Gas Barrier Properties of Biodegradable Polymer Nanocomposites Films

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Abstract

Bionanocomposites from biopolymers and inorganic nanoparticles are of great interest for packaging materials due to their enhanced physical, thermal, mechanical, and processing characteristics. In this study polylactic acid and titanium oxide (PLA/TiO_2) films were prepared by casting method. The effect of structural, mechanical , thermal, and barrier properties of the nanocomposites were studied . Fourier transform infrared spectroscopy confirmed that no change in bonds of PLA /TiO_2. Increased glass transition temperature and thermal stability, compared with pure PLA. Mechanical properties (Tensile strength, Young Modulus) increased when add 1, 3,and 5wt% TiO_2 compare with PLA(2.3, 2.5, 2.8 and 3)Gpa. Barrier properties (oxygen transmission rate) was decrease when the concentration of TiO_2 is increased in PLA/TiO_2 film as (18, 16, and 14) cm^{3}·mm/m^2.day.atm, compare with neat PLA was 20 cm^{3}·mm/m^2.day.atm

Key Words: Biodegradable, polylactic acid , titanium oxide , mechanical properties , thermal , and barrier properties **.**

1.Introduction

Poly(lactic acid) (PLA) is an aliphatic polyester made up of lactic acid. It is also a biodegradable and compostable thermoplastic derived from renewable plant sources, such as starch and sugar. Historically, the uses of PLA have been mainly limited and to discovery of new expanded use which allow the economical production of goods and packaging applications. Because PLA is compostable and derived from renewable sources, it has been considered as one of the solutions to alleviate solid waste disposal problems and to lessen the dependence on petroleum-based plastics for packaging materials [1]. The use of biodegradable plastic is one of method to resolve these problems, Poly(L-lactide) or PLA is one of biodegradable plastics, synthesized from lactic acid which can be produced from farm and agricultural product such as cassava, rice, corn and corncob by bacterial or fungal fermentation. Moreover, it has good properties such as high melting point (175 °C), high degree of transparency [2]. It is widely studied as a sustainable biodegradable material for use product applications such as medical application, packaging materials and mulching film . However, some of the other properties, such as gas barrier properties and melt-viscosity for further processing, are frequently not good enough for a wide-range of applications .To overcome this problem, biodegradable polymer nanocomposites are used with different ingredients which approve physical properties of polymers such as barrier and mechanical [3].To improve the physical properties of the polymers, barrier improvements for shelf life of the foods and mechanical properties. It can be done by several approaches such as blending, copolymerization or nanofillers addition, several nanoparticles are used such as nanoclays, carbon fibers, carbon nanotubes, titanium oxide, etc[4].

However, to achieve the mentioned positive effects of nanoparticles on properties, adequate dispersion of nanofillers within the polymeric matrix is required. However, different parameters like polymer type and morphology, type and size of nano fillers, the interaction of nano fillers with the polymeric matrix and its volume content could influence the characteristics of nanocomposites[5]. Among many different types of nano sized fillers, TiO2 nano powder is increasingly being investigated because it is non-toxic, chemically inert, has broadband UV filter properties, is anti-bacterial from its photo-irradiation effect, corrosion resistant and has high level hardness, high refractive index and low cost [6]. The addition of TiO2 nanoparticles could increase the degree of crystallinity of nanocomposites. Other parameters like melting point, glass transition, and crystallization rate could also change according to polymer structure [7]. Titanium dioxide (TiO2) nanoparticles have been investigated in recent years because of the capability to absorb UV light ($\lambda < 388$ nm) and generate oxygen species that decompose various organic chemicals such as aldehyde, toluene, and polymers such as polyethylene (PE) , polypropylene (PP) , poly(vinyl chloride) (PVC) , and polystyrene (PS).It is well known that the photocatalysis reaction of TiO2 produces active oxygen species such as O2, HO2, and HO radicals from H2O or O2 byoxidative or reductive reactions under UV exposures. These active oxygen species will lead to photodegradation reactions by attacking the interfacial polymer chains, forming carbon-centred radicals, and accelerating chain cleavage[8].

