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Research Article

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Development of PLA Based Nanocomposites Evaluating of Physical, Chemical, and Mechanical Properties

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Abstract

This study investigates the enhancement of poly(lactic acid) (PLA) composite films through the incorporation of cellulose, chitin, and starch, guided by comprehensive analyses using Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and universal testing machine (UTM). FTIR results elucidate the interactions and structural changes within the composite matrices, showcasing distinctive peaks corresponding to specific functional groups. TGA reveals the thermal degradation behavior of PLA composites, indicating improved thermal stability with the addition of cellulose and starch. Mechanical properties, assessed through UTM, demonstrate increased tensile strength, modulus, and elongation at break in the presence of fillers. Notably, PLA/starch films exhibit superior tensile strength, highlighting the potential for tailored mechanical properties. The study's culmination affirms that simple blending of bio-inspired additives enhances both thermal and mechanical characteristics, promising advancements in sustainable materials for diverse applications. The findings contribute valuable insights into designing PLA composites with improved performance and stability, crucial for promoting sustainable materials in various industries.

Keywords

Polylacticacid, Nanocomposite, Thermogravimetric analysis, Universal testing machine, Fourier transform infrared spectroscopy

Introduction

Due to rapid population growth and industrial expansion, polymers and plastic materials have been widely used. Plastics and polymers derived from petroleum have caused concern for the environment and the depletion of fossil fuel resources. On the other hand, many researchers have developed more renewable biomass-based biopolymers to replace petroleum-based plastics, and the market has recently seen rapid growth [1]. Polylactide acid or PLA is one of the biomass-based biopolymers which has attracted a lot of attention due to its relatively good performance and reproducibility. PLA belongs to the aliphatic polyester family and is generally made from α- hydroxy acids, including polyglycolic acid, or poly-mandelic acid, and is considered biodegradable and compostable. PLA is produced by polymerizing lactic acid by ring-opening polymerization of lactide (cyclic dimer of lactic acid, intermediate) [2,3]. PLA has higher strength, high-modulus thermoplastic polymer that can be manufactured annually from renewable resources to produce products for industrial packaging or the biocompatible/bio-absorbable medical device market [4].

Although PLA shows interesting mechanical properties, however, the brittleness of PLA and low heat deflection temperature [5], low impact resistance, low point elongation at break, gas permeability, sensitivity to hydrolysis, and slow crystallization rate have hindered their use in technical applications [3]. In this regard, the profile of PLA properties like stiffness, dimensional stability, heat deflection temperature, etc., can be improved by the techniques such as plasticization, copolymerization with additives such as micro- and nano-fillers, impact modifiers, flame retardants, plasticizers; and melt blending have been used to resolve brittleness, with most toughness improvements accompanied by reduced modulus and strength, industrial relevance and biodegradability [3, 5]. A well-engineered PLA, can be a suitable thermoplastic with a reasonable shelf life, allowing to be hydrolyzed with harmless natural products [6]. PLA blends with various elements like glucose monoesters, glycerol, oligomeric lactic acid, diethyl bishydroxymethyl malonate and citrate esters, polyethylene glycol [6], acrylonitrile-butadiene styrene [7], and various bio-fibers [8] are used. Recently, PLA has been finding many applications in construction, dental, biomedical, railway [9], and consumer products [10]. In the current study, additives like natural polymers, starch, cellulose, and chitin were blended with pure PLA. The PLA/starch, PLA/cellulose and PLA/chitin composites were confirmed by FTIR spectra patterns. The modified properties of PLAs were investigated through TGA, and UTM.

Materials and Method

Production of PLA composite films

Four different levels (10, 20, 30, and 40%) of additives like starch, cellulose, and chitin were mixed with standard PLA (Table 1) and dissolved in chloroform (1 g/10 ml) under constant stirring for 3 h at room temperature. A sealed glove bag [11] was pre-incubated with chloroform for 24 h to conceal chloroform vapors. The PLA composite solution was dried on a Petri dish in a sealed glove bag in a controlled drying process, thus a uniformly flat surface of films was obtained. Finally, the film was then carefully recovered and used for different characterization methods.

