"EFFECT OF MONTMORILLONITE NANOCLAY ON THE THERMOMECHANICAL AND BARRIER PROPERTIES OF BIOPOLYMER BASED NANOCOMPOSITE FOR FOOD PACKAGING APPLICATIONS"

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ABSTRACT

The main objective of this study is to prepare starch based LDPE packaging film with and without nanoclay & study the effects of Montmorillonite nanoclay on thermomechanical & barrier properties of the Sago/LDPE film. A series of low density polyethylene (LDPE)/sago starch compounds with different loadings of sago starch content were prepared by twin screw extrusion and glycerol was added to enhance its processability. Film Samples were made by the blown film process. Studies on their thermomechanical and barrier properties were carried out. The presence of high starch contents had an adverse effect on the properties of LDPE/sago starch blends. However, the addition of nanoclay to the blends improved the interfacial adhesion between the two materials, hence, improved the properties of the films. High content of starch also was found to increase the rate of water vapour transmission to LDPE/sago starch films which is undesirable in a packaging film. Nanoclay was found to decrease water vapour transmission rate to the packaging film and enhance the mechanical & thermal properties of the biopolymer film.

Keywords : *Sago Starch, LDPE, montmorillonite , nanoclay, thermal, WVTR, biopolymer, nanocomposite.*

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1. INTRODUCTION

Plastics have been widely used all over the world but it has become a major problem when the plastic cannot degrade even after hundred years. Approximately 140 million tonnes of synthetic polymers are produced worldwide each year to replace more traditional materials, particularly in packaging. Over 60% of post consumer plastics waste is produced by households and most of it as single use packaging . Plastics are manufactured and designed to resist the environmental degradation and also more economical than metal, woods and glasses in term of manufacturing costs and energy required. Due to these issues, plastics resins have become one of the most popular materials used in packaging.

To date, the production and use of non-biodegradable materials or plastics as food packaging materials have significantly increased. These types of materials are usually derived from petroleum products and cause the problem in waste disposal. To meet the increasing demand for sustainability and environmental safety, a growing number of investigations have been directed towards development of food packaging materials that could rapidly degrade and completely mineralize in environment. Biopolymers have been one of the favorable alternatives to be exploited and developed into eco-friendly food packaging materials due to its biodegradability. Used food packaging materials produced from biopolymers can be disposed into bio-waste collection for further compose, leaving behind organic by-product such as carbon dioxide (CO_2) and water (H_2O).

Unfortunately, the use of biopolymers as food packaging materials has drawbacks such as poorer mechanical, thermal, and barrier properties as compared to the conventional non-biodegradable materials made from petroleum. Due to this, many research efforts were made to improve the properties of the biopolymers. This include the use of the nanocomposite concept. From the researches done, nanocomposite was established as a promising route to enhance mechanical and barrier properties of biopolymers. Bio-nanocomposite is a multiphase material comprising of two or more constituents which are continuous phase or matrix particularly biopolymer and discontinuous nanodimensional phase or nanofiller (<100 nm). The nano-sized fillers play a structural role in which they act as reinforcement to improve the mechanical and barrier properties of the matrix. The matrix tension is transferred to the nanofillers through the boundary between them.

The incorporation of nanofillers such as silicate, clay, and titanium dioxide (TiO2) to biopolymers may improve not only the biopolymers' mechanical and barrier properties but also offer other functions and applications in food packaging such as antimicrobial agent, biosensor, and oxygen scavenger. The bio-nanocomposite can be an active food packaging whereby the food packaging can interact with food in some ways by releasing beneficial compounds such as antimicrobial agent, antioxidant agent, or by eliminating some unfavorable elements such as oxygen or water vapor. The bio-nanocomposite can also be a smart food packaging whereby it can perceive property of the packaged food such as microbial contamination or expiry date and uses some mechanism to register and convey information about the quality or safety of the food.The development of bio-nanocomposite materials for food packaging is important not only to reduce environmental problem but also to improve the functions of the food packaging materials.

2. MATERIALS & METHODS

2.1 Materials

LDPE: Low-density polyethylene (LDPE) film grade (24FS040) supplied by Reliance Polymers was used in this research. The density of the polymer was 0.922 g/cm^3 according to ASTM D1505. It had a melt flow of 4 g/10 min according to ASTM D 1238 and a melting temperature (Tm) of 110 °C.

