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RESEARCH ARTICLE

SYNTHESIS AND CHARACTERIZATION OF FLAME RETARDANT JUTE-G-POLY (2-ETHYL HEXYLACRYLATE)/MONTMORILLONITE COMPOSITES

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ABSTRACT

Chemically modified jute fiber (Tossa variety) was grafted onto 2-ethyl hexylacrylate (2-EHA) to prepare copolymer using *in situ* developed transition metal complex initiating system; CuSO₄/glycine/potassium monopersulfate (KMPS). Then its composites were prepared by incorporating montmorillonite (MMT) clay. The above samples were characterized by Fourier Transform-Infrared (FTIR) spectroscopy and surface morphology by Scanning Electron Microscopy (SEM). The thermal behavior and tensile strength of the samples were studied. The fire retardant properties were studied using oxygen consumption cone calorimeter. The biodegradability of the composites was tested to see if it is ecofriendly by nature and viable for better commercialization.

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INTRODUCTION

Jute fiber (JF) (tossa variety) is an environmentally and ecologically friendly product. The grafting of vinyl/acrylic monomers onto natural polymers such as starch (Fu *et al.*, 2002 and Athawale *et al.*, 1999) cellulose (Samal *et al.*, 1984), wool (Sahoo *et al.*, 2002) JF (Sahoo *et al.*, 2003; 2005) etc. is of great importance to develop new materials having the properties of both natural and synthetic polymers. Jute is a low-cost, multicellular, lignocellulosic fiber (Sahar *et al.*, 1991) produced in large quantities every year in India. On chemical treatment of jute fiber such as the reduction of lignin by bleaching and then grafting on its back bone, so forth expected to open a new demand for its use in various industries like transport, building etc. In our previous work we have studied grafting of poly acrylamide onto the backbone of JF (Sahoo *et al.*, 2005), to prepare a superabsorbent and waterabsorbant materials (Sahar *et al.*, 1991 and Kozlowski *et al.*, 1999). But there are very few articles on flame retardant JF composites by using MMT clay. In addition to its application in the automotive and transport industries, forced a higher use of natural biodegradable resources for its safety and comfort (Kozlowski *et al.*, 1999; Kizkiwski *et al.*, 1999; Schnipper *et al.*, 1995 and Horrocks and Price, 2001).

The natural fibers are mainly used in the interior parts of automotive and transport industries. But its use in this sector is suppressed due to their flammable nature. The modern transport industries need to be highly comfortable, relatively light, flame and heat resistance as well as with an aesthetic characteristic. It can be used as flexible barrier materials in the form of non-flammable interlayer by making flame retardant upholstery. Earlier flame/fire retardant polymer materials were prepared by addition of halogen, phosphorous or silicate etc, in to the virgin polymer. But in the case, of chlorine as additive, most important disadvantage is the evolution of toxic gas (Crivello *et al.*, 1997). This type of material is the reservation of production in Europe and USA. Another type of additive material used for flame/fire retardants is phosphorous, which acts as an intumescent coating. In this method, an intumescent coating agent provides a thermal and physical barrier to the underlying substrate. This barrier inhibits gaseous products and shields the substrate against heat and air when exposed to fire. This creates protective barrier on the surface. In case the surface is damaged, there may be a fire hazard (Tsuchida *et al.*, 1997). Recently a new type of flame retardant has been developed in which silicate is used as a filler to prepare fire retardant material. Even addition of relatively small amount of silicate compounds to various materials can significantly improve their flame/fire retardancy, through both char forming in the condensed phase and the trapping of active radicals in the vapor phase. These are considered to be 'environmentally friendly' additives because their use leads to a reduction in the

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harmful impact on environment as compared with existing materials unlike halogen compounds (Wang *et al.*, 2000; Hsiue *et al.*, 2000; Zaikov *et al.*, 1998; Kojima *et al.*, 1993 and Messersmith *et al.*, 1995). Organic-inorganic nanocomposites, from silicon materials such as clay, kaolin, emerge in the literature as a new concept (Gilman *et al.*, 1998). In the present work, JF-g-PEHA copolymer is reinforced with a new clay additive, MMT to form fire retardant composites. The synthesized composites were characterized by FTIR, XRD and SEM in order to study the micro structural interaction of the grafted matrix with MMT along with the study of fire retardancy and biodegradability properties. It was noticed that synthetic composite became fire retardant material with substantially increase in biodegradable properties due to strong interfacial adhesion between MMT and copolymer matrix.

