Free radical induced grafting of acrylonitrile on pre-treated rice straw for enhancing its durability and flame retardancy

Aparna Mukherjee, Seema Halder, Deepshikha Datta, Kumar Anupam, Biren Hazra, Mrinal Kanti Mandal, Gopinath Halder*

* Corresponding author. Fax: +91 3432754078.
E-mail address: gopinath_halder@yahoo.co.in (G. Halder).

Peer review under responsibility of Cairo University.

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.jare.2016.12.003

2090-1232 © 2017 Production and hosting by Elsevier B.V. on behalf of Cairo University.

This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
Introduction

Exploration and introduction of promising technique for the utilization of naturally abundant biodegradable materials towards addressing the environmental sustainability have been a subject of significant research over the past few decades. Rice husk, rice straw, wheat straw, corn stover, and peanut husk are few under-utilized, biodegradable and renewable agricultural by-products which can be processed into valuable industrial products to eradicate ecological problems [1]. Modern research demands attention towards energy efficient, cost-effective and low carbon building techniques to fulfill the aim of better environmental management. Subsequently the novel cellulose based components have been envisioned to be used in modern architecture [2]. Rice straw buildings can be found in many tropical places across the world especially in rural areas. The UK department of Trade and Industry has recently recognized this by funding a study into construction materials from crops [3]. Rice straw could be used as a plentifully obtainable low cost roofing material competing with other lignocellulosic biomasses subject to the elimination of drawbacks of decay and degeneration related to biodegradability and flammability.

The global rice production has the maximum percentage from Asia (90%) with the contribution of 28.7% and 19.5% shares from China and India respectively [4]. America, Africa, Europe and Asia contribute to the production of 731 million tons of rice straw yearly [5]. India and some other south-east Asian countries have been utilizing only a minor part of the total rice straw production as feedstock in paper and pulp industries, as feed for animals and as fuels for house heating, cooking and organic fertilizer. Finding no other proficient use, on-site burning of rice straw had become as one of the rice residue management methods commonly found in many of the SAARC countries [6–10].

The constraints involved in the usage of raw straw for thatched roofs could be overcome by means of grafting to produce a cross linked network forming an isolative surface barrier of carbonaceous char, which inhibits biodegradation and combustion of rice straw. In the recent years, grafting onto the solid surface of polymer matrix has received a major momentum of interest towards modification of surface properties of polymer matrix for its competent utilization. Many intensive works have been reported in the literature towards implementation of grafting onto various types of fibre such as jute [11], pineapple leaf [12], wheat straw [13], kenaf [14], and oil palm empty fruit bunch [15] by various mechanisms but free radical grafting on rice straw towards its potential utilization as a value added product is still limited.

Rice straw, an inexpensive, waste material has been utilized by the researchers in several ways. In an attempt of grafting onto rice-straw with oxycellulose modified by diethylene triamine, an impressive grafting percentage was observed [16]. Grafting of acrylonitrile onto delignified cellulose was accomplished to make it suitable for water absorbance [17]. The extent of grafting of methyl methacrylate (MMA) onto non-mulberry silk fibre was studied over the influence of different parameters viz. amount of initiator used, monomer concentration, reaction temperature and time [18]. Houssini performed the grafting of precyanoethanylated rice straw without any pre-treatment to utilize the rice straw as a potential low cost water absorbent hydrogels [19]. The stimulating effect of hydrogels prepared from rice straw on some micro-organisms using H₂O₂/ferrous ammonium sulphate was investigated [20]. Study on the graft polymerization of acrylonitrile onto wheat straw using FeSO₄- H₂O₂ initiator system was conducted [21]. In general the grafting mechanism is initiated by oxalic acid (C₂H₂O₄), which decomposes to produce free radical species (C₂O₄⁻) shown in reaction (2) in Fig. 1. Chemical initiation methods or radiation technique is generally used for the generation of reactive sites on the cellulose backbone [22]. The process is accelerated by the addition of MnO₄⁻ as co-catalyst. In redox initiation of graft copolymerization induced by hydrogen abstraction from cellulose fibre the radical species C₂O₄⁻ is expected to be reactive [23]. The C₂O₄⁻ radical having the compatibility to abstract the hydrogen from the Ph—OH group of the polymeric substrate that is the rice straw produces a free radical on it, known as the phenoxy radical, thereby creating an active site for graft copolymerization to take place as shown in reactions (3) and (4). The next step is the propagation where the free radical initiated chain reacts with the monomer acrylonitrile to yield graft co-polymer. The monomer molecules that are in the vicinity of the polymeric substrate become the acceptor of the radical resulting in chain initiation as shown in reaction (6). The phenoxy radical accelerates the formation of graft co-polymer by reacting with acrylonitrile monomers, and there after they become the free radical donors to the neighbouring molecule [24–26]. In this way the grafted chain usually grows. The last step is termination in which large straw fibre acrylonitrile free radical finally combines to give graft co-polymer as indicated in reaction (7). The probability of reaction (5) is indicated by the small extent of quinoid structure as suggested by Chen et al. [27].