TiO2 nanoparticles are incorporated into polymer matrix ,these active oxygen species will lead to photodegradation reaction by attacking the interfacial polymer chains, forming carbon-centered radicals, and accelerating chain cleavage[9]. By adding photosensitive TiO2 nanoparticles into biodegradable PLA and acts by a photocatalytic mechanism, its major drawback would be the requirement of UVA light. PLA nanocomposites can possess both photodegradable ability and biodegradability, and thus the degradation can be promoted under any conditions. The nanocomposite materials could be used as packaging films for a variety of oxygen-sensitive food products .Therefore, controlling barrier properties of polymer films is necessary to extend shell-life of food. Oxygen permeation value of polylactide was found to be the same as polystyrene and polyethylene tetraphthalate and it permeates moderate amount of oxygen with respect to other biopolymers. Moreover, degree of crystallinity in polylactide polymers affects the permeability value[10] .

The objective of this study was to investigate the effects of TiO_2 on mechanical ,thermal and oxygen transmission rate of the films.

2.Materials

Poly (lactic acid), Pure grade PLA AI - 1001, with density 1.25 g/ cm^3, was supplied by (Shenzhen Esun Industrial Co., Ltd. Chain).TiO2 nanoparticles were supplied by Nanoshel LLC (USA). The average diameter of the particles (as recorded by the company) was about (20 -50)nm. Chloroform Solution was purchased from Applied Chem. (Darmstadt, Germany).

2.1-Preperation method

Pure polylactide films were prepared by solution casting method by using chloroform. Films were cast on the glass plates and then kept at 60 C° in room temperature for 24 hour to ensure complete solvent removal. Nanocomposite films were prepared by add titanium oxide swollen in chloroform by mixing for 24 hours while polylactide dissolved in chloroform then TiO_2 solution was sonicated from homogenizerSoniprep-150 MSE for an hour to increase distribution . The amount of TiO_2 in PLA was varied between(1,3,and 5)wt% . Finally, films were cast on the glass plates and then kept at 60 C° in room temperature for 24 hour to ensure complete solvent removal. Determination of Thickness of PLA and PLA/TiO_2 films calculated by electronic digital micrometer (293-821, Mitutoyo) sensitivity was used to measure the thickness of PLA and PLA/TiO_2 films and find 110μm .

2.2-Fourier Transform Infrared (FTIR) Analysis of PLA and PLA/TiO_2 Films

FTIR analysis gave the chemical structures information of the nanocomposites films, presence of polylactide and titanium oxide . IR spectra were taken in the range of 400 to 4000 cm-1 with a FTIR Schimadzu 8201 Model. 48

2.3- X-Ray Diffraction (XRD) Analysis of PLA and PLA/TiO_2 Films

The structure of polylactic acid and nanocomposites film were characterized by Phillips X'Pert Pro MRD (Cu Kα radiation (λ=1.54 nm),40 kV,40 mA) between 20and 60 .

2.4-Thermal Analysis of PLA and PLA/TiO_2 nanocomposite Films

Glass transition and melting temperature of the PLA and PLA/TiO_2 were measured by differential scanning calorimetric DSC. Crystallization temperature of the PLA and PLA/TiO2 were determined with the following procedure. Initially. Differential Scanning Calorimeter (DSC) using (Shimadzu DSC-60) was performed to determine

glass transition temperature Tg , Tm , Xc. The films were heated up to 250 C° with the heating rate 5C°/min ,the analyses were performed in a dry nitrogen atmosphere . Tg regarded as the most important parameter for evaluating the thermal properties of polymer and polymer matrix composites. Melting and cold crystallization temperatures and enthalpies (Tm, Tc ΔHm and ΔHc) were determined from the first heating scans while glass transition temperature (Tg) were measured from the heating and cooling scans. Crystallinity was calculated by equation (1)[7]

$$Xc=\Delta Hm-\Delta Hc/\Delta Hm° \qquad \ldots\ldots\ldots 1$$

Where**:**

Xc degree of crystalline , ΔHm enthalpies of fusion and ΔHc enthalpies of crystallization, ΔHm = 93 J·g–1 is the enthalpy of fusion of 100% crystalline poly(lactic acid).