EXPERIMENTAL PROCEDURE

MATERIALS AND METHODS

Monomer, 2-EHA was purchased from E Merck, Germany and purified by washing with 5%NaOH solution followed by 3% H₃PO₄ to neutralize the excess NaOH (approximately thrice each). The monomer was then washed properly with distilled water, dried over anhydrous CaCl₂, distilled under vacuum and stored in the refrigerator. CuSO₄, EDTA was purchased from E Merck India and used as such. Initiator KMPS was purchased from across, USA. The MMT clay with Cation Exchange Capacity (CEC) of 90mequiv/100g was purchased from HiMedia Pvt. Ltd. India. Jute is the local product. Bleaching of Jute fiber was done by standard CEH (Chlorination, Extraction and Hypochlorite) (Rapson, 1966) sequence technique with total chlorine consumption of 7.26% as per earlier report. Chlorination of jute fiber was carried out with 3.7% chlorine and 5% consistency for 60 mins at room temperature, when P^H was maintained about 2 to 3. Then the fiber was washed with 2% NaOH for 45 mins at 50-60°C. Followed by repeated washing with water until it was free from alkali. The alkali treated fiber was then treated with 1.5% NaClO₂ and warmed a little at 40-50° C for 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 oven at 60°C. Bleaching was done to remove lignin the retarder of chemical grafting and also to increase the thermal stability of the fiber.

Preparation of graft copolymer

The grafting of polymer of JF was described in our previous papers (Sahoo *et al.*, 2002; 2003). In this paper, JF was first presoaked in monomer 2-EHA for 12 hrs at 35° C. Then it was transferred to reaction vessel containing water. The requisite amount (0.1M) each of Cu (II) SO₄, glycine was added to it. The reaction vessels were deaerated by passing nitrogen gas for 15 min and then sealed with a rubber septum. The vessels were kept in a constant temperature bath until the mixture attained thermal equilibrium. Then the requisite amount of initiator (KMPS) was injected carefully in to the reaction system. Turbidity appears within 15 min of the reaction time. After the described time was over, the polymerization was arrested by quenching the vessel in ice bath, and dried it under

room temperature as described elsewhere (Sahoo *et al.*, 2002). This was the preparation of grafted composites by *in situ* method. The gross polymer thus obtained was refluxed with toluene for 48 hrs at 40°C to remove the homopolymer (PEHA). The JF-g-PEHA copolymer, thus obtained was vacuum dried at 40-50°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 JF (Wi) and the weight of JF-g-PEHA copolymer (Wg) using the following relationships:

$$G \% = [(Wg - Wi) / Wi] \times 100$$

$$Rg = (w \times 1000) / V \times t \times M$$

Where *w* is the weight of monomer; *V*, the total volume of the system; *t*, the time of reaction in second; and *M*, the molar mass of monomer.

Preparation of (JF-g-PEHA)/MMT Composite

The (JF-g-PEHA)/MMT composites were prepared by adding the requisite amount of aqueous montmorillonite (MMT) solution, prepared on a weight percentage basis. The grafting procedure described as above followed and the mixture was slowly heated to 80°C followed by addition of KHSO₅ dissolved in water. Emulsion polymerization was carried out with a constant stirring speed at 80°C. After 3h of reaction; polymerization was terminated by addition of a 0.1M solution of ferrous ammonium sulfate solution. The coagulated products were purified by washing with distilled water, and dried at 65°C.

