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Design of Environmentally Useful Bio-Polymer Composite Films for Infra-Red (IR) Reflecting Coating Applications

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Abstract

The new IR reflective yellow inorganic pigment was developed as $Ti0_2$ doped $Bi_2Ce_{1.5}Ti_{0.5}O_7$. Different proportion (1%, 3%, 5%) of this inorganic pigment were loaded in PLA films. Further, inorganic pigment loaded PLA films were characterized by physical (contact angle, water absorbance chemical, oil resistance) and mechanical properties by tensile test. Thermal properties were studied by TGA and IR reflectance, UV resistance was characterized by UV DRS method. FT-IR study clearly indicating the interactions between PLA and the loaded inorganic pigment. The pigment loaded PLA films were strong light and chemical stability. Application study of the selected pigment loaded bio films showed strong IR reflectance and UV resistance were demonstrated. The antimicrobial properties of the film samples were also tested by coconut and baked bread as carriers and the inorganic pigment shows better anti-fungal properties than the neat film. The developed pigment loaded PLA based bio-composite films could be environmentally friendly and can be used for UV resistance films and coatings.

Keywords: Anti reflection filler; Inorganic filler; Semi-Crystalline PLA; PLA-PCL, Bio- composites; Bio-polymer films

Introduction

Inorganic pigments have been utilized in many applications since ancient times and are still widely used to colour materials such as paints, polymers, plastics, ceramics and glasses [1]. There are no such other alternates for inorganic pigment for colouring the material which are exposed to elevated temperature during processing. Most of the inorganic yellow pigments are employed on the industrial scale are generally toxic compounds [2]. The use of above pigments is strictly controlled and banned government due to environmental regulations. Thus, serious ecological and industrial needs to continue to seek for better substitution for inorganic pigments and free from the above toxic regulations and it's a drawback for the inorganic pigments. In general, the IR reflectance coatings were made with the matrix acrylic, melamine alkyd, epoxy and polyurethane etc [3]. These synthetic matrices were harmful to environment already, if we loaded the inorganic pigments with this matrix it leads to more toxic. So that, in such case we decide to go with bio polymer or biodegradable plastics to reduce toxicity and to reduce the harmfulness to the environment.

The IR reflective and UV resistance coatings are much essential needed in current trends. Due to the global warming unwanted UV and IR radiations are entering our world and affecting the package products. In order to reflect the IR and resist UV radiation we were developed inorganic pigment-based PLA films for industrially useful coating applications [6].

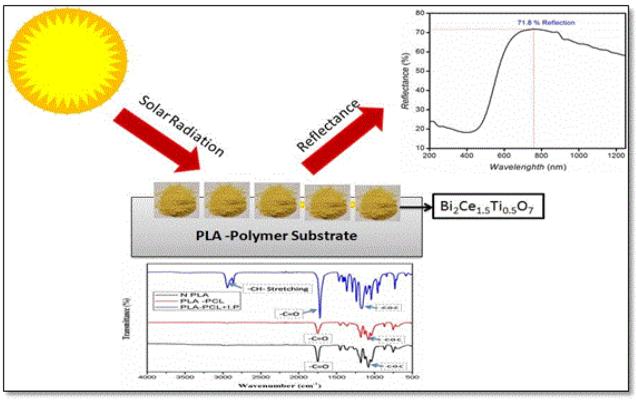

Figure 1: Graphical abstract of the work.

Much interest has been tried in the inorganic material/ pigment with high solar reflectance and thermal emittance. Solar radiation consists of 5% UV radiation, 43% visible radiation and 52% near- infra red radiation (NIR; 780-2500 nm) [7-8]. The heat producing region of the infrared radiations ranges from 700 to 1100 nm. Colour coatings with conventional pigments tend to the absorb NIR radiation that bears >50% of the power in sunlight resulting in heat built-up. Inorganic NIR pigments are mainly metal oxides and are primarily employed in two major applications namely visual camouflage and reduced heat build-up applications. Most of the literature on NIR reflective pigments exists as patents, which indicate their vast potential application [9-10]. Complex inorganic pigments based on mixed metal oxides (e.g., chromium green, cobalt blue, cadmium stannate, lead chromate, cadmium yellow and chrome titanate yellow), which have been used in camouflage, absorb visible light but reflect the NIR portion of incident radiation. However, many of these pigments are toxic and there is a need to develop novel colour, NIR-reflecting inorganic pigments that are less hazardous to the environment. Recently, the industrial utilization of lanthanides has increased rapidly because of their low toxicity; consequently, a large number of rare earths based NIR reflective pigments have been proposed as alternatives to traditional pigments [11-12]. During the last two decades, considerable attempts have been made to develop biodegradable polymers and composites. Aliphatic polyesters such as Polylactic acid (PLA), Polycaprolactone (PCL), poly (3-hydroxybutyrate) (PHB) and Polyglycolic acid (PGA) represent important biodegradable polymers, which are now finding commercial applications in combination with bio-based material. Out of all biodegradable polymers, PLA is a great biodegradable and biocompatible polymer that has been used extensively in environmental and biological systems. Products utilizing PLA include packaging material and fibres in both woven and non-woven products [13]. The use of PLA as a packaging material is a great benefit due to PLA's ability to environmentally degrade, diminishing the environmental impact resulting from all the disposable products used today