Hence, a considerable amount of investigation has been performed on application of various naturally available fibres towards their uses in many areas through grafting mechanism. Nevertheless, researches regarding the utilization of rice straw as an efficient roofing material are still scarce.

Keywords:
Rice straw
Delignification
Polymer grafting
Free radical
Flame-retardant
Durability
Therefore the objective of the present investigation was to use an efficient technique to enhance durability and flame retardancy of rice straw through three-step process consisting of delignification, dispersion of inorganic salts, and polymer grafting aimed at well-organized competent utilization of rice straw. The limiting oxygen demand, biodegradability and thermal properties of the developed rice straw were determined to justify its applicability as an efficient roofing material. The effect of different parameters on polymer grafting was extensively studied.

Material and methods

Rice straws of different quality were procured from nearby local markets of Durgapur, West Bengal, India. Delignification of rice straw was done by using chemicals such as sodium hydroxide, sodium chlorite, aluminium trihydrate, boric acid, and urea purchased from Merck India Limited (Mumbai, India). Aluminium trihydrate, boric acid, and urea were used to complete the process of delignification. Initiators such as oxalic acid and potassium permanganate and surfactant such as sodium lauryl sulphate were procured from Qualigens Fine Chemicals (Worli, Mumbai, India). Finally the free radical grafting was performed with acrylonitrile from Sigma-Aldrich (St. Louis, USA) and sodium silicate from Nice Chemicals Pvt. Ltd. (Kerala, India).

Preparation of flame retardant rice straw

Delignification of rice straw

The procured rice straw was air-dried under intense sunlight and chopped into long strips of 15 cm each for further treatment. 100 g of the sample was washed about eight times with 3 litres of water and was then thoroughly dried underneath the sun again. It was then taken in a small sized vat containing 1800 mL of water in which solid sodium hydroxide pellets of about 36-45 g by weight were dissolved. The vat was warmed for two hours at a temperature of 35 ℃ followed by thorough water wash to remove sodium hydroxide. 36 g of sodium chlorite solution dissolved in 1800 mL of water was then poured to the treated mass and kept for two hours at this temperature [28]. Delignification was continuously monitored by the addition of glucal acetic acid at various intervals at a temperature.
of about 80 °C with gentle swirling until the samples were chemically judged to be sufficiently delignified. While the yellowish solution containing lignin was drained off, the treated material was cooled and subjected to subsequent washing with tap water to eliminate sodium chlorite. The remaining straw fibres were dried thereafter for two days under the sun.

Dispersion of inorganic materials in delignified straw for preparation of composite material

Delignified straw was treated with batches of 20 g sodium silicate, 12 g aluminium trihydrate dissolved in 100 mL of 0.5 N HCl solution, 15 g boric acid dissolved in 100 mL of lukewarm water, and 15 g of urea in a vat whose total volume was made 1000 mL by adding water. Inorganic salts were dispersed to substitute those spaces in the polymer matrix that were previously evacuated during delignification. Delignified sample was immersed in salt solution and was kept in an oven for at least half an hour at 50 °C. These treated fibres were then taken in another vat to dry under sunlight for at least 8 h.

Polymer grafting

Various parameters such as the rate of mass loss during combustion of the salt-layered composites, peak heat release rate and char structure were monitored and their alternation was carried out by the synthesis of polymer composites in situ through an emulsion polymerization of acrylonitrile in the presence of sodium silicate. Sodium laurel sulphate was used as a surfactant while oxalic acid and potassium permanganate initiator was employed for grafting. In a typical batch about 500 mL of hot water was taken in a vat along with 7 mL of acrylonitrile, 5 g of sodium laurel sulphate and 5 g of oxalic acid to prepare a solution. The dried straw was then immersed in the above solution for a period of 1 h in room temperature. The immersed rice straw was then dipped in another vat containing 1000 mL of 0.1–0.2% of potassium permanganate solution by volume. These soaked straw fibres after being heated to 50 °C for at least two hours were transferred to another vat, dried in the sun for one day and were subsequently tested thereafter to substantiate its potentiality as a roofing material.

