Open Access Journal of Chemistry
Volume 2, Issue 4, 2018, PP 53-59
ISSN 2637-5834

Mechanical, Color and Barrier, Properties of Biodegradable Nanocomposites Polylactic Acid/Nano Clay

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ABSTRACT

To improving the properties of biodegradable polylactice (PLA) as packaging material by application of nano composite technology because that PLA is attracting considerable interest more eco-friendliness from its origin as contrast to the petrochemical-based polymers and its biodegradability and compatible during their service time could occur after prolonged exposure to water vapor and high temperature condition.

Poly (lactic acid) and nano clay composites films were prepared by casting method at weight percentage nano clay (1, 2, 4, and 6%). Physical, mechanical, barrier and color test of the nanocomposite were studied. X-Ray diffraction and Fourier Transform Infrared characterizing estimate the nanoclay distribution in the matrix material .Mechanical test (Tensile strength, Young Modulus, Tear Strength) increased when add 1, 2, 4, and 6% compare with PLA. Barrier test(oxygen transmission rate and water vapor permeability) of nanocomposite films were measured at 38°C and at a relative humidity of 90% show that decrease and moved down when the concentration of nano clay is increased in 1-6 wt% nano clay. Color test show that the PLA/clay nanocomposites doesn't have any change effects on films transparency and that the key research challenges in the development of nanocomposites based on biodegradable polymer used in packaging food application and other application .

Keywords: *Polylacticacid ,Nano Clay , Mechanical Test , Barrier Test, Color Test .*

INTRODUCTION

PLA is aliphatic linear polyester thermoplastic derived from monomer lactic acid, which is obtained from the fermentation of 100% renewable and biodegradable plant sources, such as corn or rice starches and sugar feed stocks. It can be produced by chemical conversion of corn or other carbohydrate sources into dextrose. Dextrose is fermented to lactic acid followed by poly condensation of lactic acid monomers or lactide.

However, the most common way to produce PLA is the Ring Opening Polymerization (ROP) of lactide monomer formed from lactic acid [1].

There are three different stereo chemical forms exist for lactide: either L-, D- or both L, D-Lactide (meso-lactide), each one having their change melting properties.

PLA is insoluble in water, ethanol, methanol and aliphatic hydrocarbons but it is soluble excellent in chloroform. Its degradation half-life goes from six months to two years, depending on its stereochemistry and molecular weight [2]. PLA exhibits many advantages; it is biodegradable, renewable and highly transparent to light and has good water vapor and humidity barrier properties, comparable to those of petroleum-based plastics, such as polyethylene tereph thalate (PET) or polystyrene (PS). Nonetheless, PLA has limited gas barrier capacity due to its hydrophobic in nature; it is very brittle, with less than 10% of elongation at break.

Some important characteristic properties of pure PLA such as weak thermal stability, low gas barrier properties, and low ductility and toughness are inadequate for food packaging applications [3, 4].

PLA has good mechanical properties, thermal plasticity, and biocompatibility and Eco friends. However, PLA is a comparatively brittle and stiff polymer with low elongation. Therefore, PLA is needed in order to compete with other flexible polymers such as polypropylene or polyethylene.

There are many techniques to modify PLA such as copolymerization, blending with other polymers, the addition of plasticizers, the addition of nucleating agents, and forming composites with fiber or nano particles materials. The improved packaging refers to addition of nonmaterial's to promote barrier and mechanical properties like nanoclay and nano silver [5].

The weight of polymer based on nanocomposites has a strong effect on the recycling of products and environmental concerns to reduce the consumption of gasoline by up to 1.5 billion liters, which in turn decreases CO2 emissions The barrier properties play an important role in the advantages of nanocomposites materials.

For example, the packing of food is one of the applications for nanocomposites [6] . In addition, the transparency of the nanocomposites is the same as virgin polymer, clays seems to behave as a nucleating agent, which induces a larger level of polymer crystalline beside the crystallization rate.

In addition, the incorporation of layered silicate enlarges the biodegradation of the resulting materials.

This action can be ascribed to the hydrophilicity of layered silicate which attracts water molecules to the mixture and ends up speeding up the hydrolytic degradation of the polymer [7].

