Isolation, Preparation and Characterization of Polylactic Acid Film Reinforced with Nano silica

Isolation, Preparation and Characterization of Polylactic Acid Film Reinforced with Nano silica

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Abstract: Lactic acid was isolated by using microbial fermentation in whey media which was carried out by local strain *Lactobacillus paraplantarum* then polymerized using the acidic medium's polycondensation method. FTIR and H-NMR were used to characterize the isolated lactic acid monomer and polyalctic acid (PLA), and the results confirmed the chemical structures of the isolated lactic acid and PLA. GPC techniques were used to determine the molecular weight and molecular weight distribution of the prepared PLA; the result showed that the Polydispersity index (PDI) was 2.51. The Biodegradable composite films of poly lactic acid (PLA)/Nano silica powder were prepared by the composite film casting method using dichloromethane as solvent. In contrast, Nano silica was synthesis from hydrolysis of tetra ethoxysilane and was loaded in PLA in 1 to5 wt. %. The films were subjected to a tensile strength study. Thermogravimetric analysis (TGA) and differential thermal analysis (DSC) were used to evaluate PLA. Also, water absorption of the prepared composites was studied, and the result showed that the thermal stability and water absorption of these prepared films were increased with an increasing percentage of Nano silica, while the percentage of crystallinity of the PLA evaluated from DSC was 28 %.

1. Introduction

Nowadays, the environmental changings in the earth make hard issues for people's life in the all aspect, due to discharging of the huge quantities from waste and gases. The most discarded waste is remaining in the environmental for long time because it is not biodegradable [1, 2] .The plastic waste is occupied high percentage and it almost cannot recycled or it is not biodegradable. In addition to this obstacle, the major sources used in the plastic production is petrochemical or non-renewable fossil [3] Which they have several disadvantages, such that, diminishing and prices growth, production high amount of carbon dioxide in both the processing and the recycling, in addition to that, some toxic monomer used in the plastic production is pollutant and may be migrating to edible materials when used for packaging of food [4].

There are many schemes to overcame this drawback and reduces the effect of pollutants on the planetary and life. One of them by using ecofriendly and biodegradable polymers. These polymers included: Polyglycolide (PGA), Polyhydroxy butyrate (PHB), L-Polylactide (PLA) and Polyethylene glycol (PEG), [5].

Among these polymers, PLA is a bio-based, biodegradable polymer which can be prepared from lactic acid produced by microbial fermentation using renewable sources such as corn and

sugarcane. It has found numerous applications in the medical and pharmaceutical fields and in the protection of goods and food [6]. Comparing with the others polymers, PLA has several advantages such as it consumes quantities of carbon dioxide during production [7]. It can be produced from renewable and benign resources, it is biodegradable, recyclable and compostable, and it's a good physical mechanical property and can be altered it through the manipulation of PLA architecture [8, 9]. Last three-decade, PLA has found numerous applications as a packing material and medical studies have shown that the amount of the lactic acid release from packaging material to food is lower than its level used in common food ingredients [10].

In this paper, we will use lactic acid produced by local strain *L. paraplantarum* bacteria to prepare PLA via polycondensation. In the present work, PLA used as a matrix and loaded it with 1 to 5 wt.% of Nanosilica and studied the effect of this filler loading on the tensile properties, thermal stability of PLA/ Nanosilica. ESM was used to characterize the silica powder prepared by the hydrolysis of tetraethoxysilane.

2. Experimental Part

2.1-Materials

Lactobacillus paraplantarum YL4 new local isolate was tested and recorded to be a local Iraqi isolate from Buffalo milk recorded under the name LP IQ MT622658, in European Nucleotide Archive (ENA), National Centre for Biotechnology Information (NCBI) and Gene Bank. MRS agar from Hi-media used for cultivation. Whey used as fermentation media, chloroform, calcium chloride, and hydrochloric acid solution (35%), potassium bromide was supplied from Fluka Comp. While dichloromethane, acetone, absolute ethanol, silicon tetrachloride, and dimethylformamide were supplied from Aldrich Comp. At the same time, solid Nano silica was synthesis in this study by the hydrolysis of precursor tetraethoxysilane monomer (prepared by silicone tetrachloride reaction with absolute ethanol). Ammonia solution acts as a catalyst, water, and ethanol, controlling the pH and temperature of the hydrolysis. The SEM technique detected the particle size of the silica.

2.2- Instruments.

2.2.1- Fourier Transform Infrared spectrum (FTIR). The Shimadzu FTIR 8400S device recorded the FTIR spectra of the lactic acid and the PLA. Each spectrum was recorded at the frequency range 400-4000 cm^{-1} using Sodium chloride cell for lactic acid, while for PLA, a Potassium bromide used. The KBr was previously oven-dried at 300°C to reduce the interference of water.

