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RESEARCH ARTICLE

MICROWAVE-ASSISTED PREPARATION OF BIODEGRADABLE SUPERABSORBENT (BNF-GRAFT-PAM)/SS NANOCOMPOSITE.

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Abstract

Betel nut fiber (BNF) graft polyacrylamide (PAM) copolymer and (BNF-graft-PAM)/Sodium silicate nanocomposite were prepared in a microwave oven using *in situ* developed transition metal complex initiating system i.e. CuSO₄/glycine/ammonium persulfate (APS) and *N,N'*-methylenebisacrylamide (MBA) as a crosslinker via nanotechnology by the inclusion of sodium silicate(SS) clay to the grafted polymer. The formation of (BNF-graft-PAM)/SS nanocomposite was confirmed by Fourier Transform Infrared Spectroscopy (FTIR). Furthermore, as evidenced by X-ray diffraction (XRD), transmission electron microscopy (TEM), the composite so obtained was found to have nano order. XRD and TEM were suggesting that SS layers were exfoliated during the polymerization process. An increasing in the thermal stability for the developed nanocomposite was recorded by thermo gravimetric analysis (TGA). The combustion behavior has been evaluated using oxygen consumption cone calorimeter and the nanocomposite exhibited good fire retardancy. The water absorption and biodegradation properties were carried out for its eco-friendly nature and better commercialization.

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Introduction:-

A large number of investigations have been done over the past decades on organic polymer-layered silicate nanocomposites due to their substantial enhanced physical properties over virgin polymers (Jeong et al., 2005, Ishida et al., 2000). These nanocomposites are most significant and new breed of composite materials due to their extensively enhanced mechanical (Wang & Pinmavaia, 1998), thermal (Wang et al., 2002), flammability (Gilman (1999), Sahoo & Samal, 2007) properties. Therefore, we have prepared nanocomposite taking natural plant fibre as reinforcing material, and these have received considerable attentions over synthetic fibres due to their low cost, low density, biocompatibility, nontoxicity, easily biodegradable and easily available in huge amount. In this work we have taken Seed fibre of betel nut (*Areca catechu*) which are available in the North-East India in large quantity and is found unutilized. The betel nut fibre (BNF) is a hard fibrous material covering the endosperm and is composed of cellulose with varying proportions of hemicelluloses (35-64.8 %), lignin (13.0-26.0 %), pectin and protopectin (Rajan & Kurup, 2005, Dhanalaxmi et al., 2012). The search for more durable and ecologically sound materials is very important in a process of technological change which is related with industry. Natural fibers offer many technological and environmental benefits when used as reinforced material in the area of composites such as high strength and stiffness quality in low density materials, high toughness, acceptable specific strength properties and good thermal property (Satyanarayan et al., 2006, Lachumanandavisavam (2006), Thomas (2007)). The development of betel nut fiber reinforced composite material which can replace synthetic plastics and provides few advantages like utilization of an abundant supply of betel nut fibre, thereby providing economic benefit to poor rural people, reducing the existing dependency on nonrenewable resources, and reducing plastic waste and associated harmful substances from the process of plastic incinerations.

On the other hand, microwave- assisted organic-polymer synthesis has received greater interest to the researchers due to the specificity of microwave heating in terms of reactivity associated with control of very fast heating rate (Cao et al., 2001, Stuerge et al., 1993). Microwave energy can be directly and uniformly absorbed throughout the entire volume of the reactive medium, causing it to heat up evenly and rapidly without heating reaction vessel (Danks (1999)). In microwave assisted synthesis the interaction between the microwave energy and molecular dipole moments of the starting materials takes place which provides an effective, selective, clean, and fast synthetic method (Fang et al., 2002), but the use of this radiation in polymer chemistry is unexplored. Microwave-assisted polymerization may be used as an alternative to thermal polymerization processes. The advantages of microwaves are increased rate of production, improved product characteristics, uniform processing, less time consuming (Stuchly & Stuchly, 1983). There are reports (Correa et al., 1998, Chia et al., 1995, Jacob et al., 1995) that show similar kinetics under both microwave-assisted method and thermal heating methods, suggesting that microwave does not alter the reaction products obtained in conventional heating process, and it also increases the yield in two or three folds. So microwave-assisted synthesis has been successfully investigated in the graft polymerization of chitosan with polyacrylic acid (Huacai et al., 2006), the cellulose on polyacrylamide (Pandey et al., 2013), bentonite on poly[sodium acrylate-co-polyacrylamide] (Kalaleh et al., 2013). Therefore, we have synthesized PAN/MMT nanocomposite (Sahoo et al., 2011), (SCBF-graft-PAM)/MMT composite (Rout & Sahoo, 2015), (SCBF-graft-PHEMA)/MMT composite (Rout & Sahoo, 2015) also.

The current work is an attempt to use rural bio-waste betel nut fiber as reinforced material, for first time, with acrylamide to prepare a nanocomposite for using as water absorbent /water retention in agricultural field. In this investigation we prepare a nanocomposite by grafting polyacrylamide on the backbone of BNF using CuSO_4 /glycine/APS as the complex initiating system with a cross linking agent MBA followed by the addition of Sodium Silicate (SS). The complex initiating system have already been used effectively as a catalytic system in the homopolymerization of acrylamide using a non conventional emulsion technique. The graft copolymer and the nanocomposite thus prepared were characterized putting special attention on their water absorption, surface morphology, flame retardancy and biodegradability for the futuristic application as an important biodegradable agro-waste.