The research gap, many of them are not done much research on inorganic pigment loaded PLA for IR reflectance and UV resistance films for packaging applications. The research gap finally, the colouring performance of the designed pigment is evaluated by casting method on PLA film and its NIR reflectance was evaluated. To overcome the environment threat, we have replaced synthetic matrix by biodegradable films (PLA). Hence, we have chosen the inorganic fillers to enhance the IR reflectance and UV resistance.

Figure 2: Image of $Bi_2 Ce_{1.5}Ti_{0.5}O_7$ Inorganic Pigment.

Material and Methods

Materials required

Laboratory level synthesized $Bi_2Ce_{1.5}Ti_{0.5}O_7$ inorganic pigment was collected from Department of Chemistry, VIT, Vellore. Ingeo ™ Biopolymer, Polylactic acid (PLA-3052D) was bought from Nature Works, USA (Density=1.24 and Mn=154.8 Kg/mol.). PCL were purchased from Sigma-Aldrich. Dichloromethane solvent was purchased from SD fine chemical company, India Pvt Ltd.

Optimization of PLA –PCL polymer blends

The neat PLA film was initially made as (reference film sample) by dissolving 10 g of PLA into the 100 g of dichloromethane solvent to make 10 weight % solution and casted on a Petri dish. The casted PLA film was dried at 30 °C for 24 hours and vacuum oven dried to remove the solvent completely. The resultant neat PLA film sample was stiff and brittle. The same observation was noticed for PLA-Inorganic pigment (IP) loaded film samples also (1%, 3%, 5% with respect to PLA).

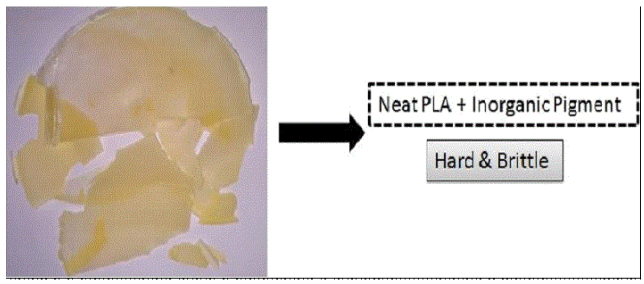

Figure 3: Image of Neat PLA with Inorganic pigment film.

To overcome the brittle issue of neat PLA film, the PLA was modified with PCL by varying the PLA: PCL percentage. The optimum PCL percentage with PLA polymer was concluded as 10 wt %, our group's another work of PLA with PCL blends also supports the PCL optimum weight percentage (10%), with this concentration, PCL and PLA forms a thermodynamically miscible blends results in stable and flexible film.

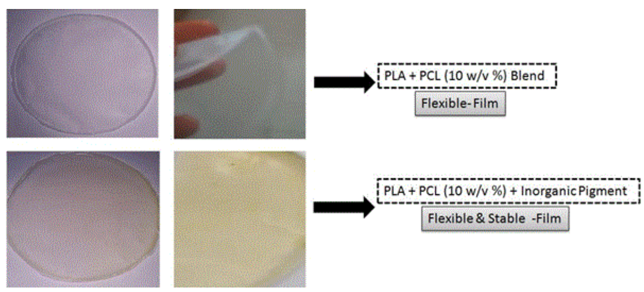

Figure 4: Image of PLA+PCL blend with Inorganic pigment film.

