

Effect of Different Filler Concentration on Polylactic Acid (PLA) for Biomedical Application

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Abstract

The present study explores the possibilities of using locally available inexpensive waste prawn shell derived chitosan reinforced and bioabsorbable polylactic acid (PLA) biocomposites to develop new materials with excellent mechanical and thermal properties for implantable application such as in bone implant. Chitosan at different concentration (1-10% of PLA) reinforced PLA were fabricated by twin screw extruder. The effect of variation of chitosan concentration on the resulting biocomposite's behavior was investigated. Mechanical, surface morphology and thermal were assessed with different characterization technique such as FT-IR, SEM and DSC. The FTIR spectra showed the characteristic peaks for chitosan and PLA in the composites. SEM images showed an excellent dispersion of chitosan in biocomposites. Differential scanning calorimetric analysis (DSC) showed that the Glass transition temperature (T_g), Melting temperature (T_m), and Crystalline Temperature (T_c) of chitosan PLA composite. The mechanical properties of the biocomposite with the increase of chitosan content indicated good dispersion of chitosan into PLA and strong interfacial actions between the polymer and chitosan. The improvement of mechanical properties and the results of anti- microbial and cytotoxicity of the composites also evaluated and revealed the composite would be a suitable candidate for implant application in biomedical sector.

Keywords: *chitosan, PLA, Biocomposite*

Introduction

Over the recent years, there was a growing scientific and industrial interest in using composites obtained by renewable sources and with potential biodegradability in order to reduce the overall environmental impact. For this reason, biodegradable polymers are considered promising materials and among these poly(lactic acid) (PLA) can be considered one of the most attractive biopolymers due to its physical properties, renewability, biodegradability finding applications in many areas of Engineering and Technology. PLA can be easily processed in a wide number of methods and it is commercially available in a considerable range of grades making it suitable for several applications. Recently, different functional groups or fillers were incorporated in the polymeric networks for introducing new functionalities and improving performance and endured reusability. In this context, natural fibres and particles as reinforcing or fillers agent in PLA-based composites has gained increasing attention. These materials permitted the valorization of agricultural or marine wastes, providing products that present final properties suitable for several applications. Different natural fibres and particles were tested as fillers for polymeric matrices such as flax, hemp, jute, kenaf, ramie and sisal, and from agricultural wastes or by-products such as coir, okra, pineapple and artichoke Nevertheless, there are some others that can be potentially used as reinforcements for PLA matrices but not yet investigated, e.g. chitosan.

Poly(lactic acid) (PLA) is a linear aliphatic thermoplastic derived from 100 % renewable resources such as sugar, corn, potatoes, cane, beet, etc. PLA is potentially degraded in soil, compost or in human body. It is intensively studied for short term applications. It was reported that the degradation of PLA in soil is slow and it takes a long time for degradation to start, probable because the slow rate of hydrolysis at low temperatures and water contents and the relative scarcity of PLA degrading organisms. In a composting environment the PLA is hydrolyzed into smaller molecules (oligomers, dimers and monomers) after 45–60 days at 50 – 60 °C. These smaller molecules are then degraded into CO₂ and H₂O by microorganisms in compost. PLA degradation was found to be higher in unsterile compost suggesting potential synergy between bacteria and fungi in PLA degradation. Also, PLA degrades into lactic acid, a normal human metabolic byproduct, which is broken down into water and carbon dioxide via the citric acid cycle. Although PLA possesses good melt processability, its weaknesses include poor gas-barrier properties, low toughness and ductility, poor thermal stability and high cost.

Chitosan, a polycationic polymer and waste product from the sea food processing industry, is an abundant natural resource that has, as yet, not been fully utilized. Advantages of this polymer include availability, low cost, high biocompatibility, biodegradability and ease of chemical modification. The physicochemical properties of chitosan, as well as its numerous applications, are reviewed with particular emphasis on its use in water treatment, pharmaceuticals, agriculture and membrane formation.

In the present we wish to fabricate laminated chitosan-PLA biocomposite by melt mixing method to use in artificial bone implant. The complete characterization of the raw materials and the composite have done and described in the following section to clinch the application of the proposed materials as a simulated form of human bones.