Characterization

The IR spectra of bleached and unbleached JF, PEHA, JF-g-PEHA and JF-g-PEHA/MMT composite, in the form of KBr pellets, were recorded with Perkin-Elmer model Paragon-500 FTIR spectrophotometer. The surface morphology of bleached JF and JF-g-PEHA were observed by using scanning electron microscope (Model 5200) of Jeol Ltd. Japan, coating it with gold at a different magnification. The X-Ray Diffraction (XRD) patterns of the fiber and the modified fiber samples were recorded and scanned by a Philips Analytical BV diffractometer. The thermal properties were measured by using a Shimadzu DTA-500 system. It was carried out in air from room temperature to 600 °C at a heating rate of 10 °C/min. The fire retardant properties were studied by oxygen consumption cone calorimeter (Weil *et al.*, 1992). The cone calorimeter is standardized as ASTM E 1354 (Huggett, 1980). The peak heat release rate is a very important factor which may be used to express the intensity of fire (Fried, 1995). The combustion of various samples was investigated using a fire testing technology cone calorimeter having dimension 100 × 100 × 4 mm in conference with 180 DISS 5660-1 (Tsuboi, 1957) at a heat flux of 35 kW/m² which is recommended heat flux for exploratory testing. All the specimens were tested in triplicate using a retaining frame with data collection intervals of 5s. The combustion parameters determined include: Time to Ignition (TTI), heat release rate (HRR), Total Heat Released (THR), effective heat of combustion, Mass Loss Rate (MLR), CO and

CO₂ yield. TTI—determined visually and taken to be the period required for the entire surface of the sample to burn with a sustained luminous flame. Peak Heat Release Rate (PHRR) is considered as the parameter that best expressed the maximum intensity of a fire indicating the rate and extent of fire spread. Fire Performance Index (FPI) (m²s/kW)—defined as the ratio of TTI to PHRR. That parameter is related with the time to flashover (or the time available for escape) in a full-scale fire situation. Average Heat Release Rate (AvHRR) (3 min), (kW/m²)—taken as the average value of the heat release rate for the period from ignition to 180 s, this parameter is thought to correlate with the heat release in a room burn situation where not all of the material is ignited at the same time. The tensile strength of the raw jute fiber, bleached, grafted and JF-g-PEHA/MMT composites were determined through measurement of stiffness at break following the method of Haque and Habibuddin (Haque *et al.*, 1980). The tenacity was expressed as g/den. After conditioning the samples they were combed and the fiber aggregates of uniform length were taken and weight and length were determined. The tensile strength was determined by means of a Dutrons tensile tester, Brand-20 Kgf capacity. The TGA of the samples was carried out using a Simadzu DTG-50 thermal analyzer. The samples were heated to a temperature of 800°C at the heating rate of 10°C per min starting from room temperature (30°C).

Biodegradation by activated sludge

Biodegradation of jute and its other samples were carried out in activated sludge water. The activated sludge water was collected from a tank area receiving toilet and domestic waste water. In most areas of our country, the waste materials after use are dumped usually near the sludge area and the sludge water contains many micro organisms (bacteria, fungi, yeast, etc.) responsible for the biodegradation of waste materials. The sludge was collected (Federle *et al.*, 2002) in a polypropylene container, which was filled completely and then fully closed. Then the waste water was brought to the laboratory immediately. After settling for about 1hr, the total solid concentration was increased to 5000mg/l. The activated sludge water and a polymer sample (0.2gm) were incubated together in a sterilized vessel at room temperature (28±2°C). Duplicate samples were removed at time intervals for biodegradation study via weight loss. Vessels containing polymer samples without sludge water were treated as control.

