ISSN No:-2456-2165

Advanced Structural Foams Based on PLA/ PP and PLA /HDPE Blends

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Abstract:- The objective of polymer blending is a practical one of achieving commercially viable product through either unique properties or lower cost than some other means might provide. The current study proposes the reparation of structural foams based on PLA/PP and PLA/HDPE polymer blends with chemical blowing agent were studied. Various ratios of base polymers were prepared and analyzed. The properties like density, hardness, tensile properties, impact properties, flexural properties, opacity, water absorption, acid resistance, base resistance, flame resistance and heat resistance are studied. The samples were also evaluated for FTIR studies and DSC. The optical images of the samples were examined. The properties of the foams were compared with the standard sheet without using blowing agent.

Keywords:- *Biopolymers, Chemical Blowing, Polymer Blend, Structural Foam, Biodegradability.*

I. INTRODUCTION

The use of polymer foams in today's world has constantly increased. Many reasons to support this growth, light weight, insulation properties, softness, excellent strength/weight ratio, material costs, energy absorption performance. There is an increasing environmental concern towards the use of biodegradable polymers. It makes greater research and development of biodegradable polymer materials as an alternative to plastics which are ecologically useful. The reasons are more and more awareness of environmental concerns and it is realized that our petroleum resources are limited. The majority of materials used for are non-biodegradable which are not satisfying the demands in environmental safety and sustainability [1].Biodegradable polymers are an alternative for these non-biodegradable materials. Polymers obtained from renewable sources are gaining popularity over their petroleum based counter parts in recent years due to their capability to address the environmental pollution related concerns emanating from the widespread usage of synthetic polymers. Polymers from renewable sources are very attractive in an environmental point of view but there are limitations and the high cost of these materials causes lower commercial applications [2].

The biodegradable polymeric materials can degrade in a limited time period without making any environmental problems. Biodegradable polymers have some limitations like higher cost, lower mechanical performances and limited thermal stability to use in packaging industry. To overcome these limitations, one of the most commonly used strategies is melt blending of dissimilar biodegradable polymers. Biodegradable polymer blends shows lower level of performance because they are thermodynamically immiscible as well as exhibit poor compatibility between the blended components [2]. Compatibilization is required to enhance the performances of the immiscible biodegradable polymer blends by enhancing the adhesion between the phases. Major studies therefore focus on various compatibilizers to enhance the performances of the resulting biodegradable polymer blends.

Poly (lactic acid) (PLA) is a bio-based and biodegradable polymers most widely referred. It has the limitations such as brittleness and relatively high cost have restricted its applications significantly. Polymer blending provides one of the economic and efficient ways to enhance the properties of PLA. Most shortcomings of PLA are theoretically surmountable by blending with abundant polymers with various properties [3].

Priyanka et al studied with PLA blend with polypropylene (PP) at various ratios with a melt-blending technique in an attempt to improve the melt processability of PLA. Maleic anhydride (MAH)-grafted PP and glycidyl methacrylate were used as the reactive compatibilizers to induce miscibility in the blend[4].Alessia Quitadamo et al studied HDPE and poly(lactic) acid (PLA) blends containing polyethylene-grafted maleic anhydride, a random copolymer of ethylene and glycidyl methacrylate as compatibilizers [5, 6].

Aleksandra Ostafinska et al report the blending of PLA with poly (ε-caprolactone) (PCL), found increase in impact strength. In an additional set of experiments, it shows the addition of TiO_2 nanoparticles slightly improves stiffness, but significantly reduces the toughness of the resulting nanocomposites [7].

PLA blends with polypropylene (PP) and polypropylene based elastomer studied for its improved mechanical properties. It uses ethylene–glycidyl

ISSN No:-2456-2165

methacrylate–methyl acrylate terpolymer as compatibilizer through a coupling reaction at the end groups of PLA by Yuewen Xu et al. Graft copolymers formed enhanced the adhesion between PLA and polyolefin phases and lowered the interfacial tension [8].Fateme Pashaei Soorbaghi tried blends of poly lactic acid with polypropylene in a combination by adding different amounts of graphene on morphology and their electrical properties were investigated [9].

To overcome the poor toughness of PC/PLA blends due to the intrinsic properties of materials and poor compatibility, thermoplastic urethane (TPU) Yueyun Zhou was added to PC/PLA blends as a toughened; catalyst di-n-butyl in oxide (DBTO) was also added for catalyzing transesterification of components in order to modify the compatibility of blends [10].

The current work proposes the use of PLA/PP and PLA /HDPE blend matrices for making cellular structure which got wide range of applications. Foams save weight of the product and increase the stiffness. It also gives higher insulation properties. Various types of blends were prepared with chemical blowing agents and all the properties were examined.

II. EXPERIMENTAL

➢ **Materials Used:**

Poly (lactic acid) pellets (INGEO 3052D) of make Nature works LLC, (Minnetonka MN, USA).
Reliance PVC, K-57 SUSPENSION GRADE 57-01.

HDPE (M60075) and PP (H050MN) are moulding grades of Reliance industries.
Sodium bicarbonate and citric acid, $CaCO_3$, TiO_2 are laboratory grade supplied by NICE chemicals.