2.5- Mechanical test of PLA and PLA/TiO_2 Films

According to ASTM D-882 standard modulus of elasticity, tensile strength, and percent elongation equipped with a 5 kg load cell in tensile mode. Tested films were cut in 10 mm width and 80 mm in length and the initial gauge length and testing speed were fixed at 10 mm/min. Two metallic grips were attached for griping both ends of the test specimen of the film. Tensile strength (σs**)**, Young's modulus (E) were determined according to the following equation:

$$\sigma s = F/(A) \quad \ldots 2$$

$$E = F\, L_0/A\, \Delta L \quad \ldots 3$$

Where: F: force exerted on an object under tension, $L_{0:}$ original length, A: cross section area, ΔL: length of the object changes

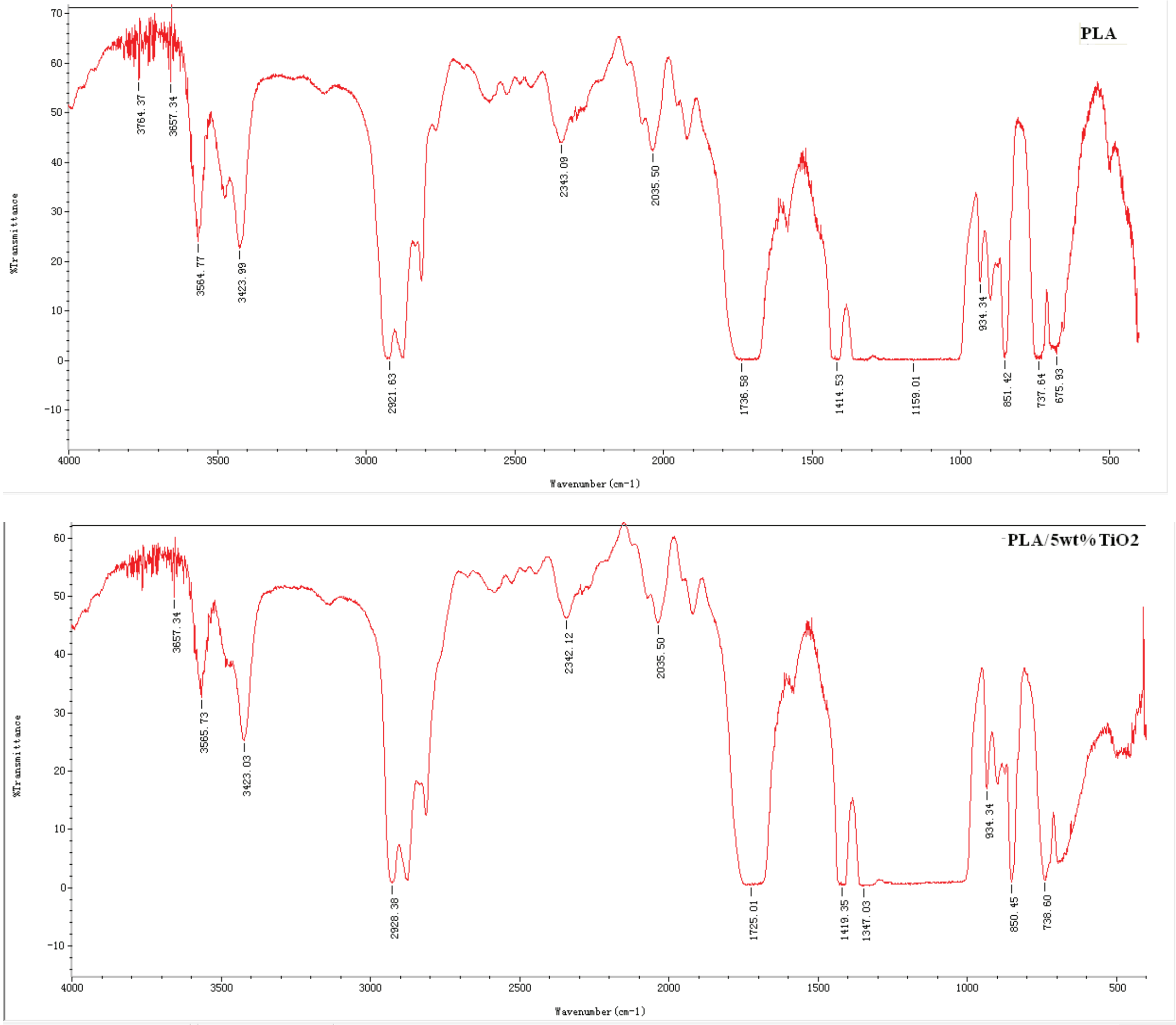
2.6-Oxygen Transmission Rate of PLA and PLA/TiO_2 Films