RESULTS AND DISCUSSION

Fourier transform-infrared (FTIR) spectroscopic study

Proof of grafting has been established by IR spectroscopy graphically in Figure 1. The detailed IR peak of the JF was discussed in our previous paper (Sahoo *et al.*, 2002; 2003; 2005). The spectra of raw jute fiber showed additional bands near 1735, 1680 and 1600cm⁻¹ and a broad band in the region of 1200-1300cm⁻¹ having maxima near 1245cm⁻¹. There was a strong broad band near 3300-3400cm⁻¹ in the spectra of jute fiber and the same was due to hydrogen bonded -OH vibration (Blackwell *et al.*, 1970). The presence of absorption band near 1680cm⁻¹ in the IR spectra is due to >C=O stretching at the carboxyl groups. The sharp bands at 1545 and 1505 cm⁻¹

showed the presence of aromatic rings in jute fiber. The spectra of lignin revealed sharp bands in these regions because of the stretching modes of the benzene ring (Herbert, 1971).

The bands near 1250 and 1235cm⁻¹ were possible due to -C-O-C- bond in the cellulose chain. (Oltus, 1968) and -OH deformation (Blackwell *et al.*, 1970) respectively. Ungrafted, unbleached and bleached JF showed the characteristic broad absorption band at 3400cm⁻¹ for a free -OH band of O-H stretching vibration and 1040cm⁻¹ C-O stretching vibration. The absorption bands at 1595 is due to carbonyl group of the carboxylate of PEHA and absorption bands 2148, 1468&990cm⁻¹ and finger print of 618cm⁻¹ are due to the Si-O bond of MMT. The observed absorption at 1468cm⁻¹ is characteristic of partially ordered phase where the chains are mobile while maintaining some orientational order (Liang *et al.*, 1960). From Figure 1 (e), there was a strong broad band near 3300-3400 cm⁻¹ in the spectra of JF due to hydrogen bonded -OH vibration.

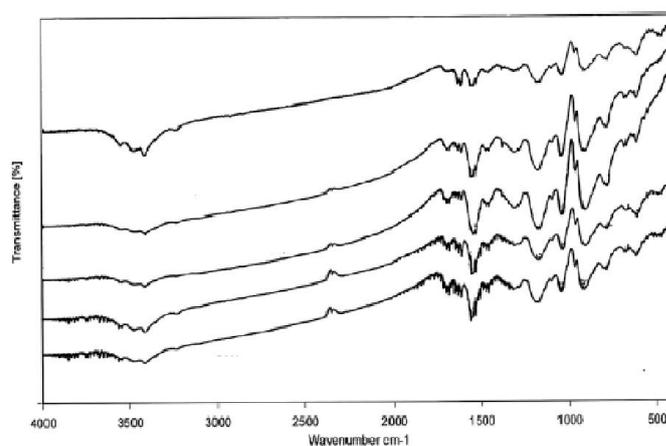


Figure 1. FTIR spectra of (a) raw JF, (b) Bleached JF, (c) PEHA, (d) Bleached JF-g-PEHA and (e) Bleached JF-g-PEHA/MMT composites

Scanning electron microscope (SEM) analysis

According to the literature, the lignin content decreases on bleaching the jute fiber. Grafting on to natural fiber increases with the decrease of lignin content which is confirmed from the grafting copolymerization of EHA on to the backbone of JF (Sahoo *et al.*, 2003; 2005). Chemically modified jute fiber with 2-EHA was characterized by its surface morphology in SEM (Hearle *et al.*, 1972) Figure 2. Especially, in the nanocomposites with JF-g-PEHA/MMT content less than 30 wt %, no obvious aggregations of nanocrystals and microphase separation were observed from SEM photographs. This indicates that JF-g-PEHA/MMT dispersed more homogeneously than JF-g-PEHA, resulting in a more chances to interact with JF, and thus formed a stronger interaction and adhesion on the interfaces of JF-g-PEHA/MMT and JF-g-PEHA molecules.