MATERIALS, gms	P1	P2	P3	Cp	H1	H2	H3	C_H
PLA	25	50	75	50	25	50	75	50
PP	75	50	25	50	75	50	25	50
$NaHCO_3$ +CITRIC ACID	3	3	3	0	3	3	3	0
PVC	10	10	10	10	10	10	10	10
TiO_2	1	1	1	1	1	1	1	1
$CaCO_3$	50	50	50	50	50	50	50	50

Table 1:- Formulations of PLA/ PP and PLA/HDPE blends

➢ **Cp: Control formulation without blowing agent PP based and C_H control formulation without blowing agent HDPE based (50/50 ratio of two base polymers)**

Table 1 shows the formulations for the compounds prepared from PLA/PP and PLA/HDPE. PLA gives the component better biodegradability compared to PP or HDPE. As of now PLA is more costly and brittle in nature. Therefore blends are tried to overcome the shortcomings. The role of HDPE and PP are as matrices to support the cellular structure. The polyolefin's are light weight and easily processable also reasonable cost. Calcium carbonate was added which act as filler to reduce cost make more dimensional stable. Titanium dioxide act as nucleating agent for the cellular structure formation, and PVC for getting the flame retardancy were added. Mixing was done as per the formulations given in table 1 in two roll mill by setting the nip gap at 1mm. The foams are proposed to use in structural components, sound insulation, and heat insulation and also to make the product light weight. This process was carried out with constant temperature 170^0C. Blowing agent combo sodium bicarbonate and citric acid was added after five minutes and mixed well. This process was carried out with a temperature of 180^0C to get a homogeneous mixture.

This processed mixture was then passed through two roll mill. This mixture was placed on the mould. This mould was coated with releasing agents for the ease removal and to avoid sticking of the product onto the mould. This process was carried by setting the timer for 30 minutes and temperature at 180^0C in a semi automatic machine. In a fully automatic machine the product can be made with 5 min time. The product was cooled down using water system. This cooled product was taken out from the mould cleaned by removing flashes. Structural foam prepared as flat sheets from the compression moulding machine.

➢ **Testing and characterization**

Various test specimens were prepared and tested for the mechanical, thermal and surface properties, as per standards. Density of the PLA/ PP blend based structural foams was determined by density balance. Density balances decide the density in liquid and air material as per the buoyancy method.

Durometer hardness (shore hardness) test was based on penetration of a specified indentor onto the surface of the object. Durometer hardness test was used for measuring the relative hardness of soft materials. Tensile properties and Flexural properties of composite samples were measured using universal testing machine (SHIMADZU, JAPAN) according to ASTM D 638-08 and ASTM D 790 respectively. The load capacity was 50 KN and cross-head speed was 100mm/min using gauge length of 115 mm. For bending tests, cross-head speed was 2.5 mm/min and span distance was 96 mm.

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Notched Izod impact strengths of the composites according to ASTM D 256-10 standard were measured using TMI 43-02 impact tester machine. The samples tested for this project were having a thickness of 3.2 mm. The opacities of the samples were measured with opacity tester (opacity tester, Elemech Pneumatic). 4×10 cm^2 sheets were cut from the sample and opacity was tested according to ASTM D 1003.

Water absorption studies were performed according to ASTM D 570-98 standard. The opacity test samples for each formulation were dried in an oven for 1hour at 110 ± 2 °C. The dried samples were weighed to a precision of 0.001 g and then immersed in distilled water at room temperature for 24hr. The specimen were taken out after 24hr and weighed immediately after wiping out the surface water.

Acid and alkali resistance studies were performed according to ASTM D 570-98 standard.3cm length and 3cm width samples from each formulation were weighed to a precision of 0.001 g and then immersed in 0.1N hydrochloric acid at room temperature for 24 hours and weighed as before. 10cm length and 1.3cm width samples were taken from each formulation and draw a line mark at 7cm. Then the samples were ignited to that mark. The time taken for the ignition of the samples was measured using a stopwatch. The flame resistance of the samples can be predicted with the help of flame proceeding time.

Ageing resistance of the specimen were determined to know the effect of heat. 5cm x 5cm samples were taken from each formulation, weighed to a precision of 0.001 g and placed in an oven for 1 hour at 110 ± 2 °C. Samples were taken from the oven and weighed after 1 hour, from weight difference % difference was calculated. The same samples were also tested for hardness difference before and after ageing.

Differential scanning calorimetry (DSC) (ASTM D3418, ASTM E1356, ISO 11357): DSC is a thermo analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured. The sample and reference were maintained at the same temperature throughout the experiment. Fourier transforms infrared spectrometry (ASTM E168, ASTM E 1252): FTIR was used as a reliable and cost-effective analytical tool for identification of polymers and assessment of the quality of plastics materials.

Optical microscopy: Image of the best sample was taken by using optical microscope of model BX51 made by Olympus having resolution 10, 20, 50,100 pixels. It used visible light and a system of lenses to magnify images of small objects. The main application was to study the morphology of the sample which can be used to obtain chemical and physical information about a polymer's structural features.

