Characterization of Mechanical and Thermal Properties of Biopolymer Nanocomposites

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***Abstract*— The research article presents the investigation of effect of nano filler material on the mechanical and thermal properties of biopolymer. For the preparation of research samples, solvent casting technique was used by dissolving pure polylactic acid (PLA) in chloroform solvent and nanoparticles (Clay) was added to the solution. The mechanical strength, morphology and thermal behavior of the PLA specimens were evaluated by using tensile test, Scanning Electron Microscopy (SEM), Fourier Transform Infrared spectroscopy (FTIR), thermogravimetric Analyzer (TGA), and Differential Scanning calorimetry (DSC). Tensile test shows significant improvement in load carrying capacity and ultimate strength of PLA/nano filler composite. Differential scanning calorimetric analysis shows, decrease in degree of crystallinity of these nanocomposites. Thermogravimetric analyzer (TGA) was used to measure the thermal weight loss of pure PLA and PLA with nano fillers. The Scanning electron micrograph (SEM) shows a good bonding between PLA and nano fillers. The nanoclay interlayer spacing was determined by X-ray diffraction.**

Keywords- Component; biopolymer, Polylactic Acid, nanoclay, chloroform, nanocomposite, Mechanical & Thermal Properties

I. INTRODUCTION

Polylactic acid is a biodegradable, biocompatible material widely used in food packing and biomedicine applications. It is a best material to replace non degradable polymer due to its transparent and eco friendly nature [1]. PLA is a very good biopolymer thermoplastic, produced from lactic acid monomer, obtained from fermentation of corn, potato, sugar cane etc. which degrades in shorter period of time (0.5 to 2yrs) compared to plastics, which takes (500-1000yrs) to degrade. PLA has good mechanical properties [2] and is soluble in most of the organic solvents such as Tetrahydrofuran, chlorinated solvents, benzene, Acetonitrile and dioxane [3]. It also known as a green polymer as it degrades into carbon dioxide and water. PLA replaces petrochemical plastics, due to its stiffness, good strength and processability. PLA has low toughness, high production cost, brittleness, poor water vapor/gas barrier properties and undesirable thermal stability making inappropriate for certain applications. To overcome these restrictions, many approaches have been adopted in developing composite and nanocomposites with organic and inorganic fillers. Polymer/clay nanocomposites have gained more interest compared to conventional composites because they often exhibit considerable improvement in mechanical, thermal, physical properties at low filler contents [4].

Various candidate fillers for PLA matrix are fiber-like natural fillers and other farming waste. Earlier studies have shown that presence of the natural fillers in eco-friendly polymers may sturdily accelerate biodegradation process and also, existence of natural filler increases water absorption, which highly influences biodegradation process of the composites, in comparison to neat polymer. The addition of fillers to PLA makes it brittle and less permeable to gases. The introduction of a few percent of nano fillers, such as layered alumino silicate clays, was known to enhance various polymer properties such as the stiffness/toughness. In the present research the developed composite specimens were subjected to mechanical and various thermal tests to understand the characteristics of PLA nano-filler composites.

Nano particle fillers

The majority application of PLA has shown enhanced properties by the reinforcement of nano-structures fillers such as carbon nanotube, nanoclays and nanoparticles etc. These reinforcements enhance the modulus of elasticity, hardness and tensile strength of material [8]. It has been reported that adding of nanoparticles to base polymers confers enhanced properties that make them usable in automotive, construction and medical areas. PLA nanocomposites have been shown to display improved tensile strength and young’s modulus compared to Pure PLA. Nanocomposites are a class of composites in which the dimensions of the reinforcing material are in the order of nanometers. Because of this nanometer size characteristic of fillers in these nanocomposites have better properties than the conventional composites due to maximizing the interfacial bond. Several nano filler materials such as calcium carbonate, ceramic, clay, graphite, kaolin, mica etc., has been tried out to obtain nano composite materials. Nano clay was a good contender for use as a filler material due to its notable increase in stiffness (elastic modulus), thermal and dimension stability, good barrier properties to gases and vapours, toughness. The introduction of clay filler initiates the interaction with the polymer matrix and based on the interaction, it can form exfoliated and intercalated structures.

