). 10% CS/PBAT (b). 20% CS/PBAT (c). 30% CS/PBAT (d). 40% CS/PBAT (e). 50 CS/PBAT (f)

Figure 6 and Figure 7 show that the tensile strength and elongation at break of the CS/PBAT composite material can be significantly decreased once the filler is introduced. The tensile strength of the composite film gradually declines as the amount of filler is increased by 10 to 20% of CS; at a filler concentration of 30%, the tensile strength reduces dramatically. The reduction of tensile strength of the composite material with the increment of filler content may be happened due to the improved stiffness of the composite that was attributed to the interaction between the PBAT and CS that weaker the polymer-polymer interaction. The elongation at break fell more sharply than the tensile strength. This may have happened since the fillers have fewer elongation values than plastics. The reduction of elongation may be caused by the limited stretching and reduced ductility of the composite materials. Therefore, the incorporation of fillers has restricted the PBAT polymer chain movement and caused the PBAT polymer matrix becomes less ductile and stiffer and leading to lower elongation at break.

When the filler loading goes up, the filler will agglomerate, which could raise the likelihood that larger agglomerates will develop in the composite material, which would then cause an uneven distribution of PBAT in the sheet and eventually cause the reduction in tensile strength and elongation at break of the composite material. The average tensile strength of the PBAT film and at a filler content of 30% are 8.28 MPa and 4.59 MPa respectively.

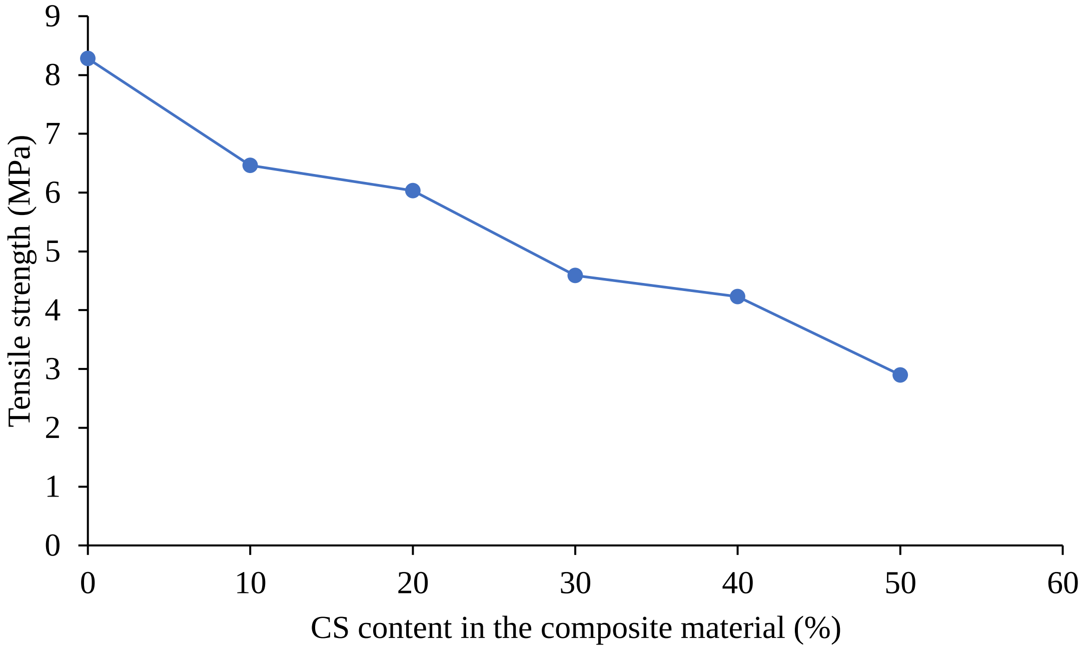


Figure 6. Effect of filler content on the tensile strength of CS/PBAT composite films.