2.2.2- Gel permeation chromatography (GPC). The number average molecular weight (Mn) and weight average molecular weight (Mv) determined by Youngling ACME 9000 GPC/SEC in DMF solvent; With flow rate 1.00ml/min, and column set length 950 nm, Injection volume was 200 µl.

2.2.3 - Differential Scanning Calorimetry (DSC). DSC measurement was conducted on Shimadzu DSC-60. Dynamic scans were carried out at the temperature range of 25-350°C at a constant heating rate of 10°C/min, under a nitrogen atmosphere at a 20ml/min flux rate. About 10-15 mg of sample was used in aluminum crucible. On the other hand, the degree of crystallinity of PLA is calculated by using the following formula [11].

$$x_c = \frac{\Delta H_m}{\Delta H_f} x100\% \quad (1)$$

Where Xc is the degree of crystallinity

ΔH_m is the heat of fusion of the sample (from DSC curve)

ΔH_f is the heat of the fusion of 100% crystalline PLA.

2.2.4 - Thermogravimetric Analysis (TGA). TGA measurement was evaluated on TGA Q50V20-13 build 39. The dynamic scan was measured in a temperature range (25-700) °C at a constant heating rate of 50 °C/min under a nitrogen atmosphere at a flow rate of 30 ml/min.

2.2.5 - Tensile strength and Elongation. The tensile strength and the elongation-to-cut ratio of the PLA film were measured using the Tensile Analyzer of the Polymer Research Center / the University of Basra, According to the American Society for Testing and Materials (ASTM) No. D-882.91 of 1996.

2.2.6 – Water absorption for PLA thin film. The specimens (dimension: 60 × 1 mm) were dried at 50°C in vacuum oven until a constant weight was attained, they were immersed in water in a thermostatic stainless-steel water bath at 30°C, 40°C and 50°C. Weight changes were recorded by periodic removal of the specimens from the water bath and weighing on a balance with a precision of 1 mg. The percentage change at any time t, (Mt) as a result of water absorption was determined by Equation 2, [12].

$$M_t = \frac{W_w - W_d}{W_d} \times 100\% \qquad (2)$$

Where, Wd and Ww denote the weight of dry material (the initial weight) and weight of materials after exposure to water absorption, respectively. The percentage at maximum water absorption (Mm) was calculated as the average value of several consecutive measurements that showed no appreciable additional absorption.

2.2.7- Nuclear Magnetic Resonance (H-NMR). ^{1}H -NMR spectrum of isolated lactic acid was obtained on a Bruker spectrometer operating at 600 MHz, at room temperature. Deuterated dimethyl sulfoxide (DMSO)-d_6 were used as solvents, and the sample concentration was 10% (w/v).

2.3 – Synthesis methods

2.3.1. Synthesis of PLA. First *L. paraplantarum* isolate cultivated in MRS agar at 37 ºC for 24-48 hrs. Which used to lactic acid production. Fermentation was carried out according to [13].The fermentation medium (whey) , pH adjusted to 6 , Inoculated with 1% inoculum with 8 ×10^7 CFU / ml and incubated at 37 °C for 3 days. Lactic acid produced by bacteria was polymerized throughout condensation polymerization, carried out using the hydrochloric acid solution (35%) as a catalyst at 90-100 ºC under nitrogen gas for 2-3 hrs. water was removed from time to time. Then the reaction mixture was cool to room temperature and washing several times with hot water to remove unreacted monomer, and remaining acid. The product was dissolved in chloroform, dried by adding calcium chloride and then filtrate. Finally, the polymer was precipitated by added methanol as white (sometimes slightly yellow) powder. Drying is carried out in an oven at 40ºC under vacuum for 3 hrs. And then characterized by the different techniques.

2.3.2. Synthesis of PLA thin films. Firstly, The PLA is dried under an inert atmosphere at 40°C for 3-4 hours to remove any solvent traces. Secondly. A 20 wt. % solution of PLA in chloroform was spread onto a glass plate with a Gardner knife to obtain a film thickness of 50 ± 5 μm. The PLA film was kept overnight at room temperature to remove most of the solvent. Final drying was accomplished in a vacuum oven at 40°C for two days.

2.3.3. Synthesis of the PLA Nanocomposites. Before processing, the PLA granules were dried at 60°C for 24 hours in a vacuum oven to remove excess moisture. The PLA was dissolved in dichloromethane solvent and several percentages of nanosilica prepared in this study (1, 3 and 5) % was added to the solution of PLA and sonication for 2 hours at room temperature in order to get homogenies mixtures. Then the samples were casting in Petri dish and kept in a desiccator for the controlled the evaporation of the solvents for 2 days. Optically clear films with thickness ranging from 500 to 700 μm were obtained and subsequently dried at 80˚C under vacuum for 2 days. The prepared films were kept in desiccator for further studies.