Preparation of PLA-PCL-inorganic filler bio-composite films

10 wt % of bio-polymer solution was prepared by dissolving (9 g of PLA+1 g of PCL) in 100 g of dichloromethane solvent until the solution becomes homogeneous and clear. Inorganic pigment (IP) with the varying weight percentage (1%, 3%, 5%) was dispersed into the PLA-PCL bio-polymer solution by ultra-sonication method individually. The obtained PLA-PCL-IP solution was transferred into a Petri dish and allowed to form a film at room temperature (30 °C/24 h). The film samples were oven dried to remove the solvent traces [14].

Figure 5: Schematic diagram of PLA-IP- bio-composite films sample preparation.

Experimental Part

Tensile strength and elongation at break

Tensile test was done according to ASTM D882. Excess mechanical strength and extensibility are generally needed for a packaging film to withstand external stress given and to maintain its integrity as well as barrier properties during applications in various packaging [15]. The tensile strength and percent elongation at break of PLA films incorporated with inorganic pigment with different concentrations were measured.

Percent elongation=(Elongation at rupture)/(Initial gauge length) × 100…(1)

Water absorption study

Water absorption properties of the neat PLA-PCL film and PLA-PCL-IP films were studied as per ASTM D570-81. The percentage of water absorption was measured using the below equation (2).

Water Absorption (%)=$(w_2-w_1)/w_1 \times 100$…(2)

Where, w_1 is the initial weight of the film sample, and w_2 is the weight of the samples after immersion in water for 24 h at 25 °C.

Chemical resistance

The chemical resistance of the film samples (neat PLA-PCL and PLA-PCL-IP) in NaCl medium was tested as per ASTM-D 543 procedure [16]. The results are given in terms of percentage solubility in that medium.

Oil resistance study

The oil resistance of film samples was tested as per the ASTM D543-06 method. The film samples were weighed in a three-digit accuracy weighing machine and immersed into the coconut cooking oil for 24 hours at 30 °C and changes were noted in appearance and weight difference as well [17].

Oil resistance, Percentage weight difference (%)=(m2-m1)/m1 × 100…(3) Where, m1 is initial mass of the sample, and m2 is mass of the samples after oil immersion.

Water Vapour Permeability (WVP)

The WVP is one of the important properties for the packaging applications. Water Vapour Permeability (WVP) of the neat film and PLA-PCL-IP film samples were measured according to the ASTM E-96-93 method using the below Eqn. 4 [13].

WVP=WVTR/[P × (R1-R2)] × L…(4)

Where, P is the saturation vapour pressure of pure water at 23 °C, R1 is the Relative humidity in the desiccators, R2 is the Relative humidity in the WVP measuring sealed bottle, and L is the thickness of the film sample (mm).

Contact angle

Contact angle test was carried out using Holm arc contact angle meter in Department of Printing Technology, CEG, Anna University. The contact angle formed between a water droplet placed at the surface of a material and the kinetics of spreading is related to the hydrophobicity of the material. Approximately 10 μL of water droplet was put on the surface of a small sample. The evolution of the droplet shape was recorded. A charge-coupled device video camera and image analysis software were used to determine the contact angle evolution, which may be used to determine the kinetics of water sorption, related to the hydrophobic character of the material [18].

Thermo Gravimetric Analysis (TGA)

Thermal resistance properties of the developed bio-composite film samples were measured by using TGA analysis. The TGA experiments were carried out from 30 °C to 800 °C with a heating rate of 10 °C/min. under a continuous flow of Nitrogen atmosphere using NETZSCH STA 409PC. Fourier Transform-Infrared (FTIR)

The Chemical interaction of PLA with added PCL and inorganic pigments were predicted by using FT-IR method. The FT-IR analysis was made by using Bruker, VERTEX 80 Series- FT-IR Spectrometers in the spectral frequency range of 4000 to 400 cm^{-1}.

UV-VIS-NIR-reflectance

The Spectro-photometric reflectance UV-VIS-NIR spectra of the samples were tested as per the ASTM E-903-12 standard. The Reflection capacity of the developed inorganic pigment was measured by UV-VIS-NIR- Spectrophotometer, Model-JASCO-V670 with the measurement range from 2500 to 200 nm.

Anti-fungal activity

The Anti-fungal activity was performed for neat PLA-PCL and PLA-PCL-IP bio- composite film samples by using baked bread slices and coconut as carriers for fungal growth at 30 °C and 70% relative humidity. The anti-fungal tests were done as per the already reported method by Ananda kumar et al. [19].

