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SYNTHESIS AND CHARACTERIZATION OF FLAME RETARDANT PINEAPPLE LEAF FIBER-G- POLY (2 ETHYL HEXYL ACRYLATE)/ MMT COMPOSITE

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ABSTRCT

Natural fibre composites have been prepared by grafting hydrophobic monomer 2-Ethyl Hexyle Acrylate (2-EHA) on to chemically modified pineapple leaf fibre (PALF) using Benzoyl peroxide as initiator in an aqueous medium with additive montmorillonite. The polymerization reaction has been studied at various temperature duration and Benzoyl peroxide at various concentrations. The overall activation energy of grafting is found to be 19.04kj mol^{-1} and the optimum time period for the reaction is 3.5h. The chemically modified PALF, PALF-g-PEHA copolymer and PALF-g-PEHA/MMT composites so obtained have been characterized by FT-IR and their morphology studied by scanning electron microscopy (SEM). The thermal behavior and tensile properties of the samples have been studied and the flame retardant properties have also been evaluated by limiting oxygen index (LOI) test and cone calorimetry. The biodegradation and water absorbency have been carried out for its ecofriendly nature and better commercialization.

KEYWORDS: Pine apple leaf fiber, Poly (2-Ethylhexylacrylate), Montmorillonite, Biodegradation, Flame retarardant.

1 INTRODUCTION

Threatened by a global ecological, environmental and energy crisis, worldwide governmental regulations are challenging manufacturers to achieve all-time high standards of sustainability and eco-efficiency. This has fueled research aiming to replace non-biodegradable petroleum-

based resins, synthetic fibers (e.g. glass and composites), with fully bio-degradable environmentally friendly lignocellulosic natural fibers. Due to their high specific strength and modulus, fiber reinforced polymer (FRPs) composites have received widespread attention. In recent years natural fibres appear to be the outstanding materials which come as the viable and abundant substitute for the expensive and nonrenewable synthetic fiber. Natural fibres like sisal, banana, jute, oil plam, kenaf and coir has been used as reinforcement in thermoplastic composite for applications in consumer goods, furniture, low cost housing and civil structures. Pineapple leaf fibre (PALF) is one of them that have also good potential as reinforcement in thermoplastic composites. It is the objective of the current research to characterize PALF and to investigate the effect of fibre treatment on the mechanical properties of PALF reinforced poly (2-Ethyl Hexyl Acrylate) i.e. PALF-g-PEHA/MMT composite. PALF was prepared from raw pineapple leaf. It was then chemically treated to hinder the water content. It was compounded using two roll mill machines and form the composite. The samples were prepared for tensile test (ASTM D638).Scanning Electron Microscope (SEM) was used to investigate the miscibility between the fibre and matrix. Pineapple leaf fiber(PALF) is a multicultural lignocellulosic fiber [1,2] obtained from the leaf of the plant *Annanus comosus* belonging to the Bromeliaceae family contains cellulose (68.5%), hemicelluloses (18.8%) lignin (6.4%), Pectin (1.1%), fat and wax (3.2%) ash (0.9%) and other substances like proteins, organic acids etc. (1.46%) [3].

It was also observed that the flexural modulus and strength of treated PALF reinforced PEHA composite increased linearly with increment of fibre loadings. The optimum fiber loading for the best performance of the composite achieved was 30 wt%. This was clarified further by SEM where fibres and matrix have shown better miscibility at 30 wt% of treated PALF. PALF composites are very cost effective materials, especially for the building and construction industry, packaging, automobile, railway coach interiors and storage devices. Composites with light weight, high strength to weight ratio, stiffness and flame retardant property are replacing conventional material like metals, wood etc.

Material scientists all over the world have focused their attention on natural composites reinforced with fibre like jute, sisal, coir, pineapple leaf etc for their light weight, recycling potential, attractiveness to green customers and to cut down the cost of raw materials as well. It is largely cultivated in tropical countries mainly for fruits. According to estimates available India has over 87,200 hectors land under pineapple cultivation. In order to develop

composites and copolymers with better mechanical properties and environmental performance it is necessary to impart hydrophabicity to the fibres by chemical reaction with suitable agents.

However, to the best of our knowledge, there has been little work on the grafting of synthetic polymer on to PALF. In the present work, the authors have modified PALF with 8%NaOH and.5% sodium chlorite ($NaClO_2$) in order to remove the lignin which is a retarder of chemical grafting4.These modified PALFs were then grafted with a hydrophobic monomer,2-Ethylhexylacrylate using Benzoyl peroxide as initiator. The commercially important properties of the grafted samples were characterized, focusing special attention on their surface morphology,biodegradability,fire retardancy,etc. for future application as an agrowaste and to reduce the environmental pollution caused by plastic waste [5-6].