II. MATERIALS AND METHODS

PLA with a density of 1300 kg/m^3, melting point of 150-170°C and molecular weight (M_W) of 197000 g/mol. PLA resins were dried in a vacuum oven at 60 °C for 24 hours before use. Organically modified fillers as Nano reinforcement, Solvents was used to dissolve PLA and to swell and disperse Nano reinforcement, Glycerol was used to grease the molds prior to casting

Method of preparation:

- In the first step of preparing the specimen, 2gms of PLA were dissolved in 100ml of chloroform solution and it is poured into a glass beaker.
- In the second step, the solution was stirred vigorously on a magnetic stirrer for dissolving the PLA into the solution for 5hrs. At the same time nano clay of 1gm was added into the solution mixture.
- In the third step, Dissolved solution was poured onto a greased glass molds and allowed to dry for 24hrs at room temperature

Preparation of films

PLA and PLA-based nanocomposites films were prepared using a solvent casting method as shown in fig 1. 2gms of PLA was dissolved in 100 mL of solvents while agitating vigorously for 5 hours at room temperature (25°C) and poured on to the glass molds, dried for 24hours to form the composite films. The Ethylhexylglycerin was used as surfactant, which helps in releasing the composite films from the glass molds. For the preparation of PLA nanocomposite films, a predetermined amount of fillers was dispersed in the solvent by vigorous stirring for 5 hours with a magnetic stirrer. They were then homogenized at 2,000 rpm for 45 min followed by sonication for 30 min at room temperature. The filler solutions were mixed with the previously prepared PLA solution and then stirred for 15 min with a magnetic stirrer. The solutions were homogenized at 2,000 rpm for 45 min and sonicated for another 30 minutes, then casted onto greased glass molds. After drying at room temperature for 24 hours, all PLA films were further dried at 60°C in a vacuum dryer to remove the remaining solvent to prevent its plasticizing effect.

Fig 1: PLA Film Preparation

Material Properties

a) Mechanical Properties

Universal Testing Machine as shown in Fig 2, was used in the present investigation to predict mechanical properties of the developed composite films as per ASTM D882. Initial grip separation was set at 200 mm and cross-head speed at 10 mm/min. The elongation was measured based on the percentage change of length in the gauge length when load was gradually applied. From the Load versus Elongation plot, the average values obtained from eight trails, the Tensile strength (TS), Elastic modulus (E-M) in the linear range were calculated.

Fig 2: tensile test equipment

b) Thermal Properties

Thermal behavior of the specimens was evaluated by DSC (Differential Scanning Calorimetry-DSC 200) as shown in Fig 3. Samples of 4-5 mg were sealed in standard aluminium dishes, using a sealed empty aluminium dish as the reference sample. The samples were exposed to varying temperatures from -10 to 200°C. Degree of crystallinity (x%) was calculated by using a value of 93 J/g for the heat of fusion of the 100% crystalline PLA. thermal behaviour of the specimens was evaluated by TGA (Thermal Gravetometric Analysis-TGA 50) as shown in fig 4,

Fig 3: Differential Scanning Calorimetry

Fig 4: Thermal Gravetometric Analysis

c) Film Microstructure

Scanning Electron microscopy was used to determine the micro structure of composite film. It is an additional test aims to correlate with the tensile test result and thermal degradation test. Samples were prepared using standard techniques, mounted on aluminium tubs, and sputter coated with gold (100 Å) at 25-30kV.

Figure 5: Scanning Electron Microscope

d) X Ray Diffraction Calorimetry (XRD)

XRD (X Ray Diffraction Calorimetry) patterns were obtained from X-ray Diffractometer equipped with radiation Co Kα beam at a voltage of 40 kV and current of 30 mA. At room temperature, relative intensity was measured for diffractive angle ranging from 2 to 45° with 1°/min angular speed at an interval of 0.02. The samples were cut in 3×3 mm^2 rectangles and placed on a glass plate, and the setup was placed inside the chamber of the apparatus.