2.3.4. Film Thickness. The thickness estimated by take average of 5 readings using hand micrometer .

3. Results and Discussion

3.1. Synthesis of PLA

PLA polymers produce by three routes from lactic acid, as shown in Figure 1.

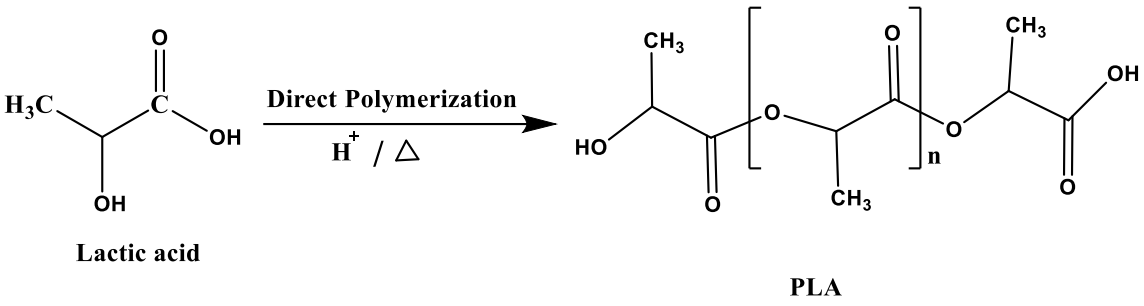

Figure 1. Scheme of polylactic polymerization

In this study , direct polycondensation of isolated lactic acid was used to obtained polylactic acid due to simple method .Here the condensation reaction obtained by the reaction of carboxylic groups and hydroxyl groups and the by product was water which was removed by distillation in order to get high yields polymers [14].Different catalyst were used to polymerize lactic acid and most of this research use antimony trioxide as catalyst [15]. Figure 2 shows the PLA powder.

Figure 2. Photo of polymer powder prepared in this study

On the other hand, in this study, Nano silica was prepared through the hydrolysis of tetraethoxysilane monomer according to literature procedure [16] as shown below.

[Hydrolysis]

$$\equiv Si - OR + H_2O \Leftrightarrow \equiv Si - OH + ROH \quad (3)$$

[Alcohol condensation]

$$\equiv Si - OR + = Si - OH \Leftrightarrow \equiv Si - O - Si \equiv + ROH. \quad (4)$$

[Water condensation]

$$\equiv Si - OH + \equiv Si - OH \Leftrightarrow \equiv Si - O - Si \equiv + H_2O. \quad (5)$$

[Overall reaction]