X-Ray Diffraction (XRD) study

The XRD method is a very useful and powerful analytical technique used for understanding crystallinity. The XRD

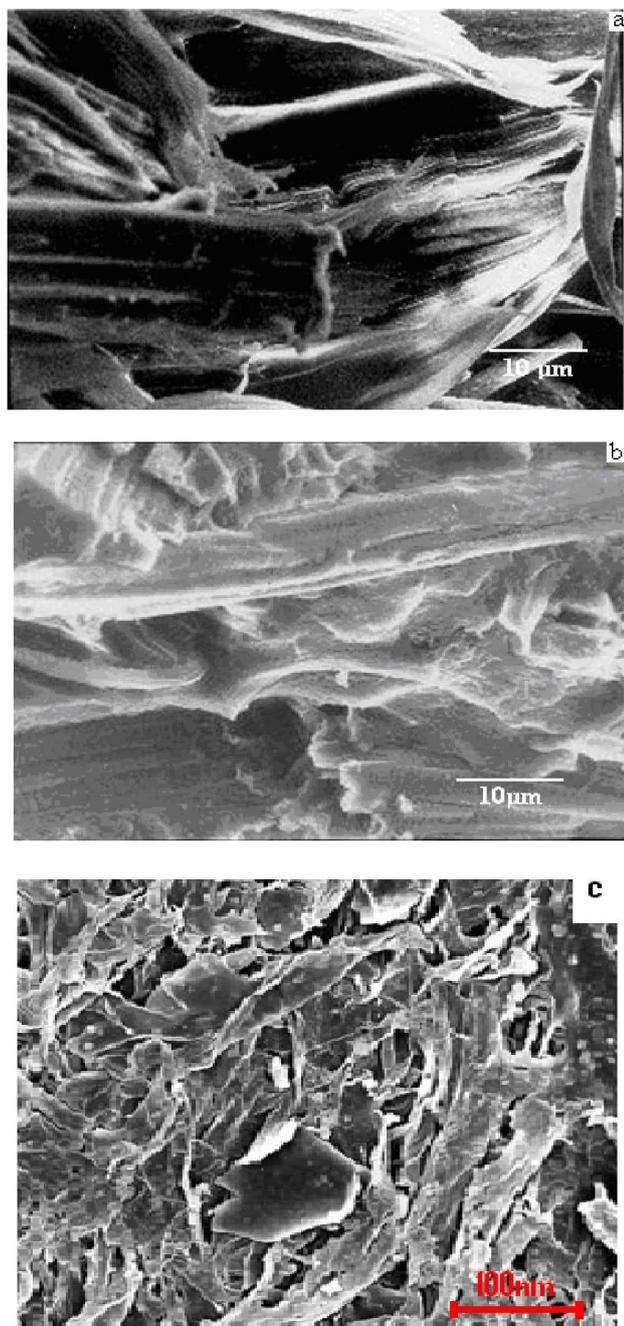


Figure 2. SEM of (a) JF, (b) JF-g-PEHA(c) JF-g-PEHA/MMT composites

pattern shown in Figure 3 reveals the degree of crystallinity in the raw fiber, modified fiber, grafted copolymer and its composite. The XRD analysis suggests the strongly hydrophobic JF-g-PEHA is increased in to the layerscrystallinity of grafted composite is increased due to presence of clay which was shown in Figure 3 (f).XRD spectra of the compound containing MMT in the small angle region under 10° on the 2θ scale (Chigwada and Wilkie, 2003). The compound containing the nonmodified MMT has one peak at 7° . Fig III reveals only a slight shift in the peak at $5.5-5.8^\circ$. In the low angle region of the data. This shift in low angle peak to higher angles after melting and cooling of organic modified MMT has been attributed to recrystallization of the treatment. Here the shift is explained by a shift from a disorder extended

bilayer to an interdigitated crystalline phase (Gilman *et al.*, 2000).