Physico-chemical characterization and instrumental analysis of rice straw

The raw, delignified and polymer grafted rice straw were characterized in terms of SEM, EDAX, TGA and FTIR to determine the degree of enhancement of flame retardancy and non-biodegradability. SEM analysis was done to determine the morphological behaviour of delignified and polymer grafted rice straw. EDAX was conducted to find out the chemical radicals present in the hay matrix after delignification and grafting. TGA gave an account of the fractional mass residue of raw and grafted rice straw. FTIR characterized the functional groups present before and after grafting.

Proximate analysis

It was conducted for the raw rice straw in hot air oven Digi-tech (Kolkata, India) to determine the moisture, ash, volatile matter and fixed carbon content (weight %) using Laboratory Analytical Procedures LAP-001 [29] and LAP-005 [30] respectively of National Renewable Energy Laboratory (NREL).

Scanning electron microscopy (SEM)

Surface morphology and the texture of the delignified and polymer grafted rice straw were examined under scanning electron microscope JEOL JSM-6360 (Mundelein, Illinois 60060, USA) for which the sample was dried and mounted on the ‘stubs’ at a height of 10 mm. A variety of adhesives such as the conductive carbon tape, epoxy resin, and colloidal silver cements were used as non-conducting specimens. Out of many coating processes vacuum evaporation and sputtering techniques were commonly used. Sputter coater (JEOL JFC-1600 auto fine coater Mundelein, Illinois 60060, USA) was used for coating the samples with palladium for 30 s in order to maintain a thickness of 8 nm under the condition of 30 mA to induce conductivity of the non-conductive sample.

Energy dispersive X-ray analysis (EDAX)

EDAX (Inca Oxford instrument, model Inca mics, UK) was used to determine the elementary percentage of materials under SEM. Every single element corresponds to a peak denoting an unique atom, thereby representing the element present along with its intensity indicated by the magnitude of the peak.

Fourier-transform infrared (FTIR) characterization

FTIR spectrometric (Smart Omni Transmission IS 10 FT-IR Spectrometer, Thermo Fisher Scientific, India) analysis characterizes the functional groups available in the raw and polymer grafted rice straw. It was carried out by KBr pellet technique. Spectroscopic grade KBr (E. Merck, Mumbai, India) that had to be used for pelletization, was dried for at least 3 h at a temperature of 110 °C [31]. Approximately 0.25 mg of rice straw was finely ground to powder form using portable blender. It was properly weighed out and mixed with ground potassium bromide in the ratio of 1:12 (by weight) in an agate mortar-pestle to obtain optimum results. The shape of a pellet was imparted to it by compressing in the mould with a mass of 6 tons. IR spectrum was obtained with 50 scans per spectrum in between 4500 cm⁻¹ and 40 cm⁻¹ by a detector of 4 cm⁻¹ resolution.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was conducted to examine the thermal behaviour of raw and polymer grafted rice straw by heating the sample from ambient temperature to 800 °C in an inert atmosphere of nitrogen under non-isothermal conditions at a heating rate of 10 °C with a flow rate of 50 mL/min. Percentage residual weight against temperature was plotted to obtain the thermograms. Thermogravimetric (TGA) analysis of the examined samples was done using DTA-TG Apparatus (Shimadzu-00290, Japan).

Durability

Durability of the rice straw can be increased by decreasing its biodegradability. Biodegradability of a substance depends on the chemistry of the lignocellulosic biomass together with the
environmental effects. Generally pre-treatment of lignocellulosic biomass with different alkalis increases the biodegradability. The presence of oxygen, microbial activity, and availability of moisture are some of the other determinants of biodegradability. Different methods are available to determine the biodegradability of polymeric substances. They are based on indirect methods of degradation calculated by either the quantity of oxygen consumed or the carbon dioxide formed. Sometimes the change in weight of the biomass could also be cited as an indicator of biodegradability. One of the simplest methods to evaluate the biodegradability is to compare the standard 5-day BOD of the sample with the chemical oxygen demand (COD). COD analysis of the polymer grafted rice straw was determined using COD digester (Spectroquant-TR-320, Merck, India).Biochemical oxygen demand of the polymer grafted rice straw was determined by Winkler’s method using BOD incubator for 5 days maintained at 20 °C.

