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Studies on Modifications of PLA Films with Nanographene Clay and Silane Treated Hydrous Clay

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Abstract: Poly (lactic acid) gains a great attention among the researchers in the recent years due to its potential to replace traditional petrochemical based polymers. Some of its properties such as barrier properties, heat resistance etc need to be modified for various applications. One of the methods to modify PLA is adding clay as filler to PLA. In the current work is the study of specially modified Nano Graphene clay and Silane treated hydrous clay on various physical and chemical properties of PLA films. Characterization methods were conducted like FTIR (Fourier Transform Infrared Spectroscopy), OTR (Oxygen transmission).
Keywords: Graphene, Treated clay, Polylactic acid, hydrous clay etc.

I. INTRODUCTION

PLA gains a great attention in many fields because of its biocompatible and biodegradable properties. But it has some defects such as low strength, Inherent brittleness, low heat deflection temperature, poor melt strength etc which affect its application and processing performance.

PLA has poor impact properties compared to more traditional polymers like crystalline polystyrene. And also PLA has a glass transition temperature of about 55°C and a melt temperature of about 165°C [1]. PLA lose its stiffness at temperature above TG. Therefore due to the low heat deflection temperature, the high temperature application of PLA such as rigid packaging for hot beverages or in the automotive industry is limited.PLA has a low crystallization rate ,whereas a high level of crystallinity is desirable in finished products as it dictates most of the mechanical and thermal properties[2] .

High water vapour and gas permeability makes PLA unsuitable for the long term storage of liquid products, moisture-sensitive products or carbonated drinks. To make PLA a suitable packaging material for this type of product, its barrier properties need to be improved [3].

Besides the chemical structure of PLA lacks reactive functional groups and it has a poor hydrophilicity which affects its application in clothing, medical supplies, and other fields [4]and its degradation rate needs to be controlled. Therefore it is necessary to modify PLA.

Clay is a natural material consisting mainly of fine-grained minerals, which behaves as plastic substances with sufficient water content and hardens when dried or fired [5]. The minerals found in clay are usually silicates less than 2 micrometers in size. There is a lot of clay on the surface of the earth. They form the rocks known as shales and are the main component of almost all sedimentary rocks [6]. The small particle size and unique crystal structure give clay materials special properties, including cation exchange capacities, plastic wetting properties catalytic ability, low permeability and swelling behavior.

Clay minerals are most often formed during long-term chemical weathering of silicate rocks. They can also form locally as a result of hydrothermal activity [7] .There are different types of clays are available. The main groups of clays include kaolinite, montmorrillonite-smectite, Chlorite, talc and pyrophylit. This category includes about 30 types of pure clays , but most natural clay are mixtures of these types with other weathered minerals.

The objectives of the present work are to prepare PLA/Clay films with different clay loading., to study and compare the properties of PLA/Clay nano composite films with neat PLA and compare and study which clay improves the properties of PLA films the most.

II. EXPERIMENTAL

A. Materials Used

PLA were purchased from Nature Tec India Pvt Ltd, Chennai. Nano graphene clay and silane treated hydrous clay under the commercial names Nanophene and Amshine were obtained from EICL Ltd, Veli, and Trivandrum. Other chemicals like Chloroform, Hydrochloric acid, calcium chloride and sodium chloride were purchased from NICE Chemicals (P) LTD; Kochi and sodium hydroxide were purchased from Labogens , India

B. The Process

A pellets were dissolved in chloroform. The resulting solution cast into thin films. Different percentage composition of nano graphene treated clay and silane treated clay were incorporated into the PLA solution and a magnetic stirrer was used to improve the homogeneity of the solution. The homogenous PLA/Nano clay composites were then casted into thin films. Blends of the two fillers were also prepared and cast into films.

The film was characterized in order to evaluate its various properties. Film Thickness, Yield, Density, Water absorption, Heat ageing, Acid and base resistance, water permeability, Membrane properties, Water vapour permeability , OTR (using PERME VAC-VBS) , DSC (Q 20 Moduled DSC), FTIR (PerkinElmer series) were carried out. Membrane properties were estimated using salt solutions.

III. RESULTS AND DISCUSSION

A. Physical And Chemical Properties

Thickness of the PLA/Nanographene, PLA/Silane treated hydrous clay, PLA/Blend clay composite films were noted by taking the average value and it is given in the table 1 below. Results shows that, as the amount of filler increases film thickness increases slightly in all types of fillers. Similarly a marginal increase in density also observed in all types of films as the fillers are having more density than the polymers.

