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Incorporation of Vitamin D Food Additive for Improved Mechanical, Barrier and Oxygen Transmission Properties of Poly(lactic-acid) Based Biocomposite Films

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Abstract

Poly(lactic acid) (PLA) based sustainable composites reinforced with Vitamin D_3 (VTD) at different concentrations (1, 3, 5 and 10 wt%) were prepared using solvent casting method. The filler dispersed readily in the PLA matrix. The properties of the PLA/VTD composite films were investigated for their thermal, barrier and mechanical properties, and also for oxygen permeability. Improvement in mechanical and oxygen barrier studies were recorded and the VTD modified PLA composite films showed improved properties. For example, the addition of the VTD in the PLA caused enhancement in the oxygen barrier and mechanical properties. The tensile property of the PLA was increased significantly to 42 MPa from 28 MPa at 3 wt% VTD. The oxygen transmission rate (OTR) was also increased by 52 % in the PLA/VTD composite. Therefore, the findings indicate that the suitable properties of the PLA/VTD composite films showed potential for food packaging applications.

Keywords: Bioactivity, Cholecalciferol, Packaging, Poly(lactic acid), UV blocking.

Introduction

Recently, there has been high demand for biodegradable packaging materials sourced from renewable avenues because of their eco-friendliness and sustainability [1, 2]. Poly (lactic acid) (PLA) has become the leading biodegradable polymer in this case due its versatility, biocompatibility, biodegradability, thermoplasticity, good processability, transparency, low cost and more importantly better mechanical properties compared to other biopolymers [3, 4]. PLA is structurally a linear aliphatic polymer whose monomers can be made from corn or sugar beets and primarily synthesised through polycondensation reaction or open ring polymerisation. PLA, given its rigidity with high transparency coupled with desirable mechanical properties has seen applications in manufacture of utensils such as plates, cups, trays, films and tubes [5,6]. PLA is a biodegradable material with water, CO_2, and small molecules been the main products of degradation in composting conditions and hence environmentally friendly [7]. Nonetheless, PLA has important drawbacks hampering its wide application for food packaging applications which include brittleness, poor water vapour and oxygen gas barrier properties, slow crystallisation and poor elongation at break [8]. In order to overcome these challenges, PLA biopolymer has been combined with both organic and inorganic fillers, other polymers, plant and animal extracts etc. to enhance films properties, improve UV-light blocking and induce bioactivity like antioxidant and antimicrobial [9].

Among the biofillers, Vitamin D_3 (VDT) is interesting, since it is an approved food additive and considered safe for human consumption. Cholecalciferol has such properties as nontoxicity, low cost, availability, robust antioxidant and antimicrobial properties [10, 11]. Biologically, cholecalciferol is essential for maintaining blood calcium and phosphorus content as well as bone mineralization [12]. Cholecalciferol is synthesized naturally in lower layers of skin in a reaction catalysed by UVB radiation, it is also found in foods of animal origins [13]. Vitamin D_3 is a secosteroid, which increases intestinal absorption of calcium, phosphate and magnesium in the intestine. About a billion people are estimated to be Vitamin D_3 deficient around the world [14, 15]. Vitamin D_3 can be taken as supplements and diets. Consequently, cholecalciferol has been considered as a bioreinforcement material in PLA for applications in food packaging. The use of cholecalciferol as a biofiller in PLA will also increase its availability to mitigate its deficiency while improving the food packaging material properties PLA.

Therefore, in the current work, the effect of cholecalciferol on the properties of PLA/VTD biocomposite films at various concentrations using solvent casting method was investigated. The main objective of this study was to fabricate PLA/VTD composite films through solution casting method and characterise same through a variety of physico-chemical analytical methods, functionality test and bioactivity. The impact of Vitamin D_3 food additive filler concentration on mechanical, structural, thermal, barrier property, antioxidant and antimicrobial properties are also carefully examined.

Material and Methods

Materials

Poly (lactic acid) Ingeo™ Biopolymer 4043D used as biopolymer matrix was obtained from NatureWorks LLC, USA. Chloroform, acquired from Sisco research laboratories Pvt. Ltd, India, was used for solubilisation purposes. Vitamin D_3 was purchased from Sigma-Aldrich, USA. Tenax, and, finally, dry food simulant was also purchased from Sigma-Aldrich, USA.