Experimental procedure:-

Materials:-

Areca empty fruits were obtained from Madhu Farm House, Nilagal, Davangere, Karnataka, India. Acrylamide (AM) monomer (E. Merck, Germany) was purified by recrystallization from acetone and dried at room temperature under vacuum. The monomer was stored in a dark bottle. A stock solution of 4M was used for experiment. *N,N'*-Methylenebisacrylamide was used as purchased from Sigma Aldrich Co. Ammonium persulfate, Copper sulfate, glycine, sodium hypochlorite and other solvents are from SRL, India Ltd and were used after purification by standard techniques. Sodium silicate was a gifted sample from PQ Corporation, the Netherlands.

Modification of BNF:-

The dried areca empty fruits were soaked in de-ionized water for about seven days. This process of wetting the areca empty fruit by water is called retting, which allow the fibre to be removed from the fruits easily. The removed areca nut fibre were separated into an individual state, and dried in oven at 50 °C for 24 hours. Then the dried BNF immersed in 1:1 benzene and methanol solution for 36 hours to remove waxes and resins. It was washed with distilled water thrice and air dried till a constant mass was obtained. Then it was bleached with 5 % solution of sodium hypochlorite to remove lignin content for 12 hours and then neutralized by 1 % HCl solution. It was washed with distilled water and dried for 24 hours at 50 °C in oven. Dried BNF was then reduced in size by a blender and screened with a sieve of mesh size number 200. It was stored in a clean plastic bag for utilization in experiment.

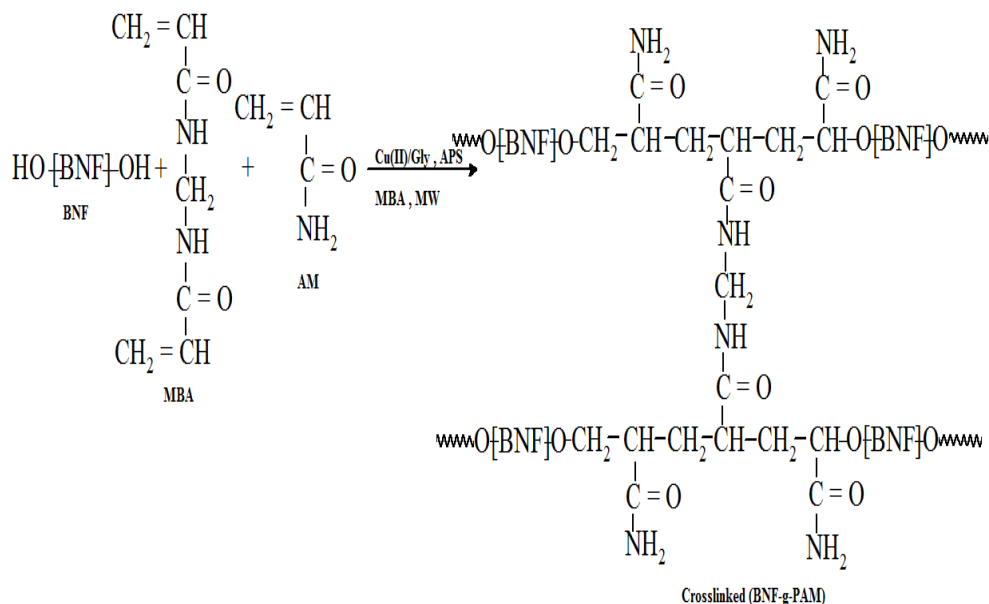
Preparation of BNF-graft-PAM:-

The polymerization experiments were carried out in a Kenstar (Model No.9811, 1200W) domestic microwave oven. The average bulk temperature at the end of the reaction was measured by inserting a thermometer in the reaction mixture. All the experiments were done with deionised distilled water and the temperature is less than 70 °C. The grafting polymerization experiments were carried out in two steps. In the first step 0.1g of modified BNF and different proportion of AM and initiator APS were taken in the reaction vessels and N_2 gas was bubbled for 15 minutes then reaction vessels were stirred at 700 rpm at room 45 °C for 45 minutes to make it homogeneous. In the second step, requisite amount of CuSO_4 , glycine and MBA were carefully added to the reaction mixture. Then N_2 gas was passed again for 10 minutes. The reaction mixture was heated with microwave oven for 180 seconds. Then