$$Si(OR)_4 + 2H_2O \xrightarrow{OH-} SiO_2 \downarrow + 4ROH. \quad (6)$$

Where R is C_2H_5

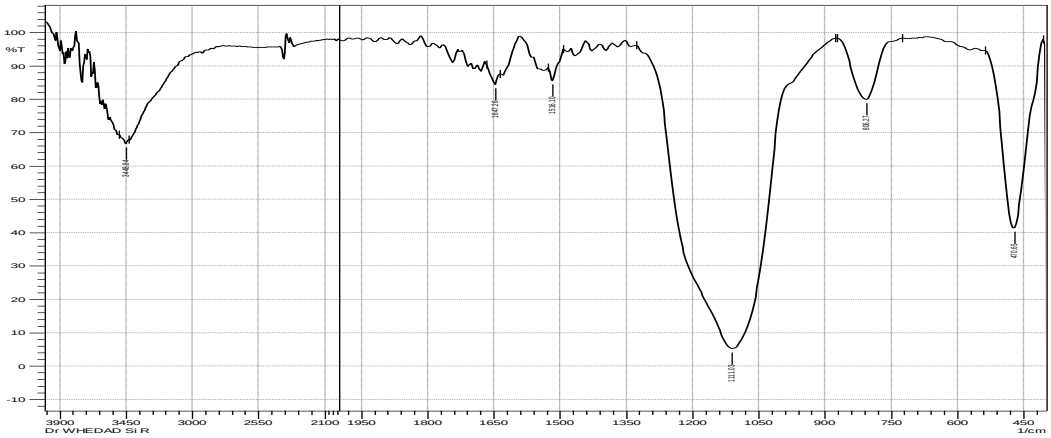

Figure 3. FTIR of the prepared silica

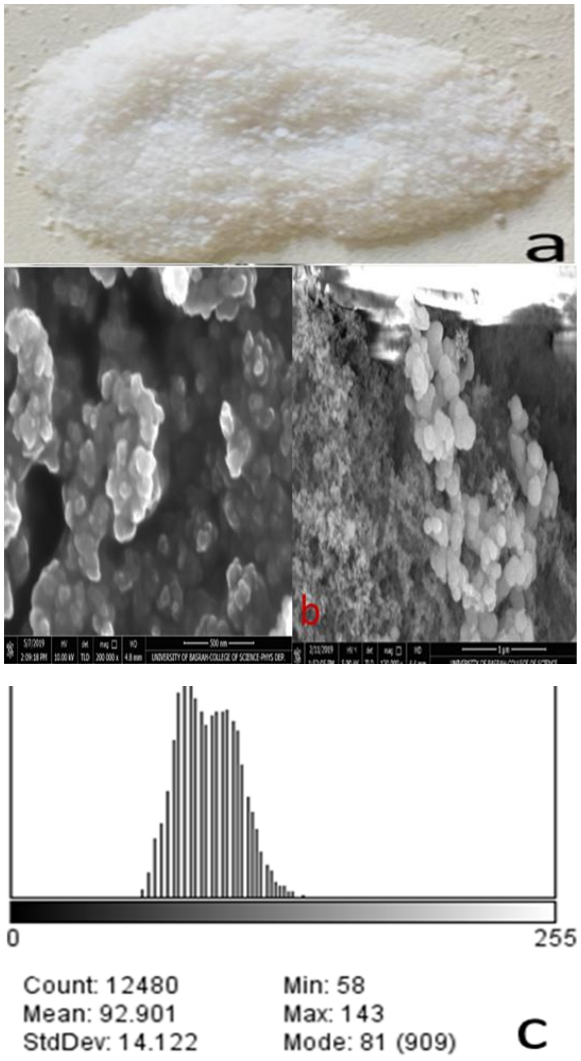

Figure 4. (a) Nano silica particle, (b) The SEM image of Nano silica powder prepared in this study and (c) The particle size distribution of Nanosilica

Figure 3. show the FTIR of the silica obtained from the hydrolysis process, the band at 3448 cm^{-1} indicate the presence of hydroxyl groups, while the characteristic band at 1111 cm^{-1} due to the Si-O-Si siloxane bond in their structures [17]. Figure 4. (a,b and c) Nano silica particle, SEM analysis of the products and the particle size distribution respectively.

3.2. Molecular weight of PLA:

GPC is an empirical method used to measure MMD and average molar masses of polymers [18]. Sometimes, the term SEC (size-exclusion chromatography) is used in the literature, but it is a more general concept for both GPC and GFC (gel filtration chromatography). In GPC, organic solvents are used as mobile phases, whereas in GFC, aqueous solvents are utilized. For the prepared PLA in this study, Figure 5 shows the molecular weight distribution and molecular weight distribution, While Table 1. show the values of the molecular weights calculated from the measurement.

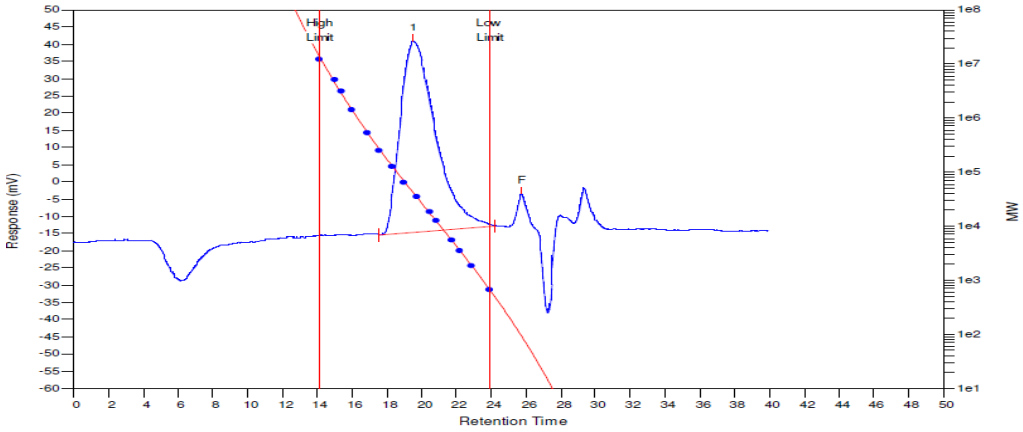

Figure 5, GPC Distribution curve of polylactic molecular weight

Table 1: The results of the molecular weights obtained from the measurement

Mn	**Mw**	**Mz**	**Mz+1**	**Mv**	**PDI**
15563	39193	63449	8449	35766	**2.5183**

Mn= number average molecular weight Mw=weight average molecular weight Mz=z average molecular weight. Mv=viscosity average molecular weight PDI= polydispersity index