From figure 1 it infers sample developed in Petri plate for pristine PLA. In figure 2, we find about 10 to 30% cellulose in steps of 10 embedded in PLA substrate is used. For figure 3, it's about chitin mixed with 10 to 30% in steps of 10 in PLA. For the third case, 10 to 30% starch used in steps of 10 in PLA as shown in figure 4.

Characterization studies of the composite films

FTIR

FTIR spectroscopy (FT-IR, NICOLET FT-IR 6700) was used to detect the interaction between the composite matrix of extracted chitin and chitosan. The radiations were passed through the membrane and the spectrum was recorded using potassium bromide pellets, from the wavelength ranging from 400 to 4000 cm^{-1} and with a resolution of 4 cm^{-1} [1].

Table 1: Coding of composites as per the quantity of additives added.

Type of additive	% of additive			
	10%	20%	30%	40%
Cellulose	A1	A2	A3	A4
Chitin	B1	B2	B3	-
Starch	C1	C2	C3	C4
Pure PLA	D			

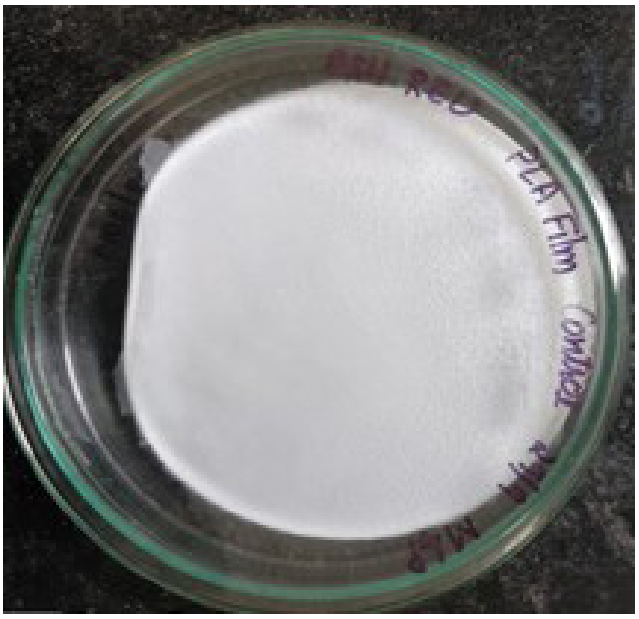


Figure 1: Pure PLA film.

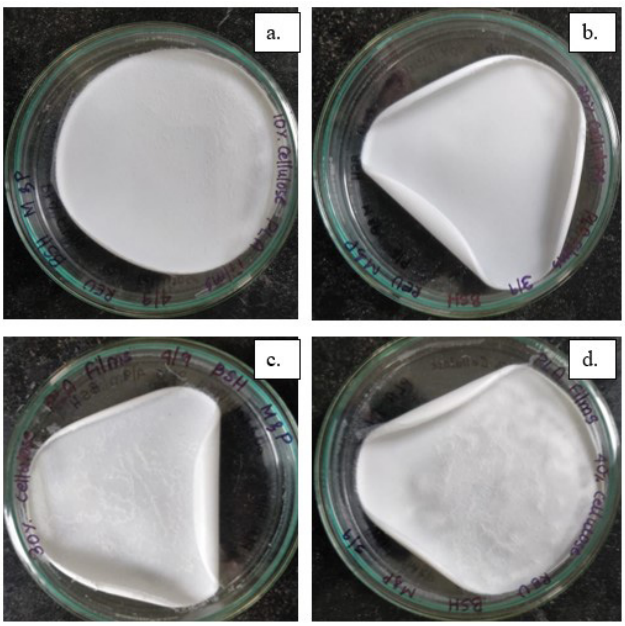


Figure 2: (a)10% PLA/cellulose, **(b)** 20% PLA/cellulose, **(c)** 30% PLA/cellulose, and **(d)** 40% PLA/cellulose composites.