Scanning Electron Microscopy (SEM)

The morphology of the neat film and film made with inorganic pigment bio-composite film samples were characterized by using Scanning Electron Microscopy (LEO 1445VP).

Results and Discussions

Mechanical analysis

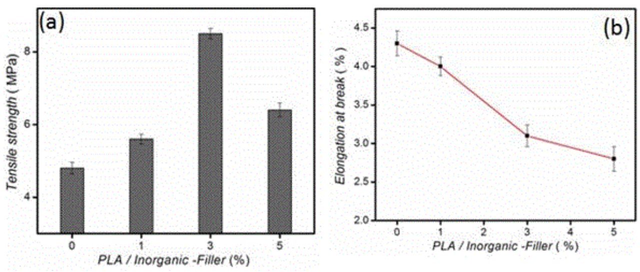

Figure 6: Tensile Strength (a) Elongation at Break (b). Illustrated the tensile properties of neat PLA and PLA/ inorganic pigment loaded bio film composites with different weight proportion of inorganic pigment (1, 3, 5 wt%).

The 3 wt% loaded inorganic pigment bio-film shows the significant improvement in tensile strength than other two proportions. The values of tensile strength stated that 5.5, 8.5 and 6.5 MPa. This increase in tensile strength might be due to the interactions that occurred between PLA and inorganic pigment. The elongation value of neat PLA was 4.32%, while the incorporation inorganic pigment reduces the elongation at break values with increasing the inorganic pigment dosage. So, the optimum dosage of inorganic pigment to load in PLA matrix was concluded with 3 wt%.

Water absorption

The water absorption rate of neat PLA based film was comparable to all three percentage of inorganic pigment (1, 3, 5 wt%) loaded PLA films in Figure 7. The addition of

hydrophobic nature inorganic pigment into PLA matrix enhances the overall hydrophobicity to the bio-composite film, results in lower water absorption.

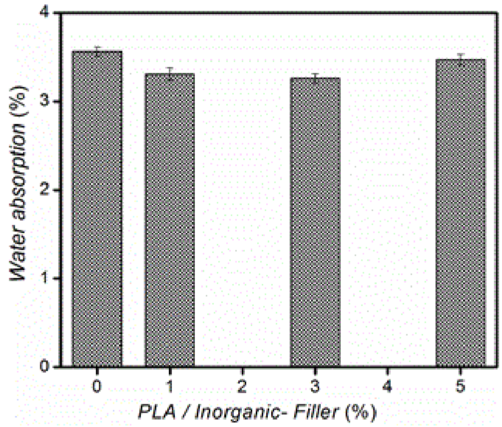

Figure **7**: Water Absorption study.

The contact angle measurement also supports this observation; the lower water absorption may be due to the strong interaction between PLA and the added inorganic pigment. The interaction leads to non-availability of oxygen leads to low in water absorption, since oxygen groups interact with water molecule. The interaction between PLA and inorganic pigment was clearly identified and reported in this manuscript at FT-IR section.

Chemical resistance

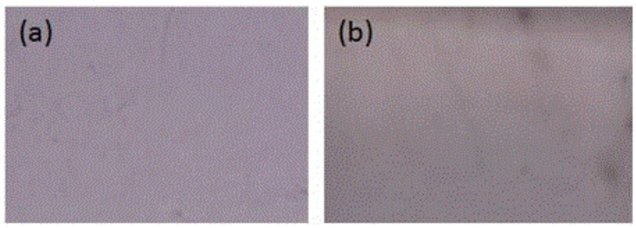

Figure 8: NaCl-Chemical Resistance Study.

The chemical resistance nature of the neat PLA based film and 3% inorganic pigment loaded film samples were tested by immersing the film samples into the 1N Sodium chloride solution. The neat PLA film and inorganic pigment loaded film samples shows relatively similar appearance without film breakage. This test is proved that, addition of PCL and inorganic pigments leads to better flexibility and stability to the PLA matrix.

Oil resistance

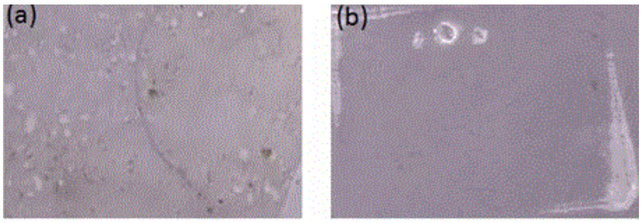

Figure 9: Oil Resistance Study.