The oxygen permeability of the films was measured according to the ASTM D-3985 standard using gas permeation instrument Qualities (Canada). In the testing method, put the specimen in test chamber and clamp it tightly. Firstly let the nitrogen flow sweeps the pipes and chambers. Then input high pure oxygen in one side of the film and high pure nitrogen in the other side of the film. Oxygen molecule permeates the specimen into the nitrogen of another side , and then is taken to the sensor . The transmission of oxygen by analyzing the concentration of oxygen detected by sensor. As for packaging container, nitrogen flows in the container, air or high pure oxygen covers the outside of the container. The measured time interval is then transformed into the gas permeability rate expressed in cm^3/m^2.day. Gas permeability's of the films were determined at constant temperature (23 C°) and relative humidity (0% RH) conditions with speedy flow between 5–10 cm^3/min gas flow.

3.Result and Dissections

3.1Fourier Transform Infrared (FTIR) Analysis of PLA and PLA/TiO2 Films:

The PLA spectrum (Fig. 1)shows the bands CH_3 stretching at (3000-2850)cm^{-1} , 3421 cm^{-1} O–H, and C=O stretching vibration (2343- 2035cm^{-1}), 2921cm^{-1} corresponding to the –CH2– asymmetric and symmetric stretching vibrations ,1414 for the –CH_3 bending vibration , 934 cm^{-1} - 851 cm^{-1} for C–C single bond , the strong C=O absorption band at 1736 cm-1 . C-O-C asymmetrical and symmetrical valence vibrations were found at 1150 cm-1. These statements are similar those described by Nikolic et al., 2010 [11]