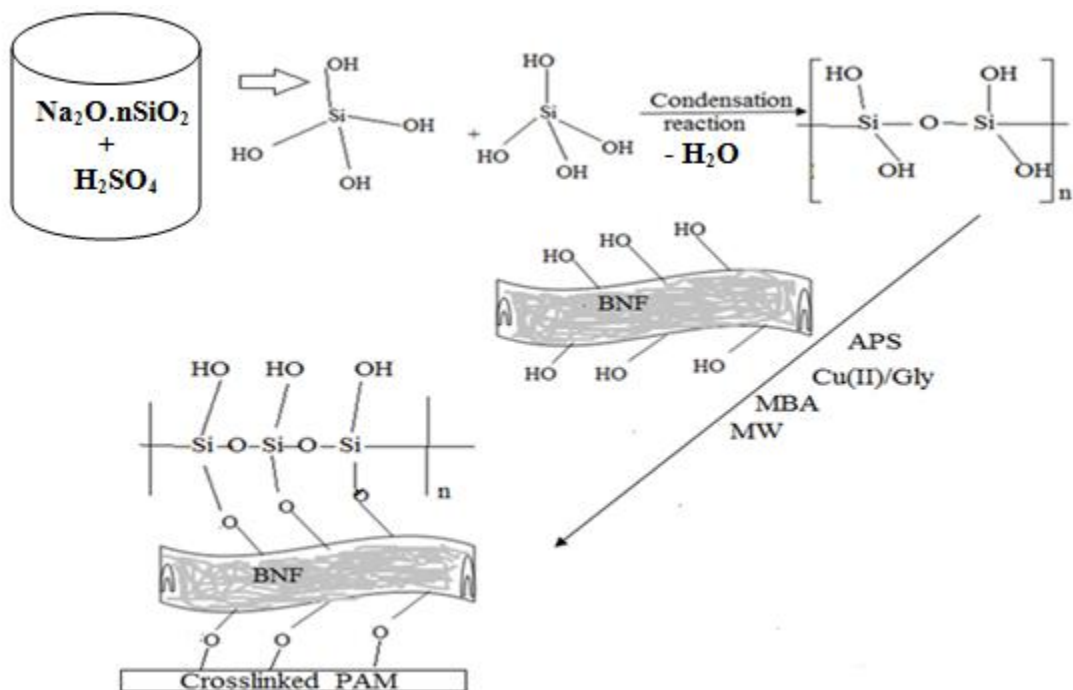
sample formed was dissolved in hot water for 24 hours to remove homopolymers, PAM. The product was filtered and washed with deionised water. It was dried in oven at 60 °C till a fixed weight of grafted sample BNF-*graft*-PAM obtained. It was kept in desiccators for characterization. It is shown in Scheme 1.

Preparation of (BNF-*graft*-PAM)/SS nanocomposite:-

For the preparation of composite same procedure was followed but in the second step requisite amount of 1 % (w/v) SS solution was added to the reaction mixture carefully with other chemicals. The variations of different components along with water absorbency and % conversion were tabulated (Table 2) and formation is in Scheme 2.



Scheme 1:- Formation of Crosslinked copolymer (BNF-*graft*-PAM)



Scheme 2:- Formation of crosslinked (BNF-*graft*-PAM)/SS nanocomposite

Characterization:-

Infrared Spectra (IR):-

The FT-IR spectra of BNF, PAM, BNF-*graft*-PAM copolymer, and crosslinked (BNF-*graft*-PAM)/SS composite were measured by FTIR Spectrophotometer (Perkin Elmer, Paragon-500 FTIR) using KBr pellets prepared by the following method (Endo et al., 2002). The KBr (0.5g) and the sample (0.01g) were weighed and then grounded in an agate mortar to obtain the mixed powder. The mixed powder (0.06g) was compressed at a pressure of 10 tones /cm² to prepare a tablet (diameter = 10 mm, thickness = 0.25 mm).

X-ray diffraction (XRD):-

XRD monitoring diffraction performed on Philips PW-1847 X-ray crystallographic (Utah, Saltlake city) unit equipped with a Guinier focusing camera CuK₂ radiation.

Transmission electron microscopy (TEM):-

Nanoscale structure and surface morphology of (BNF-*graft*-PAM)/SS nanocomposite were investigated by means of TEM (H-7100 Hitachi Co, Dako, CA) operated at an accelerating voltage of 100 kV.

Thermogravimetric Analysis (TGA):-

Thermogravimetric analysis (TGA) of the samples was carried out using a Shimadzu DTG-50 thermal analyzer. The samples were heated to a temperature of 500 °C at a rate of 10 °C/ min starting from room temperature (28 °C) under nitrogen atmosphere.

Scanning Electron Microscopy (SEM):-

Scanning electron microscopy (SEM) micrographs of modified BNF, BNF-g-PAM copolymer, and crosslinked (BNF-*graft*-PAM)/SS composites were recorded with a Jeol Ltd, Japan, Model No 5200 scanning electron microscope.

Fire Retardancy:-

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 Release (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 heat expressed the maximum intensity of a fire indicating the rate and extent of fire spread. Fire Performance Index (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 180s. 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.

Water absorbency:-

The water absorbency Q of the modified BNF, BNF-*graft*-PAM, and crosslinked (BNF-*graft*-PAM)/SS composites were determined by immersing the dry samples (W₀ = 0.1g each) in deionised water at room temperature for 24 hours. After the required time period, the samples were drained for 30 min for the elimination of excess non-absorbed water and then the weight of the swollen samples (W_s) was recorded. The water absorbency was calculated using the equation

$$\% Q = [(W_s - W_0) / W_0] \times 100$$

Biodegradation:-

Biodegradation of modified BNF, copolymer BNF-*graft*-PAM, and crosslinked (BNF-*graft*-PAM)/SS composites were studied under sludge water, soil burial degradation, and cultured medium in order to compare the extent of biodegradation at different conditions.

Sludge Water Degradation:-

0.1g of prepared samples were immersed in the supernatant of standard activated sludge and were incubated at 40 °C. The activated sludge water was collected from a waste dump area, on the day of test. It was centrifuged, and the supernatant liquid was taken for study.

Soil Burial Degradation:-

Soil burial (Chandra & Rustogi 1997) degradation method is a traditional and standard method for degradation because of its similarity to actual conditions of waste disposal. Biodegradability of the prepared samples was studied by weight loss of the samples over time in a soil environment. Sample of 1g weight was buried in the soil for upto one year. The soil was maintained at approximately 20% moisture by weight, and samples were buried at a depth of 20 cm. The buried samples were dug out at certain intervals throughout the year, washed with deionised water, dried in a vacuum oven at 50 ± 1 °C for 24 h before evaluation and were equilibrated in a desiccators for at least a day. The samples were then weighed to determine the weight loss.