The Oil resistance nature of the neat PLA based film and 3% inorganic pigment loaded film samples were tested by immersing the film samples into cooking grade coconut oil. The neat PLA film shows relatively higher oil absorption than the inorganic pigment loaded samples, this may be due to that added pigment which resists the oil absorption. The inorganic pigment added film sample shows stable structure without any wrinkles and breakages.

Water vapour permeability

The water vapour permeability is one of the important properties for barrier and coating applications. The water vapour permeability of neat film shows relatively higher permeability, the addition of inorganic pigments delays the permeability process by increasing the tortuous path of water vapour results in lower WVP [20].

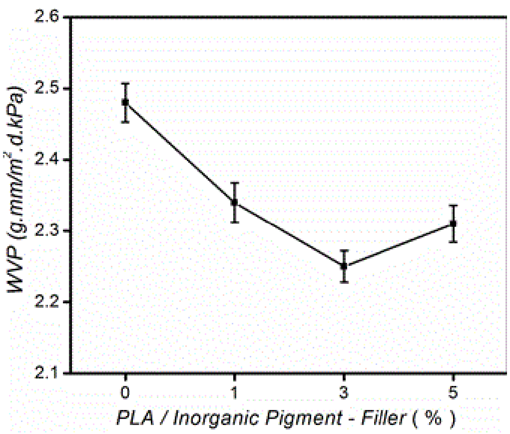

Figure 10: Water Vapour Permeability of Bio-composite film samples.

The inorganic filler, which contains hydrophobic nature inherently, which resist the water vapour percolation, the FT-IR interactions, contact angle, and water absorption tests also supports the obtained properties.

Contact angle

The contact angle is one of the important parameters to explain the hydrophobicity of the polymer materials. The neat PLA film shows a contact angle value of 74.6, which implies its moderate hydrophobic nature. The addition of hydrophobic inorganic pigment forms the uniform distribution into the PLA matrix and enhances the overall hydrophobicity which cause higher contact angle values

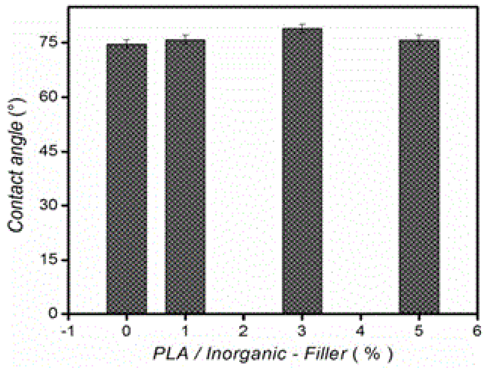

Figure 11: Contact angle of Bio-Composite film samples.

Thermo Gravimetric Analysis (TGA)

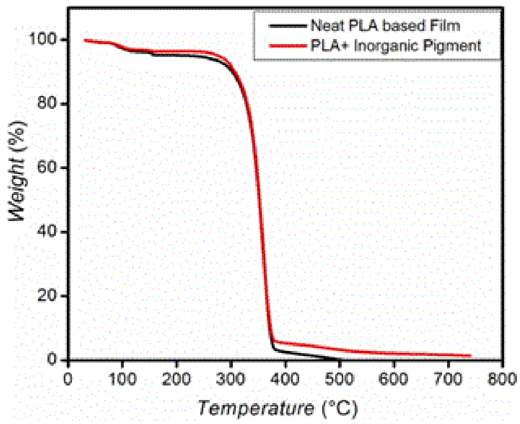

Figure 12: TGA-Analysis of neat film and PLA+PCL+IP (3%).

The TGA thermal analyses of Neat PLA film and PLA with inorganic pigment (3%) are depicted in above figure. The neat PLA shows 5% weight loss at 231.16˚C, whereas PLA based inorganic pigment (IP) film weight loss was noticed at 277.17 °C, which is 46 °C higher than the neat PLA based film. The 10% weight loss was noticed at 302.37 °C (neat PLA based film) and 307.2 °C for PLA-IP film sample, which indicates almost 5 °C increase in thermal stability. The remaining weight percentage at 400 °C for the neat PLA based film was 2.52%, whereas for PLA-IP film was 5.31%. At 500 °C, the neat PLA based film shows 0.15% remaining weight, but the PLA-IP film shows 3.25% remaining weight. The neat PLA based film becomes zero residues at 507 °C, but the PLA-IP film shows 1.34% char yield even after 800 °C, which clearly proves the effect of inorganic pigment incorporation into PLA matrix. The thermal stability improvement is may be due to the strong interaction between PLA with inorganic pigments and the inherent thermal behavior of inorganic pigment.