2 MATERIALS AND METHODS

2.1 Materials

Pineapple leaf fibre was obtained from the National Institute of Research on Jute and Allied Fibre Technology, Kolkata, India. It was treated with 8%NaOH and 5% $NaClO_2$ separately in two different containers overnight. Fibre sample treated with $NaClO_2$ enhancing its bleaching action. The sample was then washed properly with triply distilled water, neutralized with 0.1% HCl and finally dried in a vacuum over at 60^{o}C for 24h. These were done to remove lignin, the retarders of chemical grafting and to increase the thermal stability of the fibre. The monomer 2-Ethyle Hexyle Acrylate (2-EHA) was obtained from EMerch, India and purified 5% NaOH & 3% H_3PO_3 & then with double distilled water three times & finally putting $CaCl_2$ to it for 12 hrs. Benzoyl Peroxide (BPO) obtained from EMerch, India .

2.2 Preparation of Graft Co-Polymer

PALF was presoaked in 2-EHA for 1h at various concentrations in a polymerization tube with a joint for passing nitrogen gas. The reaction vessels were deaerated by passing nitrogen for 15 min & then sealed with rubber septum. The vessels were kept in a constant temperature bath until the mixture attained thermal equilibrium. Then the requisite amount initiator (BPO) was injected carefully in to the reaction system. Turbidity appeared within 15 min of reaction time. After the desired time was over, the polymerization reaction was arrested under ice bath followed by the addition of a small amount of hydroquinone to consume the unreacted free radicals. The graft copolymer thus obtained was washed thoroughly with deionised water to remove unreacted BPO and hydroquinone.

The gross polymer thus obtained was refluxed with toluene for 48h at 40^{O}c to remove the homo polymer PEHA. The cross linked PALF-g-PEHA, thus obtained was vacuum dried at 40^{o}-50^{o}c for 24h till it attained a constant weight. The percentage graft yield (G %) and rate of grafting (Rg) were calculated from the initial weight of PALF (w_i) and the weight of cross linked PALF-g-PEHA (w_g) using the following relationship.

$G\% = [(w_g - w_i)/w_i] \times 100$

$R_g = (w \times 1000)/ (v \times t \times M)$

Where W= wt of monomer

V= Total volume of system

T= Time of reaction in sec

M= Molar mass of monomer

2.3 Preparation of PALF-g-(2-EHA)]/MMT composite

The [PALF-g-(2-EHA)]/MMT composites were prepared by adding the requisite amount of aqueous MMT after 2h of the reaction time carried out in the grafting procedure described above.

2.4 Characterization & properties

2.4.1 FT-IR spectra

The FT-IR spectra of bleached PALF, PEHA homopolymer, [PALF-g-poly (2-EHA)] copolymer and [PALF-g-poly (2-EHA)]/MMT composite were taken using the KBr pellets in a Perkin Elmer paragon 500 FT-IR spectrophotometer.

2.4.2 Thermo gravimetric Analysis

The TGA of the samples were carried out using a shimadzu DTG-50 thermal analyzer. The samples were heated to a temperature of 500^{o}C at the heating scale of 10^{o}c per min starting from room temperature (30^{o}c)

2.4.3 Flame retardancy

The flame retardancy of the composites was assessed by LOI test according to ASTM D 2863, Apparatus from Fire Instrument Research Equipment Ltd. with a digital read out of oxygen concentration to +0.1%. The dimension of the compression mold sample is (100×6.5×3) mm. The LOI value corresponds to the minimum concentration of oxygen in the mixture of oxygen /nitrogen necessary to burn the sample during 3min or over a length of

80mm. The cone calorimetry is one of the effective methods for studying the flammability of fire retardant polymers [7].The horizontal orientation using a Stanton Red CROFT Cone Calorimeter[8] in accordance with the procedure outlined in AS/NZS 3837; 1998, which was based on ISO 5660-1; 1993, with dimensions 100×100×4 mm^3 at a external heat flux (9)+ 35kw/m^2 . The peak HRR is known to be an important factor in predicting fire hazards, when exposed to a 35kw/m^2 , a multilayered silicate heat flux, as measured by cone calorimeter.

Table. 1: Cone Calorimetric Data and LOI Values of PALF, PALF-g-PEHA, and (PALF-g-PEHA)/MMT (10%w/v) Composite

Samples	TTI(s)	PHRR (kW/m^2)	AvRHR (kW/m^2)	THR(MJ/m^2) MLR(g/s)	MLR (g/s)	AvCO (kg/kg)	PSEA (m^2/k)	LOI
ALF	64	554±12	156±5	21±2	0.045	34	154	18.8
PALF-g-PEHA	69	543±12	163±5	24±2	0.043	37	189	20.4
(PALF-g-PEHA)/MMT	55	423±12	148±5	17±2	0.036	39	172	24.8

2.4.4 Tensile Behavior

The tensile behavior of the samples before and after biodegradation was evaluated by measuring the tensile strength as per the method supported by Haque and Habibuddowala 10. The tensile strength was determined from the tenacity [11] (g/den) and elongation-at-break by using the following relationship.