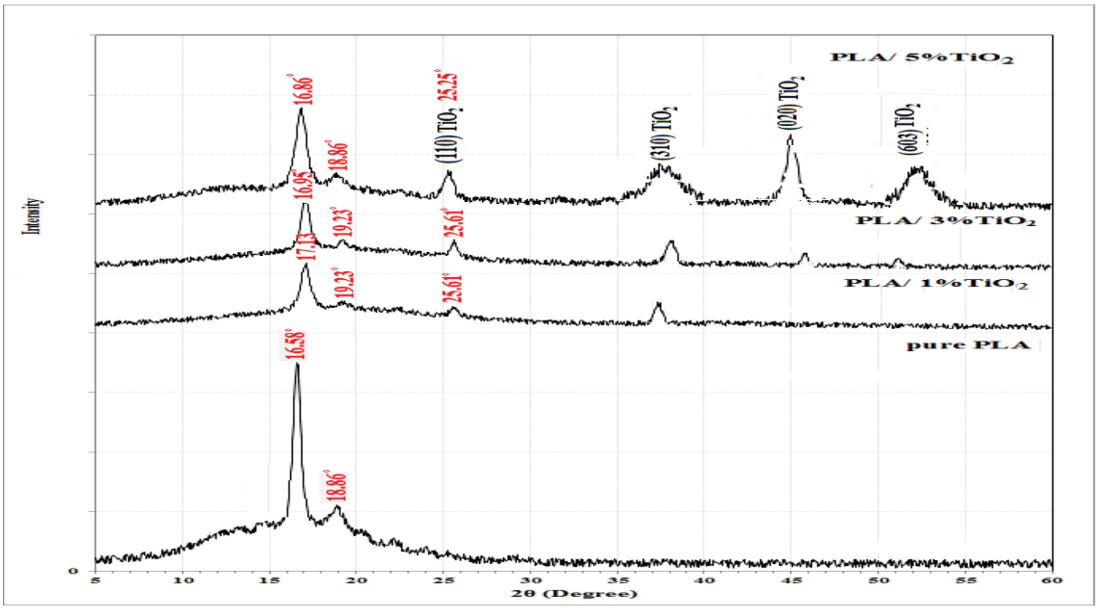


Fig(1) :FTIR of PLA and PLA/5wt%TiO2 composites

In All nanocomposite films of PLA/TiO2 appear all bonds between activity sites of TiO_2 and -C=O groups of PLA, 1347 symmetrical stretching C-O-C . A comparison between PLA and PLA/TiO2-5wt% showed that absorption peak at 850-738 cm^{-1} is assigned to (Ti-O-Ti) stretch peak, the bands at 1756, 1384, 1330cm-1 were caused by the vibrations of C=O and C-O groups from PLA/TiO2 chains. Besides, new bands appeared at 1421cm-1 due to the coordination between Ti atoms and the carboxylic groups of lactic acid[12]. FTIR results indicated that PLA chains were successfully onto TiO2 .because showed similar spectra as pure PLA, and the typical spectrum of nanocomposites containing 5wt% TiO2 was presented in Figure(1) .

3.2X-Ray Diffraction (XRD) Analysis

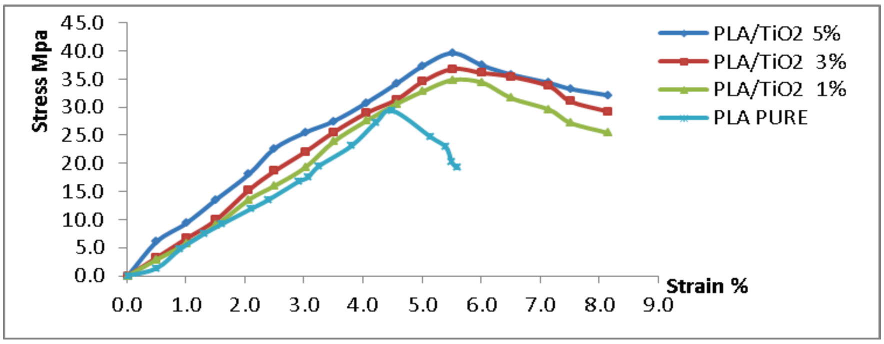
X-ray diffrction pattern of polylactic acid shows two peaks located at 2θ= 16°.58 and 18.86° with sharp peak for first peak indicating semi crystalline structure as shown in Fig.2 which agree well with results reported by Batteazzone et.al [13,16] as reported of PLA finds that pattern of PLA is characterized by a 2θ = 16.6º, 19.1°. In PLA/ 5wt%TiO2 showed four main peaks at 2θ = 25° ,38°, 48 ° and 54° being indicative of the PLA and titanium oxide which agree with Xi.li et .al [5,] that appear peak at 25°, 39°, 47°, and 55° .



Fig(2) :XRD patterns of pure PLA and PLA/5wt%TiO2 composites

3.3Mechanical properties:

The improvement in the mechanical performances of nanocomposites is due mainly to the nanosized dimensions of the fillers which results in an extremely large aspect ratio and strong polymer-filler interactions that may affect the effectiveness of load transfer between the nanofillers and the polymer matrix. The tensile strength and Young Modulus of pure PLA and PLA/TiO2 5wt%, is shown in Table(1).Usually, strong nanopartical / polymer-matrices interfacial bonding is desired to produce the stronger mechanical properties compared to only a matrix polymer. The tensile property of PLA/TiO2 5wt% was increased compared in pure PLA; mean that depended on the size of TiO2 (20-50nm) at relatively high contents such as 5 wt%. The nanocomposite of titanium increased (Young‘s modulus and Tensile strength) over that of the neat PLA when a uniform dispersion is achieved in nanoscale size and that agree with Norio N.et.al find that tensile strength increased when used nano TiO2 in 10wt% [12].