Table 1 Physical property of the films casted

	Thickness (microns)			Density , gm/cm^3		
(%) Filler	Graphene	Silane	Blend	Graphene	Silane	Blend
0	313			1.24		
0.5	321.66	622.66	243.33	1.30	1.25	1.27
1	325.32	624.33	438.32	1.38	1.26	1.28
1.5	336.66	639.33	622.33	1.42	1.28	1.33
2	392.56	651.25	625.33	1.43	1.31	1.37
2.5	433.33	653.66	633.33	1.45	1.32	1.40

B. Heat Ageing

Figure1 shows the heat ageing results. It is the difference in weight before and after heat aging. The results show that the difference decreases as the amount of fillers increases. PLA has poor heat resistance because of its high mobility near its glass transition temperature. PLA films shows significant weight loss when it was heated at a temperature of about 80°C. Compare to neat PLA, PLA/Nano graphene clay composite films and PLA/Blend films shows less weight loss when heated than PLA/Silane treated hydrous clay composite films. It is due to the high thermal conductivity of Nano graphene clay. Among these films, blend clay loading of PLA shows more decrease in weight loss than other PLA film. Among all fillers graphene based films shows a steady decrease value. This indicates more stability of graphene fillers.

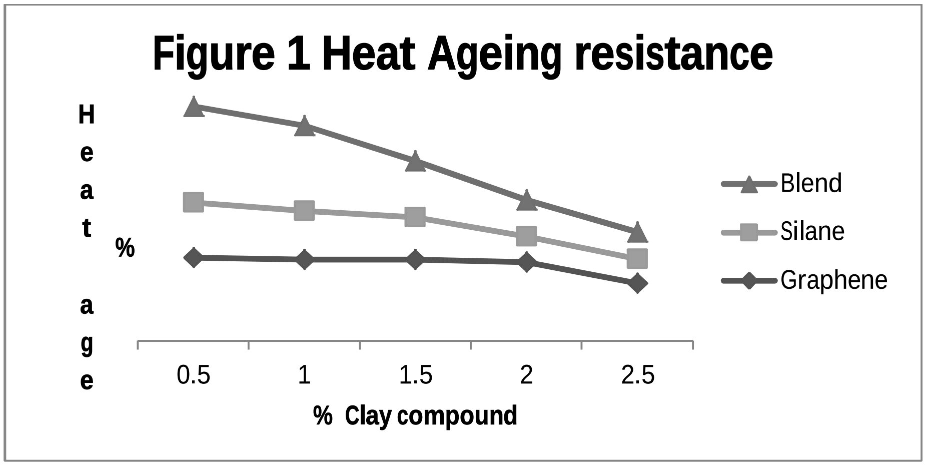
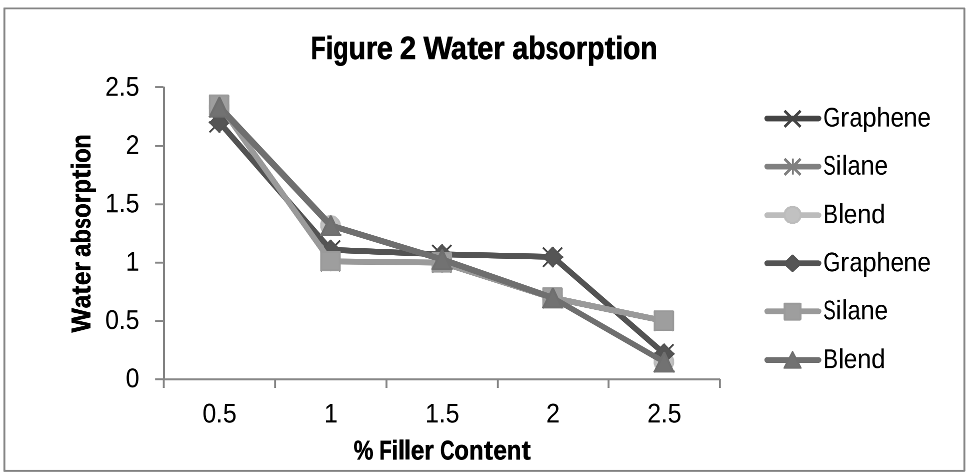