Materials and methods

Materials

The prawn shells were purchased from a local market. They were washed and crushed in a sample mill. Poly(lactic acid) (PLA) used in this study was of 2002D type from NatureWorks LLC (Minnetonka, MN, USA), with a density of 1.24 g/cm³, melt flow index (MFI) of 5–7 g/10 min (at 210 °C/2.16 kg). PLA has a Mw of 14.27 x 10⁴ g/mol, Mn of 7.54 x 10⁴ g/mol and polydispersity index (PDI) of 1.88. It is a semicrystalline polymer obtained from renewable annual resources, with a D-lactide content of 4 % (96 % of L-lactide) and is accepted by the Food & Drug Administration (FDA). Sodium hydroxide pellet (Shah sales corporation, Ahmedabad), Hydrochloric acid (Shah sales corporation, Ahmedabad), sodium chlorite, extra pure, Phosphorus pentoxide (Shah sales corporation, Ahmedabad) and Methane sulfonic acid (Shah sales corporation, Ahmedabad) were purchased and used in this work as obtained.

Extraction of chitin from prawn shell

The prawn shells were washed, dried and milled. The pulverized shell was stirred by magnetic stirrer with 2N HCl for 2 h for demineralized and treated with 2N NaOH at 50 °C for 2 h for deproteinization and 50% NaOH at 121 °C for Deacetylation, Deacetylated shell was washed and dried at 60 °C in an oven to obtain dried chitosan.

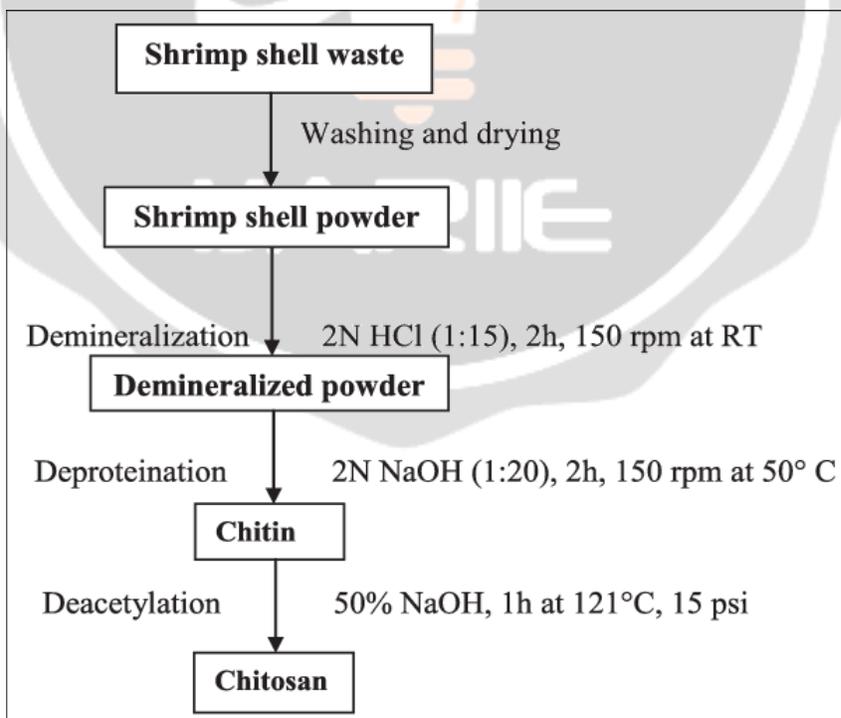


Fig. 1 Flow Chart for Preparation of chitosan from prawn shell.

Phosphorylated Chitosan

One of the water soluble derivatives of chitosan is phosphorylated chitosan, which has significant importance for bone implant. Phosphorylated chitosan have the ability to form polyelectrolyte hydrogels and to make complexes with metals. They have anti-inflammatory property, and blood compatibility.

Preparation Methods of Chitin and Chitosan Phosphorylation

Phosphorous pentoxide in methanesulphonic acid can be used to carry out phosphorylation in chitosan at low temperature. Water soluble products with high degree of substitution were obtained. Methanesulphonic acid acts both as a perfect solvent for chitin and chitosan, and as a catalyst.