III. RESULTS AND DISCUSSION

A. Physical Properties of the Structural Foam

Table 2 shows density, hardness and opacity of structural foams based on PLA /PP and PLA/HDPE blends. Density decreases with increasing the amount of polypropylene from 25% to 75% as more blowing take place and the same is observed in HDPE based blends. Table 2 clearly shows the reduction in density due to the presence of blowing agent. The hardness of the sheets also decreases as the blowing agents are added. The effect is common in PP and HDPE blends. On addition of PP or HDPE to PLA can cause increases in hardness, while due to the presence of blowing agent there is a significant difference in density and hardness for the blends. Opacity values give evidence that foaming of structure happened due to the presence of blowing agent both in HDPE and PP blends.

SAMPLE	DENSITY, gm/cc	HARDNESS (SHORE-D)	OPACITY
Control PLA/PP (without blowing agent)	1.3093	67	3.88
PLA/PP 75/25	0. 819	55.2	1.53
PLA/PP 50/50	0. 818	50.8	1.12
PLA/PP 25/75	0.809	50.4	1.03
Control PLA/HDPE (without blowing agent)	1.313	60	3.28
PLA/HDPE 75/25	0.82	56	1.82
PLA/HDPE 50/50	0.819	51	1.81
PLA/HDPE 25/75	0.80	50	1.80

Table 2:- Physical Properties of the structural foam

B. Tensile Properties

Tensile properties such as tensile strength, modulus and elongation are the most important properties of materials, which measures the ability of materials to withstand the force that tends to pull it apart and determines to what extend the material stretches before breaking.

Figures 1, 2 and 3 show the tensile strength, modulus and elongation at break for the structural foam samples. Control sample was made of the blend of polymers (50/50 ratio) without any blowing agent. It is found that tensile properties are increasing with increasing the concentration of polypropylene from 25% to 75%.Sample with 25/75 PLA/PP shows highest value while the sample with 75/25

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PLA/PP show lowest value. Tensile modulus is related to stiffness of a material. Similar pattern observed for PLA/HDPE blends. Higher the modulus of elasticity, higher is the stiffness of material. Stiffness is the one of the important advantage of structural foams. The figure give an idea while foams are prepared tensile strength, modulus and elongation decreases but as the amount of PP increases strength increases. Once matrices are converted to cellular structure the amount of polymer will be reduced and there will be incorporations of gases, this causes the reduction in tensile strength, modulus and elongation of the structural foams.