FWHM allows researchers to obtain important information about the surface state of materials, which is related to grain distortion, dislocation density and residual stresses. On increase in stacking faults & structural disorders, widens the XRD Peaks. Increase in hardness & density of point defects, affects the crystallinity and grain boundary mobility, which in turn causes a linear increase in the full width at half max (FWHM) of XRD Peak. Presence of tensile stress in material causes increase in FWHM.

$$\mathrm{FWHM}\ (2\theta) = (K\lambda/L\cos\theta)$$

Fig 6: x ray diffraction Equipment

e) FT-IR Characterization

The interactions of polymer composites can be identified by means of FT-IR Spectra (Fourier Transform Infra Red Spectroscopy) as shown in **Error! Reference source not found.**.. The neat polymer with the completely immiscible blends will not yield notable FTIR spectrum. However, if two polymers are compatible, distinct chemical interaction and hydrogen bonding exists between their chains, causing the appreciable change in FT- IR spectra.

Fig 7: FT-IR Spectroscopy

Results & Discussion

a) Mechanical Properties

Mechanical Properties reflect the durability of films and their ability to enhance the mechanical characteristics. Mechanical Properties of PLA nanocomposite films with various clay contents resulted from the tensile test are shown in graphs.

Fig 8: Pure PLA Load Vs Displacement Curve

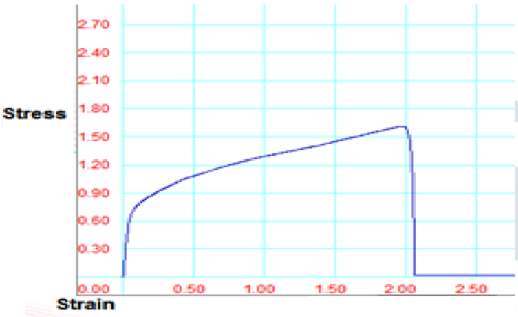

Fig 9: Pure PLA Stress Vs Strain Curve

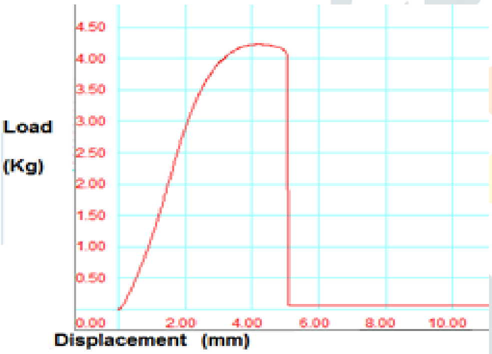

Fig 10: PLA Nanocomposite Load Vs Displacement Curve

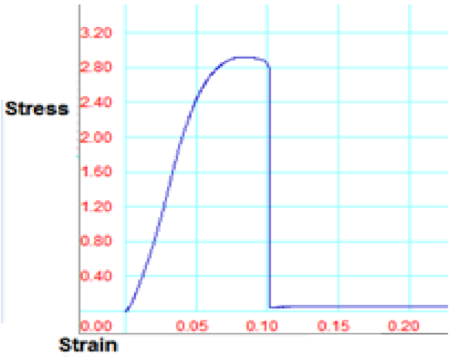

Fig 11: PLA Nanocomposite Stress Vs Strain Curve

Figure 8 shows the curve of load and displacement of pure PLA film and Figure 9 shows the curve of tensile stress and strain of pure PLA film. Figure 10 shows the curve of load and displacement of PLA nanocomposite film and Figure 11 shows the curve of tensile stress and strain of PLA nanocomposite film. Comparing the above curves, It is observed that the ultimate tensile stress and load carrying capacity of the PLA composite has increased with the addition of nano filler clay. In addition the brittleness of the composite has also increased. Which was predicted due to the formation of Hydrogen bonds between PLA and nanoclay.