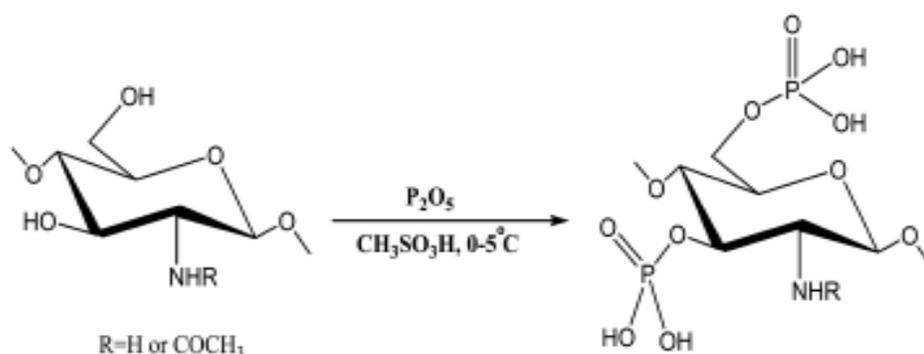


Fig. 2 Chemical reaction of Phosphorylated Chitosan

Compounding

PLA and phosphorylated chitosan, were predried at 80 ± 5 °C for 2 hrs prior to compounding. chitosan (0-10 wt%) were added to PLA. The composites were prepared by using melt mixing technique using co-rotating, twin screw extruder (Specific Engineering and Automates, ZV 20) at L/D ratio of 40:1 and screw speed of 120 rpm. The temperature profiles in barrel were maintained from 190, 200, 210, 220, 230, 220 °C from feed zone to die zone. The extrudates were water cooled at room temperature, cooled to room temperature and pelletized.

PLA and chitosan Composition

Sr. No.	Wt % of PLA	Wt % of Chitosan	Nomenclature
1	100	0	PLCH
2	97	3	PLCH1
3	95	5	PLCH2
4	93	7	PLCH3
5	90	10	PLCH4

Characterization

Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared (FTIR) spectra (transmission) of chitosan measured by a FTIR spectrophotometer (FTIR, Agilent Technology).

Thermal analysis

To analyze the thermal behavior differential scanning calorimeter (PERKINELMER, Diamond DSC) was used to determine the glass transition, melting temperature, crystalline temperature of biocomposite.

Scanning electron microscopy (SEM)

A high-performance scanning electron microscope (SEM) (Tescan Wega) with a high resolution of 3.0 nm at 5 kV was used to determine the surface morphological characteristics of chitosan, PLCH, PLCH1, PLCH2, PLCH3, PLCH4. A small portion of the samples was fixed on conductive carbon tape and mounted on the support and then sputtered with an approximately 5 nm layer of graphite.

Mechanical properties

Tensile strength (TS) and percent elongation at break (Eb) and E modulus of PLCH, PLCH1, PLCH2, PLCH3, PLCH4 biocomposite were analyzed by Universal Testing Machine (P.S.I. SALES LTD).

Water uptake test

Water uptake of the PLCH, PLCH1, PLCH2, PLCH3, PLCH4 biocomposite were calculated to observe the water absorptivity and sustainability in water. The water absorption was determined by using the ASTM test method D570-81.