Anti-fungal properties study

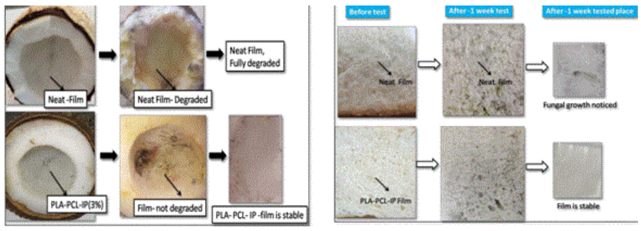

Figure 13: Anti-Fungal Properties-Using Coconut (a), and bread (b).

The anti-fungal nature of the developed organic-inorganic bio-composite film was tested by using Coconut and baked bread as carries by In-Situ method [19]. For coconut carrier system the test was conducted for 72 hours. For bread carrier the test was prolonged for one week (7 days). In coconut carrier, the neat PLA based film samples destroyed and degraded with the fungal growth. The inorganic pigment loaded film sample was not destroyed or degraded fully, it with stand against fungal attack. This improvement in anti- fungal properties may be due to the addition of inorganic pigment which contains anti- microbial agent TiO_2. The Titanium dioxide is well known anti-microbial agent which resist the fungal and microbial attack. The same effect was noticed in bread carrier system also.

UV-VIS-NIR-resistance study

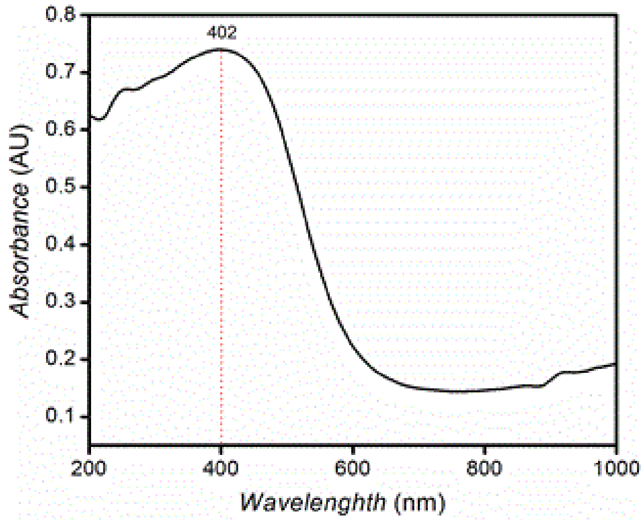

Figure 14: UV-Absorbance Study.

From the UV-absorption spectroscopy we can clearly see the strong absorption at 402 nm, which results in yellow colour to the pigment. The reason for yellowish colour for the developed pigment may be due to the charge- transfer transitions from the filled valance band to empty conduction band. The similar observation was reported by Sheetu Jose et.al [21].

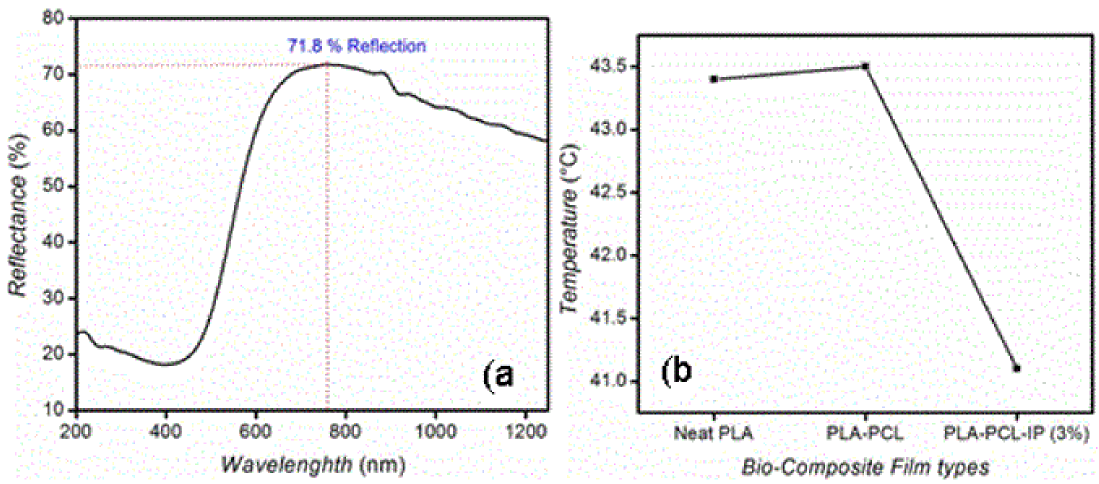

Figure 15: UV-VIS-NIR-Reflectance Study (a), Temperature test under sunlight (b).