Fig(3): Mechanical properties of PLA and PLA/5wt% TiO2 composites

Table 3.Value of Tensile Strength , Young Modulus for all samples

Sample	Tensile strength(MPa)	Young modulus (GPa)
PLA	29	2.3
PLA/1wt% TiO2	35	2.5
PLA/3wt%TiO2	37	2.8
PLA/5wt%TiO2	39	3.0

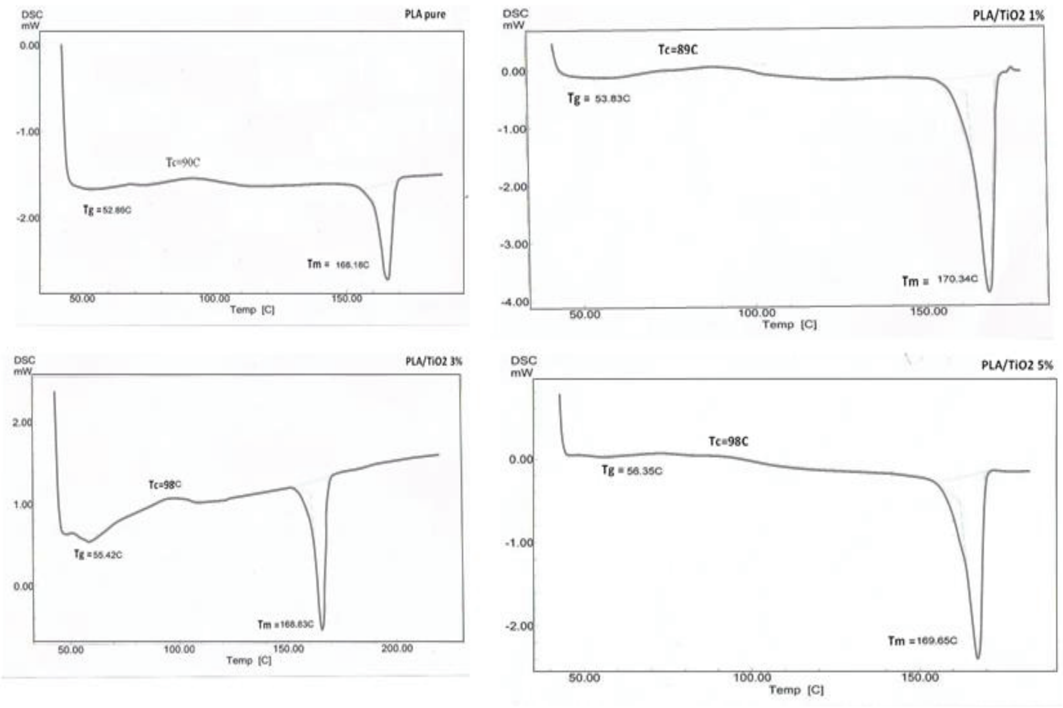
3.4 Differential Scanning Calorimetry (DSC) Analysis

DSC analyses of the prepared nanocomposite samples showed no significant effect of titanium oxide content in thermal properties of nanocomposites compared to pure PLA films. As can be seen from the DSC results given together in the Table 2, variations in glass transition, melting and crystallization temperatures as well as degree of crystallinity of PLA nanocomposites were observed. However, crystallization temperature of PLA/TiO_2 nanocomposites were decreasing with titanium loading(1wt%) and increased in (3wt% and 5wt%) nanocomposite films were increased about 10 C° that agree with *D*. Battegazzore et.al [13,14]. .

The Tg for all samples is seen Fig.(4) Such an observation Tg of neat PLA (52C°) is slightly increased in the case of all the PLA/TiO_2 composite .This may be due to the favorable interaction between PLA matrix and TiO_2 particles this is due to the strong adsorption of PLA /TiO_2 because FTIR ,X-ray analysis (refer to Fig1,2) did not change of any bonds chemical interaction and appear that peak of crystallization between the PLA matrix and TiO_2 nanoparticles.