**Flame retardancy**

This parameter evaluates the flame retardant properties of a substance. The minimum oxygen concentration in the oxygen/nitrogen mixture required to maintain flame combustion of 3 min or that burns 5 cm of the sample, kept vertically upward can be used to determine Limiting oxygen index (LOI). LOI can be expressed by Eq. (8) [32].

\[
\text{LOI} = \frac{[O_2]}{[O_2] + [N_2]} \times 100
\]

Oxygen depletion calorimetry (ISO 5660 standard) has been cited as the best measurement to find out LOI [33]. It is carried out in a cone calorimeter. This investigation is on the basis of the concept that the heat evolved during the burning process is directly proportional to the empirical oxygen required during the combustion process. The mass loss during the experiment was evaluated by placing the sample (100 × 100 × 4 mm³) on a load cell where it was irradiated by a conical radiant electrical heater from above. The combustion was triggered by an electric spark.

**Percentage of grafting (%)**

The percentage of polymer grafted can be evaluated from the following Eq. (9) [34]:

\[
\text{Grafting} (%) = \frac{P}{Q} \times 100
\]

where \( P \) is the amount of polymer grafted on the surface of rice straw (g) and \( Q \) is the weight of rice straw used for the purpose (g).

Grafting percentage is usually calculated by the change in weight when the sample is heated in a hot air oven around a temperature of 50 °C. The percentage of grafting is plotted against time and its effect with rise in temperature is discussed.

The graft yield percentage based on nitrogen content of polyacrylonitrile (25.41 wt%) can be also calculated to estimate the grafting efficiency more accurately using the following expression [35]:

\[
\text{Graft yield (%) } = \frac{100(N\% \times 0.05306)}{100 - (N\% \times 0.05306)} \times 100
\]

where 0.05 is the molecular weight of acrylonitrile divided by 1000.

**Results and discussion**

**Proximate analysis**

Proximate analysis was done to determine the moisture, ash, volatile matter and fixed carbon content (weight %) in the rice straw and it has been represented in Table 1.

Normally the quantity of moisture present in the rice straw should be within 10–20% [36] as the presence of high moisture lowers the combustion efficiency of the sample. The amount of moisture present in the sample was computed to be 6.01%. The slight deviation of moisture content from normal value ensures its flame retardancy. However, typical ash content of straw was found to be around 5–10% as shown in Table 1. The presence of higher ash content further leads to additional disposal problems. A higher contents of volatile matter of up to 85% on dry basis of rice straw compared to coals and other agricultural residues, enable appreciable grafting percentage of it due to the formation of more active sites on the surface. Higher fixed carbon content of 16.11% ensures the non-biodegradability of the sample.

**SEM analysis of the sample at different stages**

For every successive step of the process, the treated composites were scanned under scanning electron microscope for observing changes in its micro-porous structure. SEM images of raw rice straw as depicted in Fig. 2 show a rigid and highly ordered structure of the surface with protruding portions and grooves.

SEM image of rice straw depicted in Fig. 2(a) shows a disordered structure after alkali pre-treatment. Generally, bundles of rice straw fibres start dismantling and get detached from the others. When the process of delignification gets completed, they become even more unstructured with the formation of completely unaltered and independent fibres. In some regions of the sample, the bundle structure was completely lost and multiple holes could be observed. Delignification could be well verified from Fig. 2(a), showing the appearance of separated cellulose fibrils amenable to grafting.

Remarkable changes in the surface of polymer grafted rice straw from those of the raw rice straw are apparent from the adjoining SEM image. SEM micrograph in Fig. 2(b) depicts that the surface of the rice straw almost gets homogenously covered with acrylonitrile after the grafting process. This synthetic polymer is strongly attached onto the fibre as it is chemically bonded and successfully grafted onto the backbone of rice straw.

**EDAX analysis of rice straw**

EDAX result represented in Table 2 shows the relative percentage of elements in delignified and in polymer grafted rice straw sample. A representative of EDAX analysis in Table 2a and in Fig. 3(a) clearly indicated the presence of carbon, oxygen, chloride and silicon in noticeable amount. The high content of carbon and oxygen could be explained by the fact that the rice straw with an intricate structure,
principally comprises three bioconstituents viz. lignin, hemicelluloses and cellulose. Relative percentage of sodium and chlorine is also observed in Table 2a since the rice straw had been previously treated with sodium hydroxide and sodium chlorite respectively during the delignification stage.