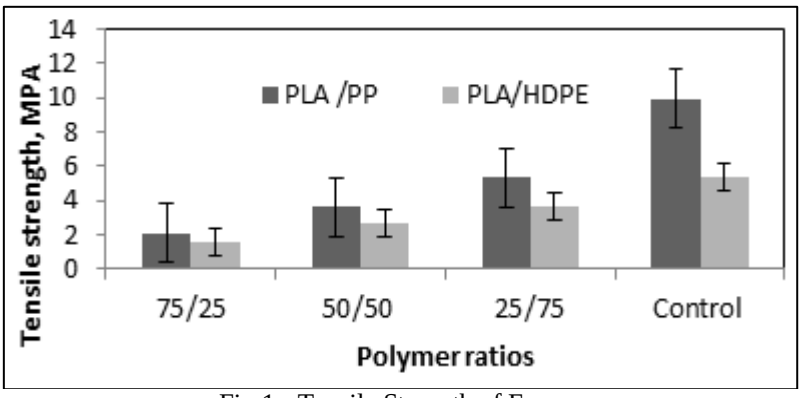

Fig 1:- Tensile Strength of Foams

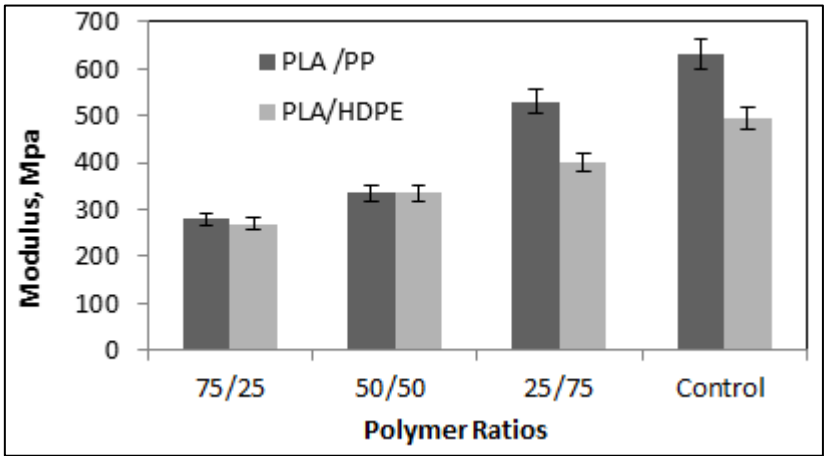

Fig 2:- Modulus of Foams

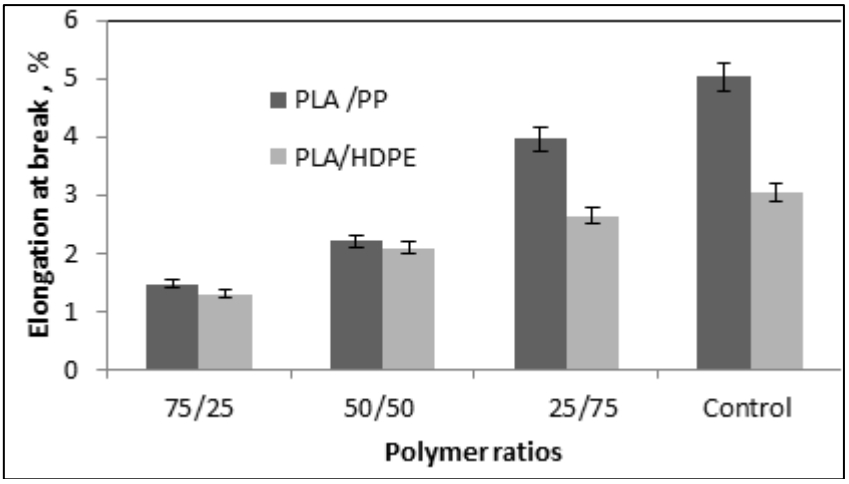

Fig 3:- Elongation at Break of Foams

C. Flexural Properties

From the figures 4 and 5, it is clear that flexural properties such as flexural strength and modulus are increasing with increasing the concentration of polypropylene and HDPE from 25% to 75%. Sample with 25/75 PLA/PP and 25/75 PLA/HDPE show highest value whiles the sample with 75/25 PLA/ PP and 75/25 PLA/ HDPE show lowest value. Similar to tensile strength cellular structures are with air gaps and flexural strength and modulus reduces which give confirmation of foamed

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structure. Flexural properties are useful for quality control or specification purposes and to classify or rank the material with respect to bending strength and stiffness. The advantage of flexural test on brittle specimen is that fracture usually can be made to originate on a moulded surface. Flexural results are more reliable and less scatter than tensile results.

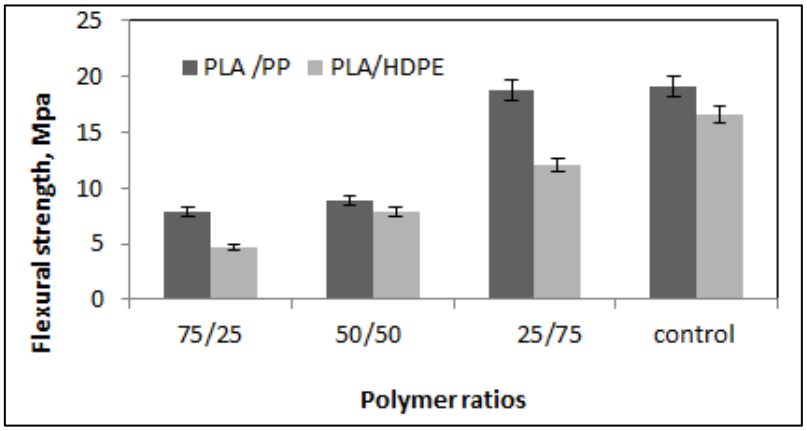

Fig 4:- Flexural Strength of Foams

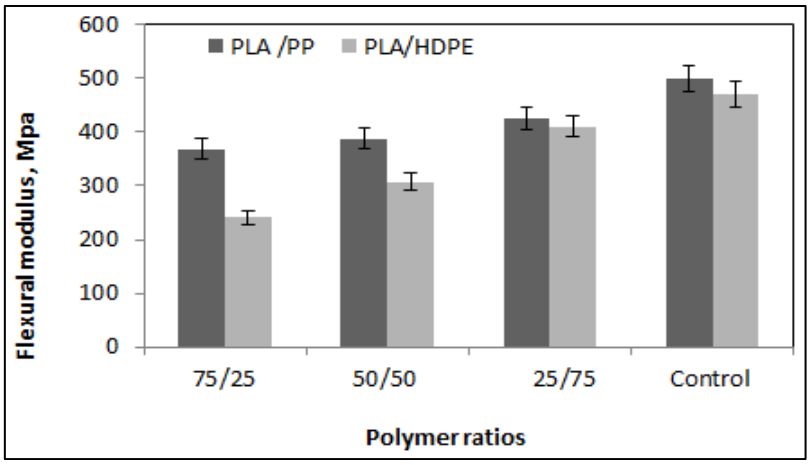

Fig 5:- Flexural Modulus of Foams

D. Impact Strength

From the figure 6, it is observed that impact strength increasing with increasing the concentration of polypropylene from 25% to 75%. Compound with 25/75 PLA/PP show highest value while the sample with 75/25 PLA/PP show lowest value, the trend is similar for HDPE. High value of impact strength is an advantage of foamed plastics. In case of impact strength the values are near to the control samples without foaming. PLA by nature have lower impact strength, as PP or HDPE is added toughness increased.