Sago Starch: Sago starch, food grade was used as filler in this research. The particle size of those starches ranged from 9.73 ŋm to 83 ŋm with an average particle size of 32.97 ŋm. The moisture content of starch is average of 11.5%.

Nanoclay (Montmorillonite): Nanoclay surface modified montmorrilonite was procured from Sigma Aldrich (product code – 682632). It contains 0.5-5 wt. % aminopropyltriethoxysilane and 15-35 wt. % octadecylamine with a base of montmorrilonite clay.

Processing Aids: Glycerol (glycerin, $C_3H_8O_3$) from Sago Chemicals (Molecular weight = 92 gmol^{-1}) were used as a processing aid to these blends.

2.2 Compounding Formulation

1. 5% glycerol was kept constant in these blends. The composition of the samples are given in table 2.1 :

Table 2.1 Sample formulation of LDPE and Sago Starch with and without nanoclay

Sample	LDPE (w/w %)	Starch (w/w %)	Nanoclay (wt. % of starch)
LDPE	100	0	0
LDPE/S : 90/10-5	90	10	0
LDPE/S : 80/20-5	80	20	0
LDPE/S : 70/30-5	70	30	0
LDPE/S/NC : 90/10/1-5	90	10	1
LDPE/S/NC : 90/10/3-5	90	10	3
LDPE/S/NC : 90/10/5-5	90	10	5

2.3 Pre-Mixing

LDPE and starch were mixed in a high speed mixer (M/s Delta Machine Crafts) . For blends with nanoclay, first the starch and nanoclay were mixed in a beaker using a glass rod for 2 minutes and then low-density polyethylene (LDPE) was mixed with this starch – nanoclay mixture using high-speed mixer, before undergo compounding process. The mixing process was done for 10 minutes with a speed of 35 rpm at room temperature.

2.4 Compounding

Low-density polyethylene and starch were dried in an oven for 24 hours at 80 °C before pre-mixing and compounding to eliminate the moisture completely specially for starch. The compounding of LDPE/starch was done using a co-rotating twin screw extruder (M/s Specific Engineering & Automats, Model No. ZV 20) . The compounding process was carried out at a speed of 110 rpm and the temperature was set at 160 °C/170 °C/170 °C/180 °C/180 °C/ 170 °C .The extrudates were palletized using a pelletizer machine for each formulation.

2.5 Sample Preparation:

The compounded samples were blown using blown film machine (M/s Konark Plastomech Pvt. Ltd., Model – KBF/32 HM/LD) to produce LDPE/starch film. This process was carried out at temperature of 170 °C/165 °C/160 °C/150 °C/140 °C/ 130 °C with drawer and screw speed of 50 rpm and 80 rpm respectively.

3. RESULTS & DISCUSSIONS

3.1. Tensile Strength

Tensile strength decreased drastically with the addition of starch, however tensile strength increased considerably after addition of nanoclay but there was not so much change after increasing the percentage of nanoclay from 3% to 5% in the sago/ldpe blend. Same was the case with percentage elongation.