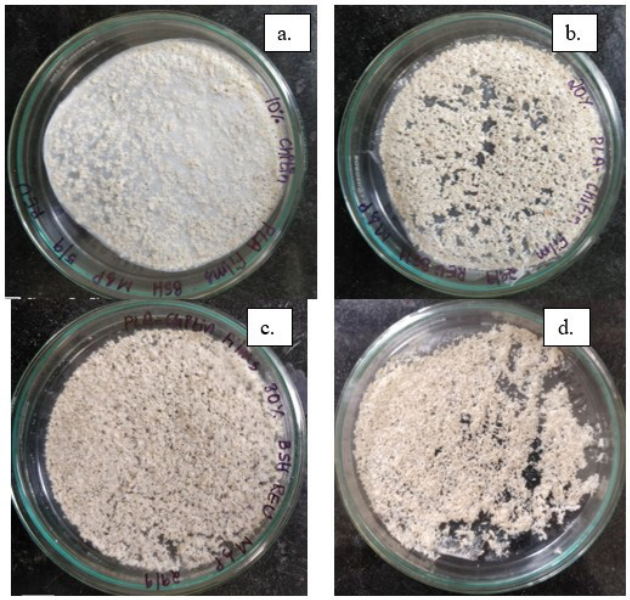


Figure 3: (a)10% PLA/chitin, **(b)** 20% PLA/chitin, **(c)** 30% PLA/chitin, and **(d)** 40% PLA/chitin composites.

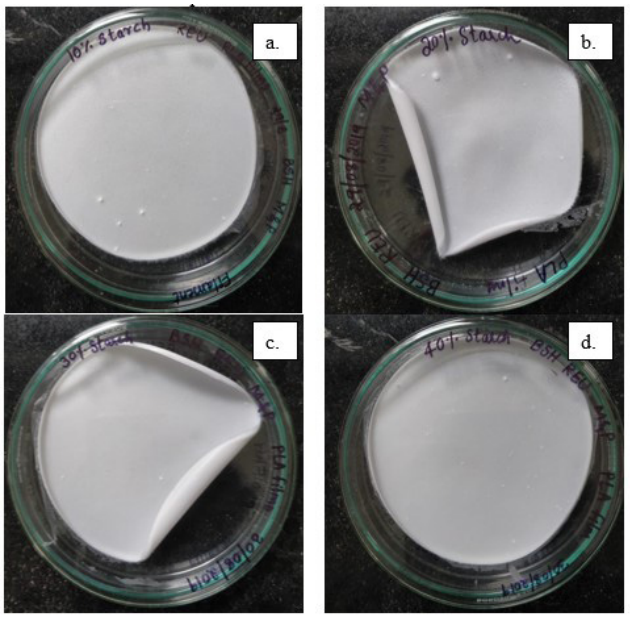


Figure 4: (a)10% PLA/starch, **(b)** 20% PLA/starch, **(c)** 30% PLA/starch, and **(d)** 40% PLA/starch composites.

TGA

The thermal property i.e., thermal degradation was examined for the chitin and chitosan samples using TGA/SDTA: 851e Mettler Teledo instrument. The weight of the samples was monitored against the temperature under an inert environment using nitrogen gas, at a heating rate of 10 °C/min and the results were recorded and analyzed.

UTM

The tensile strength of the PLA, PLA composite films were used to represent the mechanical properties of the films. The tensile strength or the ultimate strength is defined as the maximum tensile stress before the material reaches the breaking point. The tensile strength was tested in a UTM: Micro Universal Testing Machine 10ST. The specimens were prepared by cutting the PLA/PLA composite films into small specimens. The crosshead speed was 10 mm/min. For each sample, the length of the gauge was adjusted, and the width and thickness of each sample was measured prior to testing. For each sample, Young's modulus, strength, and elongation at break were determined and average values were reported [6].