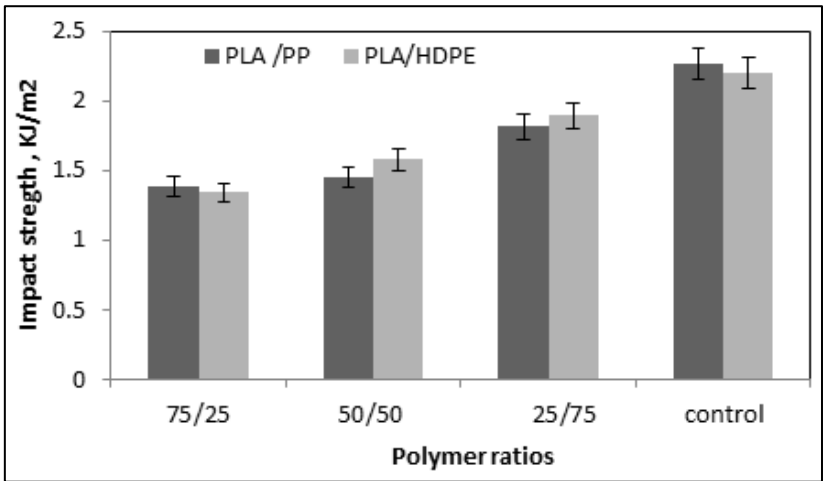

Fig 6:- Impact strength, KJ/m2

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E. Water Absorption

Figure 7 shows the water absorption in percentage decreases with increasing the concentration of polypropylene from 25% to 75%.Sample with 75/25 PLA/PP show highest value. When compared to control samples foam samples show higher rate of water absorption. That means the sample 75/25 PLA/PP show high water resistance. PLA due to its polar nature shows higher water absorption and hydrophilic in nature. As the amount of PP or HDPE is added water absorption decreases drastically. Maximum water absorption is visible when PLA is foamed and the cellular structure can absorb more moisture. Due to the synergistic effect highest water absorption is obtained for 75/25 PLA/PP or PLA/HDPE.

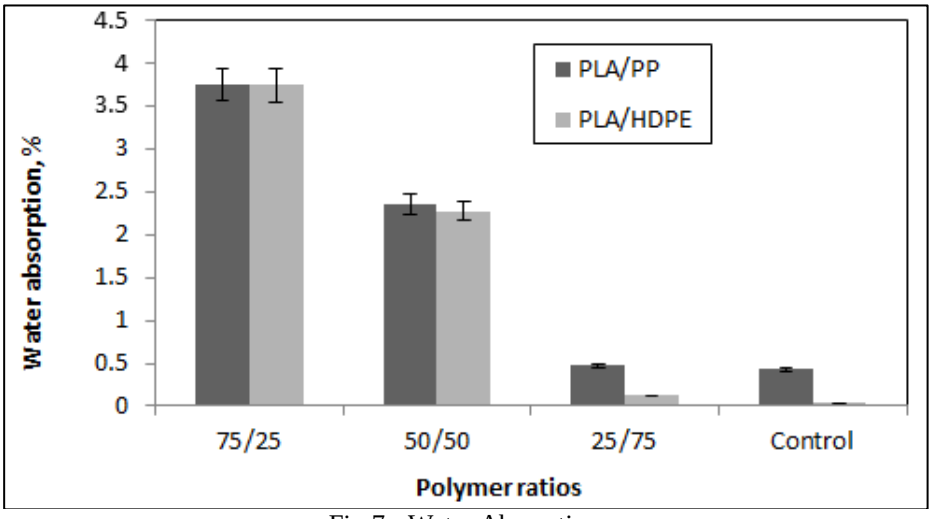


Fig 7:- Water Absorption

F. Acid Resistance

From the figure 8 there is a gradual decrease of weight loss in percentage in acid attack with increasing the concentration of polypropylene from 25% to 75%.Sample with 25/75 PLA/PP and PLA/HDPE show lowest weight loss. That means that the sample show high acid resistance. When compared to control composite, foam samples show comparable acid resistance.