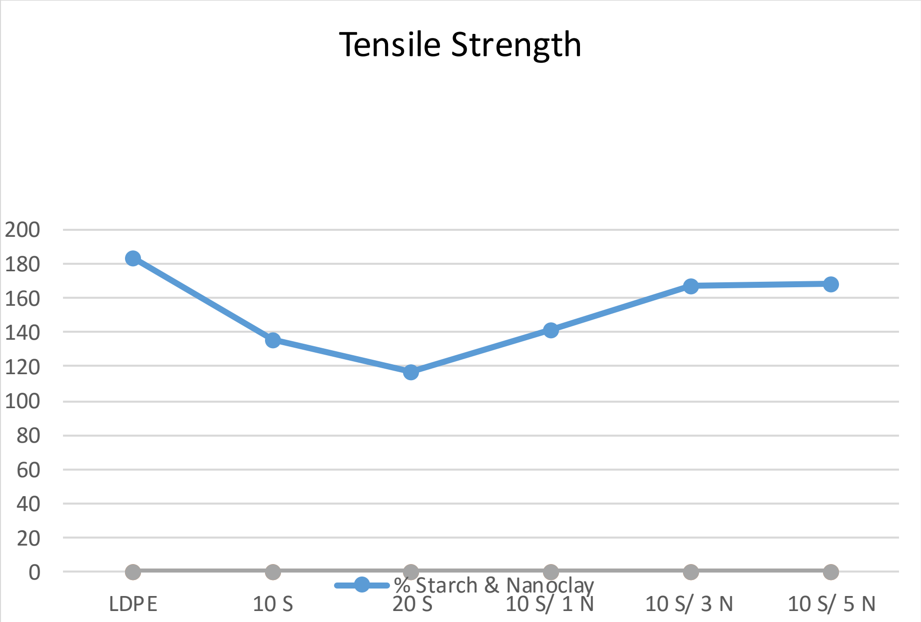

Fig. 3.1 Graph of tensile strength (kg/cm^2) v/s % Starch & Nanoclay

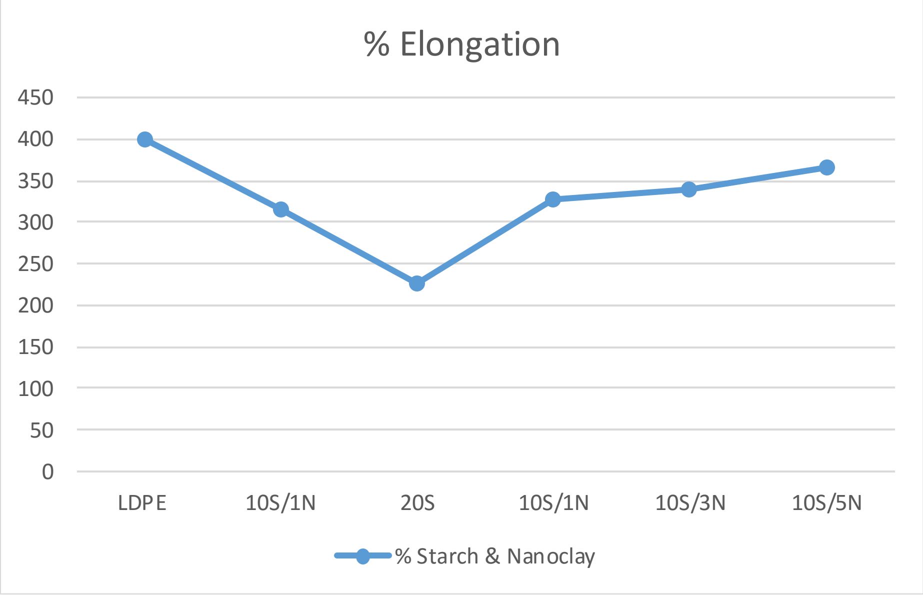

Fig.3.2 Graph of % Elongation v/s % Starch & Nanoclay

3.2 Tear Strength

The tear strength is measured both in MD & TD . From the graph it is evident that tear strength decreases with addition of sago starch to LDPE but it increases with addition of nanoclay. 3% nanoclay is the optimum choice for increasing tear strength since there is not much difference between strength of 3% & 5% nanoclay blends.