Results and Discussion

FTIR analysis

The information regarding the interactions between the composite matrices was revealed by FTIR. The spectra of pure PLA film exhibited characteristic bands at 1755 cm^{-1} and 1078 cm^{-1} which represents the backbone ester group of PLA. The peak observed at 1078 cm^{-1} signifies the -C-O- stretching vibration from the ester units. The peak at 3505 cm^{-1} determines the terminal position of -OH of L-lactic acid. The bands at 2885 cm^{-1} and 3001 cm^{-1} represent the -C-H symmetric and asymmetric vibration of $-CH_3$ groups of the side chains. The band at 2945 cm^{-1} signifies the -CH- groups present in the main chain of PLA. From the FTIR spectra of the chitin and PLA, the bands around 1550, 1599, and 1654 cm^{-1} were assigned to amide II (-NH), amino ($-NH_2$), and amide I (C-O) of chitin in the organic matrix, respectively. The FTIR spectra of cellulose and PLA represents a new broad intense band around 1,200 - 1,000 cm^{-1} and a distinguished peak at 1,260 cm^{-1} that reflects the stretching vibration of the S=O bond can be observed. On the contrary, the absence of the characteristic peaks after the acid treatment of cellulose at 3,340 cm^{-1}, assigned to the -OH stretching of intra molecular hydrogen bonds, suggests the diminution of cellulose -OH bonds. The FTIR spectra of starch and PLA at the peak, 1731 cm^{-1} represent the C-O stretching vibration peak (Figure 5, figure 6, and figure 7).

TGA analysis

TGA is an essential method used to study the thermal decomposition of polymeric substances. The loss in weight of the substance (polymer) was due to the formation of a volatile product after the degradation. This is monitored as a function of temperature or time. The TGA results of PLA/cellulose and PLA/starch composite films are summarized in table 2 and table 3, respectively. T_d represents the thermal degradation temperatures whereas T_{max} represents the maximum temperature at which weight loss is maximum. The figure 8 and figure 9 illustrates the relation between weight loss percentage and temperature. In figure 8, the blue line represents PLA which has the lowest thermal degradation temperature. The red, green, yellow, and black lines represent 10% PLA/cellulose, 20% PLA/cellulose, 30% PLA/cellulose, and 40% PLA/cellulose films respectively. In figure 9, the blue line represents the PLA which has the lowest thermal degradation temperature. The black, yellow, red, and green lines represent 10% PLA/starch, 20% PLA/starch, 30% PLA/starch, and 40% PLA/starch composite films.

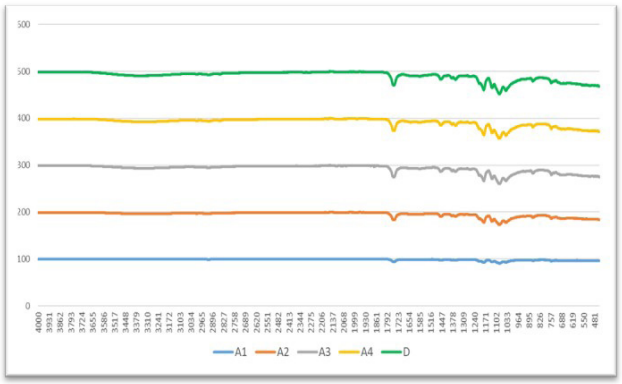


Figure 5: FTIR spectra of PLA/cellulose.

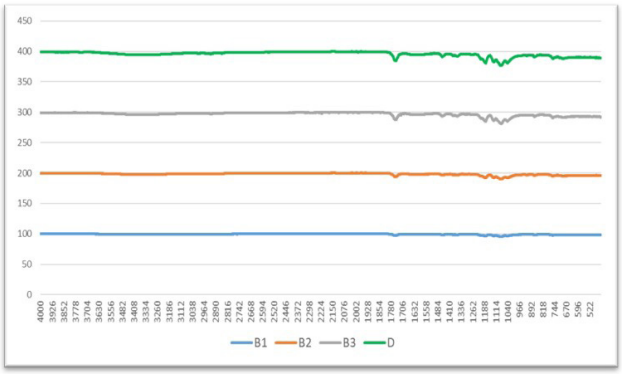


Figure 6: FTIR spectra of PLA/chitin.