In cultured medium:-

Nutrient agar medium was prepared by mixing peptone (5.0g), beef extract (3.0g), and sodium chloride (NaCl)(5.0g) in 1000 ml deionised water and the pH was adjusted to 7.0. Finally, agar (15.0g) was added to the solution. The agar medium was sterilized by autoclaving at 121 °C for 30 min at a pressure of 15 lb. *E.coli* bacteria was inoculated in this medium and the pure culture was maintained separately in the incubator. Then to 10 ml of sterilized broth 0.100g each of the samples i.e BNF, crosslinked BNF-graft-PAM, crosslinked (BNF-graft-PAM)/SS composite were added aseptically in separate test tubes and each tube of samples was supplemented with inoculums of the bacterial strains separately.

The degradation of samples by *E. coli* was monitored in time intervals of 1, 8, 15 and 30 days. After the required time period, the samples were washed repeatedly with deionised water, oven dried at 40 ± 1 °C for 24 h. Then the samples were weighed to determine the weight loss. Biodegradation through *E. coli* was studied by the amount of CO₂ evolved during the incubation periods of 1, 8, 15, and 30 days.

Quantitative estimation of free CO₂

Chemicals requirement: Na₂CO₃, phenolphthalein indicator.

Procedure: The cultured sample ('X' ml) and blank tube was titrated against Na₂CO₃ (N/50) ('Y' ml) using phenolphthalein indicator until the pink color persists for at least 30s. This was continued till getting a concordant reading.

Calculation:-

$$N_1 V_1 = N_2 V_2$$

$$(\text{CO}_2) \quad (\text{Na}_2\text{CO}_3)$$

$$\Rightarrow N_1 \times X = (1/50) \times Y$$

$$\Rightarrow \text{Strength} = (Y \times 22) / (50 \times X)$$

$$\Rightarrow \text{Free CO}_2 = [(Y \times 22 \times 1000) / (50 \times X)] \text{ mg/l}$$

$$\Rightarrow \text{Free CO}_2 = [(440 \times Y) / X] \text{ ppm}$$

Result and discussion:-**IR-Spectra:-**

In the IR of modified BNF (Fig 1-a) peaks at 3442.6 and 1048 cm⁻¹ indicating the stretching vibration of O-H group and C-O group respectively, and former peak also indicates the presence of more number of OH groups in the backbone of BNF. Another peak at 1727.6 cm⁻¹ indicating the ether and ester crosslink between cellulose and hemicelluloses or between cellulose and lignin which is absent in modified BNF indicating the breaking of ether bond or ester bond, Peaks between 1100 – 1600 cm⁻¹ suggesting the presence of hemicelluloses. These peaks are less intense indicating removal of some hemicelluloses from BNF (Lai & Mariatti 2008). For PAM (Fig 1-b) the peaks obtained at 3401, 1649, and 1600 cm⁻¹ indicate the N-H stretching, the C=O stretching and N-H bending of amide bands, respectively, which are characteristics of the -CONH₂ containing in the acrylamide. In addition, -C-N stretching band is observed at 1390 cm⁻¹ and a weak band for N-H out of plane bending is observed at 599 cm⁻¹. All the above IR peaks are observed both in copolymer BNF-graft-PAM (Fig 1-c) and nanocomposite (BNF-graft-PAM)/SS (Fig 1-d) with slight changes in their position. Comparing the IR peaks of BNF-graft-PAM copolymer and crosslinked (BNF-graft-PAM)/SS composite a very strong peak was observed at 1100 cm⁻¹ to 1040 cm⁻¹ due to

Si-O-Si stretching indicating the composite formation and presence of sodium silicate in the copolymer. Another weak peak was observed at 920 cm^{-1} which indicates that silanol network is present which is responsible for increasing the water absorbency which is due to hydrogen bonding of OH group of silanol with O – of water.

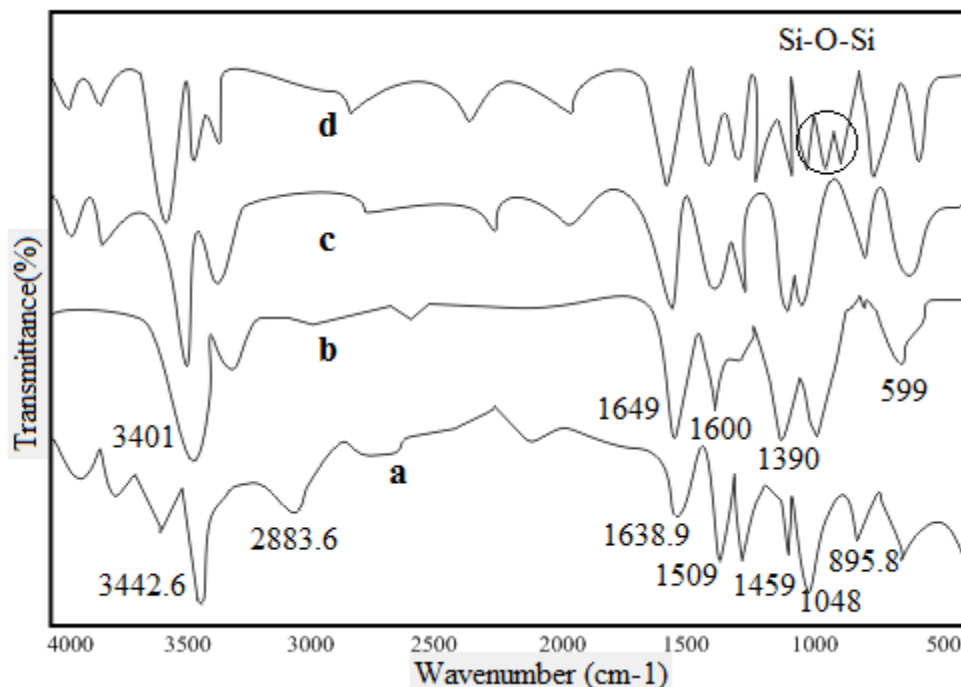


Fig 1:- FTIR Spectra of (a) modified BNF, (b) PAM, (c) BNF-graft-PAM copolymer, and (d) (BNF-graft-PAM)/SS nanocomposite