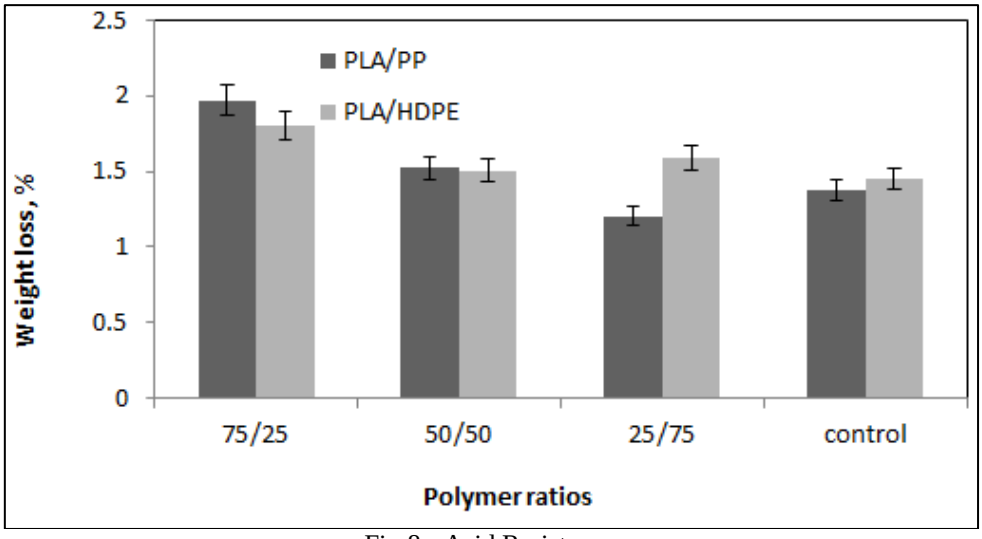


Fig 8:- Acid Resistance

G. Alkali Resistance

From figure 9, it is observed that there is a gradual decrease of weight loss in percentage in alkali attack with increasing the concentration of polypropylene from 25% to 75%.Sample with 25/75 PLA/PP and PLA/HDPE show lowest weight loss. Similarity in HDPE based blends also. That means that the sample show comparable alkali resistance with control samples.

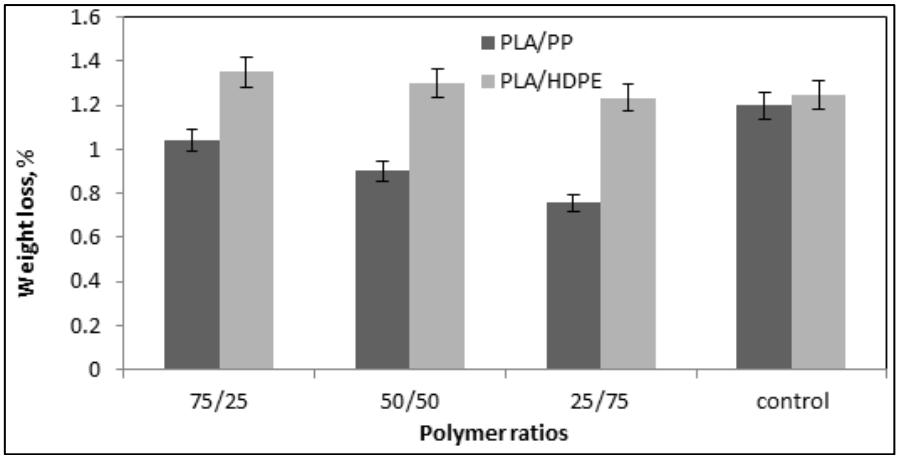


Fig 9:- Alkali Resistance

H. Flame Resistance

From figure 10 the flame resistance of the compounds is obtained, there is a gradual increase of time taken to burn the sample with increasing the concentration of polypropylene from 25% to 75%.Sample with 25/75PLA/PP and same in HDPE, take more time to burn. This means that the samples show high flame retardant property. When compared to composite, foam samples show high flame resistance were in the processing, flame retardant such as PVC is added, product shows burning tendency.

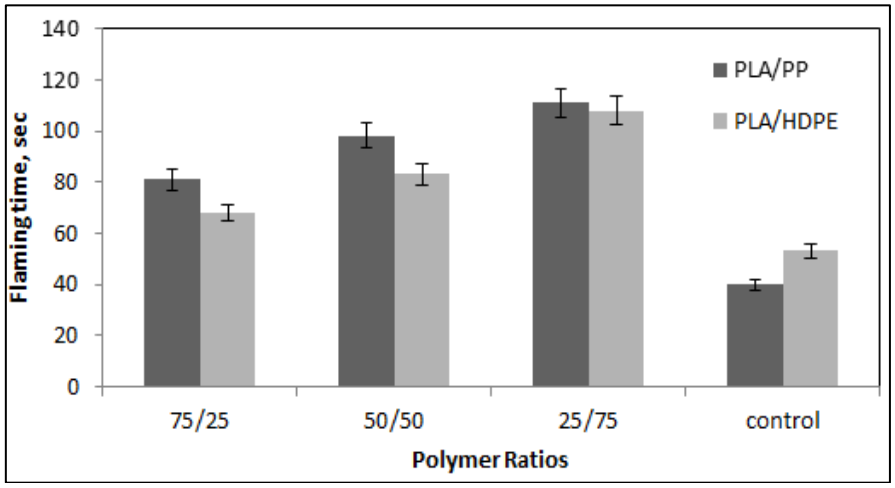


Fig 10:- Flame Resistance

I. Heat Resistance

Figure 11 shows gradual decrease of weight loss in percentage with increasing the concentration of polypropylene from 25% to 75%.Sample with 25/75PLA/PP as in HDPE show lowest weight loss. This means that the sample show high heat resistance. When compared to composite, foam samples show high heat resistance.