From the results, we noted that the order of the different molecular weights according to their values is as follows:

$$M_n < M_w < M_z < M_v$$

This agreement to the most reported values of the molecular weight of polymers. With regard to the Polydispersity index, it value can be calculated from the equation below:

$$PDI = \frac{M_w}{M_n} \qquad (7)$$

We note that the PDI value is 2.518, which means that the high molecular weight package is broad. These values depend on the type of polymerization process and its conditions. The research indicates that PDI values for additive polymers are in the range 1-1.5, while its values for condensing polymers are less than 2. When the number closes to the limits of 2 means, the high molecular weight is

narrow. Thus the crystallization ratio is high. According to the prepared polymer, it gave a low percentage of crystallinity, which is around 28%, calculated from the DSC.

3.3. FTIR-analysis

The FTIR spectra were measured within a 400-4000 cm^{-1} range, for the isolated LA and PLA on sodium chloride and potassium bromide disk. The peak at 3510 cm-1 in the spectrum of the isolated LA as shown in Figure 6. Indicates to a hydroxyl group (OH), while the peaks (2993, 2947, 2885) cm^{-1} indicate the binding of C-H [19] .The peak at 1454 cm^{-1} is attributed to the CH3 group. The C-O-C within the region (1000-1300) cm-1 refers to the stretching vibration. The main peak, which is considered a clear indication of acid formation, appears at 1751 cm^{-1}, attributed to the carbonyl group as reported by [20].

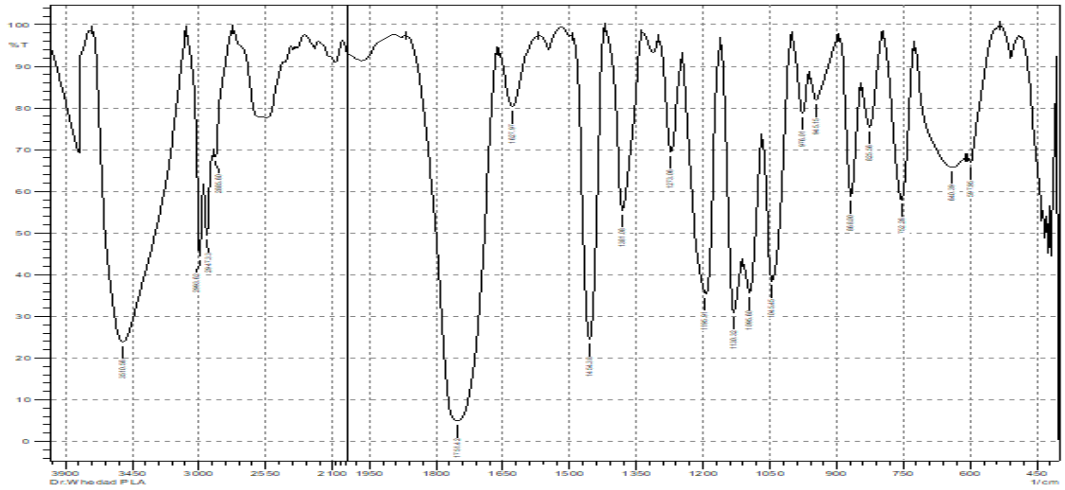

Figure 6, the FTIR of LA

On the other hand FTIR spectrum of PLA is shown in Figure 7. We noticed a decrease in the intensity of the beam belonging to the hydroxyl group 3506 cm^{-1}. This is evidence of the polymerization process. In addition to that, the presence of (2947, 2997) cm^{-1} peaks returns to the stretching C-H bond. The carbonyl group's peak in the acid 1751 cm^{-1} is shifted to 1759 cm^{-1}, with a stronger intensity in the polymer, which belongs to the ester group, which gives evidence of the polymerization of the acid. The peak at 1458 cm^{-1} refers to the CH_3 group. These results agreement with some researches [21, 22].