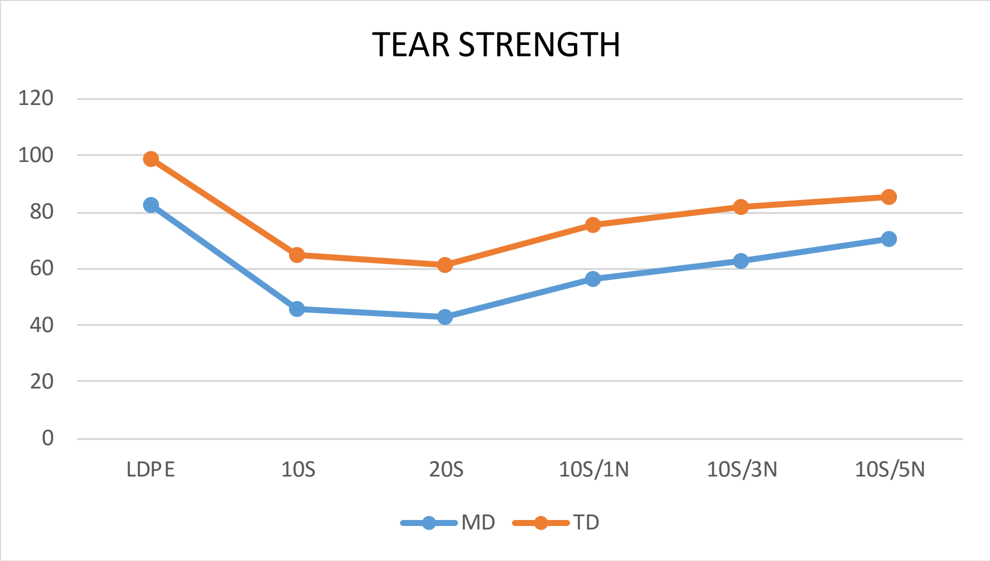

Fig. 3.3 Graph of Tear Strength (gm/mil) v/s % Starch & Nanoclay

3.3 Burst Strength

Burst Strength of each sample was tested with 5 specimen for each sample. It was observed that burst strength decreased with addition of sago starch to LDPE and increased with incorporation of nanoclay to Sago Starch/LDPE blend. 3% & 5% nanoclay blend had the same burst strength

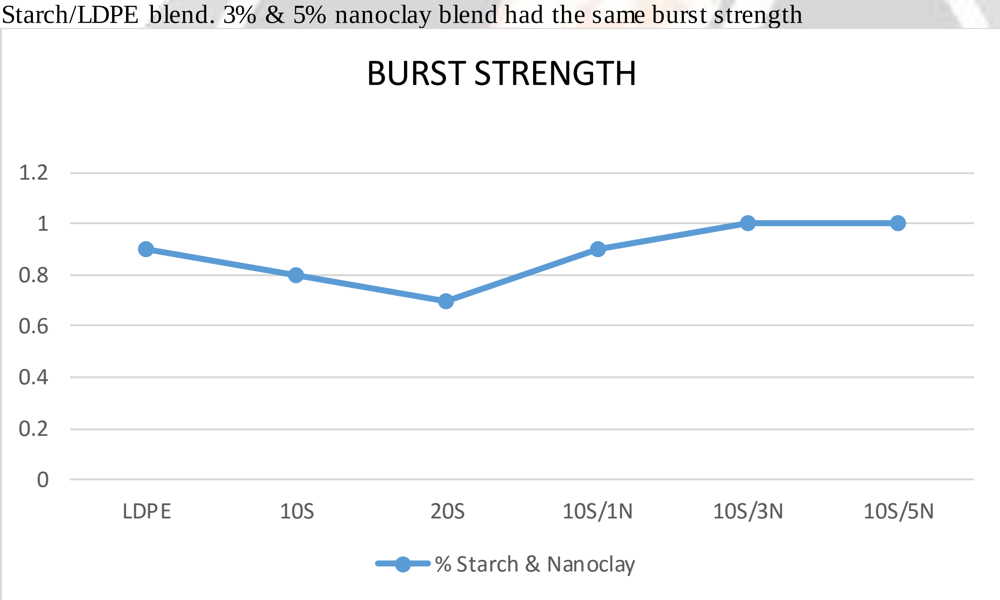

Fig. 3.4 Graph of burst Strength (kg/cm^2) v/s % Starch & Nanoclay

3.4 Water Vapour Transmission Rate

WVTR was calculated for the following six batches as given in the table 3.5. It was noted that due to addition of sago starch, WVTR increased which is not acceptable in food packaging industries. WVTR decreased drastically after addition of nanoclay. The composition with 5% nanoclay showed the least water vapour transmission rate.