Results and discussion

FTIR analysis

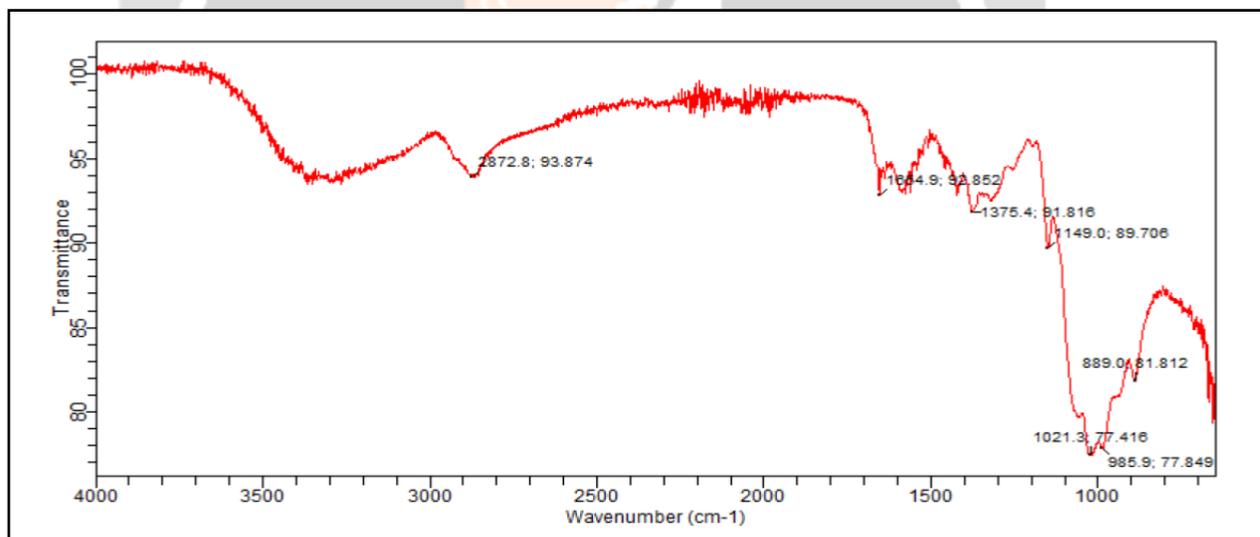


Fig. 3 FTIR graph of chitosan

FTIR data revealed very important information about the chitosan. The bands (chitosan) and 3285 cm^{-1} (chitosan oligomers) are determined by $\nu(\text{OH})$ overlapped on $\nu(\text{N-H})$. The band from 2867 cm^{-1} is determined by $\nu(\text{C=O})$ of the amide group CONHR of the chitosan. The bands 1568 cm^{-1} (chitosan) and 3285 cm^{-1} (chitosan oligomers) are determined by $\nu(\text{C=O})$ of the proton amide group, and $\delta(\text{NH}_3)$ is determined by the proton amide group. The bands 1417 cm^{-1} (chitosan) and 1419 cm^{-1} (chitosan oligomers) are determined by $\delta(\text{OH})$. The bands 1372 cm^{-1} (chitosan) and 1375 cm^{-1} (chitosan oligomers) are determined by $\delta(\text{-CH}_3)$. The bands 1318 cm^{-1} (chitosan) and 1317 cm^{-1} (chitosan oligomers) are determined by $\nu(\text{-CH}_3)$ third amide $\omega(\text{-CH}_2) + \text{OH}$ deformation in plane. The bands 1152 cm^{-1} (chitosan) and 1148 cm^{-1} (chitosan oligomers) are determined by $\nu(\text{C=O})$ oxygen bridges resulting from the deacetylation of the chitosan. The bands 1060 cm^{-1} (chitosan) and 1081 cm^{-1} (chitosan oligomers) are determined by $\nu(\text{C=O})$ by the bindings C-O-H, C-O-C and CH_2CO . The bands 892 cm^{-1} (chitosan) and 892 cm^{-1} (chitosan oligomers) are determined by $\omega(\text{C-H})$ from the polysaccharide's structure.

Morphological study

shows the SEM photographs of prawn shell derived chitosan which exhibited rough and thick surface morphology under electron microscopic examination at 65 magnification. At higher magnification (3000), chitosan from shrimp was found to be distinctly arranged in a microfibrillar crystalline structure. Similar observation was also observed in the literature. The PLA is transparent and heat treated laminated PLA surface was observed uniform. A figures represented SEM images of PLCH, PLCH1, PLCH2, PLCH3, and PLCH4 exhibited a relatively smooth.