Tensile strength = Tenacity at break/Elongation at break ×100

After conditioning the samples, they were combed. Fibre aggregates of uniform length were taken and their weight and length determined by means of a Dutrons tensile tester (Brand-20kg of capacity)

2.4.5 Scanning Electron Microscopy

The SEM micrographs of bleached PALF,PEHA homopolymer PALF-g-PEHA copolymer and [PALF-g-PEHA]/MMT composite were recorded by using scanning electron microscope (model 5200) of Jeol Ltd, Japan.

3 Water absorbency

The water absorbency (12) (W_{abs}) of the PALF, PALF-g-PEHA an (PALF-g-PEHA)/MMT composite was determined by immersing the dry samples (W_0=1g each) in deionized water at room temperature for 24h. After the required time period, the samples were drained for

30min for the elimination of excess non absorbed water, and the weight of the swollen samples (Ws) was recorded. The water absorbency was calculated using the following equation;

$Q\ (gH_2O/g_{sample}) = [(Ws-W_0)/W_0)]$

4 Biodegradation

The biodegradation of bleached PALF, PALF-g-PEHA, and (PALF-g-PEHA)/ MMT composite were studied in sludge water, soil burial and bacteria culture medium to compare the extent of biodegradation under these conditions.

4.1 Sludge water degradation

Fiber samples (0.1) g were immersed and incubated at 40oc in the supernant liquid taken from standard activated sludge collected from the waste dump areas where both solid and liquid wastes were collected. The water collected was centrifuged and the supernant liquid was taken for the study.

5 RESULTS AND DISCUSSION

Infrared spectra (FTIR)

According to the literature, the lignin content decreases with bleaching the PALF, Graft copolymerization of natural fiber increases with a decrease in the lignin content[13]. Figure 1 shows the graft copolymerization of PEHA on the backbone of PALF. In the case of bleached PALF**,** there is a strong broad peak at3360cm^{-1}due to the characteristic hydrogen bond$(OH)_{str}$ vibration as reported earlier[14]**.** When compared to PALF, in the case of PALF-g-PEHA, absorption bands at1545, 1406, and 1015cm^{-1}, assigned to the carbonyl group of the carboxylate of PEHA, the new peak obtained at 1755cm^{-1} is the stretching vibration of carbonyl group present in the monomer. There are other bands near 2980cm^{-1}corresponding to the normal (C-H) str, 1450$cm^{-1}$for (C-C) str, 1350cm^{-1} for $(C-H)_{def}$ and 1080cm^{-1} for (C-O)str.

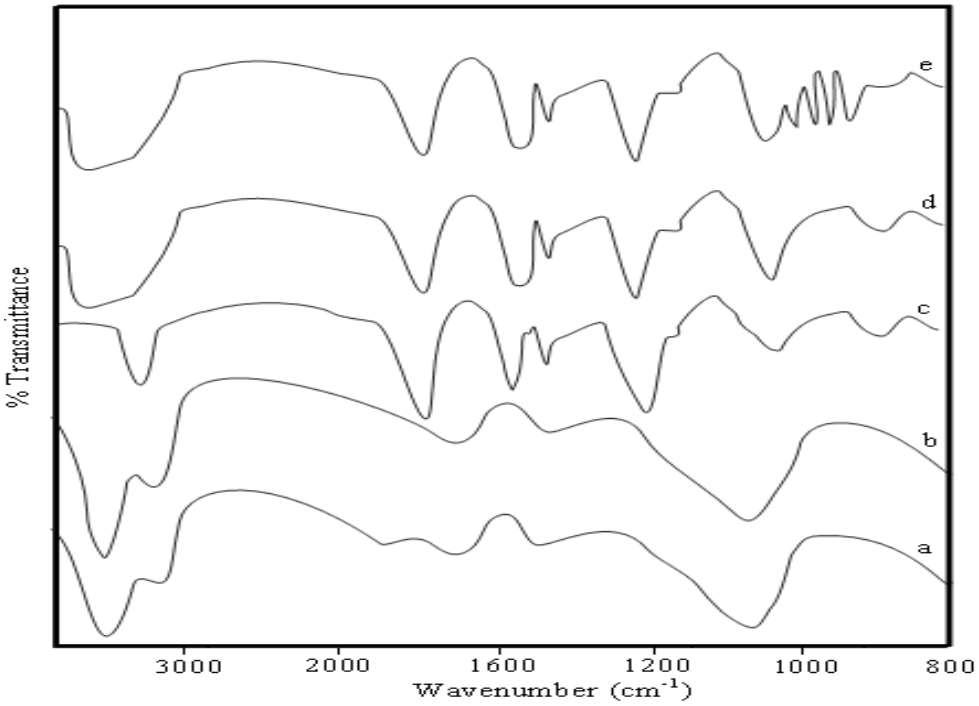
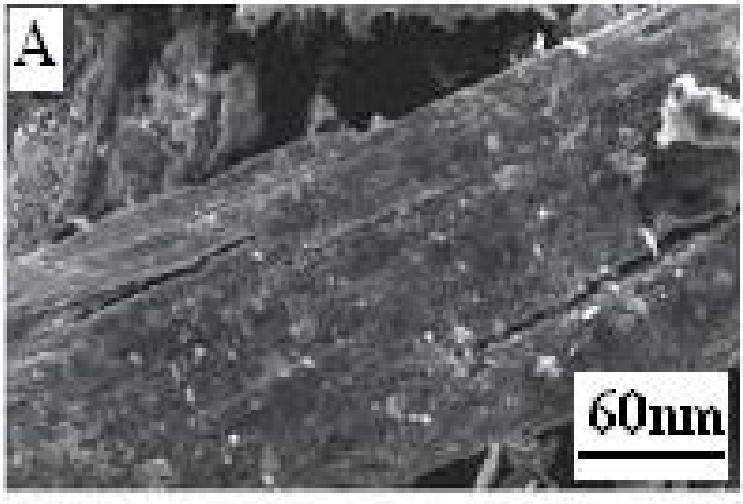