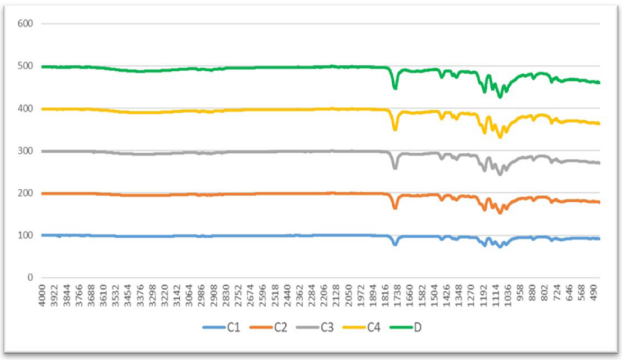


Figure 7: FTIR spectra of PLA/starch.

Table 2: TGA results for PLA/cellulose composite films.

PLA/cellulose	T_d (°C)	T_{max} (°C)
10%	360	500
20%	370	400
30%	375	600
40%	380	800

Mechanical properties by UTM

Tensile properties of PLA composites were studied using UTM and a typical stress-strain curves of the films are illustrated in figure 10. The characteristic values of tensile stress, tensile modulus, and elongation at break is summarized in table 4. The pure PLA show modulus of 1.854 GPa and then abruptly breaks at 0.423%.

Table 3: TGA results for PLA/starch composite films.

PLA/starch	T_d (°C)	T_{max} (°C)
10%	200	400
20%	370	800
30%	390	550
40%	400	800

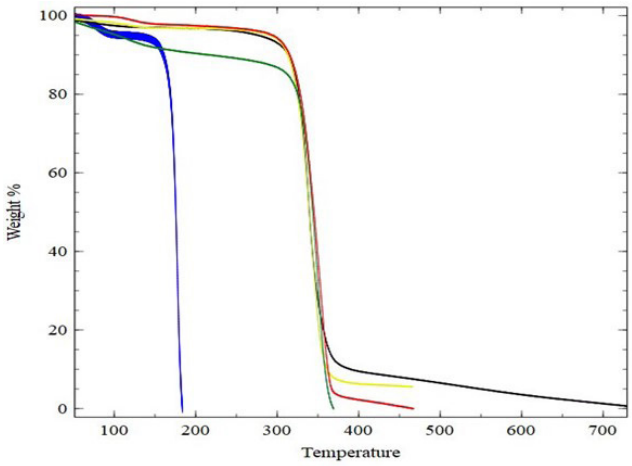


Figure 8: TGA analysis of PLA/cellulose composite film.

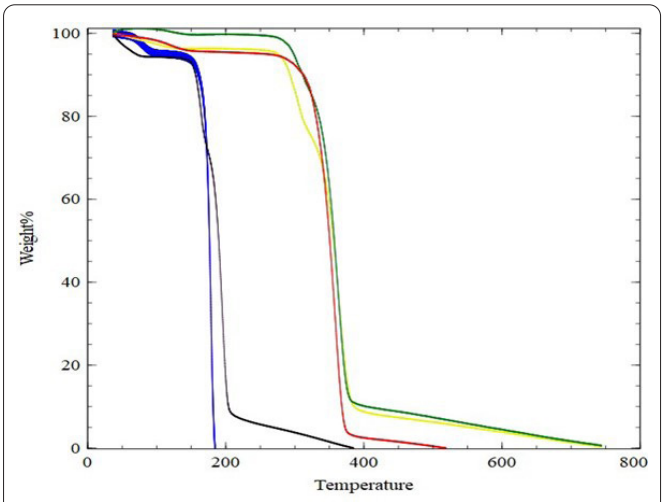


Figure 9: TGA analysis of PLA/starch composite film.