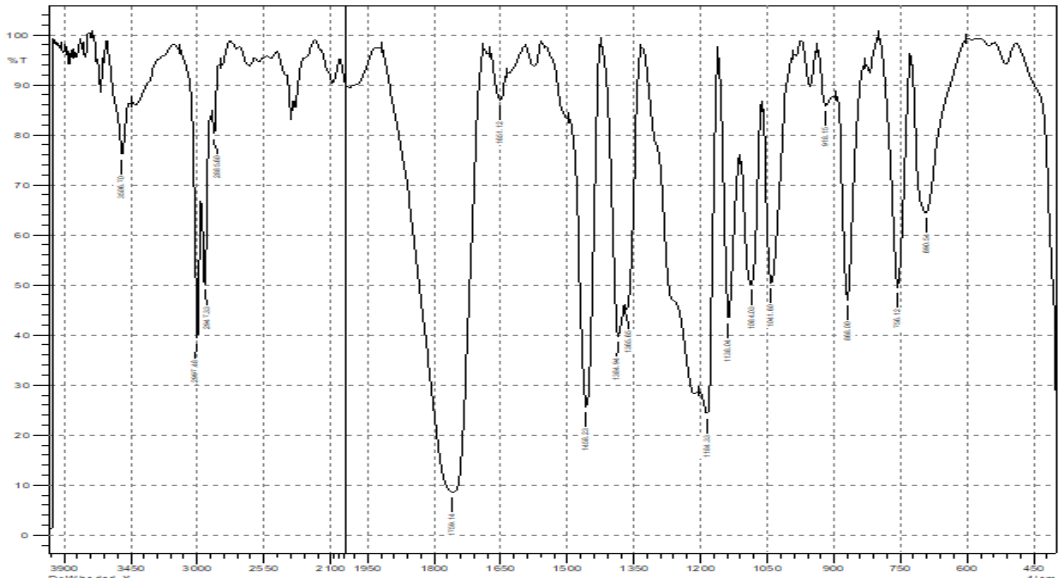

Figure 7, the FTIR of PLA

3.4. H-NMR analysis

The 1H-NMR spectrum of isolated lactic acid is shown in Figure 8. The resonance signal at 1.3-1.6 (d, 3H, CH_3) is assigned to methyl protons (-CH_3), The resonance signalat (δ = 4.28) corresponds to the methine linked to the OH group (23), while the peaks around 4.8 ppm due to deuterated solvent (D_2O) .

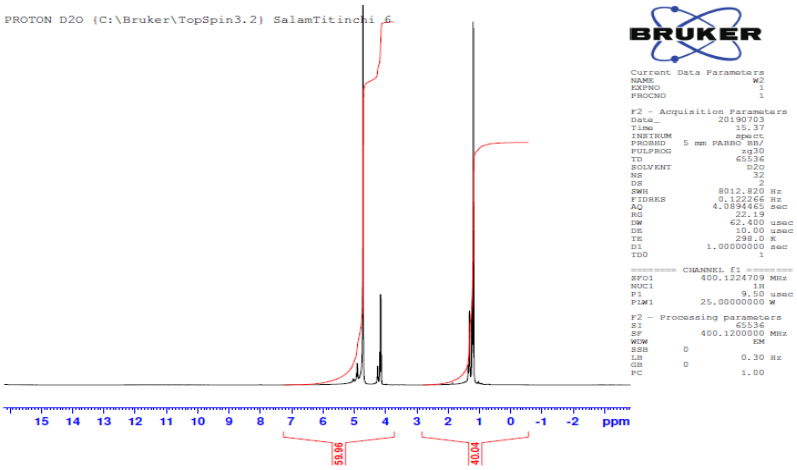

Figure 8. H-NMR spectrum of isolated lactic acid

3.5. DSC analysis

To investigate the thermal behavior of PLA, DSC measurements were carried out. PLA thermogram consists of a glass transition and melting endotherm peaks (Figure 9). The glass transition temperature, Tg, PLA, is 65.89 ◦C, and the specific heat capacity Cp, PLA 0.67 J/ (g ◦C). These values compare well with Tg = 61 ◦C and Cp ∼ 0.55 J/ (g ◦C), as[24], While the endothermic peak at 158 ° C is attributed to the polymer's melting point [25]. On the other hand degree of crystallinity was determined from this analysis and was equal to 28.07, this mean that the prepared polymer has low degree of crystallinity.