XRD:-

The structure and apparent interlayer spacing (d-spacing) of the (BNF-graft-PAM)/SS nanocomposites synthesized by microwave method intercalation have been detected by X-ray diffraction. Figure 2 shows the XRD patterns for the modified BNF, sodium silicate, BNF-graft-PAM copolymer and the nanocomposites. The d-spacing of SS has calculated to be 1.89nm from a diffraction peak at $2\theta = 6.4^\circ$ using Bragg's equation $n\lambda = 2d \sin\theta$. The modified BNF shows two peaks at $2\theta = 17.5^\circ$ and 24.56° . In case of copolymer these two peaks are shifted towards lower 2θ regions, but in the composite no diffraction peaks are observed in the 2θ range from 1 to 28° , indicating polymer, copolymer have no ordered structure in this dimension range. The diffraction peak of the SS perhaps is shifted towards lower 2θ region in the composite This indicates that the layered SS is delaminated in the aqueous medium by the PAM polymer when the SS content is relatively low, whereas the intercalated structure of SS in polymer matrixes is dominant when the SS content is higher than $1 \times 10^{-2} \text{ mol.dm}^{-3}$. This phenomenon accords with the conclusion drawn in the literature (Ray et al., 2003) about the dependence of the nanocomposite structure (exfoliated or intercalated) on the silicate content.

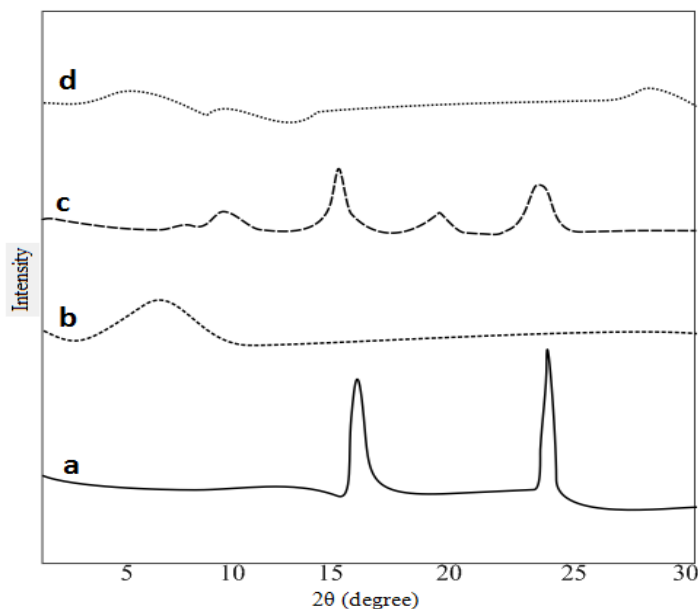


Fig 2:- XRD of (a) modified BNF, (b) SS, (c) BNF-graft-PAM, and (d) (BNF-graft-PAM)/SS nanocomposites

TEM:-

TEM studies are necessary for confirming the extent of exfoliation /intercalation achieved in the copolymer matrix to form nanocomposite as shown in figure 3 (a) and 3 (b). From figure it is shown that the SS layers are well dispersed in the nanocomposite. Although the SS layers still retain their orientation to some degree, the SS layer are highly delaminated into some thin lamellas with a dimension of about 1-4 nm in thickness. Here the silicate layers are partially exfoliated, i.e destroyed their orientation, which are supported by XRD result. On the basis of the evidence from XRD and TEM, the (BNF-graft-PAM)/SS nanocomposites with a partially exfoliated or intercalated structure have been successfully prepared via an in situ intercalation process in the aqueous media.

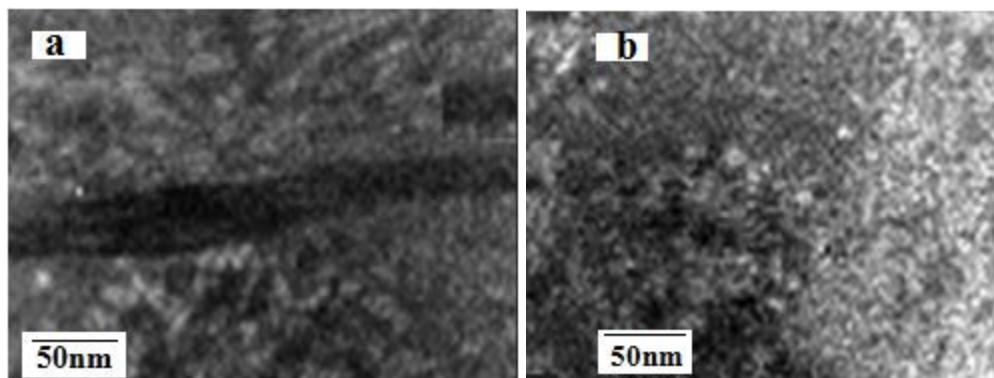


Fig 3:- TEM (a) Copolymer BNF-graft-PAM, and (b) (BNF-graft-PAM)/SS nanocomposite

TGA:-

Comparing the thermogram (TGA) curves of PAM, modified BNF, BNF-graft-PAM copolymer and (BNF-graft-PAM)/SS nanocomposite, it was found that the temperature of decomposition (T_D) is very much influenced by the addition of sodium silicate. T_D values and residual mass indicate that on addition of sodium silicate the composite becomes resistant to thermal action.