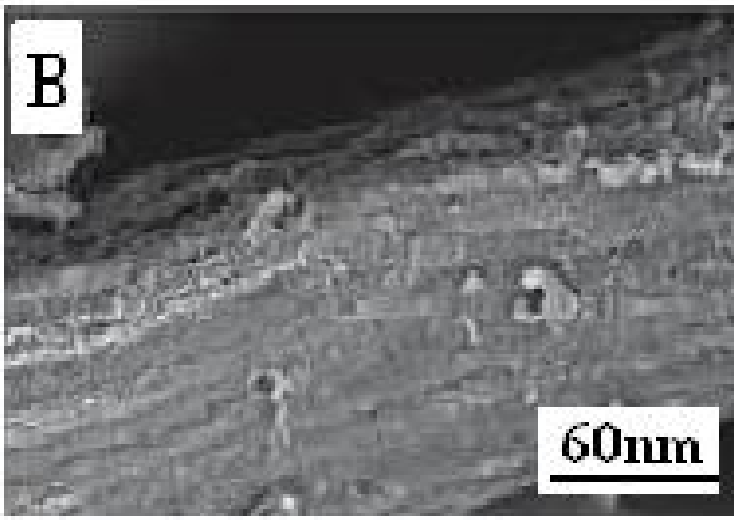
Figure I. FTIR spectra of (a) raw PALF, (b) Bleached PALF, (c) PEHA, (d) Bleached PALF-g-PEHA and (e) Bleached PALF-g-PEHA/MMT composites

Scanning Electron Microscopy

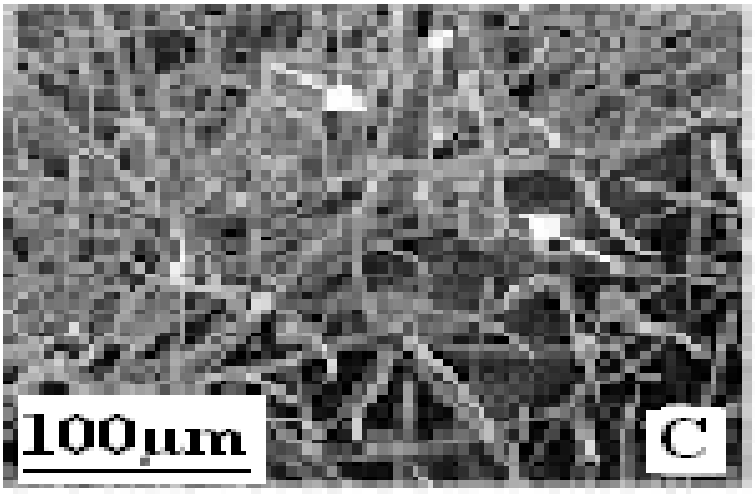
The surface morphology of PALF-g-PEHA and (PALF-g-PEHA)/MMT composite are shown in Figure 2 . On grafting with 2-EHA, the surface morphology of PALF is changed as shown Figure 2(b), Figure2(c) shows the presence of MMT embedded on the surface of the PALF.On addition of MMT to a crosslinked sample,i.e. (PALF-g-PEHA)/MMT, the property increases, and as a result the composite sample is compelled to carry more water than the PALF-g-PEHA copolymer.