Table 1: Results of Tensile Test

Parameters	Pure PLA	PLA Nanocomposite
Peak Load (Kg)	2.101	4.226
Elongation at Peak Load (mm)	99.13	4.22
Percentage Elongation (%)	198.26	8.44
Yield Strength (N/mm2)	15.794	28.66
Ultimate Modulus (Mpa)	189.997	666.68

b) *Thermal Properties*

Thermal behavior of specimens was evaluated by DSC and TGA analysis. Thermal conductivity of all crystals was measured using hot wire method and thermal stability of films are determined. Thermal analysis of PLA with the addition of nano filler clay have better thermal properties, which makes these composites suitable for food preservation/packaging.

i. *Differential Scanning Calorimetry (DSC) Property*

Glass transition temperature (Tg), Melting temperature (Tm) and their degree of crystallinity were analysed using DSC. The Tg of the PLA nano filler composite shows the marginal improvement, where the material undergoes structural transition from an amorphous solid state (glassy state) to a viscous state (rubbery state). The Tm values were found to be similar in range for PLA/clay nanocomposites and for neat PLA.

Degree of crystallinity of PLA matrix decreases with increasing the amount of clay content. Degree of crystallinity is calculated by,

$$\mathbf{X\% = 1.63 + (1.27 \times \Delta H)}$$

Where X% is Degree of crystallinity and ΔH is Heat flow

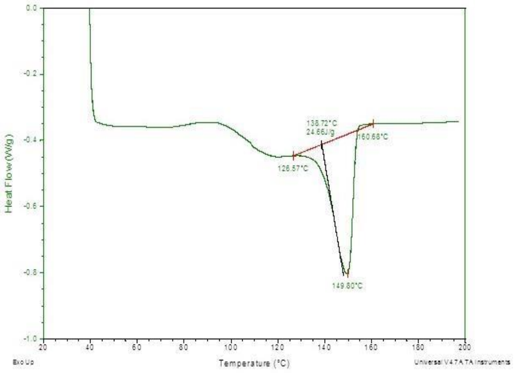

Fig 12: DSC graph for pure PLA

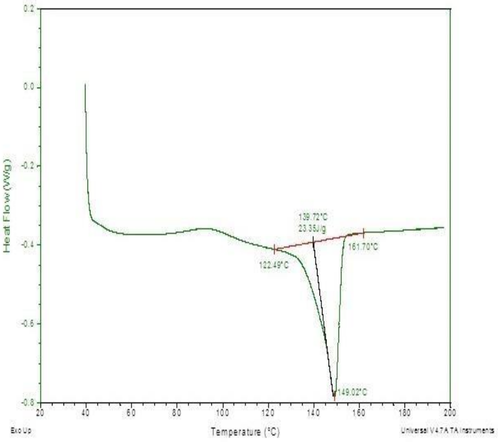

Fig 13: DSC graph for PLA Nanocomposite

The results of Tg, Tm and crystallinity percentage of neat PLA and PLA/clay nanocomposites were shown in Fig 12 and Fig 13 and also presented in the table 2.

Table 2: Comparison of DSC Property

Parameters	Pure PLA	PLA Nanocomposites
Heat Flow (J/g)	24.66	23.35
Tg (°C)	138.72	139.94
Tm (°C)	149.80	149.02
X %	48.77	36.81

Thermal analysis of PLA and its nanocomposites were heated up to 200°C and glass transition temperature and melting temperature were predicted. There is no significant change in T_g and T_m. Degree of Crystallinity decreases for nanocomposite.

ii. Thermogravimetric Analysis (TGA) Property

Thermal conductivity of all crystals were measured using hot wire method. By this analysis Thermal Stability of films are determined. Organic modified clays begins to degrade around 180° C and with stand Temperature up to 450°C, where as pure PLA start degrade around 280°C - 300°C and with stands Temperature up to 400°C. Out of 10 mg of polymer film, in TGA analysis, 1.149 mg weight loss occurs at temperature 158.71°C and 9.470 mg of weight loss takes around temperature of 414.82°C for the clay filled PLA composite.