Improvement in barrier properties is one of the most notable successes of polymer/clay nanocomposites. Some quite dramatic reductions in permeability with relatively low additions of nanoclay. The objective of this study was to investigate the effects of nanoclay on barrier, mechanical and color properties of the films.

Materials

Pure grade PLA AI - 1001 with density 1.25 g/ cm^3 supplied by (Shenzhen Esun Industrial Co., Ltd.Chain).Nano clay supplied by Nanoshel LLC (USA) with average diameter of the particles (as recorded by the company) was about < 80 nm. Chloroform Solution was purchased from Applied Chem. (Darmstadt, Germany)

Preparation Method

Polylactide films were prepared by casting method by using 3 gm in 30 ml of chloroform than was putted in glass tubes on a magnetic stirrer at temperature 60°C for one hour. After that, the solution was stay at room temperature for one day to ensure complete solvent removal.

PLA/nano clay composite films were prepared by add nano clay swollen in chloroform by mixing for one hours while polylactide dissolved in chloroform at 60 °C then nano clay solution was sonicated from homogenizer Soniprep-150 MSE for an hour to increase distribution .

The amount of nano clay in PLA was varied between weight percentage (1,2, 4,and 6)wt% .

Characterizations

Thickness

Determination of thickness of pure PLA and PLA/nanoclaycomposites calculated by electronic digital micrometer type (293-821, Mitutoyo) sensitivity was used to measure the thickness of composites films and find that is 105µm.

X-Ray Diffraction (XRD) Analysis

The structure curve pure of polylacticacid and PLA/nanoclay composites film were characterized by Phillips X'Pert Pro MRD (Cu Kα radiation (λ=1.54 nm) in (40 kV, 40 mA) between 5° and 60°.

Fourier Transform Infrared (FTIR) Analysis

The infrared spectra were recorded with the help of Shimadzu type FTIR -7600 in range 400 to 4000 cm^{-1}.

Mechanical Properties

Tensile Strength

According to ASTMD-882[8] standard modulus of elasticity, tensile strength, and elongation equipped with a 5 kg load cell in tensile mode. Tested films were cut into 10 mm width and 80 mm in length and the initial gauge length and the speed were fixed at 10 mm/min. Tensile strength (*σs*), Young's modulus (*E*) were determined according to the following equation:

$$\sigma s = F / A \qquad (1)$$

$$E = F\, L_0 / A\, \Delta \qquad (2)$$

Where: *F*: force exerted on an object under tension, L_0: original length, *A*: cross section area, Δ*L*: length of the object changes

Tear Strength

Tear strength of films was determined on the same Universal Electronic Dinamometer according to ASTM D-1922[9] by the trouser tear method.

The sample size was 100 mm long and 63 mm wide having a cut of 50 mm at the center of one end.

A pendulum impact tester is used to measure the force required to propagate slit a fixed distance to the edge of the test sample.

Optical Properties

Color test and Brightness

Color properties were evaluated measuring color coordinates in the CIELAB color space L* (lightness), a*(redness - greenness) and b* (yellowness - blueness) were analyzed using a Konica CM-3600d color. Average values for samples were calculated by the color a difference (ΔE) was evaluated by Equation (3) [7]

$$\Delta E=\sqrt{\Delta a2\ +\ \Delta b2\ +\ \Delta L2} \qquad (3)$$

Where: ΔL = Lstander*-Lsample ,Δa = a stander*– a sample , Δb = b stander*-b sample , Stander values for white plate were L = 96.86, a = - 0.02 and, b = 1.99 respectively for pure polylactic acid .

Barrier Properties

Oxygen Transmission Rate (OTR)

Oxygen Transmission Rate of the films was measured according to the ASTM D-3985[10] using gas permeation instrument Qualities. The diffusing oxygen is measured by a gasdetector that is sensitive only to oxygen, after 12 -16 hours test was completed .Before each measurement, the samples were kept dry in vacuum oven in nitrogen gas and the gas permeability rate expressed in cm^3/m^2.day that keep at temperature (23°C) and relative humidity (0% RH) with test Area $50cm^2$and thickness ≤ 3 mm.