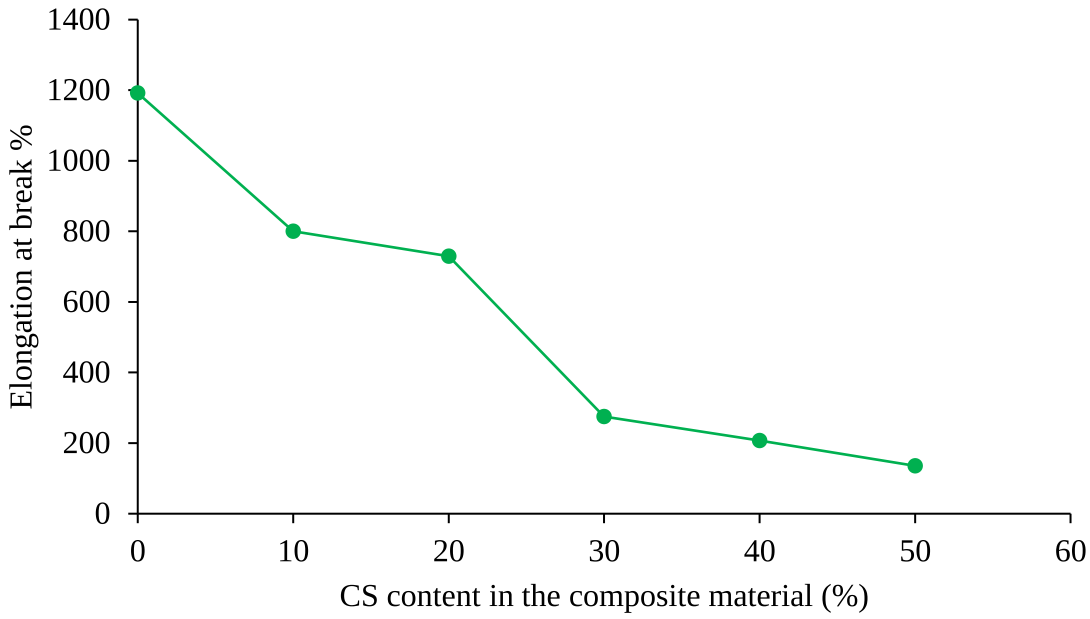


Figure 7. Effect of filler content on the % elongation at break of CS/PBAT composite films.

Figure 8 shows that the tear resistance of the CS/PBAT composite material can be significantly decreased once the filler is introduced. This may be caused due to the decrease in polymer-polymer interactions as the filler loading is increased. The average tear resistance of the PBAT film and at a filler content of 30% are, 59.11 N/mm and 20.85 N/mm respectively.

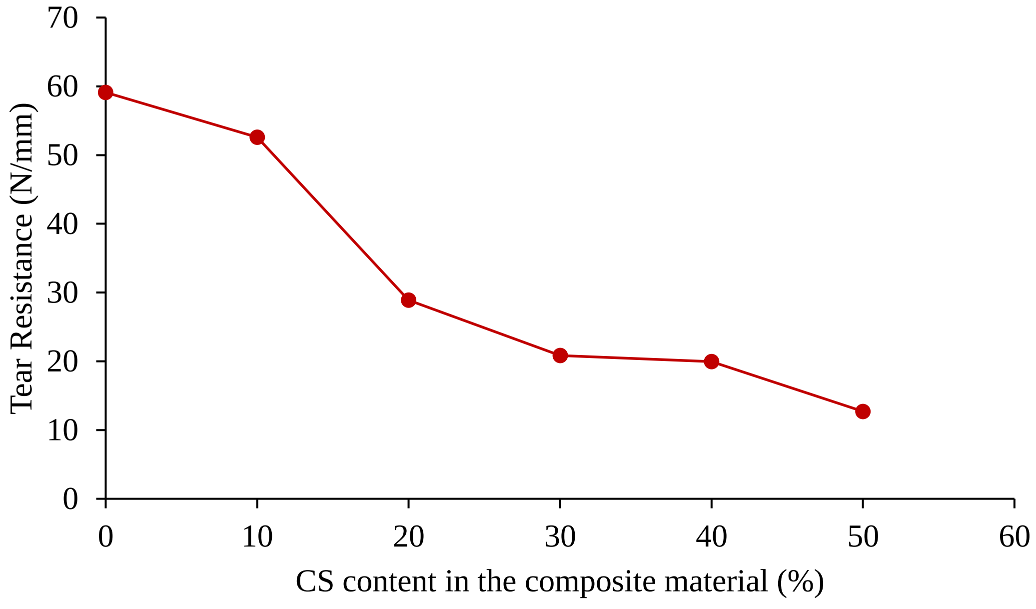


Figure 8. Effect of filler content on the tear resistance of CS/PBAT composite films.

3.2.3. Total migration of aqueous and fatty foods

Table 3. Total migration of aqueous and fatty foods

Test Sample	Total Migration-Distilled water (mg/dm^2)	Total Migration-95% Ethanol (mg/dm^2)	Total Migration-Isooctane (mg/dm^2)
10% CS/PBAT	112.1	210.5	118.8
PBAT (Control)	272.0	384.8	298.8
20% CS/PBAT	155.8	221.9	138.4
PBAT (Control)	278.0	392.0	298.8
30% CS/PBAT	97.2	164.0	68.6
PBAT (Control)	263.6	391.2	453.2
40% CS/PBAT	122.2	157.4	82.7
PBAT (Control)	279.6	495.2	341.6
50% CS/PBAT	197.8	147.9	77.5
PBAT (Control)	303.2	485.6	352.4