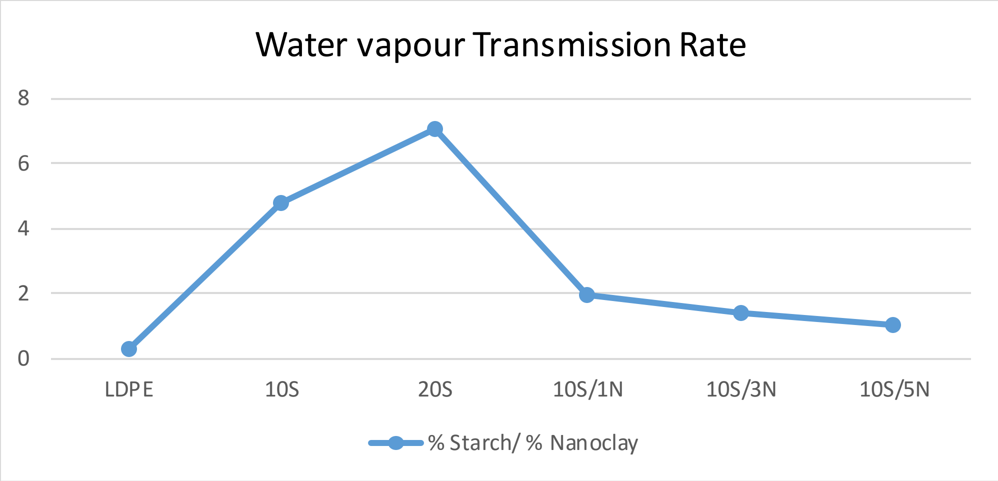

Fig.3.5 Water Vapour Transmission Rate(gm/m^2-24 hrs) v/s % Starch &Nanoclay

3.5 Melt Flow Index

The melt flow index was calculated for all the samples as given in the table 3.6 . MFI gives the processability of a material. MFI decreased with increase in Sago Starch content and decreased still further after addition of nanoclay.

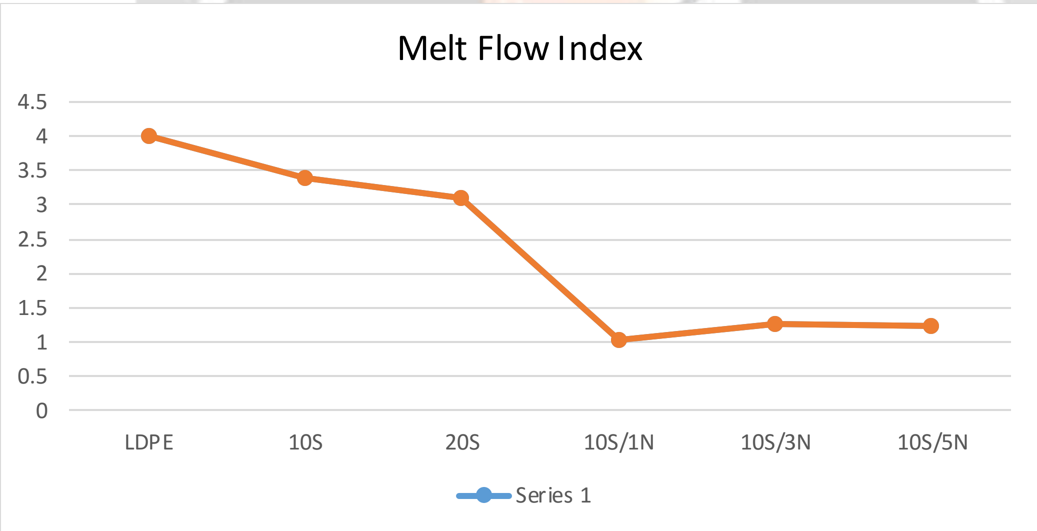

Fig.3.6 Graph of Melt Flow Index (gm/10 min) v/s % Starch & Nanoclay

3.6 Differential Scanning Calorimetry

DSC test was done on all film samples. The starch films were subjected to two heating cycles in two temperature intervals. The first was from 30 to 400 °C followed by cooling and the second was from 30 to 350 °C. The DSC analysis of Sago Starch/LDPE/Nanoclay film shows same Tg. So it's evident that when nanoclay is added to LDPE, the quantity of nanoclay does not have any effect on the glass transition temperature.