Figure 1 Heat aging resistance of PLA films with clay

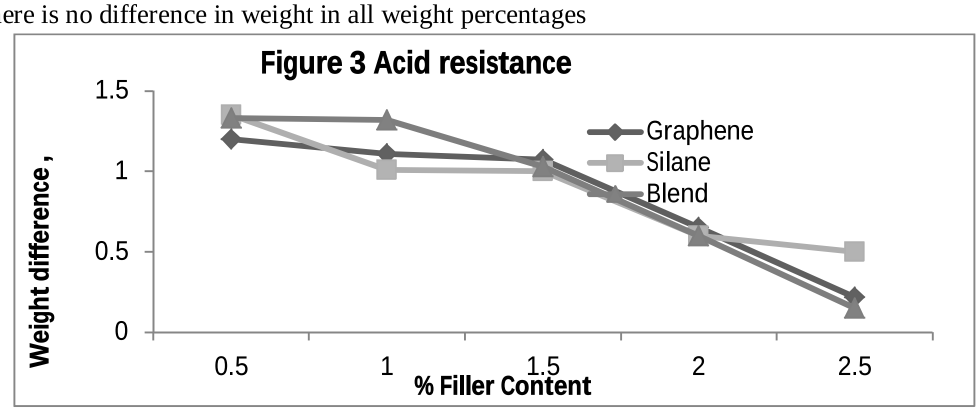
C. Water Absorption

Figure 2 shows the water absorption for neat PLA and PLA/Clay composite films. The result exhibits that the water absorption for the PLA/Nanographene clay composite film is decreasing as compared to neat PLA, PLA/Silane treated hydrous clay and PLA/Blend filler films. PLA/Silane treated hydrous clay composite shows little water absorption and on further adding of clay shows no water absorption. It is due to the reduction in water permeation property of Nanographene clay and silane treated hydrous clay.



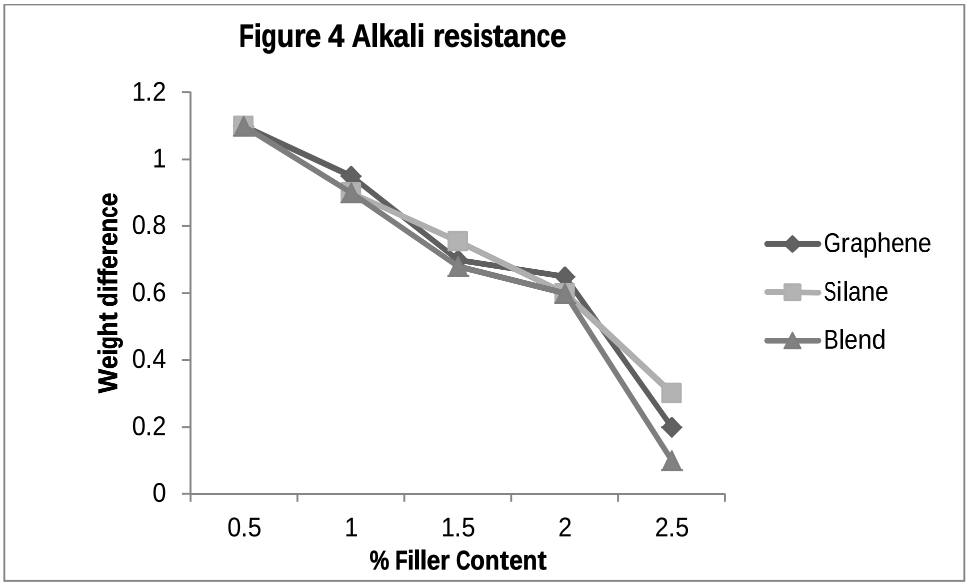
D. Acid Resistance

Figure 3 shows acid Resistance for neat PLA film, PLA/Silane treated hydrous clay, PLA/Nanographene clay and PLA/Blend films obtained was that there is no difference in weight in all weight percentages