The UTM result reveals the strength of the material and the elasticity of the polymer. Higher strength means a harder the material, thus the material is less deformable. Therefore, the deformed material breaks at low strain. Conversely, if the material is more elastic or plastic then the material is less strong but breaks at higher deformation. In this study, poor adhesion of the filler matrix at the interface can seriously weaken the composite material and the filler may not act as a reinforcing material but as a defect in the matrix. If this happens, the strength will decrease, and therefore the elongation at break will increase. Chitin PLA composite has lower elas-

Table 4: Summary of tensile properties of PLA blended with various concentrations of cellulose, chitin, and starch.

Material	Concentration	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)
PLA/cellulose	10%	6.07	3,413	0.423
	20%	4.29	2,316	0.256
	30%	4.49	2,936	0.229
	40%	2.53	2,565	-0.00247
PLA/chitin	10%	2.92	1,342	0.283
	20%	0.52	258	-0.0138
	30%	159	0.2	5.63
PLA/starch	10%	4.41	2,898	0.355
	20%	3.81	1,974	0.273
	30%	4.36	2,914	0.439
	40%	4.26	2,510	0.351
Pure PLA	-	4.31	1,854	0.661

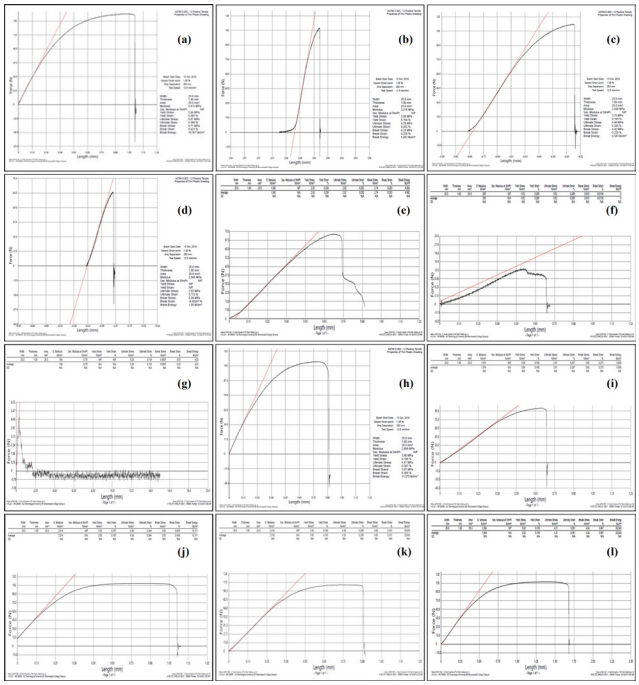


Figure 10: UTM of **(a)** A1, **(b)** A2, **(c)** A3, **(d)** A4, **(e)** B1, **(f)** B2, **(g)** B3, **(h)** C1, **(i)** C2, **(j)** C3, **(k)** C4, and **(l)** D films.

ticity, while starch PLA composite has better elasticity. Tensile strength increases with the addition of fillers to pure PLA. Compared to pure PLA film, the composite material has 20% to 25% higher tensile strength, 8% to 10% higher elongation at break, and a high modulus of elasticity.

Conclusion

PLA films are semi-transparent like many other plastic films. Low concentration (10%, 20%) PLA composite films are also semi-transparent. As the concentration increases, PLA/starch films become opaque while PLA/cellulose and PLA/starch films become white. There are also pores and discontinuities in high concentration PLA/chitin films. A simple blending of starch, cellulose, and chitin to PLA, improved the thermal and mechanical properties. The tensile strength of PLA/starch films is the strongest among all the test samples. The tensile strength of PLA composite films increases as the concentration of the additives increases. PLA/starch has the highest tensile strength among the PLA composite films at high concentrations. PLA has the lowest thermal degradation temperature; starch has the lowest. For PLA/starch and PLA/cellulose, the thermal degradation temperatures are in between PLA and the corresponding additives. The result cannot verify the existence of a chemical reaction during the fabrication process. PLA has better mechanical properties than starch, cellulose, and chitin; by blending materials with lower tensile strength and degradation temperature, PLA composite film may be fabricated with a better degradation rate and better stability.

Acknowledgments

None.

Conflict of Interest

None.

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