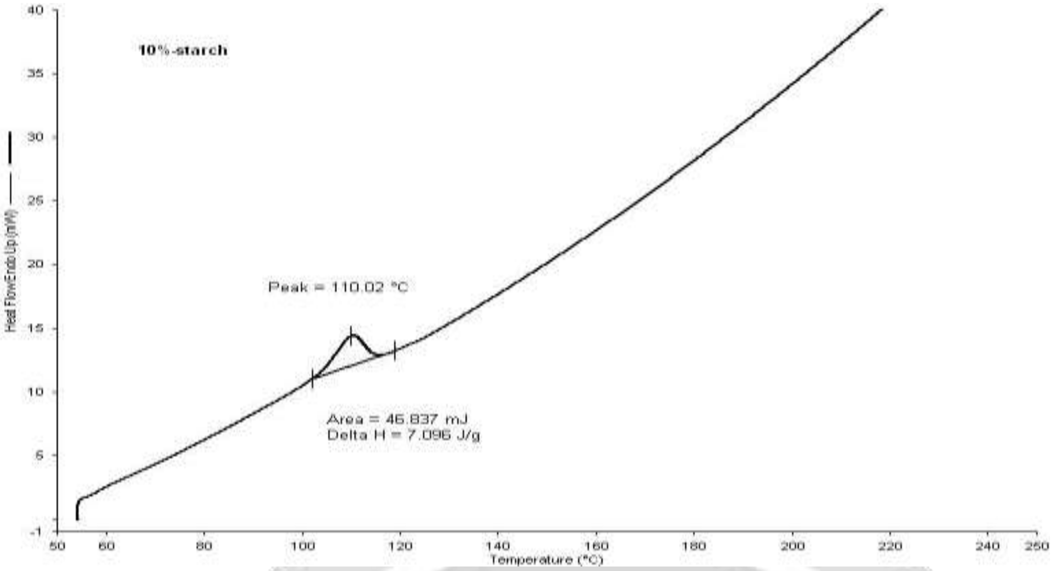

Fig. 3.7 DSC graph of LDPE/10S

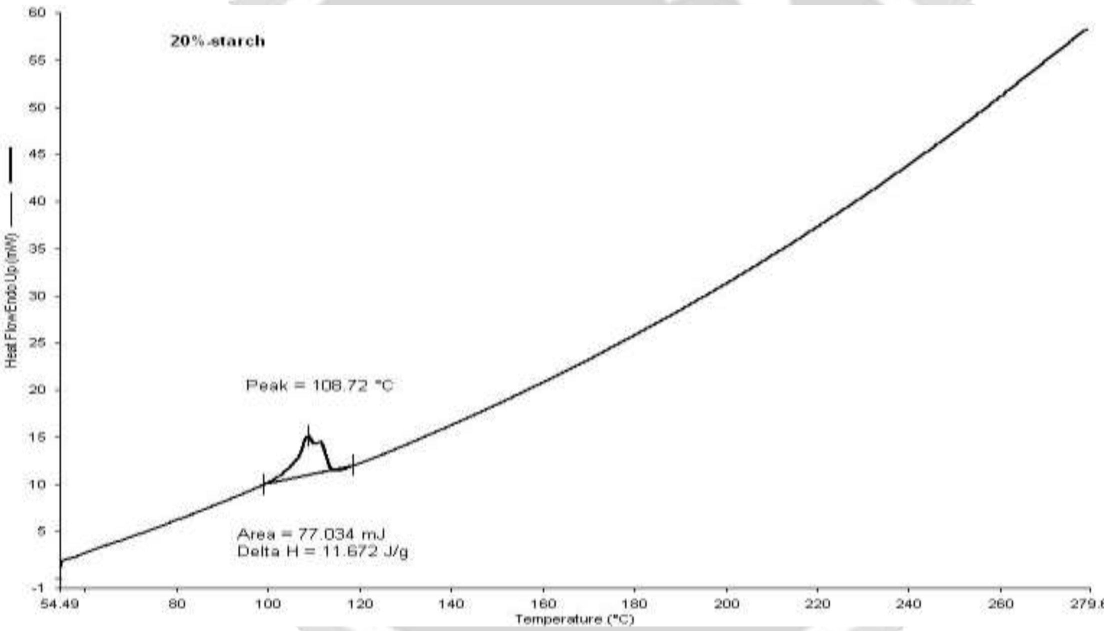

Fig. 3.8 DSC graph of LDPE/20S

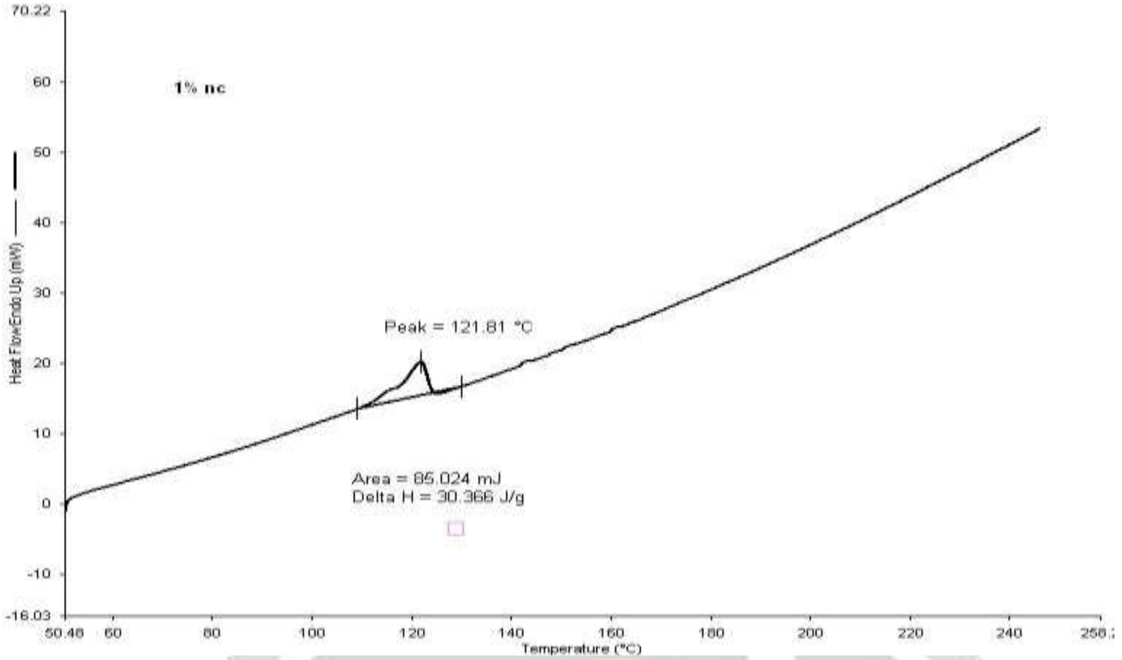

Fig. 3.9 DSC graph of LDPE/10S/1NC

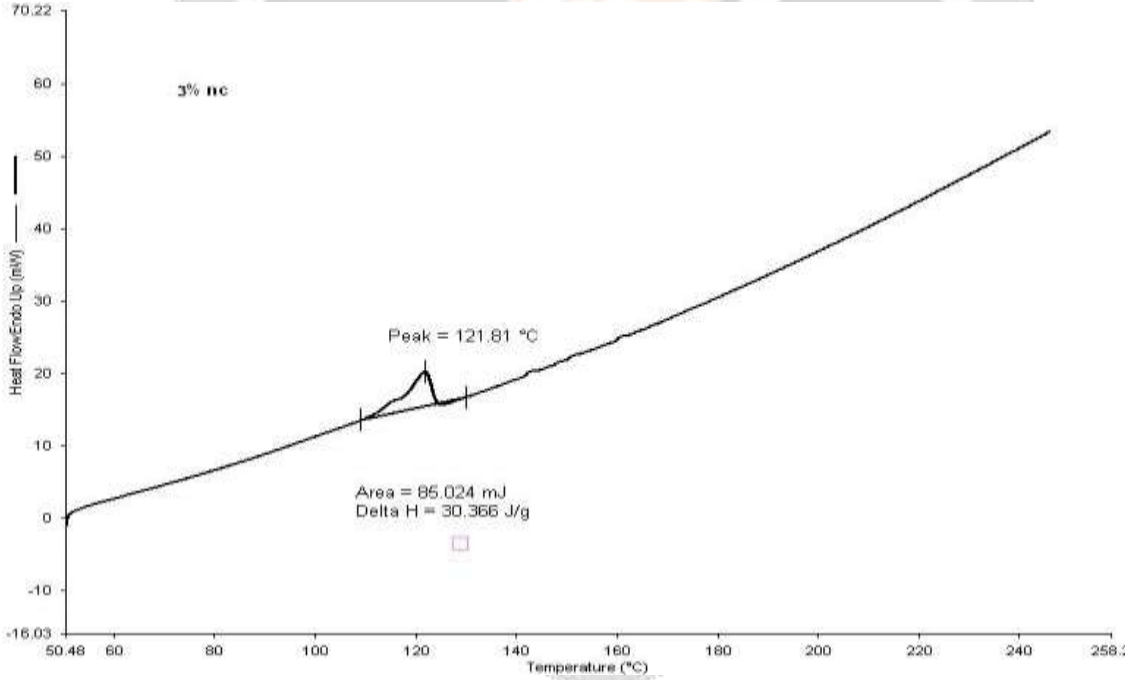

Fig. 3.10 DSC graph of LDPE/10S/3NC

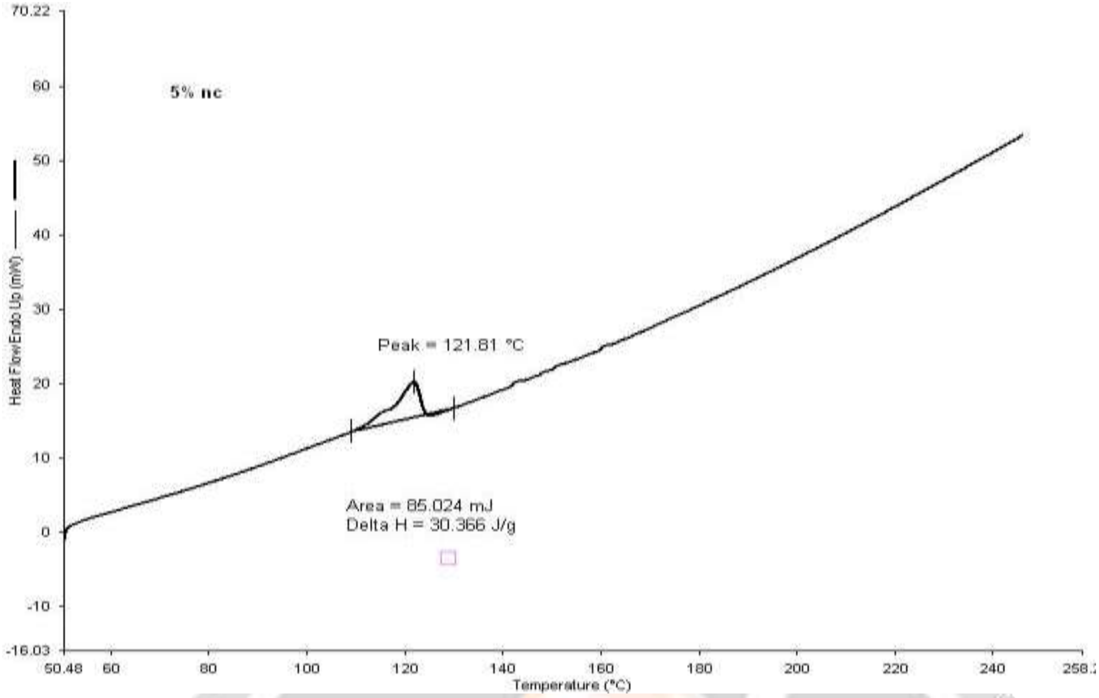

Fig. 3.11 DSC graph of LDPE/10S/5NC

4. CONCLUSION

Based on results obtained in this study, it will be appropriate to conclude that starch strongly affected the thermomechanical & barrier properties of LDPE/starch blends. As the content of starch increased in LDPE, there was significant decrease in mechanical, thermal & barrier properties Starch imparts an adverse effect upon the mechanical properties wherein decreased the tensile strength and elongation at break. This less effectiveness is due to the hydrophilic nature of starch that is not compatible to hydrophobic nature of LDPE, that result in weakness of interfacial adhesion. However, incorporation of nanoclay has increased the tensile strength & tear strength considerably and also it decreased the water vapour transmission rate. The DSC graph showed variation after nanoclay was added but the quantity of nanoclay did not pose any effect on the glass transition temperature.

Among the Sago Starch/LDPE blend with nanoclay (1%, 3% & 5%) the composition of Sago Starch/LDPE film with 3% nanoclay was found to be the most optimum since it showed most improved properties. It showed good mechanical properties. Melt Flow Index decreased drastically due to increase in viscosity. Water Vapour Transmission Rate decreased with the increase in percentage of nanoclay while Sago Starch/LDPE/Nanoclay (3% & 5%) showed similar tensile and burst strength.

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