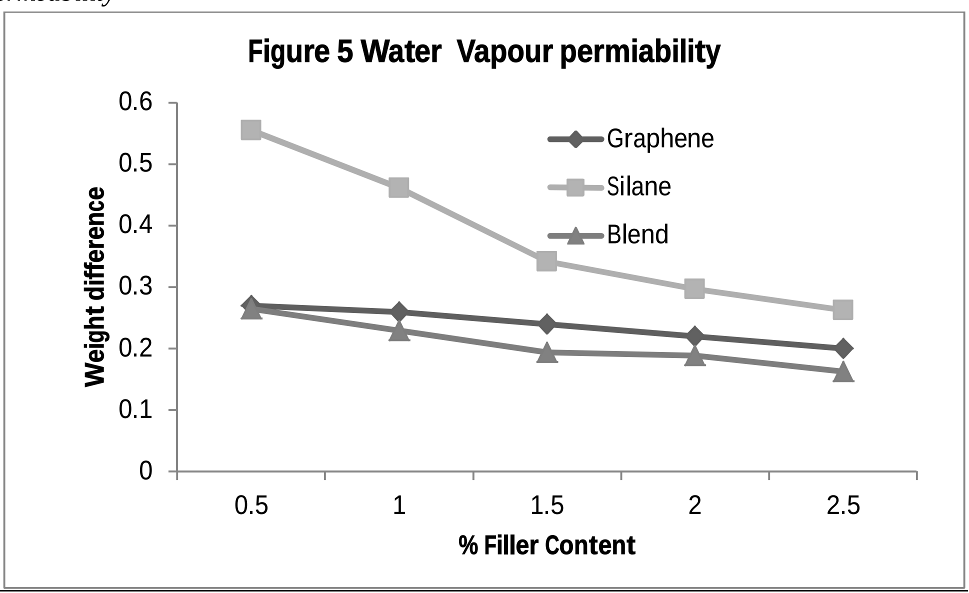


E. Alkali Resistance

Figure 4 shows base resistance for neat PLA film, PLA/Silane treated hydrous clay, PLA/Nano graphene clay and PLA/Blend films result indicates that, Neat PLA, PLA/Nano graphene clay and PLA/Silane treated hydrous clay composite films are resistant to sodium hydroxide. This is due to the comparatively stable nature of PLA towards bases.



F. Water vapour Permeability



The result shows that (figure 5) the water vapour permeability for the PLA/Blend is less than that of pure PLA and it showed a trend of increase in the weight difference up to 1.5% clay loading and then the weight difference decreases. The water vapour permeability is very less in 0.5% clay loading of PLA/Blend films.

The water vapour permeability of PLA/Nano graphene clay composite films showed an increasing trend up to 1% clay loading and then it decreases and low water vapour permeability is shown at 0.5% clay loading. Except at 1% clay loading, the water vapour permeability of PLA/Nanographene clay composite films are less that of pure PLA. This is due to the ability of nano graphene clay to reduce water vapour permeability. The water vapour permeability of PLA/Silane treated hydrous clay showed a trend of decreasing up to 1% clay loading and then it increases.

Silane treated hydrous clay modify the water vapour barrier property of PLA upto 1.5% clay loading only. Adding further amount of clay increases the water vapour permeability of PLA films. Comparing to the three PLA/Clay composite films, PLA/Blend composite films shows high water vapour barrier properties.

G. FTIR Analysis

FTIR SPECTRA of PLA/Nano graphene clay composite film of 1.5% clay loading (figure 6), shows absorption bands attributed to C=O stretching at 1747.5 cm^{-1} which is the backbone of PLA chain. The peak corresponds to stretching of C-H bond is found at 2853.13 cm^{-1} and C-O-C stretching is found at 2853.13 cm^{-1}. The peak revealed at 1081.67 cm^{-1},1382.7 cm^{-1} and 1454.67 cm^{-1} establishes the O-H stretching, symmetric and asymmetric C-H vibrations in the $CH(CH_3)OH$ end groups of PLA respectively. Nano graphene clay is a premium grade graphene composite developed as a performance filler in rubber and polymer applications. And Graphene is a crystal with flat mono atomic graphite sheets composed of sp^2 hybridized carbons arranged in a 2D hexagonal honeycomb lattice. There are no significant peak corresponds to graphene in FTIR [8].