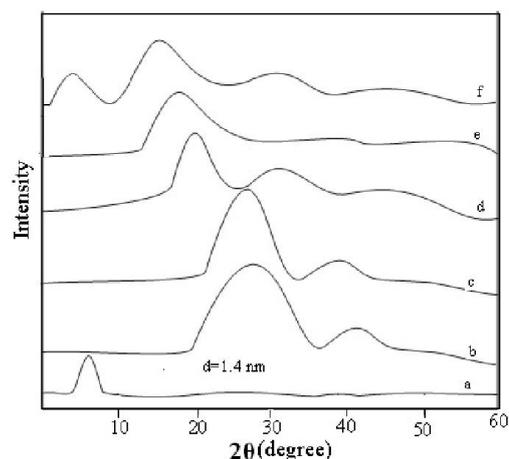


Figure 3. XRD of (a) MMT, (b) unbleached Jute, (c) bleached Jute, (d) PEHA, (e) Jute-g-PEHA and (f) Jute-g-PEHA/MMT composites

Thermo gravimetric analysis (TGA)

One can understand the course of the thermal degradation from TGA Figure 4.

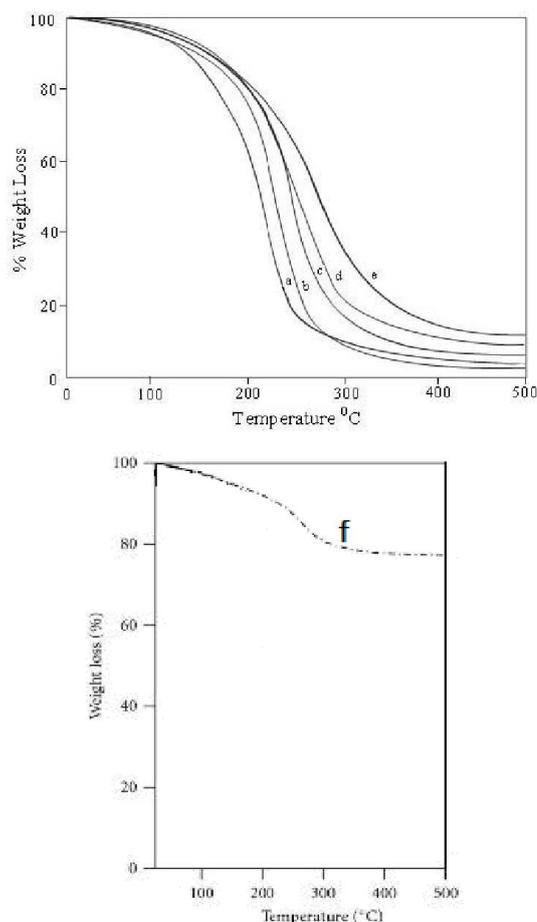


Figure 4. TGA of (a) Bleached JF, (b) Unbleached JF, (c) PEHA, (d) Bleached JF-g-PEHA (e) Bleached JF-g-PEHA/MMT composites and (f) MMT

The important parameters are the onset temperature of decomposition (T_d) for unbleached and bleached JFs, JF-g-PEHA and JF-g-PEHA/MMT composite. From the Figure 4, it was found that the thermal stability of JF-g-PEHA/MMT composite is shifted towards a higher temperature with increased MMT content. The enhancement in thermal stability occurs when JF-g-PEHA is intercalated in to the MMT (Bradly *et al.*, 2002). Due to the presence of clay the decomposition temperature of The JF-g-PEHA/MMT nanocomposite exhibited higher thermal stability due to the higher decomposition onset temperature than that of JF-g-PEHA copolymer, which can be attributed to the nano scale MMT layers preventing out diffusion of the volatile decomposition product. On the other hand, since the inorganic part (MMT) of the nanocomposite film almost did not loose its weight during the heating period, the shift of weight loss to higher temperature region might be simply due to that the nanocomposite film processed relatively small amount of organic polymer which contributed to the weight loss.