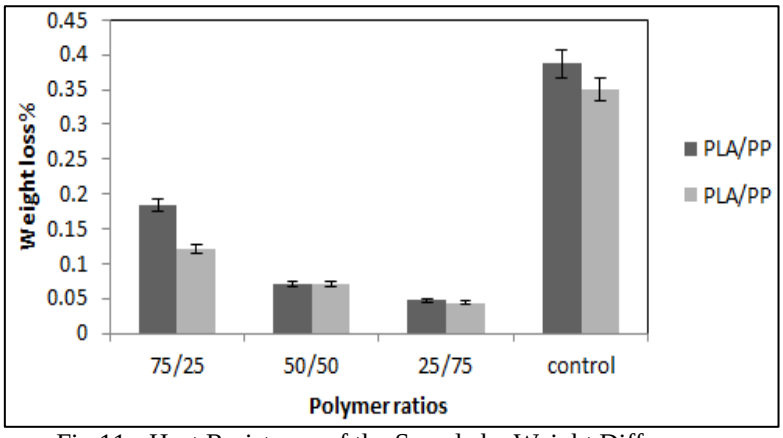


Fig 11:- Heat Resistance of the Sample by Weight Differences

ISSN No:-2456-2165

As per figure 12 there is a gradual decrease of hardness loss with increasing the concentration of polypropylene from 25% to 75%.Sample with 25/75 PLA/PP show lowest hardness loss exactly same as HDPE blends. This means that the sample show high heat resistance. When compared to composite, foam samples show high heat resistance.

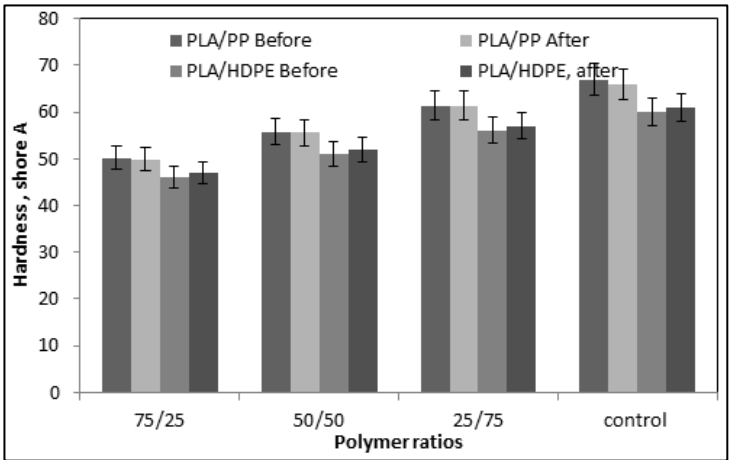


Fig 12:- Loss of Hardness on Ageing

J. Differential Scanning Calorimetry(DSC)

DSC of the best sample 25/75 PLA/PP and PLA /HDPE were done. Results are shown in the figure 13and figure 14 respectively.

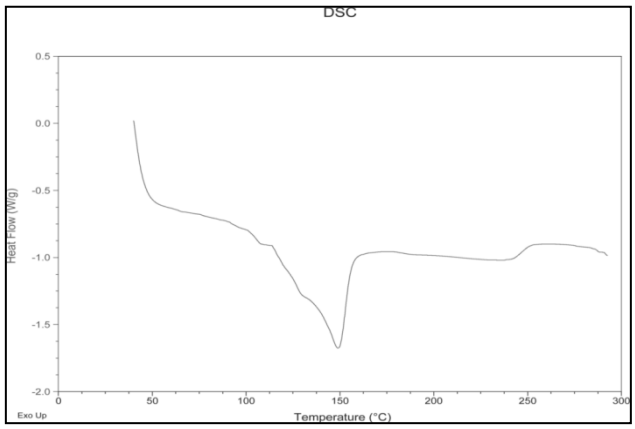


Fig 13:- DSC Plot of PLA/PP: 75/25

Figure 13 it was found that, the melting point of the sample is 150^0C. All other transitions are not significant. It is thus clear that by the addition of PLA and blowing agents melting point does not decreases. Similar is the case in PLA/HDPE blends melting is observed at 140 ^{0} C as per figure14, and it indicates that there is not much difference in melting point on foaming.