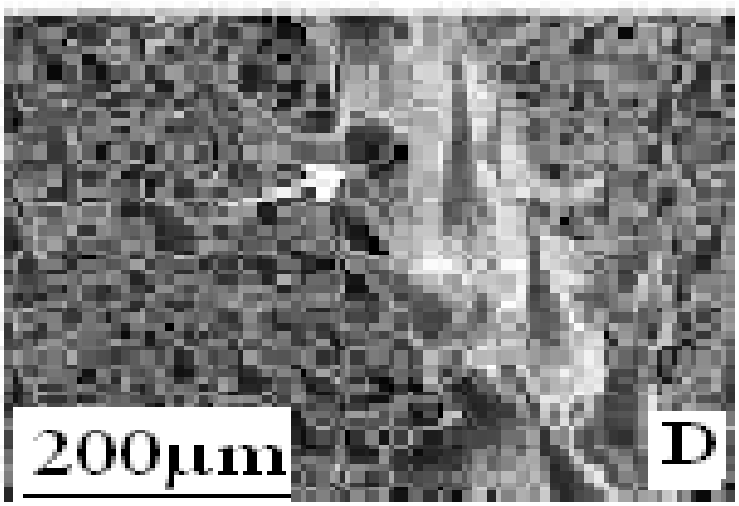
(A) SEM figure of Unbleached Pineapple leaf fiber



(B)SEM figure of bleached Pine apple leaf fiber



(C) SEM figure of PALF-g-PEHA



(D)SEM figure of (PALF-g-PEHA)/MMT

Thermogravimery analysis(TGA)

In this study, the Thermo gravimetric (TGA) curves were used to determine the thermal degradation and thermal stability of each material. The TG analysis of pineapple leaf fiber (PALF),PALF-g-PEHA and (PALF-g-PEHA)/MMT composite are presented in *Fig. 3(a,b,c)*. The thermal decomposition of each sample took place in a programmed temperature range of 25°C to 800°C. The thermal decomposition of PALF under nitrogen atmosphere comprises of a two-step process. The first step process that was shown at temperature 25°C to 103°C had a weight loss of 2.4%. Several previous studies [15-16] (e.g. Threepopnatkul *et al*., 2009; De Rosa *et al*., 2010) revealed that the loss weight of this stage was due to the release of absorbed moisture or vaporization of the water from the fibres [17]. George *et al*. (1996) reported that the weight loss of pineapple fiber at 100°C was about 6%, while at 200°C and 300°C, the weight loss were about 7.6% and 16%, respectively. The second stage of weight loss occurred at 126°C - 542°C, with the peak of this transition at 339°C. This weight loss indicated the decomposition of cellulose [17]. In their study, the thermal decomposition of pineapple fibre was obtained at 350°C. Meanwhile, the residual weight of PALF in the temperature that ranged between 25°C - 800°C was 17% (*see* Table 2). The temperature of decomposition (T_D) is very much influenced by the addition of MMT. From the curves, TD was found to be 205 ^{0}C for PALF-g-PEHA and 2500C for the (PALF-g-PEHA/MMT composite. Residual mass for PALF-g-PEHA and PALF-g-PEHA/MMT composite was found to be 9% and 15% respectively. Thus T_D values and residual mass indicates that on addition of MMT, the (PALF-g-PEHA)/MMT composite becomes somewhat resistant to thermal action.