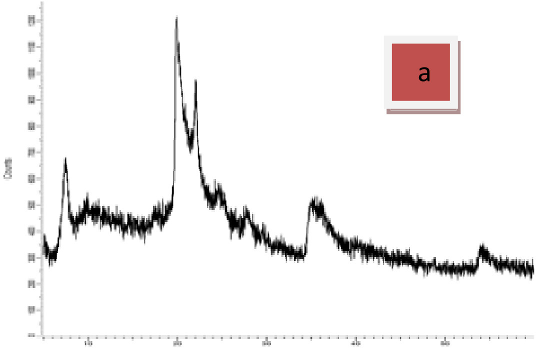
Water Vapor Transmission Rate

The water vapor transmission rate of the films was measured according to the ASTM E-96[11] using water permeation instrument Qualities .Film specimens were mounted horizontally on poly (methylmethacrylate) cups filled with distilled water up to 1 cm under the film. The cups were weighed every hour for a period of value was noted usually after 6-8 hours and measure the weight loss versus time in unit gm $/m^2 \cdot 24h$ at 37°C and (90%RH) with $50cm^2$ area and thickness is ≤ 3 mm.

RESULT AND DISCUSSION

X-Ray Diffraction of powder Nano Clay

XRD patterns of the claynano powder is given in Fig (1a) shows the XRD of the clay nanopowder typical peaks around 2ϴ= 5°, 20°, 25°,30°, and 35 ° of the (001), (002) (111), (003) (005),reflections corresponding to Na –montmorillonit



In **Fig(1b)** *shows the XRD of the PLA/nano clay nanocomposites peaks at 2θ= 13°,17°,20°,23°,30°,38°,40° where 2θ =17°, 20° of pure PLA that mean is semicrystallineit was shown by Nadia et.al [12]. Incorporation of nano clay in polymer matrix(PLA) causes an increase in intensity and sharpness of PLA peaks at 2θ = 17°, 30 °, which can be attributed to improvement of matrix crystallinity.*

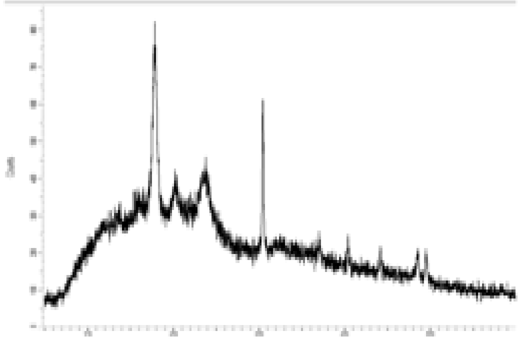


Fig (1a, b): *XRD of nano clay and PLA/nano clay nanocomposites*

Fourier Transform Infrared Analysis of Nano Clay, Pure PLA and PLA/Nano Clay

FTIR analysis of a chemical substance shows marked selective absorption in the infrared (IR) region. Nano clay is prepared by adding 1–2 mg clay in equal amount of KBr and ground to fine powder, Solid casted pellet is placed in the path of light source at wave number ranges from 400 to 4000 cm^{-1}.In Fig (2a) It has been reported that peak intensity at $3421cm^{-1}$, 3340 cm^{-1} corresponding to O-H stretching for the silica and water and 1633 cm^{-1} related to (O-H bending) may be due to presence of water

molecules from moisture. Si-O-Si bond is confirmed from 1043 cm^{-1}. The peaks at920cm-1 to from Al-OH-Al deformation of alumina , there are also unique bands due to tetrahedral SiO_4 near $700cm^{-1}$ in layer silicate that be used for specific mineral identification .Bands at $2930cm^{-1}$, 1314cm-1 to C-H vibrations of methylene groups (asymmetric starching and bending) and 484 and 520 cm^{-1} ascribe the presence of bonds such as Si-O-Al and Si-O-Mg.