Preparation of PLA/VTD composite films

The PLA/VTD composite films were made using solvent casting method. Concisely, different concentrations of VTD food additive biofiller (1, 3, 5 and 10 wt. % based on pure PLA) were evenly solubilised in 30 ml of chloroform with a probe sonicator for 1 h to make a homogenised mixture. Thereafter, ~1 of neat PLA was also dissolved in chloroform until a clear and uniform solution was formed. The two solutions were mixed and sonicated for 2 h to have a proper homogeneous PLA/VTD solution. The resultant composites were casted in flat petri dishes and dried at room temperature for 24 h. The films were peeled-off and further dried in the oven at 40 °C for another 24 h to remove all traces of chloroform. The prepared PLA/VTD composites films were designated as PLA/VTD-1, PLA/VTD-3, PLA/VTD-5 and PLA/VTD-10 respectively. The neat PLA biopolymer film was prepared similarly as described.

Characterization

Fourier Transform Infrared (FTIR) spectroscopy

FTIR spectra for neat PLA and PLA/VTD composites were observed using FTIR spectrophotometer (Bruker, Germany with model: TENSOR 27) in attenuated total reflectance (ATR) mode. The resolution of the equipment was 4 cm^{-1} and spectral peaks were recorded between wavenumber of 4000-400 cm^{-1}.

2.3.2 Mechanical analysis

The mechanical properties of the neat PLA and PLA/VTD composites films which include tensile strength (TS), elongation at break (EB) and elastic modulus (EB) were measured by ASTM D 882 using with aid of a universal testing machine (Make: Tinius Olsen, USA with model: H5K). The samples were cut to a size of 15 cm x 1 cm and the machine grip separation was set at 20 mm at a crosshead speed of 20 mm/min. multiple samples of five were tested for each sample with mean values reported. The TS (MPa) and EB (%) were calculated with the formula below.

$$TS(MPa) = {F_{max}}/{A} \qquad (2)$$

$$EA(\%) = \frac{\Delta L}{L_o} \times 100 \qquad (3)$$

Where, F_{max} is the maximum force used on the film (N), A is the area of the films (m^2), ΔL is the change in length at break, and L_o is the initial length of the film. The elastic modulus (EM) of each film was calculated using the slope of the stress-strain curve.

Oxygen transmission rate (OTR) analysis

The oxygen (O_2) permeation analysis for neat PLA and PLA/VTD composite films was carried out with using of a gas permeability tester (GTR) (M/S Labthink, China with model: PERME VAC-VBS). For this analysis, a constant temperature of 30 °C at 50% relative humidity were maintained. Oxygen gas inlet pressure was operated at 5 bar and the test was conducted between 0.1 to 100,000 cm^3/m^3. 24 hr. 0.1 MPa. This test complied with ASTMD 1434 standard method and proportional mode was followed during the test period. The samples were test in triplicates for each analysis to arrive at the average OTR value for the neat PLA and PLA/VTD composite films.

Results and Discussion

FT-IR analysis

The FTIR spectra of the VTD powder, the PLA film and the composites are presented in the Figure 3. With respect to vitamin D3 spectrum, the peak at 3286 cm^{-1}, is assigned to the O-H stretching vibration. Two peaks at 2929 cm^{-1} and 2866 cm^{-1} was attributed to the CH3 asymmetric and CH2 symmetric stretching. The characteristic peak of VTD positioned at 1637 cm^{-1} is associated with H-C=C-H stretching vibrations and the peak at 1460 cm^{-1} belongs to C-O-H bending vibrations. Finally, series of peaks were observed in the range of 1400 cm^{-1} – 800 cm-1 related to C-H stretching and bending vibrations [16-18]. The typical peaks of PLA appeared at 2993 cm^{-1} and 2937 cm^{-1} were related to asymmetric and symmetric stretching of CH_3 groups. A strong distinctive vibrational peak obtained at 1747 cm^{-1} was due to the −C=O stretching vibration of ester group present in PLA backbone. The appearance of peaks positioned at 1452 cm^{-1} and 1357 cm^{-1} ascribed to the asymmetric and symmetric bending of $–CH_3$ group respectively. The peak at 1182 cm^{-1} is ascribed to the asymmetric stretching of −C−O−C in PLA. The peak at 1261 cm^{-1} is associated with C=O bending vibrations [19]. A triplet peak appears at 1124 cm^{-1}, 1082cm^{-1}, 1039 cm^{-1} were due to CH_3 rocking vibrations, C−O stretching vibrations of the −CO−O− group and C -CH_3 stretching vibration mode respectively. And two peaks positioned at 866 cm^{-1} and 750cm^{-1} are related to –C–C– stretching, which is associated to the amorphous and crystalline phases of PLA [20].