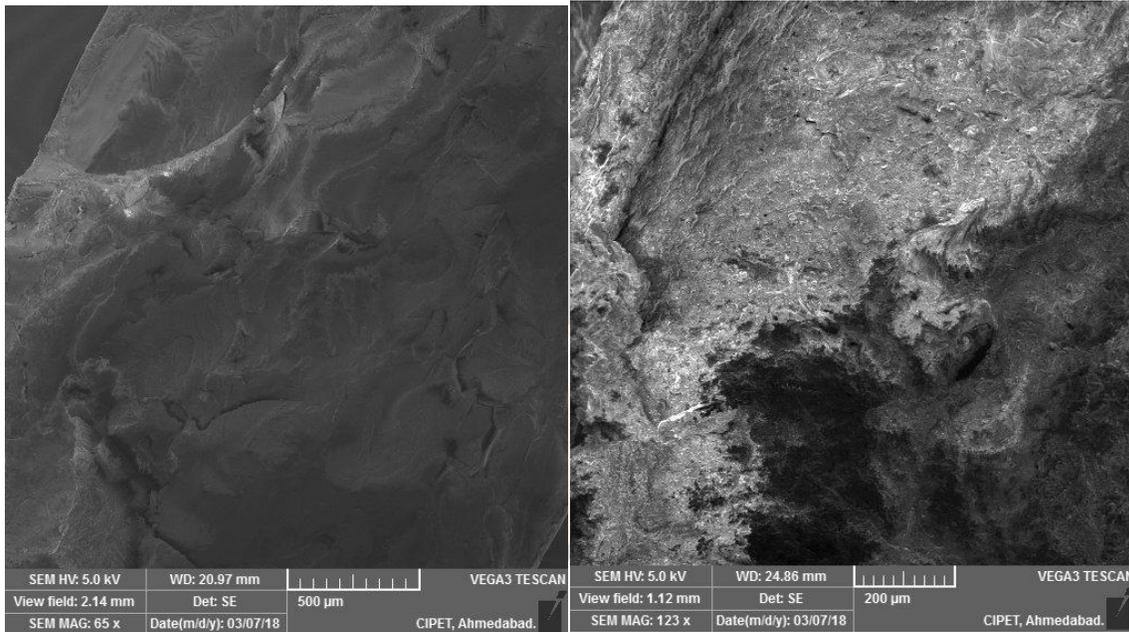


Fig. 4 and 5 SEM images of PLCH and PLCH1



Fig. 6 SEM images of PLCH2

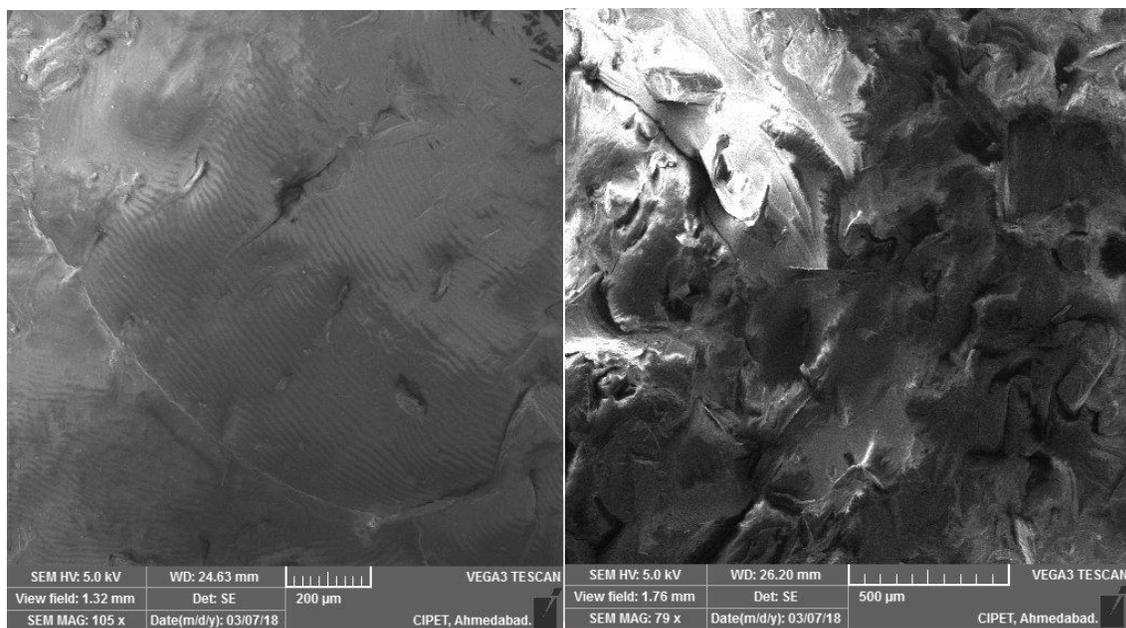


Fig. 7 and 8 SEM images of PLCH3 and PLCH4

surface, indicating a high compatibility between PLA and chitosan or a good uniform dispersion of chitosan in the reinforced biocomposites. The composites also showed better entanglement of chitosan and PLA in the surface.