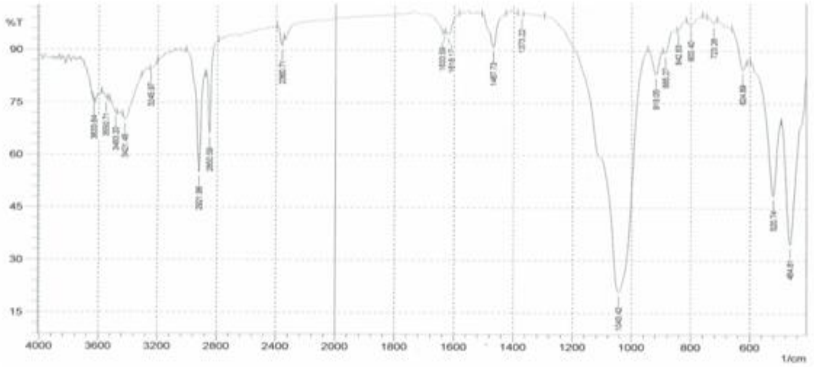
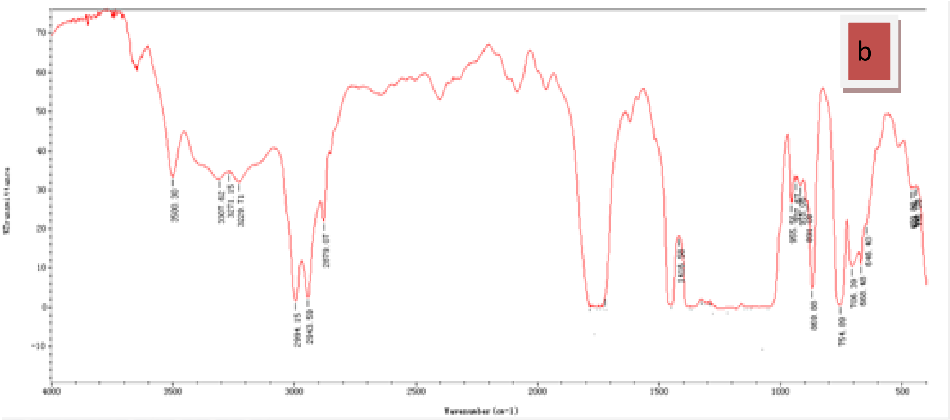


Fig. (2b) *shows the of pure PLA and appear peaks at 1418, 2994 and 3600 cm^{-1} were assigned to the C–O, C–H(double) and O–H stretching of the –CH(CH3)–OH end group of PLA, respectively. The band at –C–O bond stretching (955 cm^{-1}) in –CH–O– groups.*



In **Fig (2c)** *shows that PLA/nano clay exhibit identical absorption peaks, suggesting lack of strong interactions between PLA molecules and nanoclay nanocomposites. In PLA/ nanoclay , the C=O and O– H stretching peaks were at (955 and 3617 cm^{-1}, respectively) and atstrong peaks are corresponding to stretching vibration of carbonyl group C=O and C-O groups at (1747, 1087 cm^{-1}). This was attributed to the strong interactions between the PLA hydroxyl end groups and the nano clay platelet surfaces, and/or the ammonium groups of the surfactant in the modified clay ,Si–O stretching (917 cm^{-1}) and Si–O bending vibration of organo clay (516-462 cm^{-1}), respectively.*

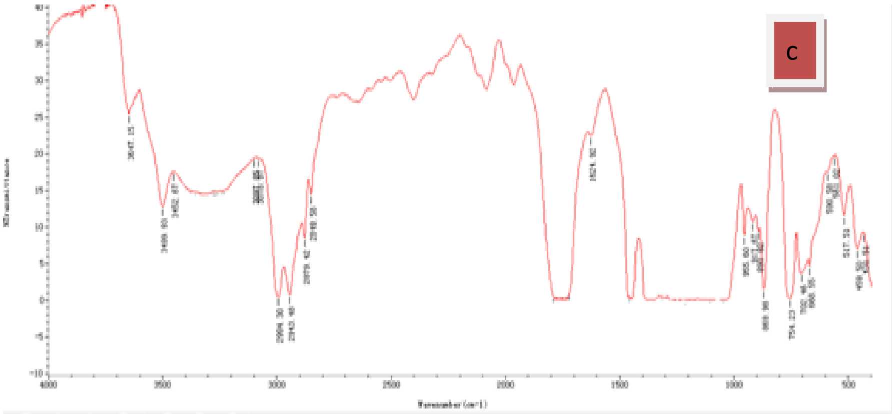


Fig (2 a, b & c). *FTIR spectra of nano clay powder , pure PLA, PLA/nano clay composites*

Mechanical Propertiespla and PLA/Nano Clay

Table (1) shows the values of mechanical properties of pure PLA and PLA/ nano clay films, tensile strength (9.34 MPa), Elongation (8%) and Young Modulus (2.8 GPa) because that PLAbased materials are rigid and brittle polymerat room temperature (RT) due to its Tg ~ 55 °C [6] .