Furthermore, Characteristic peaks of PLA are found in all PLA/VTD composite films. The films showed the same peaks as the PLA film due to the formation of weak interactions, such as Van der Waals forces and hydrophobic interactions between vitamin D3 and PLA, which were unaffected by molecular vibration. However, the presence of VTD can be confirmed by slight shifts in peaks recorded in the composite films, the shifts from 1747 to 1749 cm^{-1} of the characteristic PLA peak and subsequent shift from 866 to 869 cm^{-1} and 750 to 754 cm^{-1} of peaks representing the crystallinity of PLA are indicative of impact of VTD in the crystallinity PLA [14,20], as corroborated the observations of XRD analysis results.

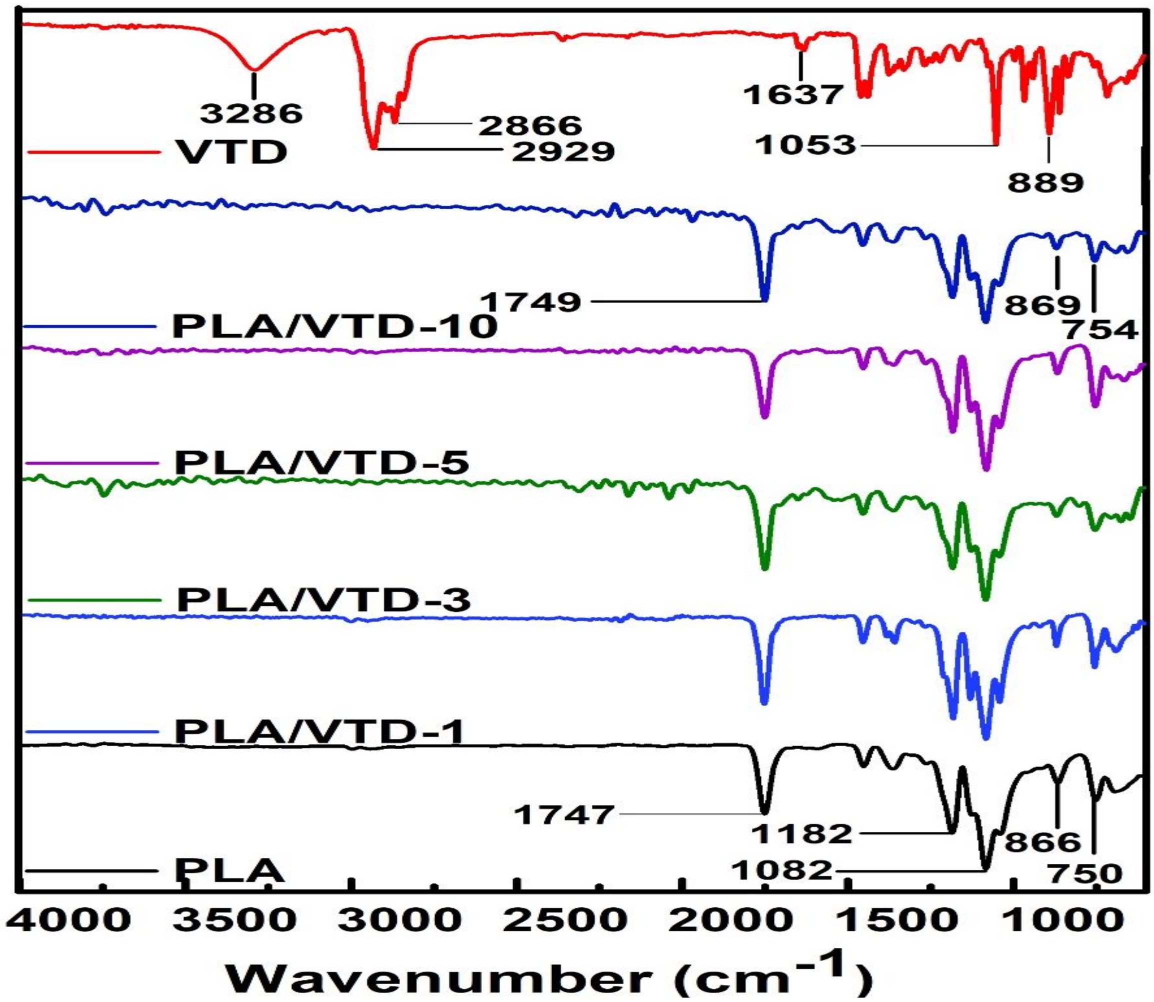

Figure 1: FITR spectra of PLA, PLA/VTD composites & VTD biofiller

Mechanical properties

Films used for packaging materials must have good mechanical properties to withstand external stress during processing, transportation, handling and storage to protect foodstuffs [21]. The sample films mechanical properties vis-a-vis tensile strength (TS), elongation at break (EB) and young's modulus (EM) of the neat PLA and PLA based VTD composites films are shown in Figure 6. The TS is defined as the highest stress withstand by a film before it breaks. The TS of neat PLA was 28 MPa and it increased significantly by ($P < 0.05$) (36 MPa) upon addition of 1 wt% VTD filler due good dispersion and interfacial interaction between PLA and VTD at 1 %. A further increase in TS was observed by adding 3 wt% of VTD in the PLA with a significance of ($P <0.01$), but TS subsequently decreased at higher concentration of VTD, for 5 and 10 wt% VTD 37 and 37 MPa was recorded. The noticeable decrease in decrease in TS of the composites at higher VTD wt% can be attributed to decreased interfacial interaction between VTD and

PLA matrix resulting in formation of agglomeration as evident in SEM micrographs. Additionally, PLA recorded EB of 3.2 %, this shows PLA is inflexible and easily brittle making its application in food packaging limited. The composite films showed enhanced flexibility (EB) which increased significantly ($p < 0.001$) with the incorporation of 1 wt% VTD to 8.4 %. The EB of 3 wt% VTD increased more the four folds to 13 % with a significance of ($p < 0.0001$). At higher concentrations of VTD flexibility reduced, which can be attributed to increasing agglomeration earlier observed on the surface of the films at these wt%. In all, the EB of composites films showed significant improvement compared to PLA film. It can be suggested that the presence of VTD aided molecular chains movement in PLA and thus increased EB. Likewise, The EM which describes the stiffness of the film increased significantly up to ($p < 0.01$) by the addition of VTD except in PLA/VTD-10. The trend of improved TS, EB and EM with incorporation of the food additive VTD shows its suitability for active food packaging applications.