$$X_c = \frac{26.28}{93.6} \times 100 = 28.07$$

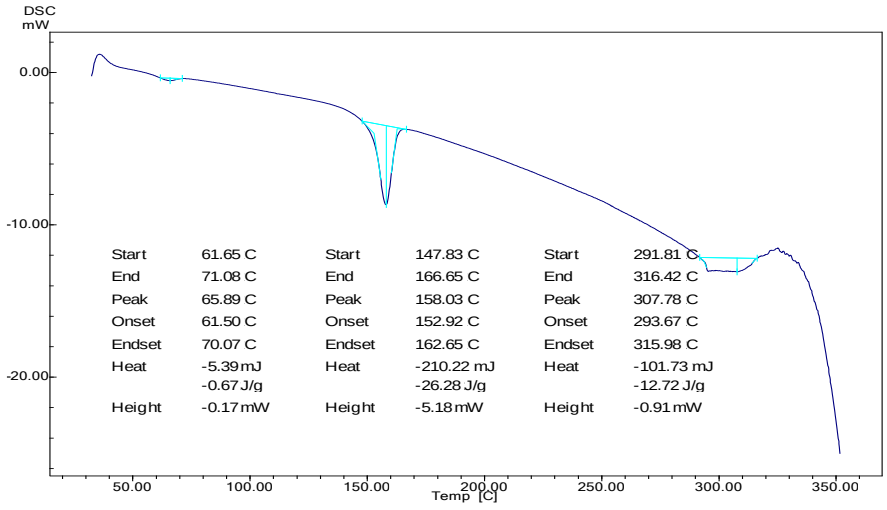

Figure 9. DSC thermogram of PLA

3.6. TGA analysis

TGA, or thermogravimetric analysis, has long been an accepted analysis method for polymers in industry . Its advantages are also easily seen from a forensic point of view, here TGA was carried out to investigate the importance of thermal degradation of PLA and PLA-composite. According to the TGA thermograms shown in Figures (10, 11), the degradation of PLA and PLA -Nano silica composite has one decomposition temperature higher than 400ºC. In contrast, On the other hand, the decomposition rate of PLA- Nano silica composite was less than the other polymers, which means that the composite was more stable than the PLA alone. Table 2. Show the thermal parameters obtained from the TGA thermograms.

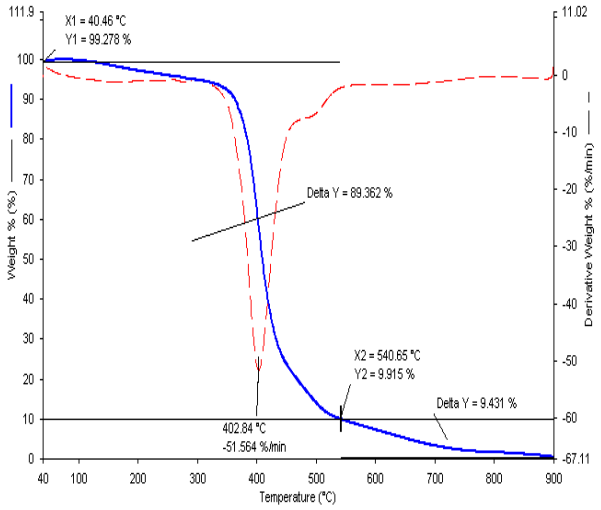

Figure 10. TGA thermogram of PLA

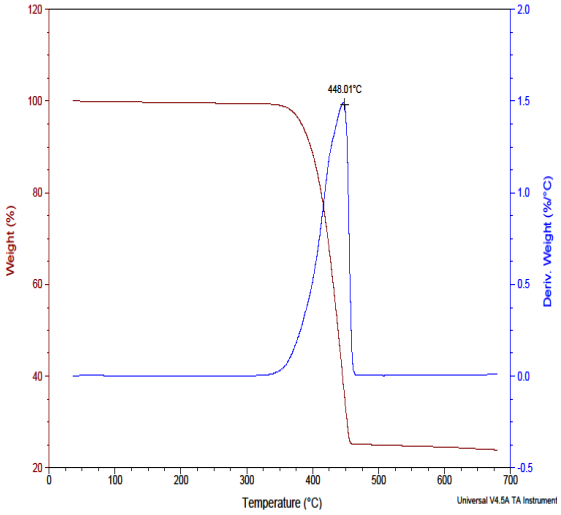

Figure 11. TGA thermogram of PLA+3%Nanosilica

Table 2. Thermal parameter of the prepared polymers

Sample No.	Decomposition Temp.C^0	Temp. of 50% weight loss C^0	Char Content % At 600 C^0	Rate of Decomposition % / min.
PLA	402	435	5	1.032
PLA-Nano silica	448	418	8	0.832

3.7. Tensile strength and Elongation of the PLA films

In order to assess the mechanical performance of PLA and PLA composite films, their tensile properties were studied. Figure 12. show the stress-strain curves of PLA Film. The effect of Nano silica loading on the tensile (strength, modulus, and elongation at break) are presented in Table 3., it can be observed that the tensile strength and modulus increased with filler content. This is probably because of better interfacial adhesion between the filler and the matrix by the van der Waals or induction interactions.