Flame Retardancy

The cone calorimeter instrument provides a method for measuring the amount of heat energy released from a material during combustion and also gives other parameters that are measured simultaneously including total smoke release, carbon dioxide & carbon monoxide generation, ignition time and also mass loss rate. The measuring principle is that of oxygen consumption. This states that there is a constant relationship between the mass of oxygen consumed from the air and the amount of heat released during the polymer degradation. The cone calorimeter is standardized as ASTM E 1354. From Figure 5 and Table 1, it was found that the time for ignition of the JF-g-PEHA/MMT was lower than that of JF-g-PEHA i.e.

ignition time for JF-g-PEHA/MMT composite was earlier than JF-g-PEHA due to the decomposition of MMT clay at lower temperature, which was correlated with Ray *et al.* (2003). HRR is one of the most important parameters associated with the flammability and combustion of materials. The samples which have low value of HRR are better flame retardant than those with high HRR value. Jute and its samples are generally flammable substances. But due to the presence of flame retardant substance it can show flame retardancy. Out of various flame retardant additives, silicon is such additive which shows flame retardancy; even when in a small amount present in sample, decreases the HRR value of silicate composites if present in the sample in an insignificant amount. From Figure 5 and Table 1, it was found that the HRR value of jute and its grafted samples were more than of any JF-g-PEHA/MMT composite. The low PHRR value of JF-g-PEHA/MMT composite was due to the formation of char residue, which acted as a protective barrier in between the flame and composites by reducing the mass transfer, which was explained by Gilman *et al.* (2000).

MLR is another factor that describes the flame retardant property. Flame retardancy of polymers is mainly dependent on HRR value. But, heat release capacity mainly depends on the mass loss rate and the heat of combustion of the decomposition products at that temperature. Therefore, the mass loss rates become another important factor that can determine the heat release rate. From Table 1, it was found that the MLR value of JF-g-PEHA/MMT composite was observably decreased with the presence of MMT in the JF-g-PEHA copolymer due to the formation of a protective barrier in between flame and sample. The value was correlated with the rate of mass loss from a polymer-silicate hybrid when exposed to heat, which was significantly reduced compared

Table 1. Cone calorimetric data of Jute and composite at 35 kW/m²

| Sample | TTI | PHRR | THR | MLR | TOC | AvCO ₂ | AvCO | PSEA |
|-----------------|-----|-------------------|-------------------|-------|-------|-------------------|-------|--------------------|
| | s | kW/m ² | MJ/m ² | g/s | g | kg/kg | kg/kg | m ² /kg |
| Bleached Jute | 64 | 812.4 | 96.5 | 0.065 | 15.87 | 3.3 | 0.02 | 174 |
| Unbleached Jute | 74 | 776.8 | 97.4 | 0.058 | 15.93 | 3.4 | 0.038 | 309 |
| PEHA | 71 | 621.2 | 83.7 | 0.045 | 14.74 | 3.0 | 0.034 | 258 |
| Jute-g-PEHA | 68 | 697.4 | 89.4 | 0.051 | 15.43 | 3.1 | 0.032 | 345 |
| Jute-g-PEHA/MMT | 59 | 567.8 | 74.7 | 0.032 | 13.29 | 2.9 | 0.024 | 224 |

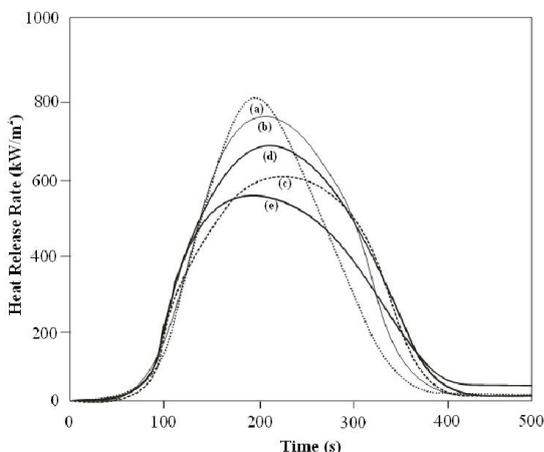


Figure 5. HRR vs. Time of (a) Bleached JF, (b) Unbleached JF, (c) PEHA, (d) Bleached JF-g-PEHA & (e) Bleached JF-g-PEHA/MMT composites