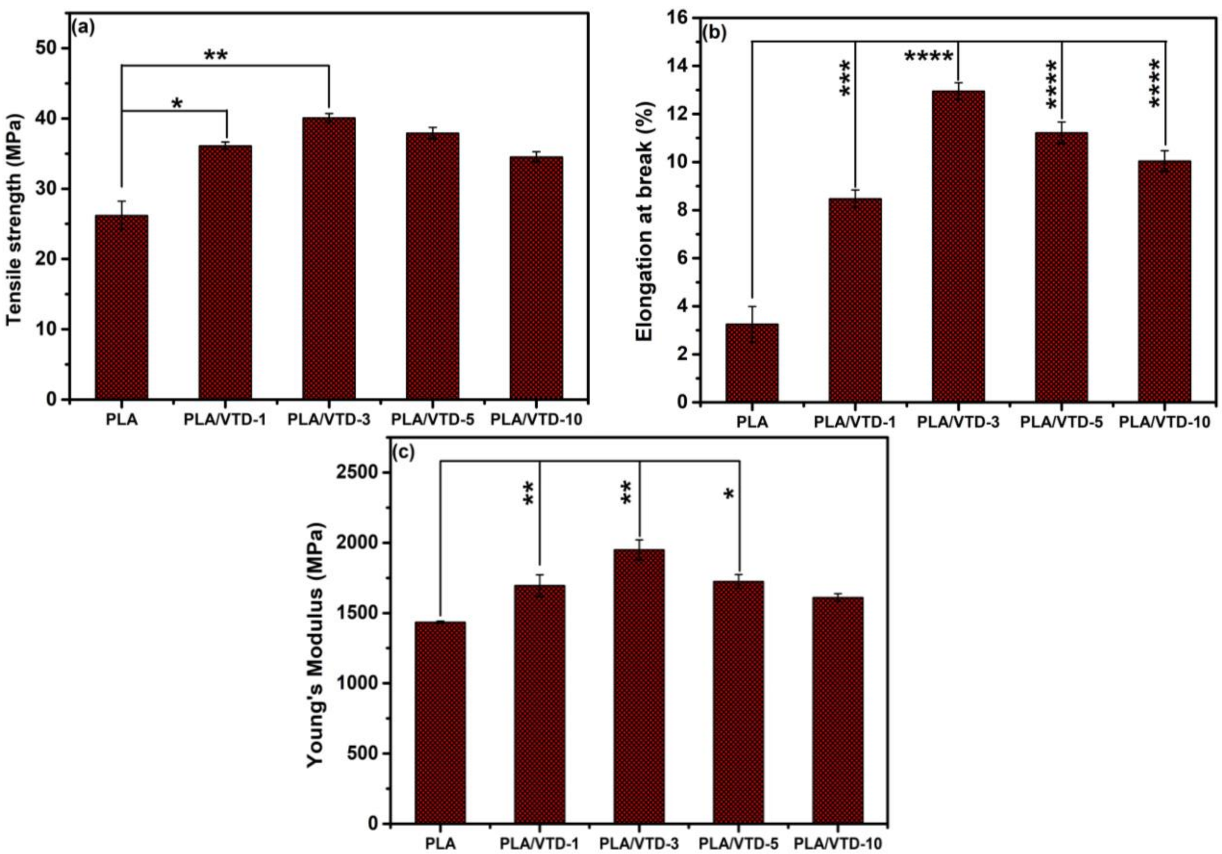

Figure 2: (a) stress-strain curve, (b) tensile strength, (c) elongation at break and (d) young's modulus of PLA and PLA/VTD composite films. (*$p < 0.05$, **$p < 0.01$, ***$p < 0.001$ and ****$p < 0.0001$ (one-way ANOVA).

Oxygen transmission rate analysis

The oxygen barrier properties of packaging materials is critical to their predictability to increase shelf and enhance food safety. An important role food packaging material to prevent the transfer of molecules between the environment and the food during storage or transport for food safety protection. The oxygen transmission rate (OTR) of the sample films were tested and the results are shown in figure 7. The neat PLA showed an OTR of 505 cm^3/m^2. 24 hr. 0.1 MPa. The OTR of the composites reduced by 10% for 1 wt% VTD inclusion in PLA and upto 52% for PLA/VTD-5 before slightly increasing to 40% for PLA/VTD-10. The enhanced OTR blocking the composite films can be attributed to impact of the VTD filler on the