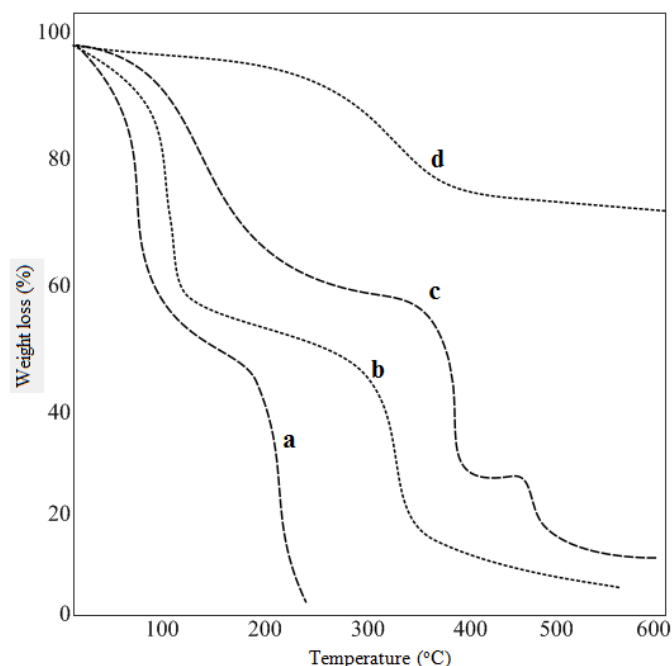


Fig 4:- TGA of (a) PAM, (b) modified BNF, (c) (BNF-graft-PAM)/SS nanocomposite, (d) Sodium silicate (SS)

SEM:-

The surface morphology of modified BNF, crosslinked copolymer BNF-graft-PAM, and crosslinked (BNF-graft-PAM)/SS composite are shown in Fig-5. Figure 5(a) stands for modified BNF. On grafting with PAM the surface morphology of BNF is changed Fig-5(b). The penetration of PAM in the lumens is seen as the white interior and surface of BNF. This is the good agreement with the result found in the literature (Sahoo et al., 2002). The presence of SS is clearly visible which is embedded onto the surface of the copolymer BNF-graft-PAM forming the nanocomposite Fig-5(c). On the addition of sodium silicate to a crosslinked composite, the porosity increases which create more room to carry more water than the copolymer. This is confirmed by the more water absorbency of nanocomposite.

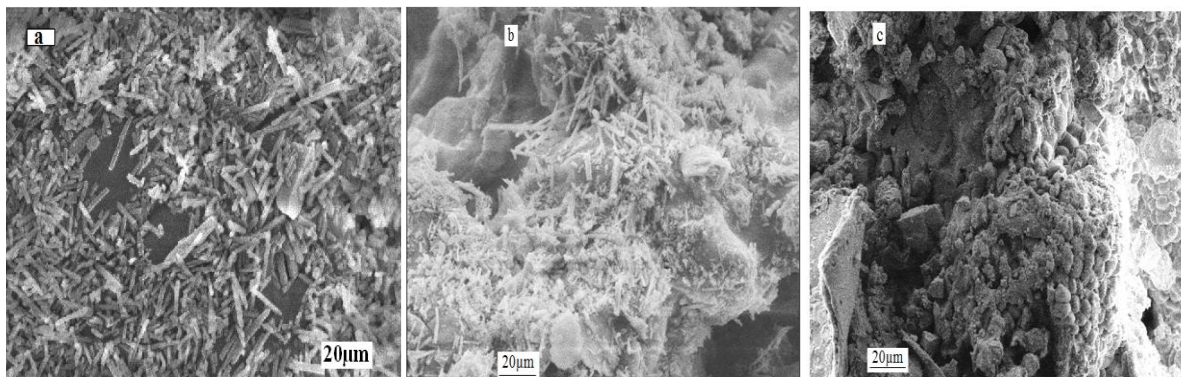


Fig 5:- SEM of (a) Modified BNF, (b) BNF-graft-PAM copolymer, (c) (BNF-graft-PAM)/SS nanocomposite

Flame Retardancy:-

The amount of heat energy released is measured by cone calorimeter when combustion of a material is done and also other parameters that are measured simultaneously including total smoke release, carbon dioxide & carbon monoxide generation, ignition time and mass loss rate. The measuring principle is that of consumption of oxygen. Measurement of these parameters based on consumption of oxygen which 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 6 and Table 1, it was found that

the time for ignition of (BNF-*graft*-PAM)/SS nanocomposite was lower than that of BNF-*graft*-PAM copolymer. It is due to the decomposition of sodium silicate clay at lower temperature, which is same as reported in literature (Ray et al., 2003). HRR is one of the most important parameter associated with the flammability and combustion of materials. The samples which have low value of HRR are better flame retardant than those with high value of HRR. BNF which is an agro-waste and its copolymer and composites 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 a most important flame retardant additive: even when in a small amount present in sample, decreases the HRR value of that silicate composite. From Figure 6 and Table 1, it was found that the HRR value of BNF and its grafted samples were more than of any BNF-*graft*-PAM/SS composite. The low PHRR value of BNF-*graft*-PAM/SS 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 in the literature (Fangrat et al., 1996, Gilman et al., 2000).