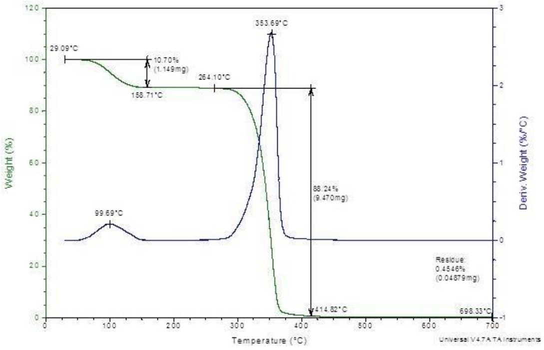

Fig 14: TGA curve for Pure PLA

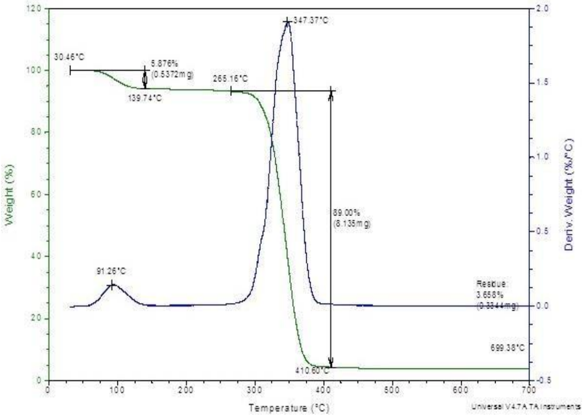

Fig 15: TGA graph for PLA Nanocomposites

The properties obtained from TGA for the Pure PLA and PLA nanocomposites were shown in Figure 14 and Figure 15 respectively and the results were presented in the table 3,

Table 3: Comparison of TGA Property

% of Weight Loss	Temperature range for Pure PLA (°C)	Temperature range for PLA Nanocomposites (°C)
10	132.15	175.37
20	338.73	347.73
30	349.80	360.48
40	357.13	368.79
50	362.99	374.44
60	368.10	379.92
70	372.85	385.32
80	377.50	391.22
90	382.46	465.58

On comparing the results of both graphs and table, with the addition of clay filler, degradation starts at 180°C and completes at around 465C. which shows PLA/Nanofiller clay composite have excellent thermal withstanding capacity.

Film Microstructure

Micro Structural study of nano composites gives relevant information about the arrangement of components in a polymer. SEM (Scanning Electron Microscopy) is the basic analysis for film micro structure.

Pure PLA has a uniform structure with holes and cracks as shown in Figure 16, which confirm the high WVP (Water Vapor Permeability) of this bio Polymers.

Micro graphs of PLA/Clay nanofiller composite shows a good distribution and interfacial adhesion of nano particles in polymer matrix which is evident from the figure 17. PLA/Clay nanofiller composite microstructure shows dense structure.