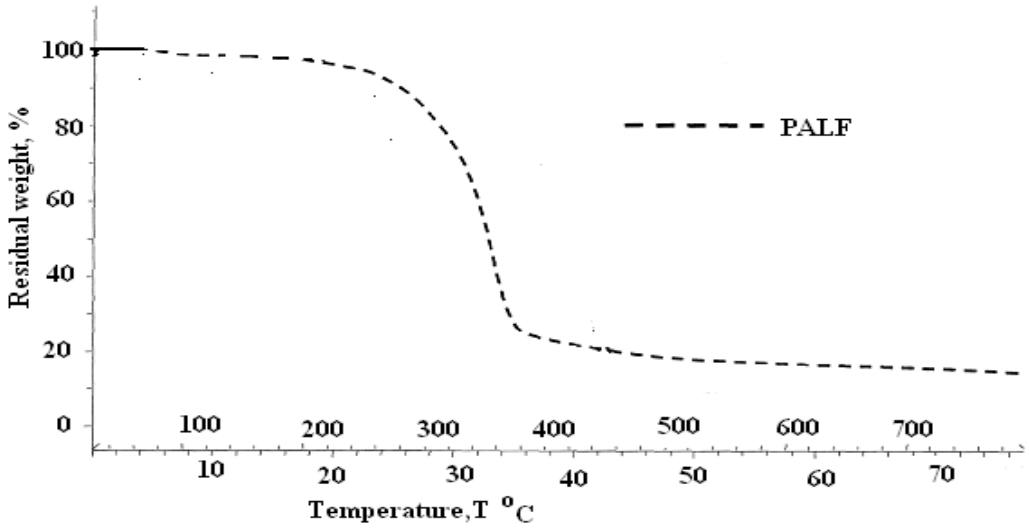


Figure 3 (a)TGA of PALF

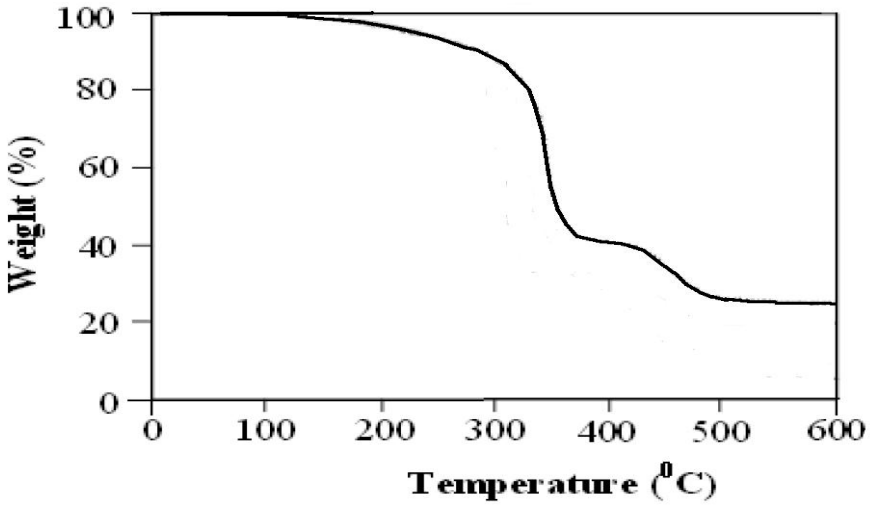


Fig3(b): PALF-g-PEHA

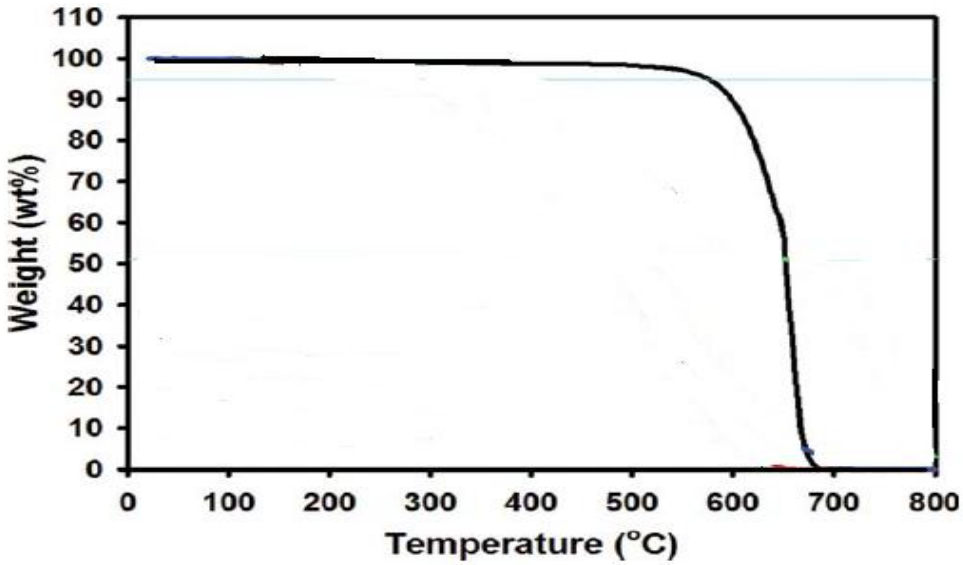


Figure 3c .PALF-g-PEHA/MMT composite

Flame retardancy

LOI is the popular research measurement to evaluate fire extinction. The errors associated with LOI measurements generally are 10.2%, and the results reported in table1 are the average of three to five determinations. A large increase in LOI is seen for the presence of MMT (18)which only 5%, but **as** the amount of MMT increases the LOI leaves out and the value is relatively constant above 15%. The evidence for protective, effective effect of layered silicate has on the composite obtained by cone calorimeter. The cone calorimeter instrument provides a method for measuring the amount of heat or energy released from a material during combustion. Other parameters that are measured simultaneously include smoke, carbon monoxide generation, ignition behavior, mass loss etc.

Rate of HRR is one of the most important parameters associated with the flammability and combustion of materials. The samples that have low value of HRR are better fire retardant than those with high HRR value. From Figure4 and Table1, it was found that the HRR value of PALF or PALF-g-PEHA was more than (PALF-g-PEHA)/MMT composite. The flammability property of a solid phase flame retardant can be the result of formation of charred residue with the silicate layer present in it. Because of the formation of char residue, layered silicate acted as a protective barrier by reducing the heat and mass transfer between the flame and the samples. In our previous article [19-20] we proved that the HRR was normally lowered because of the presence of MMT such as clay which was explained by Gilman et al [21] and others [22, 23].