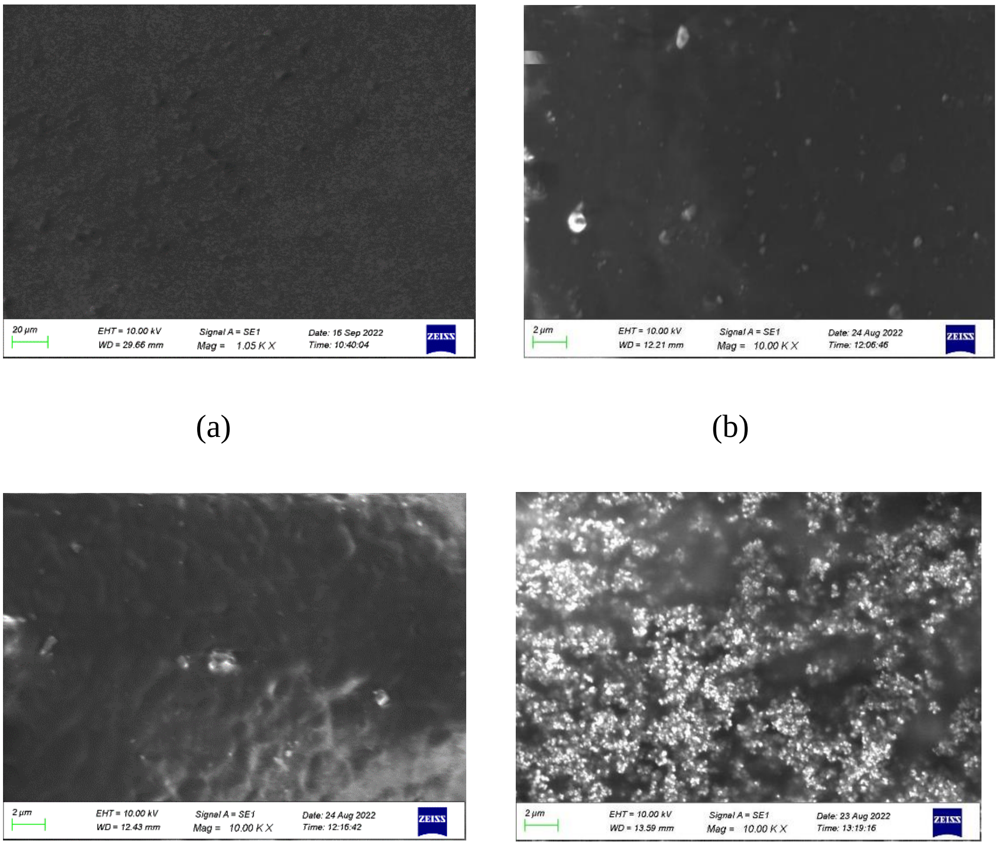
The overall migration of residue (aqueous foods and fatty foods) on the surface of the CS/PBAT sample, which is supposed to come in contact with meals, wasn’t within permissible limits (<10 mg/dm^2).

3.2.4. SEM analysis of CS/PBAT composite films

Figure 9 shows the surface morphology of the PBAT and CS/PBAT extruded films. The micrograph of the PBAT film (Figure 9 (a)) reveals a homogeneous, smooth structure devoid of pores and with no significant flaws.

A smooth surface can also be noticed in the surface morphology of the 10% CS/PBAT film (Figure 9 (b)). Nevertheless, it is possible to spot starch granules that did not fully rupture during the extrusion process. There were no fissures in the polymer matrix despite the starch grains. Furthermore, rough surface and unruptured starch granules are increased with increased CS content.

In contrast to PBAT, which predominantly consisted of hydrophobic hydrocarbons with benzene rings, CS was composed of large amounts of hydrophilic hydroxyl groups and was very hydrophilic. As a result of that, phase separation in the microscale of the films may have happened due to the less compatibility of PBAT and CS that weaker the polymer-polymer interaction with the increment of CS. This is further verified by the decrease of tensile strength, elongation at break and, tear resistance of composite film with the increase of CS content.



(a) (b)

(c) (d)

Figure 9. The microstructures of the PBAT and CS/PBAT extruded films (diameter is 2 µm) - PBAT (a). 10% CS/PBAT (b). 20% CS/PBAT (c). 30% CS/PBAT (d).

3.2.5. Heavy metal analysis

Heavy metals were not detected in the 30% CS/PBAT composite film sample.

Table 4. Heavy metal analysis of 30% CS/PBAT composite film

Type of heavy metal	Results (mg/l)
As	Not detected (<0.001)
Cd	Not detected (<0.001)
Sb	Not detected (<0.001)
Pb	Not detected (<0.001)

4. CONCLUSIONS

The observed moisture content of “CS” was 5.82%. Neither the peak position nor the intensity of the films distinctive infrared absorption peaks was altered by the addition of CS to PBAT. As a result, it is clear from the findings that adding CS to PBAT is solely a physical process. With an increase in CS content, the composite film's tensile strength, elongation at break and, tear resistance gradually declined, while the elongation at break declined more than the tensile strength. This may be happened due to the weaker polymer-polymer interaction. Heavy metals were not detected in the 30% CS/PBAT composite film sample. The "30% CS" included composite film was selected as the optimized composition, per the mechanical and physical evaluation, since it is economically feasible while acquiring the required physical properties to be a better fit as a packaging material. But the overall migration of residue (aqueous food and fatty food) of the surface of the “30% CS/PBAT” sample, which is intended to come into contact with foodstuffs, wasn’t in the acceptable range (<10 mg/dm^2). Therefore, to use the final product as a food packaging material, the extrusion process needs to be further modified.

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