The reflectance nature of the developed pigment was tested by using UV-VIS-NIR- Spectrophotometer. The above figure clearly indicating the reflectance nature of the developed pigment, which can reflect 71.8% of the UV-VIS-NIR wavelength from sunlight. The intensity of the Sunlight source is very much higher in visible region, in the same time it emits relatively higher amount energy in invisible ultraviolet (UV-Region) and near infrared (NIR) region also [22]. The inorganic pigment used in our study is very well reflecting the sunlight energy source through which we can make industrial products with better environmental benefits. The samples were kept under sunlight for two hours from 12 pm to 2 pm and the temperature were tested and reported in above Figure 15(b). The PLA-PCL-IP shows low temperature due to reflectance nature of the developed bio-composite film.

Fourier transform-infrared spectroscopy

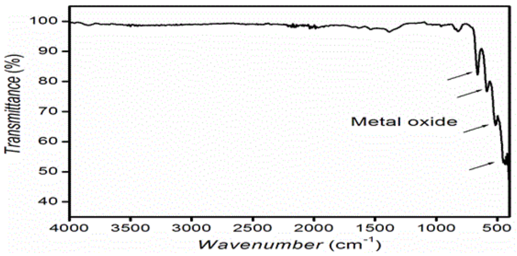

Figure 16: FT-IR of Developed inorganic Pigment.

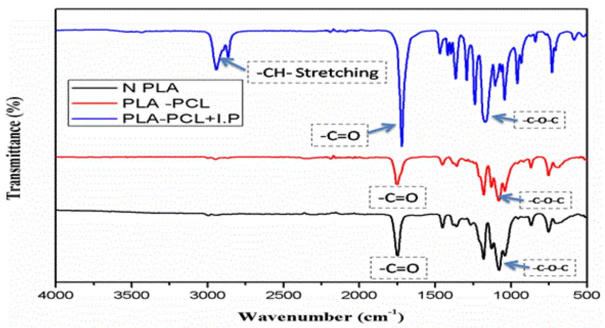

Figure 17: FT-IR of neat PLA, PLA-PCL and PLA-PCL-IP.

Table 1: FT-IR band assignment for the chemical groups.

Type of vibrations	Chemical group	Neat PLA	PLA-PCL -10%	PLA-PCL-IP -3%
		Band position (cm-1)		
C=O Stretching	C=O	1750	1751.4	1720.5
CH3-Asymmetric stretching	CH3	1452	1452	1469.76
CH3-Symmetric stretching	CH3	1382	-	-
CH-Bending	CH, (CH3)	1361	1358	1365.6
CH+COC-Bending	CH+C-O-C	1267	-	1238.3
COC- Asymmetric stretching	C-O-C	1181.4	1180.5	1172.7
CH3- Rocking	CH3	1128.4	1130.3	-
COC- Symmetric stretching	C-O-C	1080	1082	1064.7
C-CH3-Stretching	C-CH3	1042	1042	1043.5
CH-Asymmetric stretching of CH3	CH	2945	2945.3	2943.37
CH-Symmetric stretching of CH3	CH	2996	-	2864.29

The inorganic pigment FT-IR spectra clearly indicated the formation of metal-oxygen bond formation, which reflects in the FT-IR band range between 400 to 700 cm^{-1}. The FT-IR spectra of Neat PLA, PLA-PCL and PLA-PCL-IP film samples were depicted in Figure: 17. The Characterized peaks of neat PLA observed at 1750 cm^{-1}, 1080 cm^{-1}, 1181.4 cm^{-1}, 1361 cm^{-1}, 2945 cm^{-1}, 2996 cm^{-1}. These peaks were corresponding to -C=O, Carbonyl group stretching, C-O-C ether symmetric stretching, C-O-C ether group asymmetric stretching, CH_3 group CH bending, CH asymmetric and CH symmetric groups respectively. The PLA-PCL blend characterized peaks were noticed at 1751.4 cm^{-1}, 1082 cm^{-1}, 1180.5 cm^{-1}, 1358 cm^{-1}, 2945.3 cm^{-1}. These FT-IR peaks were corresponding to -C=O stretching, C-O-C ether symmetric, C-O-C ether asymmetric stretching, CH_3 group CH bending, CH asymmetric groups respectively.