Mechanical properties

Tensile properties. The tensile properties of the biocomposite (PLCH, PLCH1, PLCH2, PLCH3, PLCH4) are given in Fig. 9. The results demonstrated that melt mixed PLA with various chitosan content showed less tensile strength than of pure PLA. It is also observed that tensile strength increases in 5% (PLCH2). The increased tensile strength of the with the increasing chitin content indicated good dispersion of chitosan into PLA and strong interfacial actions between the polymer and chitosan. The orientation of chitosan effectively occurred in PLA matrix and, therefore, the TS rises. The overall mechanical performance of composites, depends on adhesion and compatibility between the polymer matrix and the additives or reinforcement and crystallinity of the polymer matrix and reinforcement. Hence the increase of TS upon the addition of chitosan is probably due to good dispersion and crystalline nature of the chitosan. Further increase of chitosan content in the PLA made brittle and the composite did not show enough strength since PLCH4.

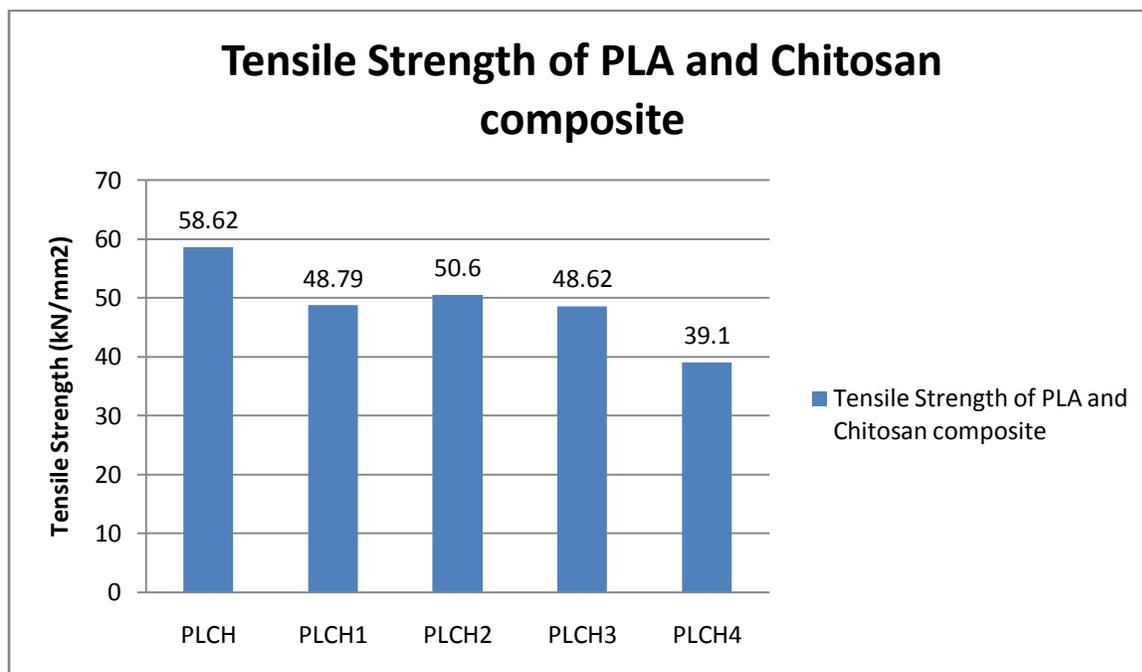


Fig. 9 Tensile Strength of PLA and Chitosan composite

Thermal properties

Differential Scanning Calorimeter (DSC)

The non-isothermal crystallization behavior of the PLA Chitosan composites were studied by DSC with the sample cooled from 235 to 40 °C at constant a cooling rate 10 °C/min. Fig. 10 shows that there is no significant change in the melting points (T_m) of both filled and unfilled samples of PLA Chitosan composites. The melting temperature are consistently scattered within the typical range of 150-170 °C for composite. DSC thermograms obtained for PLA Chitosan composites sample shows the glass transition, exothermic crystallization peak and the endothermic peak of crystalline phase melting.