with the pure polymer given by Le *et al.* (1998). This deficiency came into effect after a couple of minutes of combustion, when the surface of the silicate-polymer had time to form char on the outer layer of the material. The JF-g-PEHA continued burning but the JF-g-PEHA/MMT composite became highly charred and stopped burning after the flame was removed. The THR due to the combustion of JF-g-PEHA or JF-g-PEHA /MMT composite was approximately same. Due to its cellulose structure, burning of JF evolves large amounts of smoke i.e. known to be hazardous in fire situation. Sample containing layered silicate (clay) produced more CO at a faster rate in the initial stage but total production of smoke is overall less than that of other samples due to the presence of layered silicate, char formed decreases and also smoke formation is decreased.

Mechanical Property

The tensile strength of JF, chemically modified JF, grafted jute and its composites was shown in Table 2. The tensile strength of JF decreased with alkali treatment. However in case of JF-g-PEHA sample, the strength increases slightly, which is an added advantage, which imparted 10-40%. However, with the addition of MMT, the tensile strength increases comparatively. The improvement in tensile properties was due to the uniform distribution of MMT platelets within the copolymer matrix. Further the intermolecular adhesion between MMT and copolymer can also be evidenced due to enhancement in tensile properties.

Table 2. Tensile strength of Jute and composite

| Sample | Tensile Strength (MPa) |
|-----------------|------------------------|
| Bleached | 20.82 |
| Unbleached Jute | 22.89 |
| Jute-g-PEHA | 25.68 |
| Jute-g-PEHA/MMT | 25.78 |

Biodegradation

Degradation by activated sludge

Biodegradation by activated sludge was less in the case of PEHA than that of JF-g-PEHA samples. The biodegradation is highest with additive MMT, as shown in Figure VI From this observation, it was confirmed that the growth of microorganisms was more in unbleached JF because of the presence of more lignin (which act as a nutrient for the degrading agent), in the sample. Because of the presence of inorganic filler increases hydrophilic property of JF-g-PEHA/MMT composite and hence the biodegradation.

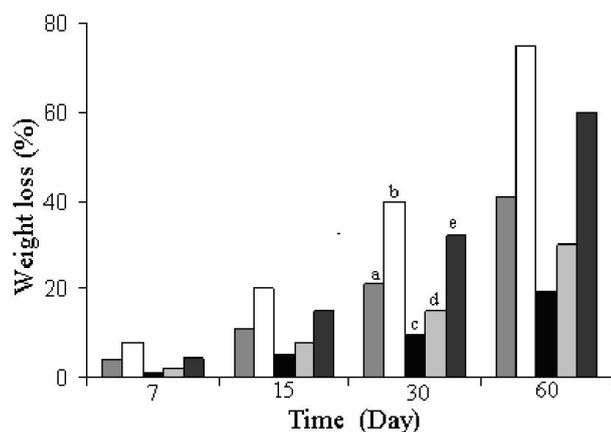


Figure 6. Biodegradation of (a) Bleached JF, (b) Unbleached JF, (c) PEHA, (d) Bleached JF-g-PEHA & (e) Bleached JF-g-PEHA/MMT composites

Conclusion

The novel flame retardant JF-g-PEHA/MMT composites were prepared by emulsion technique. The significant properties thereby inducing hydrophilic character to the hydrophobic PEHA matrix are noticed. The nanocomposites are characterized by FTIR, XRD, and SEM. XRD result showed a

disordered layer structure due to intercalation of copolymer in to the silicate layer of MMT. TGA exhibits higher thermal stability and cone calorimeter gives better flame retardancy than copolymer matrix. As the synthesized nanocomposites are ecofriendly, it may open the door for use as good commercial fire retardant materials.

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