The pure PLA as a brittle material the reasons for this brittle behavior for the pure PLA is due to the low entanglement density (Ve) and the high value of characteristic ratio (C∞), a measure of chain stiffness [12]

Table1. *Mechanical test of pure PLA, PLA/nanoclaycomposite*

Samples	Tensile Strength MPa	Elongation %	Young Modulus GPa	Tear Resistance mN/mm
Pure PLA	9.34	8.0	2.8	12.5
PLA/clay%1	35.3	7.11	8.1	13.4
PLA/ clay%2	36.8	6.85	8.5	16.7
PLA/ clay %4	38.6	5.49	8.7	19.6
PLA/ clay %6	39.9	5.41	9.2	23.3

When add nano clay increased in Tensile Strength , Young Modulus between (35.3-39.9)MPa and (8.1-9.2)GPa respectively appear in Fig (3) because that due to the hydrogen bonding interaction between PLA and nano clay and the structure of PLA consists of two hydroxyl groups at the end of its polymer chains these prepared PLA/nano clay composites embedded in a network of PLA polymeric chains and the origin hydrogen bonds formed between the PLA molecules and nano clay and these new hydrogen bonds would improved the mechanical properties. The main reason for this behavior may be attributed to the resistance exerted not only by the clay itself with high surface area high aspect ratio and vary high elastic modulus, but also by the stronger interfacial interaction between the matrix and layered silicate due to the vast surface exposed to the clay layers [14,15]. Good dispersion of the nanoclay in polylactic acid reduced tensile ductility and increased tensile strength compared with pure polymer that mean the complete dispersion of clay nano layers in a polymer optimizes the number of available reinforcing elements for carrying an applied load and deflecting cracks. Nano clay decreased in elongation between (7.11-5.41)% with increase in nano clay concentration.

Tear resistance is the force it takes to rip a plastic film, generally plastic sheet with a property of brittleness will have very low tear resistance; this is clearly proved from the Table (1), pure PLA is a brittle material it shows low tear resistance is 12.5 mN/mm. When addition of nano clay improvement in tear resistance shown between (13.4-23.3 m N/mm) by considering that the nano clay contain silicate layers are able to inhibit or at least to slow down crack propagation by deviating their tear path. The higher tear strength of the samples appear in 6% nano clay because the interfacial bonding between the clay and the PLA matrix suffices to produce a strengthening effect as demonstrated.

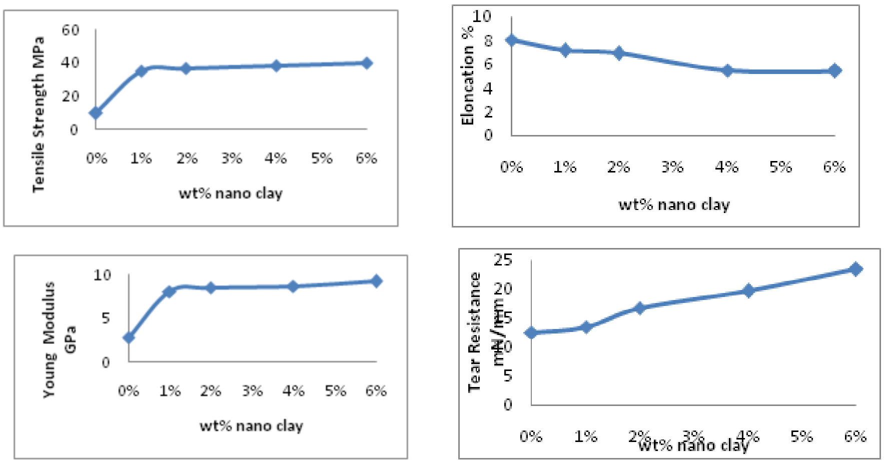


Fig3. *Mechanical test of pure PLA, PLA/nano clay composites*

Optical Properties PLA, PLA/Nano Clay

Color is veryimportant factors to be considered in food packaging since it could influence consumer acceptance and commercial success of a food product. Table 2 shows Color test of pure PLA, PLA/nano clay composites