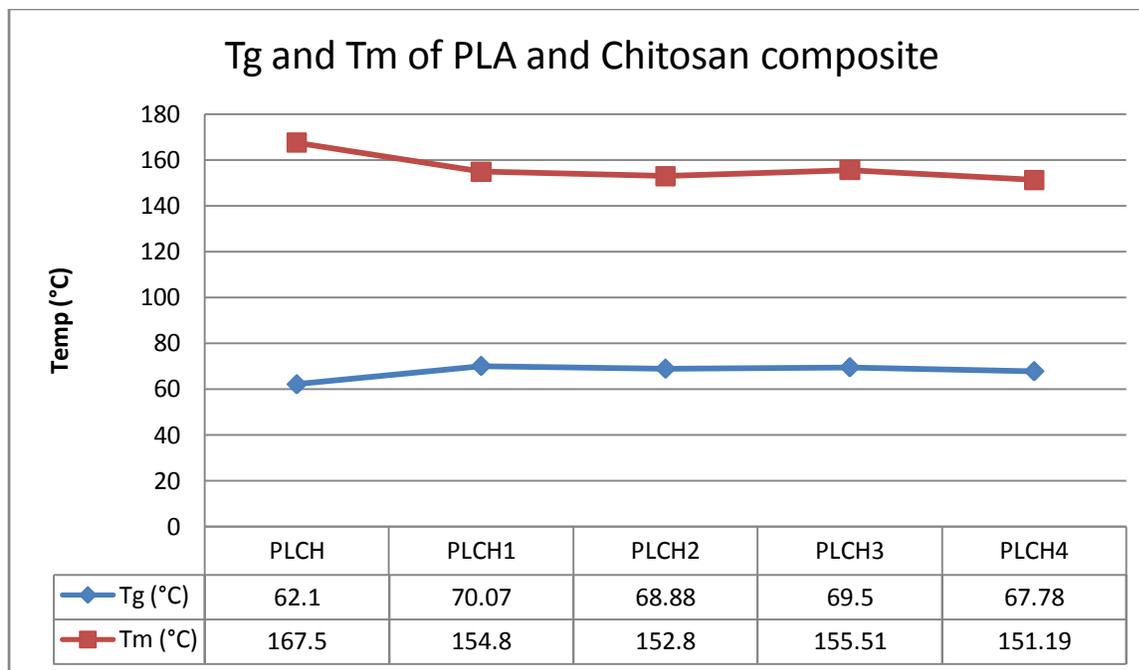


Fig. 11 Tg and Tm of PLA and Chitosan composite

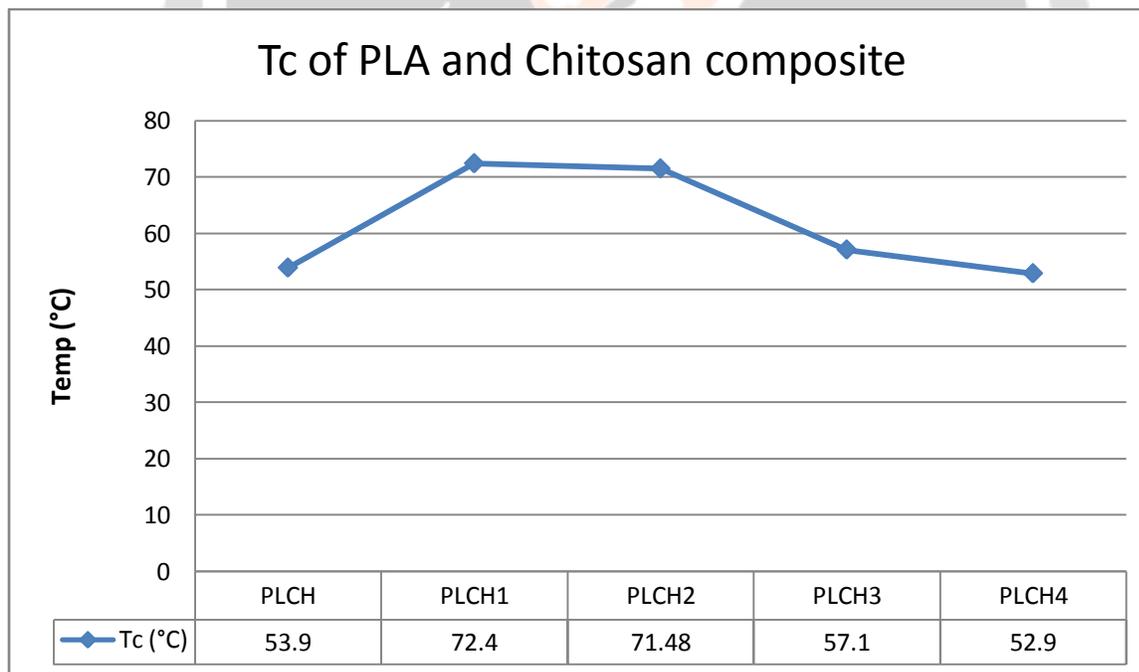


Fig. 12 Tc of PLA and Chitosan composite

Water uptake test

Fig 13 showed the water absorption behavior of PLA (PLCH), 3% chitosan-PLA film (PLCH1), 5% chitosan-PLA film (PLCH2), 7% chitosan-PLA film (PLCH3), and 10% chitosan-PLA film (PLCH4), for 24 h duration. Interestingly

pure PLA film showed 2.9% water absorption up to 24 h although it has hydrophobic nature. After the incorporation of chitosan (PLCH2) the graph displayed less water absorption than pure PLA film. It absorbed 2% water in a 24 h period. The absorption of water decreases after 2 h. The films containing higher