Table 2. crystallinity (%)of PLA composites determined by DSC thermal scans

Samples	**Tg C°**	**Tc C°**	**Tm C°**	**Xc%**
PLA	**52**	**90**	**168**	**12.8**
PLA/1wt%TiO_2	**53**	**89**	**170**	**13.1**
PLA/3wt%TiO_2	**55**	**99**	**170**	**13.9**
PLA5wt%TiO_2	**58**	**91**	**169**	**14.2**



Fig(5): DSC of PLA and PLA/ TiO_2 composites

3.5 Oxygen transmission rate

Oxygen permeability plays an important role in packaging application to control shell-life of the foods, drinks and goods. Therefore, when a polymer film has low oxygen permeability coefficients, the oxidation is retarded and the shelf-life of the product extends [15]

The OTR gas permeability values of pure PLA and composites are presented in Table(3) showing that oxygen permeability of PLA taking into account of 20cm^3.mm/m^2.day.atm which agree with Amita et.at which found that value is 20 cm^3.mm/m^2.day.atm [16]and compare with K. Fukushima et.al which found that value is 18cm^3.mm/m^2.day.atm [10] .

When addition of (1,3,and 5wt% TiO2) leads to a decrease of the PLA oxygen permeability that because the concept of the tortuous path of nanomaterials , given to its high dispersion, according to X-ray analysis lead to improvements in barrier properties of polymer nanocompositesare attributed to formation of a tortuous path by the incorporation of nano-size fillers .That is, when impermeable nanoparticles are incorporated into a polymer, the permeating molecules are forced to wiggle around them in a random walk, and hence diffuse through a tortuous pathway. Oxygen permeability depends on chain flexibility, phase and physical state of the polymer and packing of its molecules. We observed that there is a great decrease in oxygen transmission rate as the percentage composition of the modified titanium increases. The deep understanding of chemical and physical interaction between TiO_2 particles and the polymer could to obtain polymer nanocomposites with the reduced oxygen permeation required for materials with high oxygen barrier properties for food packaging applications is widely common the use of Polystyrene (PS), Polypropylene (PP) and Polyethylene terephthalate (PET), given their good mechanical and oxygen barrier properties and compare with this polymer contributing to the development of new bio-based polymer composites for food packaging applications [7,14].

Table 3: Oxygen gas permeability of PLA and PLA/TiO_2 composites , at 23°C and 0% R.H.

Oxygen Transmission Rate (OTR) cm^3.mm/m^2.day.atm.	
PLA	**20**
PLA/1wt%TiO2	**18**
PLA/3wt%TiO2	**16**
PLA5wt%TiO2	**14**

The dispersal of nano-sized fillers into the polymer matrix affects the barrier properties of a homogeneous polymer film in the first way is by creating tortuous path for gas diffusion. Because the filler materials are essentially impermeable inorganic crystals, gas molecules must diffuse around them rather than taking a (mean) straight line path that lies perpendicular to the film surface. The result is a longer mean path for gas diffusion through the film in the presence of filler ,essentially the tortuous path allows the manufacture attain larger effective film thicknesses while using smaller amounts of polymer. The second way that nanoparticulate fillers influence the barrier properties is by causing changes to the polymer matrix itself at the interfacial regions. [8, 16].

4.Conclusion

Throughout the research study, polylactide /titanium nanocomposite (PLA/TiO_2) films were investigated as an alternative to conventional polymer composites. XRD and FTIR analysis were performed to characterize the PLA/TiO_2 films. FTIR analysis was used to be sure about no presence of nanotitanium in PLA matrix. Structure of the nanocomposite had significant influence on the physical properties of the nanocomposites as the dispersion of the titanium in polymer matrix. The tensile property of PLA/TiO2 5wt% was increased compared in pure PLA (29-39)Mpa. The crystallization temperature of PLA/TiO_2 nanocomposites were decreasing with titanium loading(1wt%) and increased in (3wt% and 5wt%) nanocomposite films were increased about 10 C°. Oxygen permeabilities were measured to investigate the barrier properties of the nanocomposites. Nano titanum addition improved barrier properties of pure PLA from 20 to 14 cm^{3}·mm/m^2.day.atm. OTR test values shows that nano titanium plays powerful role in increasing the gas barrier properties .several applications, such as in transparent functional packaging and biomedical applications.

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