The characterized peaks for PLA- PCL- IP film sample was noticed at 1720.50 cm^{-1}, 1064.7 cm^{-1}, 1172.7 cm^{-1}, 1365. 6 cm^{-1}, 2943.37 cm^{-1}, 2964.29 cm^{-1}, which correspond to C=O stretching, C-O-C symmetric, C-O-C asymmetric stretching, CH3 group CH bending, CH asymmetric and CH symmetric groups respectively. From the FT-IR study, the PLA polymer is having very strong interaction with inorganic pigment results in better barrier properties. The carbonyl group stretching vibration was shifted from 1751 cm^{-1}(neat film) to 1720.50 cm^{-1}, which is almost 30 cm^{-1} shifted, this change in wave number is clearly indicating the strong interaction. The symmetric and asymmetric C-O-C ether group characterized peak also shifted from 1082 cm^{-1}, 1180.5 cm^{-1} to 1064.7 cm^{-1}, 1172.7 cm^{-1} respectively. The CH symmetric and asymmetric group peaks intensity was increased than the neat PLA and PLA-PCL. The wavelength shifts in carbonyl, ether groups, and CH groups in PLA-PCL-IP film sample is clearly indicating the interactions between the polymer and pigments. The reason for interaction may be due to the Carbonyl group adsorption, the electrostatic interactions with incorporated metal cations that lead to polarization of adsorbed Carbonyl molecule (Stark effect). Another probable reason for the red shift in frequency, the electron back donation from filled state of metal substrate to the CO $2p^*$ anti-bonding orbital which results in frequency shift reported by Wang Y et al. [23]. The interactions lead to better water and water vapour barrier, mechanical, anti-fungal, IR reflectance by forming a stable bio-composite film.

Scanning Electron Microscopy (SEM)

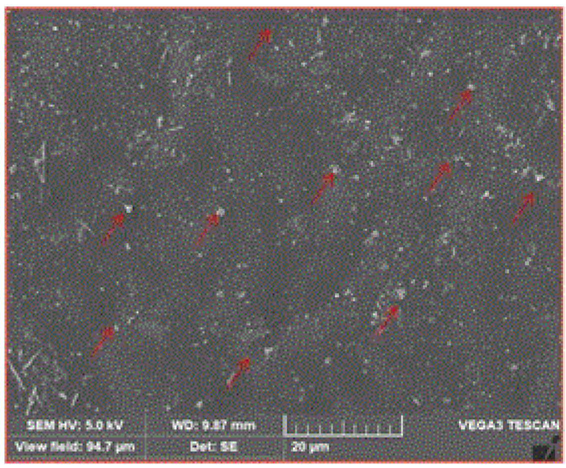

Figure 18: SEM-Image of PLA-PCL-IP (3%)

The SEM images of PLA-PCL-IP (3wt%) was depicted in above Figure; the SEM image supports the data's obtained from previous tests. The added inorganic pigments were well dispersed into the PLA matrix and form the continuous film structure results in better properties. Generally, dispersion of inorganic fillers into the PLA matrix is complicated, since the added fillers forms agglomeration and leads to settling instead of dispersion. Here in our study, the PLA is having strong interactions with added pigment which leads to better dispersion and better properties.

Conclusions

The new IR reflective yellow inorganic pigment was developed as $Ti0_2$ doped $Bi_2Ce_{1.5}Ti_{0.5}O_7$ was loaded into the PLA-PCL polymer blend and organic-inorganic bio- composite film developed with optimum 3 wt% pigment loading. The developed film possesses better water resistance, water vapour resistance, NaCl and Oil resistance. The mechanical test clearly indicates that the addition of inorganic pigment enhances the tensile strength, and reduces elongation at break. The contact angle measurement and water absorption results reveal to indicate the hydrophobic nature of the developed pigment. TGA analysis proved the improvement in thermal stability of the bio-composite film. The FT-IR study, confirms the interaction between incorporated pigment with PLA polymer, the interaction leads to better barrier, thermal stability, and stable bio-composite. The UV-VIS-NIR spectroscopy analysis indicating the developed material can reflect 71.8% solar radiation, through which development of environmentally beneficial industrial products can be made.

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