From Figure 4 and Table 1 the time to ignition (TTI) value of (PALF-g—PEHA)/MMT composite was lower than the others because the first decomposition of silicate formed a charred residue like clay on sample. Further, the flame retardancy of polymer is explained by mass loss rate (MLR) value. But HRR mainly depends on the MLR value, i.e., the substance having lower MLR have lower HRR. From Table 1, it is found that the (PALF-g-PEH/MMT has low MLR than others. The decrease of MLR during combustion in cone calorimeter is due to the formation of charred residue on samples, which is coincided with data of Lee et al.

TABLE II.

Tensile strength of PALF, PALF-g-PEHA and (PALF-g-PEHA)/MMT Composite

Sample	Elongation at break (BL%)	Tenacity (g/den)	Tensile strength (N/m^2) Tensile strength after 28 days (N/m2)	Tensile strength after 28 days(N/m2)	Strength Retain (%)
PALF	28.8	0.087	37.8	5.6	14.81
PALF-g-PEHA	40.4	0.426	48.7	7.1	14.45
(PALF-g-PEHA)MMT	38.5	0.389	49.7	6.4	14.00

The tensile properties of PALF, PALF-g-PEHA, AND (PALF-g-PEHA) MMT composite are given in table II. The results show that PALF has the lowest tensile strength than other samples. The tensile strength of fibers mainly depends on the presence of lignin and binding materials, and the substances having less lignin and binding materials have lower tensile strength. Presently, in PALF the lignin and binding materials are removed by alkali treatment; hence, the tensile strength is decreased .From Table II, the tensile strength of PALF-g-PEHA copolymer is more because of the grafting of PEHA on to the back bone of PALF. The presence of MMT in (PALF-g-PEHA)/MMT composite is the cause of the

decrease in the tensile strength than that of PALF-g-PEHA [24].

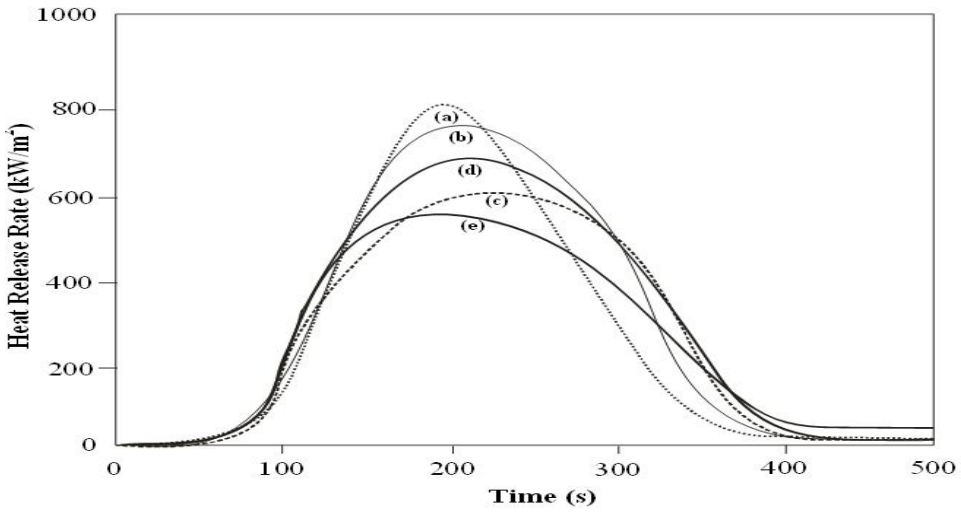


Figure 4. HRR vs. Time of (a) Bleached PALF, (b) Unbleached PALF, (c) PEHA, (d) Bleached PALF-g-PEHA & (e) Bleached PALF-g-PEHA/MMT composites.

Water absorbency

Figure 5 shows the absorption of various samples in deionised water. It is found that the water absorption of PALF is low because of the absence of lignin and binding materials. But the water absorption of PALF-g-PEHA shows low value when compared to PALF because of the increasing hydrophobic nature by grafting of hydrophobic PEHA on to the backbone of PALF. The water absorption of (PALF-g-PEHA)/MMT composite is increased with increasing hydrophilicity because of the presence of hydrophilic MMT. The water absorption also depends up on porosity, i.e. the substance having more porosity has more water absorbency. Addition of MMT facilitates more water absorption and increases the porosity of the composite.