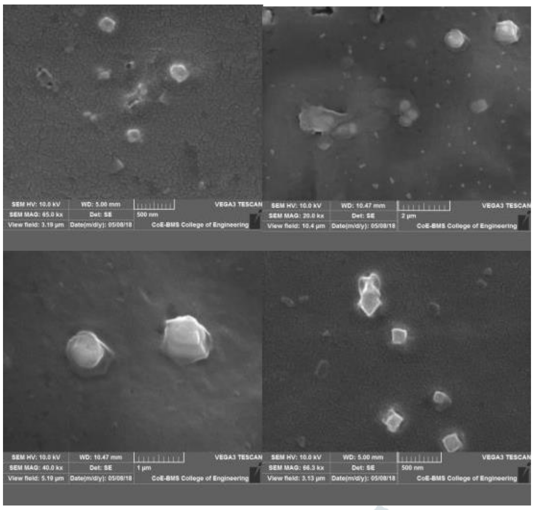

Fig 16: SEM images for Pure PLA

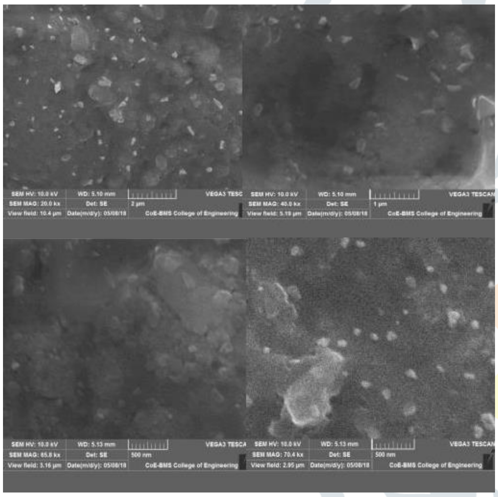

Fig 17: SEM images for PLA Nanocomposites

Polymers containing clay fillers have exhibited uniform distribution and good adhesion to polymer matrix. The pure PLA polymer structure has uniform structure containing holes and cracks.

c) X-Ray Diffraction (XRD) Pattern

XRD results shows that the nano composite films with different filler concentrations have exhibited variation in intensity of the diffraction peaks. XRD Patterns, indicating polymer chains have penetrated the gallery and clay clusters lose their layered identity and were separated into single sheets with in the continuous polymer phase. This may be due to the high affinity between polymer and clay.

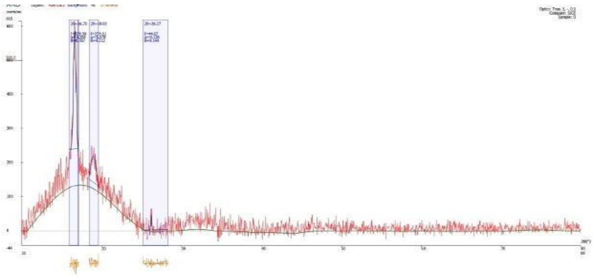

Fig 18: XRD Pattern for Pure PLA

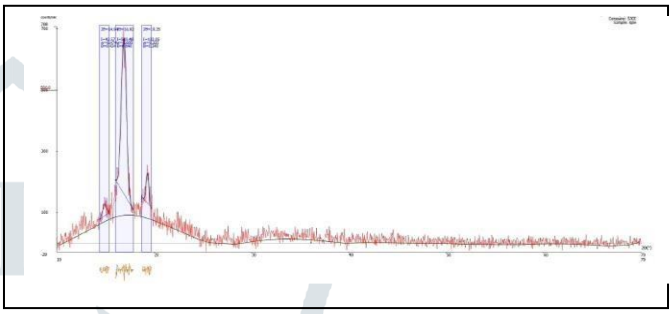

Fig 19: XRD Pattern for PLA Nanocomposites

The Pure PLA and nano composites based on PLA where characterized by X-Ray diffraction as shown in figure 18 and Figure 19 respectively to study the effect of incorporation of nano reinforcement and its content on the structure and crystallinity of PLA.

Incorporation of filler in polymer matrix causes an increase in intensity and sharpness of PLA’s peaks, which can be attributed to improvement of matrix crystallinity of PLA. Peak reference of XRD for Pure PLA and PLA Nanocomposites are shown in Table 5and Table 6 respectively.

Table 4: Peak Reference of XRD for Pure PLA

Pos. [°2θ]	Height [cps]	FWHM Left [°2θ]	d-spacing [Å]	Rel. Int. [%]
16.7	359.5	0.3993	5.30439	100.00
19.0266	259.6	1.5776	4.66066	19.37
26.2732	44.7	0.1364	3.38929	16.65

Table 5: Peak reference of XRD for PLA Nano Composites

Pos. [°2θ]	Height [cps]	FWHM Left [°2θ]	d-spacing [Å]	Rel. Int. [%]
16.70	359.5	0.3967	5.3044	100.00
19.03	259.6	1.5776	4.6607	19.65
26.27	44.7	0.1364	3.3893	10.92

d) Fourier Transform-Infra Red (FT-IR) Characterization

Interaction of polymer composites can be identified by means of FTIR Spectra as a result; FTIR can identify segment interactions and provide information about the phase behavior of polymer composite. The results indicated that hydrogen bonds forms among hydroxyl groups of the cellulose surfaces and terminal hydroxyl, terminal carboxyl and carbonyl groups of PLA.