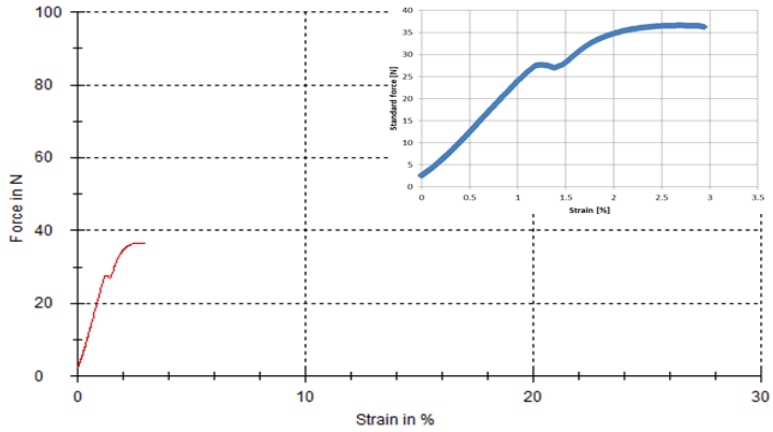

Figure 12. Stress-strain curve of PLA.

Table 3: Tensile properties of Nano silica-reinforced PLA as a function of silica content

Sample No.	Maximum Stress (Map)	Yong Modulus (Map)	Elongation at break %
PLA	19.8	986	2.9
PLA- 1% Nano silica	21.6	1011	2.7
PLA- 3% Nano silica	24.2	1045	2.6
PLA-5% Nano silica	31.8	1098	2.1

Table 4: Maximum water absorption of PLA Nanocomposites

Sample No.	**Mm value %**		
	25 C^0	**35 C^0**	**50 C^0**
PLA alone	0.513	0.973	1.310
PLA-1 % Nano silica	0.721	1.427	1.732
PLA – 3% Nano silica	1.427	1.756	2.216
PLA-5% Nano silica	1.732	1.987	2.712

3.8. Water absorption

Table .4, shows the maximum water absorption (*Mm*), The *Mm* values of all PLA/silica are higher than that of unfilled PLA at immersion temperature of 30°C, 40°C and 50°C. This indicates that the presence of hydroxyl group in Nanosilica is prone to water absorption, which can be associated with its hydrophilicity. The *Mm* values of Nanosilica filled PLA (with and without impact modifiers) at 35°C

and 50°C increased dramatically compared to the samples immersed at 30°C. It is suggested that at higher immersion temperatures (i.e., 35°C and 50°C), the swellable Nanosilica and the polymer chains became more flexible which create more free volume in PLA nanocomposites to enable more penetration sites for water molecules, and thus increase the *Mm* value. Figure 13.show different image of PLA.

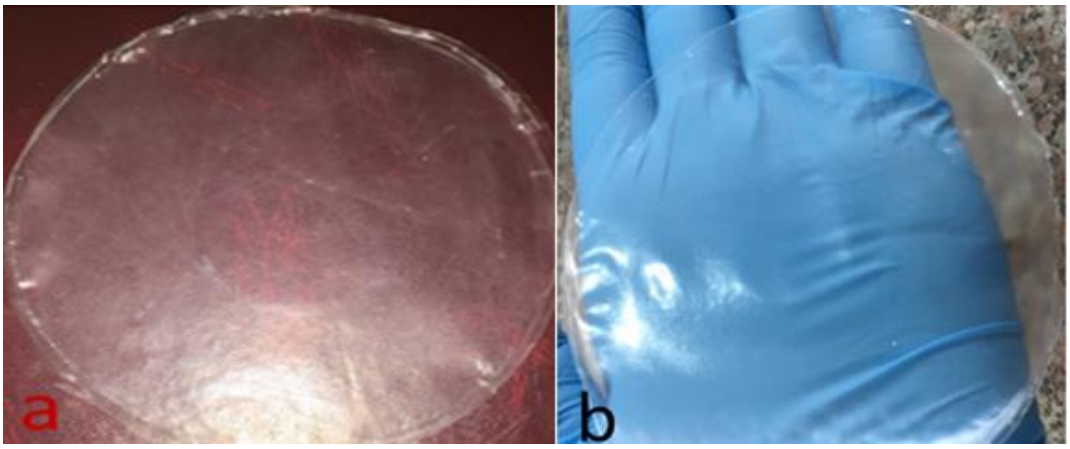

Figure.13: Image of, (a) PLA thin film alone, (b) PLA with Nanosilica film Conclusion

4. Conclusion

In this study lactic acid isolate and ,Then polymerized to Polylactic acid in acidic medium .FTIR and H-NMR used to characterized the product ,Thermal of PLA was evaluated using TGA and DSC techniques and from the result it has been found that the degree of crystallinity of PLA was 28% ,on the other hand composite thin film using Nanosilica was prepared and study of some mechanical properties the result shown that the tensile strength and modulus was increase with increasing percentage of Nanosilica.

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