The heat release capacity mainly depends on the maximum mass loss rate (MLR) and heat of combustion of the decomposition products at that temperature. So the MLR is another factor that describes the flame retardant property. From Table 1, it was found that the MLR value of BNF-*graft*-PAM/SS nanocomposite was decreased as compared with the MLR value of copolymer BNF-*graft*-PAM due to the formation of a protective layer in between flame and sample. This decrease came into effect after a few of minutes of combustion, when the surface of the silicate-polymer had time to form char on the outer layer of the material.

Table 1:- Cone calorimetric data of BNF and composite at 35 kW/m²

Sample	TTI s	PHRR kW/m ²	THR MJ/m ²	MLR g/s	TOC g	AvCO ₂ Kg/Kg	AvCO Kg/Kg	PSEA m ² /Kg
BNF	85	780.7	99.8	0.061	18.80	4.3	0.046	368
Modified BNF	80	820.6	98.6	0.068	16.98	4.2	0.041	188
BNF- <i>graft</i> -PAM	78	701.5	92.6	0.059	16.68	4.2	0.032	386
BNF- <i>graft</i> -PAM/SS	70	585.9	74.7	0.038	14.59	3.1	0.031	238

The BNF-*graft*-PAM continued burning but the BNF-*graft*-PAM/SS composite became highly charred and stopped burning after the flame was removed. The THR due to the combustion of BNF-*graft*-PAM or BNF-*graft*-PAM /SS composite was approximately same. Due to its cellulose structure, burning of BNF 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.

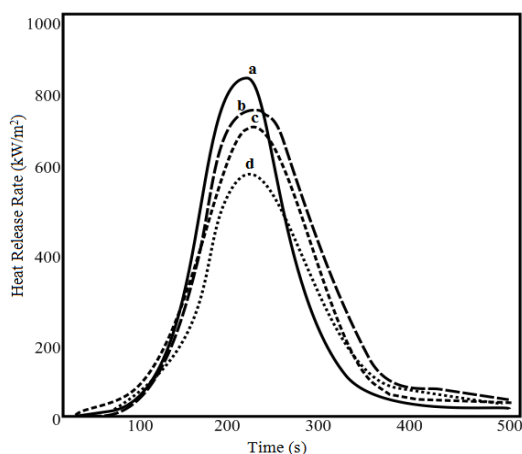


Figure 6:- HRR vs Time of (a) Modified BNF, (b) Unmodified BNF, (c) BNF-*graft*-PAM, (d) (BNF-*graft*-PAM)/SS nanocomposite

Water absorbency:-

Water absorption capacity of the samples is illustrated by the Figure 7. From the figure it was found that modified BNF has very low water absorption capacity within 36 h. But for BNF-*graft*-PAM copolymer, the superabsorbency is maximum at 24 h and then remain same. Upon grafting and addition of sodium silicate, the superabsorbency

becomes the highest within 24h and then remain same. This is because on addition of SS to the crosslinked copolymer porosity increases which facilitates maximum water absorption and also water absorption of composite is influenced by the hydrophilic nature of PAM in copolymer as well as in nanocomposite..

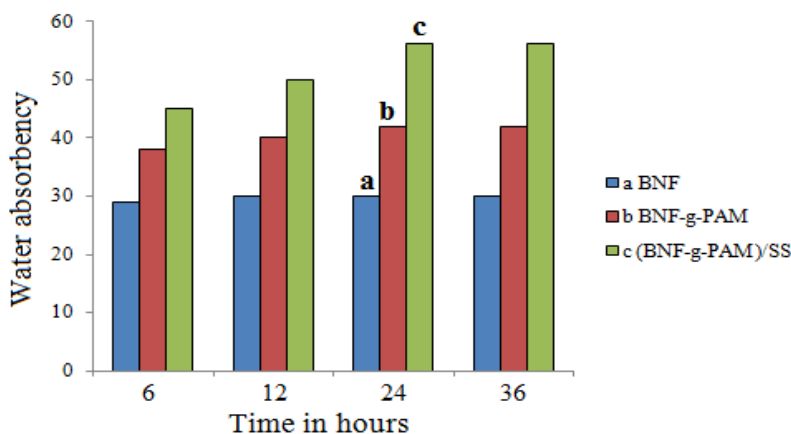


Fig 7:- Water absorbency of (a) modified BNF, (b) BNF-*graft*-PAM copolymer, and (c) crosslinked (BNF-*graft*-PAM)/SS nanocomposite

Biodegradation:-

The biodegradation of modified BNF, crosslinked copolymer BNF-*graft*-PAM and nanocomposite (BNF-*graft*-PAM)/SS in the sludge water (Fig 8), soil burial method (Fig 9) and in cultured medium (Fig 10) are shown. Weight loss due to microbial degradation for BNF in three cases is small as compared to crosslinked copolymer BNF-*graft*-PAM which is lesser than that of nanocomposite (BNF-*graft*-PAM)/SS. This is due to availability of good environment for growth of microbial which is supported by increase in water absorbency, because of hydrophilic nature of PAM and sodium silicate. Therefore, synthesized nanocomposite may be a good green superabsorbent.