FT-IR Peak Spectrum of Pure PLA and PLA Nanocomposites were shown in Figure 20 and Figure 21 respectively. Results were tabulated in Table 6 and Table 7,

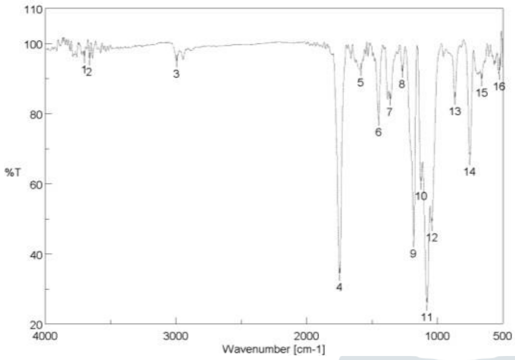

Fig 20: FT-IR Peak Spectrum of Pure PLA

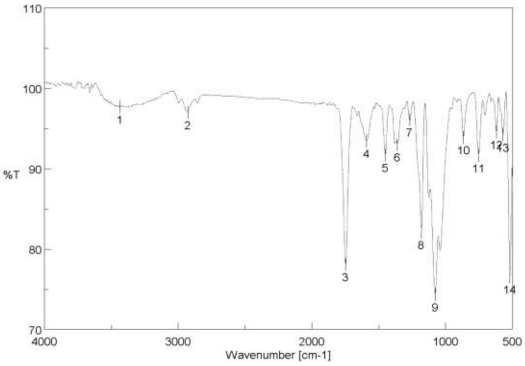

Fig 21: FT-IR Peak Spectrum of PLA Nanocomposites

Table 6: FT-IR Peak Spectrum of Pure PLA

Peak	X (cm-1)	Y (%T)	Peak	X (cm-1)	Y (%T)	Peak	X (cm-1)	Y (%T)
1	2999.46	95.1	6	1181.26	36.11	11	755.26	76.5
2	1749.54	34.0	7	1127.93	54.52	12	699.69	90.5
3	1453.67	80.9	8	1082.48	22.3	13	667.85	89.47
4	1382.58	82.6	9	1045.16	56.77	14	623.95	89.8
5	1360.03	83.0	10	869.28	87.48	15	607.68	89.52

Table 1: FT-IR Peak Spectrum of PLA Nanocomposites

Peak	X (cm^{-1})	Y (%T)	Peak	X (cm^{-1})	Y (%T)	Peak	X (cm^{-1})	Y (%T)
1	2990	97.1	6	1182.82	62.13	11	706.15	88.97
2	1756.08	65.31	7	1131.49	70.48	12	694.72	92.51
3	1455.0	90.53	8	1084.68	54.3	13	656.51	93.43
4	1383.15	91.76	9	1043.63	68.94	14	623.92	87.59
5	1360.31	90.39	10	870.71	91.5	15	608.17	86.73

If two polymers form completely immiscible blends, then there are no appreciable changes in the FT-IR spectra, when compared with those of each component. However, if two polymers are compatible, a distinct chemical interaction exists between their chains, causing the IR spectra of the composites to change.

CONCLUSION

In the present work, Mechanical and Thermal behavior of PLA and PLA nanocomposites were studied.