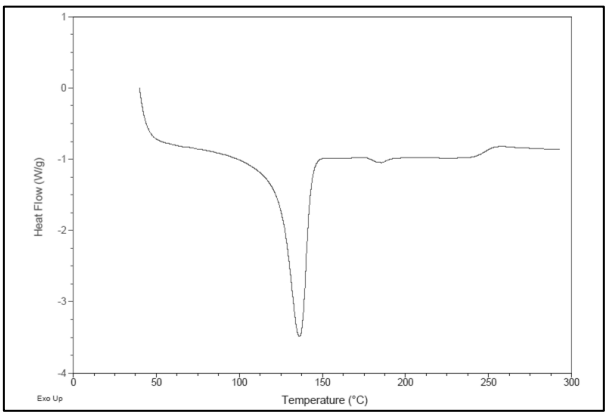


Fig 14:- DSC Plot of PLA/HDPE: 25/75 Melting Point at 140 ^{0} C

❖ *Fourier Transform Infrared Spectrometry (FTIR)*

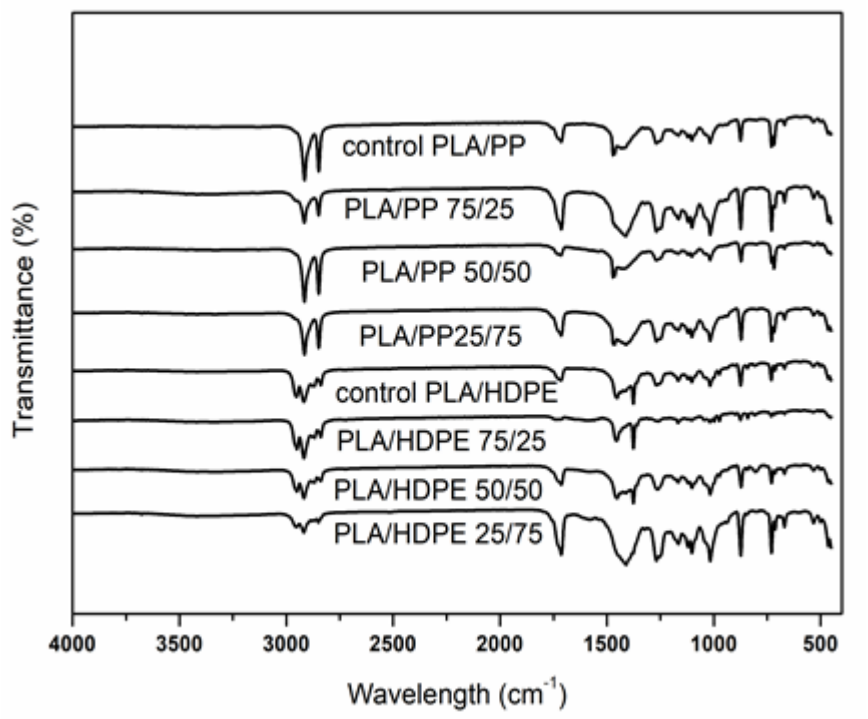


Fig 15:- FTIR of the PLA/PP and PLA/HDPE Blends

From the figure 15 it can be found that, the transmittance bands corresponding to PP are at 2950-2838, 1455-1453, and 1376 cm^{-1} referred to CH stretching, CH_3 bends, and C-H bending, respectively. The transmittance bands corresponding to PLA are at 1749, 1181, and 1080 cm^{-1} referred to C=O stretching, symmetric C-O-C stretching, and asymmetric CH_3, respectively. A carbonyl band will be present at 1700 cm^{-1}.From the graph the transmittance bands corresponding to HDPE are at 2950-2838, 1455-1453, and 1376 cm^{-1} referred to CH stretching, CH_3 bends, and C-H bending, respectively. A carbonyl band will be present at 1700 cm^{-1}. The transmittance bands corresponding to PLA are at 1749, 1181, and 1080 cm^{-1} referred to C=O stretching, symmetric COC stretching, and asymmetric CH_3, respectively.

K. Optical Microscopy

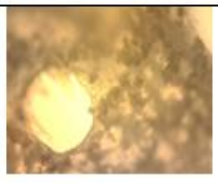
PLA-PP :Control	PLA/ PP 75/25 structural foam	PLA/PP 50/50 Structural foam	PLA/PP 25/75 Structural foam	Unmagnified image PLA/PP Blend foam
				
PLA/HDPE:Control	PLA/HDPE 75/25 structural foam	PLA/HDPE 50/50 Structural foam	PLA/HDPE25/75 Structural foam	Unmagnified image PLA/HDPE Blend foam
				

Table 3:- Optical Microscopy Images of All Specimens

Table 3 shows the optical microscopy images of all specimens of PLA/ PP and PLA/ HDPE blends. Cells are formed in compounds containing blowing agents. Light passes through the cells and it is very much visible from the normal photograph also. This confirms the cellular structure formation in the compounds with the use of chemical blowing agents.

IV. CONCLUSIONS

PLA/ PP and PLA/HDPE blends based structural foams was successfully prepared by moulding process. Sodium bicarbonate and citric acid are used as blowing agent, $CaCO_3$ is used as the filler, titanium dioxide is used as nucleating agent and PVC is used for flame retarding additive. The product is expected to have a wide range of applications and will be a promising product for the current needs in different fields. A Comparative study was conducted with PLA/PP and PLA/HDPE blends based structural foams. Physical, Mechanical, thermal strength and surface morphology characteristics were analyzed.

Density decreases with increase in concentration of PP.Tensile strength, elongation, tensile modulus, flexural properties such as flexural strength, modulus , hardness, impact strength found increased with increase in concentration of PP.Opacity increases with increase in concentration of PP.Water Absorption tests revealed that water absorption is lower with the increase in concentration of PP. Acid resistance, Alkali resistance, Flame resistance and Heat resistance increases with increase in concentration of PP.Thermal property study such as DSC show the melting point of the best structural foam is 150^0C and 140 ^{0}C for HDPE blends.

FTIR study show nature of functional groups present in the structural foam. The cellular structure of foam is observed by optical microscope which shows that the foam has uniformly distributed cellular structure. The developed foams with PLA/ PP and PLA/HDPE with 25/75 loading showed better dimensional stability. The prepared product can satisfy the requirements for larger extend for building construction. It can replace conventional materials like metal, wood and glass with a very high weight saving.

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