Table2. *Color Properties of pure PLA and PLA/nanocomposite*

Sample	L	a	b	Brightness%
Pure PLA	90.05	-14.38	-2.76	80.88
PLA/CLAY %1	88.85	-19.18	-1.61	74.63

PLA/ CLAY%2	86.80	-21.10	-0.76	71.62
PLA/ CLAY%4	85.06	-22.01	-0.07	69.32
PLA/ CLAY%6	84.64	-22.60	-0.05	68.75

When nano clay is added to the film sample, slight decrease in lightness values (L) was observed when increasing nano clay content and about 84.64 for nanocomposites with 6% nano clay and 90.05for pure PLA. While, a parameter reduced that mean the red color value of samples decreased and green color value is increased, b parameter did not show regular changes this results mean nature of nano clay agreed with visual observation.

Brightness is percentage reflectance of light at wavelength 457nm show that high brightness in pure PLA that is 80.88% and for PLA/ nano clay is ranged (74.63-68.75) % that appear high transparency of PLA compare PLA/nano clay composites because the structure of nanocomposites will be optically clear which is traced to the thickness of each nano clay layer that is smaller than the wavelength of visible light.

Barrier Properties (OTR, WVTR) of PLA and PLA/Nano Clay

The main limitations of PLA as a packaging material are a high gas permeability (O_2, and water vapor) that show in Table (3) .Higher oxygen permeability coefficients and water vapor transmission rate are an indication of lower barrier protection that appear in pure PLA. The high molecular weight glassy polymers (PLA) with rigid chains have very high oxygen permeability. Polylactic acid is showing that OTR and WVTR taking of (488.96 $cm^3.mm/m^2.day.atm$)and(181.818 $g.mm /m^2$ .day)respectively that mean pure PLA suffers from some serious drawbacks such as its great sensitivity towards moisture and its poor water vapor barrier property because is hydrophobic significantly tend to be non-polar , that mean exhibit a high contact angle but is sensitive to water vapor that appear in Table (3).

Table3. *Barrier test of PLA, PLA/nano clay composites*

Samples	Oxygen Permeability Coefficients ($cm^3.mm/m^2.day.bar$)	Water Vapour Transmission Rate ($g.mm /m^2 .day$)
Pure PLA	488.9	181.8
PLA/clay %1	239.4	97.2
PLA/ clay%2	209.3	87.7
PLA/ clay%4	183.6	72.3
PLA/ clay%6	186.1	58.1

In PLA/nanoclaycomposites shown in Table (3) samples found that significant reduce in OTR and WVTR with increasing clay content at 6 weight %, due to the 'tortuous path' that improvement in barrier properties ,nano clay contain platelets forming complex barriers to gases and water vapor. As more tortuosity is present in a polymer structure, higher barrier properties will result in 1-6% of nano clay to polymer matrix due to the impermeable clay layers distributed in polymer matrix consequence increasing the effective diffusion path length [18] .

CONCLUSIONS

- The nanocomposites PLA/nanoclay are studied, XRD, FTIR show strongly associated with the dispersion of nanoclay in polylactic acid.
- The nanoclay is used at (1, 2,4, 6%) increases in mechanical , optical and improvement the barrier test for industrial manufacture and packaging application .
- Measured values of barrier properties of OTR, WVTR permeability of the PLA/ nanocomposites were compared with pure PLA showing good barrier properties at 6% nano clay by creating a maze or tortuous path that retards the diffusion of gas molecules through the polymer matrix.

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Citation: *Ali H. Mohsen and Nadia A. Ali. "Mechanical, Color and Barrier, Properties of Biodegradable Nanocomposites Polylactic Acid/Nano Clay". Open Access Journal of Chemistry, 2(4), pp.53-59*