crystallinity of PLA as shown in the XRD results which in this case framed a tortuous part preventing the diffusion of gas molecules and slowing their movement through it.

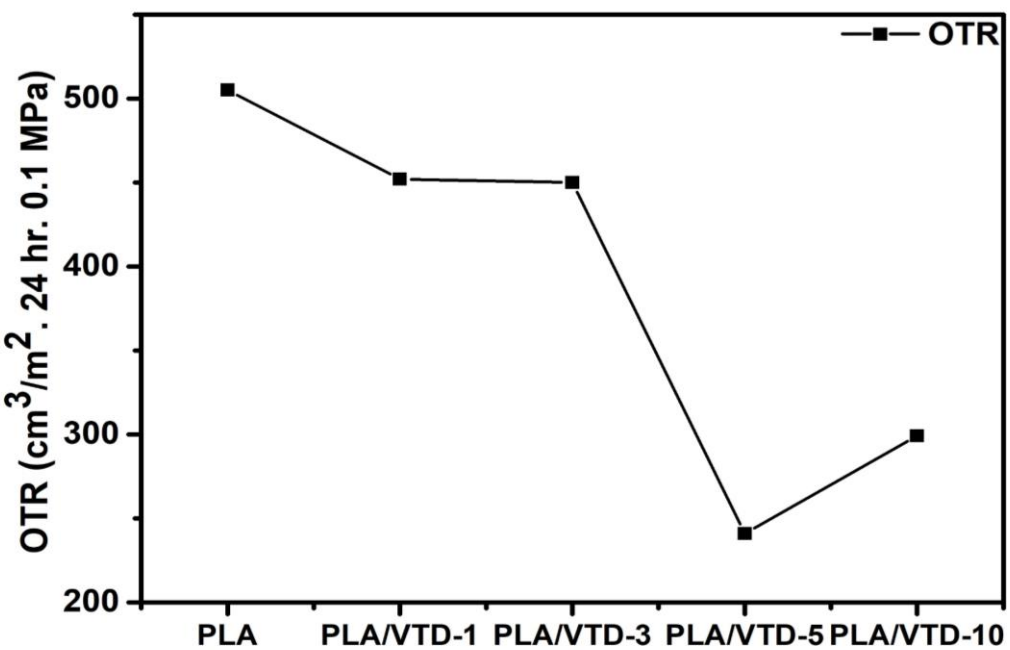

Figure 3: Oxygen permeability measurements for neat PLA and PLA/VTD composites

Conclusion

Herein, the fabrication of PLA reinforced with VTD was carried out. Studies of FTIR, and OTR showed the impact of the interaction between the components. The filler was uniformly dispersed at lower concentrations. The FTIR showed the good compatibility and intermolecular interaction of VTD in the PLA matrix. The addition of the VTD in the PLA caused enhancement in the oxygen barrier and mechanical properties. The tensile property of the PLA was increased significantly to

42 MPa from 28 MPa at 3 wt% VTD. OTR was also increased by 52 % in the composite. These findings have indicated a potential use of the PLA/VTD bio-composite in the food packaging industry.

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