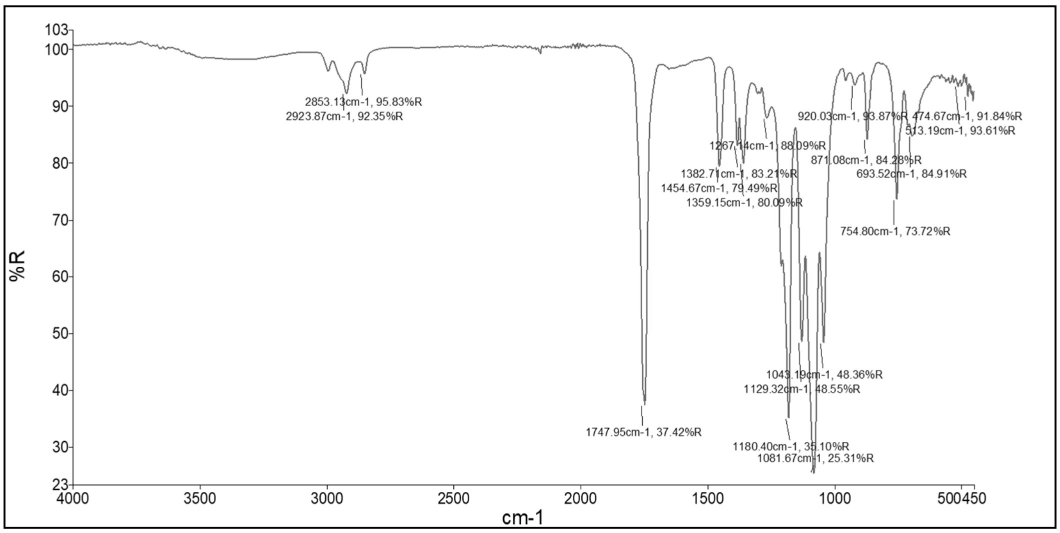


Figure 6 FTIR spectrum of PLA with Graphene clay 1.5 % loading

H. DSC Analysis

DSC result of the PLA/Nano graphene clay composite film of 1.5% clay loading is shown in the figure 7. The exotherm observed with peak maxima at 156.65°C was attributed to the melting temperature (T_m) of PLA/Nano graphene clay composite.

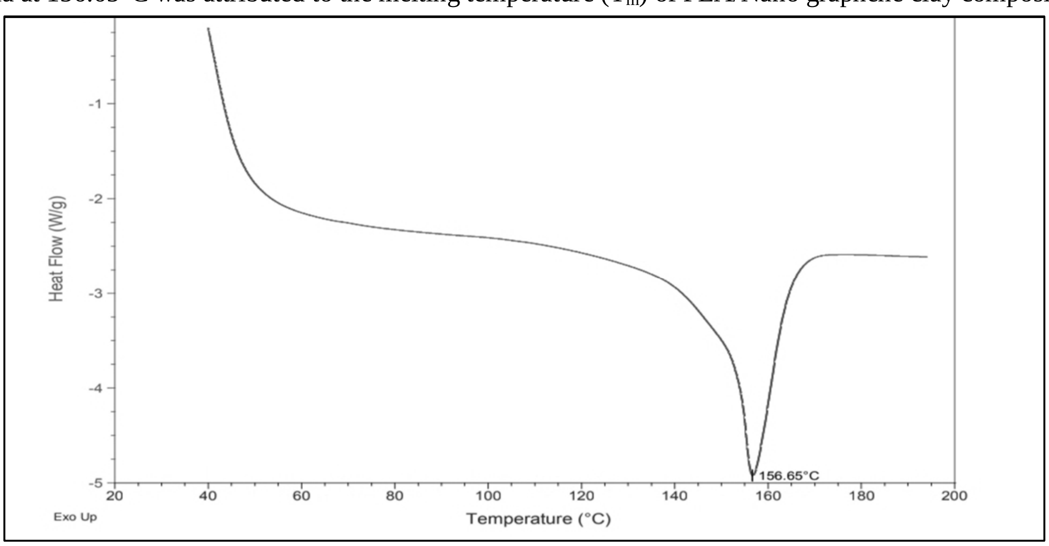


Figure 7: DSC GRAPH

I. OTR Analysis

The OTR results were shown in Table 3 .The oxygen transmission rate of PLA/Nano graphene clay composite film was found to be decrerasing as the filler laoding increases. The average oxygen transmission rate of neat PLA was 76.6 $cm^3/m^2/24$ hr [9]. The presence of Nano graphene clay results in the reduction of oxygen transmission. The reduction of OTR from the addition of clay was due to the decrease in polymer chain flexibility [10]. So nano graphene clay improves the oxygen barrier property of PLA, which has an important role in packaging.

Table 3 OTR analysis of PLA composite films.

Sample (PLA/Nano graphene)	Temperature(°C)	Humidity(%RH)	Oxygen transmission rate($cm^3/m^2/24$ hr)
0	28.4	40.8	76.6
0.5%	28.4	40.8	75.23
1.0%	28.4	40.8	73.53
1.5 %	28.4	40.8	71.13
2.0%	28.4	40.8	70.12
2.5 %	28.4	40.8	68.23

IV. CONCLUSIONS

Poly (lactic acid) gains great importance due to its various properties over traditional petroleum based polymers. The objective of the work was the studies of specially modified Nano Graphene and Silane treated hydrous clay on PLA films.2% silane treated hydrous clay-PLA film was found to be more heat resistant than neat PLA. The water absorption of PLA/Nano graphene composite film is none compared to neat PLA and PLA/Silane treated hydrous clay.PLA was found to be acid and base resistant and both the clay didn't affect its resistance towards the acid and base. PLA/Blend films improved the water vapour barrier property of PLA films the most. Nano graphene clay improves the water vapour barrier property of PLA films than silane treated hydrous clay. OTR results proved that 1.5% Nano graphene clay effectively improved the gas barrier property of the films. So the reduction in barrier properties helps in packaging applications of PLA. In short, both the clay modifies the physical and chemical properties of PLA to certain extend.

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