- In tensile test, PLA Nanocomposite shows a increased load carrying capacity and yield strength which results in higher young's Modulus. But decrease in percentage of elongation.Results in brittleness of theseccomposites compared to pure PLA.
- Differential scanning calorimetry (DSC) shows a decrease in heat flow rate with increase in clay content. Glass Transition (T_g) temperature increase with decrease in melting temperature (T_m) and overall degree of crystallinity decreases with addition of nanoparticles into a PLA.
- Thermogravimetric Analysis (TGA) shows that PLA with nano particles starts its degradation at 180° C and major degradation (% Weight loss) takes place around 465^0 C. Which shows the clay content polymer has long withstanding temperature with respect to time/heat flow.
- Scanning Electron Microscopy (SEM) shows, a polymer containing clay content will give uniform distribution and adhesion.
- X-ray Diffraction, with different filler concentrations has exhibited variation in intensity of the diffraction peaks. XRD Patterns, indicating polymer chains have penetrated the gallery and clay clusters
- FTIR analysis indicated the formation of some polar interaction, resulting in enhanced tensile property of a nanocomposite.

REFERENCE

[1] Cheolho Lee and Sungyeap Hong **“**an Overview of the Synthesis and Synthetic Mechanism of Poly (Lactic acid)” volume 2, issue 4 /10.4172/2329-6798.1000144

[2] A Porras, A. Maranon “Development and characterization of a laminate composite material from polylactic acid (PLA) and woven bamboo fabric” composites: part B 43 (2012) 2782-2788 https://doi.org/10.1016/j.compositesb.2012.04.039

[3] Mousam Choudhury, smita mohanty, sanjay nayak “Effects of different solvents in solvent casting of porous PLA scaffolds – in Biomedical and tissue engineering applications”. J Tissue Sci Engg 6: 142. Doi:104172/2157-7552.1000142 https://doi.org/10.1166/jbt.2015.1243

[4] Reza Arjmandi, Azman Hassan, Stephen J. Eichhorn, M.K. Mohamad Haafiz, Zainoha Zakaria and Faisal Amri Tanjung “ Enhanced ductility and tensile properties of hybrid Montmorillonite/cellulose nano whiskers reinforced polylactic acid nanocomposite” April 2015, Volume 50, Issue 8, pp 3118–3130

[5] A. A. Yussuf • I. Massoumi • A. Hassan “Comparison of Polylactic acid/kenaf and polylactic acid/Rise husk Composites: the infulence of the natural fibers on the mechanical, Thermal and biodegradability properties” J Polym Environ (2010) September 2010, Volume 18, Issue 3, pp 422–429

[6] Suryani, Harry Agusnar, Basuki Wirjosentono, Tenku Rihayat and nurhanifa “ Improving the quality of biopolymer (poly lactic acid) with the addition of bentonite as filler” IOP Conf. Series: Materials Science and Engineering **222** (2017) 012008 http://iopscience.iop.org/journal/1757-899X

[7] Mostapha EI Jai, Iatimad Akhrif, Laila mesrar, Raouf Jobrane “mechanical characterization of new micro-composites composed by natural clay matrix and PEG 6000 fillers” IOP Conf. Series: Materials Science and Engineering **353** (2018) 012015 http://iopscience.iop.org/volume/1757-899X/353 Volume 353, conference 1

[8] Aswini Kumar mohapatra, smita mohanty, “ Modeling of the mechanical properties of polylactic acid/clay nanocomposites using composite theories” Int J Plast Technol (December 2011) 15(2):174–187 Int J Plast Technol (2011) 15: 174. https://doi.org/10.1007/s12588-012-9022-8

[9] Avérous, L. (2008), “Synthesis, Properties and Applications, In Monomers, Polymers and Composites from Renewable Resources”, Poly Lactid Acid, 21, hal 433-435 https://doi.org/10.1016/B978-0-08-045316-3.00021-1

[10] M.N. Azmi, S A Rafeq, R.Nadlene, M.A.M.Irwan, A.M.Aishah, “tensile and harness properties of kenaf-PP/PLA Composite filled nanoclay”, 3rd International Conference on Engineering and ICT (ICEI2012), melaka, Malaysia, 4-5 April 2012