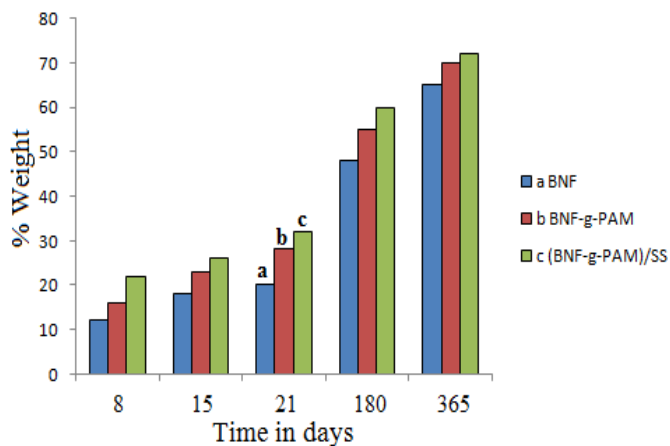


Fig 8:- Biodegradation in sludge water of (a) modified BNF, (b) BNF-*graft*-PAM copolymer, and (c) crosslinked (BNF-*graft*-PAM)/SS nanocomposite

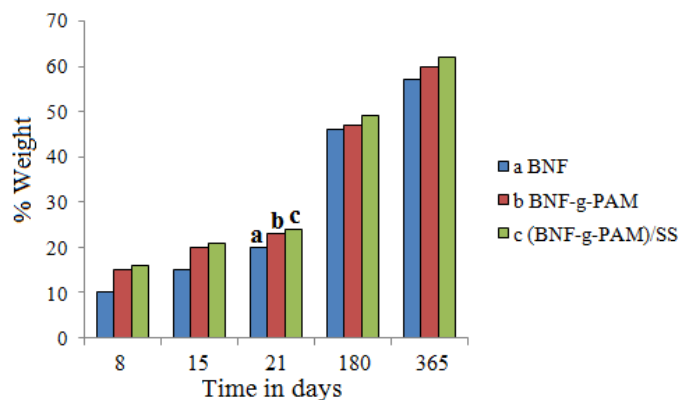


Fig 9:- Biodegradation in soil burial method of (a) modified BNF, (b) BNF-*graft*-PAM copolymer, and (c) crosslinked (BNF-*graft*-PAM)/SS nanocomposite

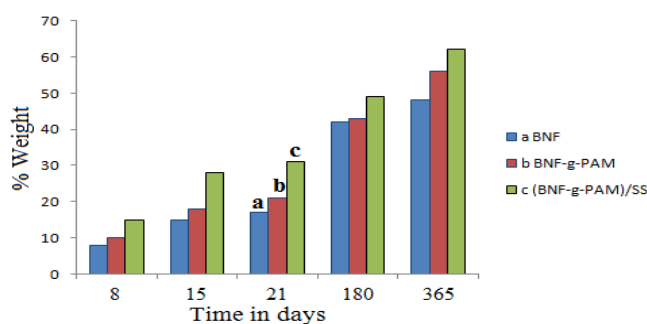


Fig 10:- Biodegradation in cultured medium of (a) modified BNF, (b) BNF-*graft*-PAM copolymer, and (c) crosslinked (BNF-*graft*-PAM)/SS nanocomposite.

Table 2:- % conversion with respect to [monomer], [initiator], [MBA], and [SS]

Code of the polymer	[AM] mol.dm ⁻³	[APS] × 10 ⁻² mol.dm ⁻³	MBA × 10 ² mol.dm ⁻³	[SS] × 10 ⁻² mol.dm ⁻³	Time in sec	% of conversion
S ₁	0.4	1.0	1.2		180	40.09
S ₂	0.6	1.0	1.2		180	44.02
S ₃	0.8	1.0	1.2		180	46.02
S₄	1.0	1.0	1.2		180	48.1
S ₅	1.2	1.0	1.2		180	45.02
S ₆	1.0	0.5	1.2		180	46.02
S ₇	1.0	1.0	1.2		180	48.1
S₈	1.0	1.5	1.2		180	49.8
S ₉	1.0	2.0	1.2		180	46.5
S ₁₀	1.0	1.5	2.4		180	50.2
S ₁₁	1.0	1.5	3.6		180	52.1
S ₁₂	1.0	1.5	4.8		180	50.0
S ₁₃	1.0	1.5	3.6	0.25	180	57.8
S ₁₄	1.0	1.5	3.6	0.5	180	60.5
S₁₅	1.0	1.5	3.6	1.0	180	75.6
S ₁₆	1.0	1.5	3.6	1.5	180	71.9
S ₁₇	1.0	1.5	3.6	1.0	90	69.3
S ₁₈	1.0	1.5	3.6	1.0	120	71.2
S ₁₉	1.0	1.5	3.6	1.0	150	72.8
S₂₀	1.0	1.5	3.6	1.0	180	75.6
S ₂₁	1.0	1.5	3.6	1.0	210	73.8

Conclusion:-

Natural fibre based composites were prepared from unused biowaste betel nut fibre through grafting with acrylamide monomer, Cu(II)/Gly/APS catalytic system and MBA as crosslinking agent. Some were then embedded with sodium silicate. The resulting composites were characterized by IR, TGA, XRD and their morphology by SEM. The observed IR peaks indicate the inclusion of silicate onto the BNF-*graft*-PAM forming a composite. TGA data reveals that on addition of sodium silicate, the composite becomes resistant to thermal action. The porous nature of the grafted composites with SS showed higher water absorbency than BNF-*graft*-PAM and modified BNF which make the composite suitable for use as superabsorbent in the conditioning the sandy soil with fertilizer making the green garden in desert area. Cone calorimeter gives the flame retardancy of nanocomposite which is better flame retardant than copolymer and modified BNF due to presence of silicate layer in composite which is a good fire retardant. It may open a new path to improve the commercial environment in the field of fire retardant materials.

Finally, biodegradation test in different methods indicate that crosslinked composite showed a significant increase in biodegradation in every case it is due to suitable environment for microorganism due to more water absorbency.

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