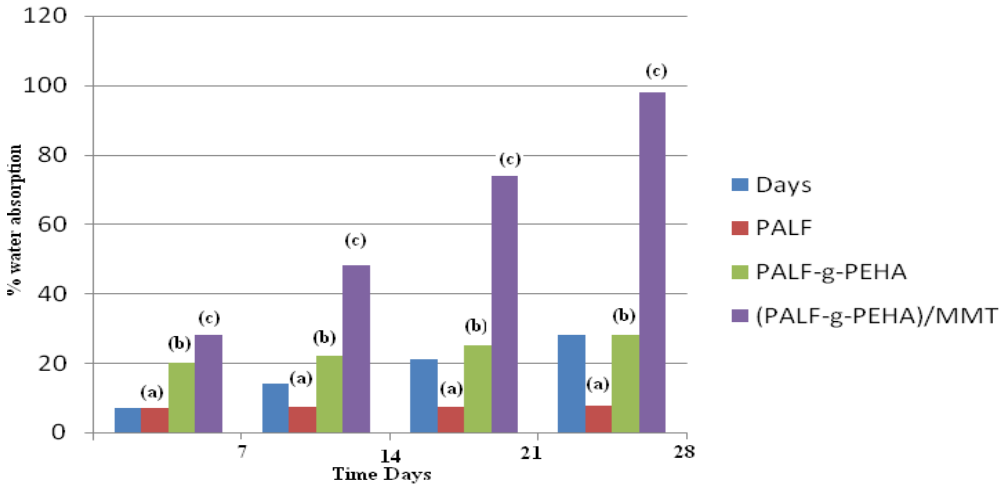


Figure 5 Water absorption of (a) PALF (b) PALF-g-PEHA (c) (PALF-g-PEHA)/MMT composite

Biodegradation

Figure 6 shows the biodegradation of PALF, PALF-g-PEHA copolymer, and (PALF-g-PEHA)/MMT by activated sludge water with their water uptake capacity .The presence of microorganisms in sludge water is the cause of biodegradation of the samples. The biodegradation of PALF is low because of the absence of lignin and binding materials. Addition of hydrophobic PEHA on to the backbone of PALF causes further decrease in the biodegradation of PALF-g-PEHA copolymer than the PALF. But the biodegradation of (PALF-g-PEHA)/MMT composite is increased with the addition of hydrophilic MMT because of the presence of dispersed silicate layers with large ratio in the composite matrix, which forces the microorganisms diffusing in the bulk of the matrix through more fortuous path. All these data are agreement with the decrease in tensile strength after 28 days in activated sludge water (Table II).

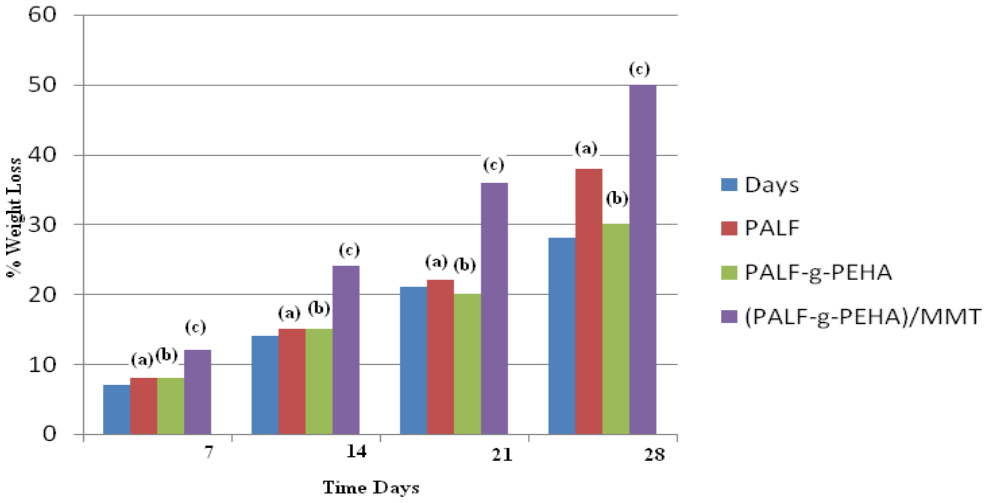


Figure 6 Biodegradation of (a) PALF (b) PALF-g-PEHA (c) (PALF-g-PEHA)/MMT composite

CONCLUSION

Natural fiber based composite was prepared from PALF through grafting with PEHA monomer and MMT. The resulting composite was characterized by FTIR, TGA, SEM, and tensile properties. The observed IR peak indicate the inclusion of MMT on to the PALF-g-PEHA forming a composite. TGA and tensile strength data reveal that, on addition of MMT the composite becomes resistant to thermal action, but is not as strong as the samples without MMT. The LOI and the cone calorimetric values show the composite with MMT is more flame retardant than the virgin fiber and copolymer. The porous nature of the PALF and the grafted composite with MMT showed higher water absorption as well as biodegradation in

activated sludge. They may find use in industries as flame retardant, tough and durable materials.

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