percentage of chitosan were very much brittle and non-uniform in character and thus absorbed more water than pure PLA.

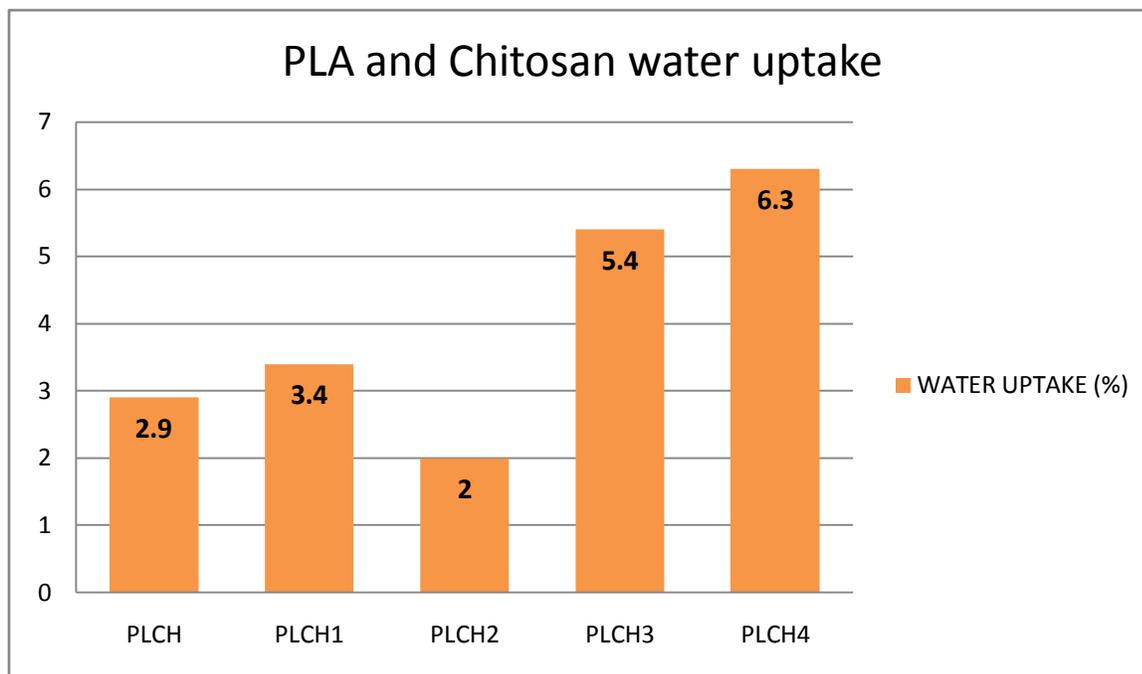


Fig. 13 PLA and Chitosan water uptake

Conclusions

The composite material (PLCH2) was found to have combined advantages of their components, namely higher tensile strength. The composite also showed suitable thermal stability as well as lower water absorption capacity suitable for using as a bone implant. Considering the various physicochemical and thermal properties it is revealed that the materials can be an excellent candidate for the replacement of traditional metallic, ceramic based implants.

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