EDAX analysis of polymer grafted rice straw shown in Table 2a and Fig. 3(b) indicates the presence of carbon, hydrogen, silicon, potassium, manganese and sodium. The presence of manganese in the sample as shown in Table 2b could be attributed to the presence of oxalic acid-permanganate initiator that was used in the process of grafting.

**FTIR analysis**

FTIR spectrum of raw and poly acrylonitrile grafted rice straw has been represented in Fig. 4a and b respectively. The significant absorption band of polyacrylonitrile at 2245 cm\(^{-1}\) as observed in Fig. 4b is due to stretching vibration of C=\(\text{N}\). The prominent band at 1265 cm\(^{-1}\) shown in Fig. 4a corresponded to methoxyl stretching. It could be inferred from Fig. 4a and b that the presence of methoxyl group in the lignin of the NaOH-treated rice straw decreased with respect to untreated rice straw due to the nucleophilic reaction between methoxyl group and NaOH. These changes had substantial influence on the rate of biological degradation of rice straw.

The absorption band corresponding to 3421 cm\(^{-1}\) in Fig. 4a indicated the stretching of \(\text{O}^-\text{H}\) groups to enhance accessibility of cellulose to reagents. The band at 1383 cm\(^{-1}\) could be attributed to \(\text{C}^-\text{H}\) bending in cellulose and hemicellulose. It was noticeable that the band displayed at 3422 cm\(^{-1}\) was due to the presence of hydroxyl groups in hemicellulose for both NaOH treated and unreacted rice straws. The intensity of this band in Fig. 4b is found to decrease after NaOH treatment, because of the disruption and breakage of hydrogen bonds.

The band between 1116 cm\(^{-1}\) and 1000 cm\(^{-1}\) was of typical xylans. The presence of a small amount of associated lignin in hemicelluloses was indicated by small band at 1606 cm\(^{-1}\) found in two spectra. The band at 1082 cm\(^{-1}\) which had been strongly influenced by the degree of branching corresponded to the \(\text{C}^-\text{O}\)\(\text{C}\) vibrations in the anomeric region of hemicelluloses indicated that the structure of hemicellulose changed after NaOH treatment.

**Thermogravimetry analysis**

The TGA demonstrates the thermal behaviour of raw rice straw in comparison with polymer grafted rice straw. The thermogravimetric curves depicted in Fig. 5 of rice straw and polymer grafted rice straw exhibited that mass loss occurs in two steps. The early mass loss from the rice straw that occurred below 100 °C resulted due to gradual evaporation of adsorbed moisture while the second step exhibited a mass loss from the polymer matrix in the range of 170–550 °C due to the decomposition of cellulose, hemicelluloses and lignin as the three major constituents of the rice straw. Usually the lignocellulosic materials are chemically active and hence they decomposed
thermochemically between 150 °C and 500 °C. Hemicellulose was found to decay between 180 °C and 360 °C. In the temperature range of 250–500 °C there was parallel decomposition of cellulose and lignin. Cellulose decomposed up to a temperature of 350 °C while lignin showed an extended degradation up to a temperature of 500 °C. The weight loss of the samples due to the release of moisture remaining in the temperature between 100 °C and 150 °C was not taken into consideration for the determination of the thermal events. In the case of non-grafted paddy straw, the degradation occurred between 200 °C and 360 °C causing a weight loss of 65% whereas with grafted straw, the degradation occurred between 300 °C and 444 °C bringing a weight loss of about 84%. The steps of mass-loss of the polymer matrix occurred slowly below 430 °C but the process became rapid above 430 °C and got completed at 800 °C as shown in Fig. 5. In fact, the total degradation process can be subdivided into three phases. The first phase of decomposition of cellulosic material took place up to 360 °C causing the decomposition of cellulose and hemicelluloses, the second phase of degradation includes the decomposition of non-cellulosic material like lignin up to a temperature of 480 °C and at last in the third phase the degradation of inorganic materials remaining in the rice straw degraded rapidly until the achievement of approximately 100% weight loss was seen at about 800 °C. Radiation chain scission and a radical chain mechanism might be the reason of thermal degradation of polyacrylonitrile. The amplification in thermal stability of grafted straw could be due to the late decomposition of polyacrylonitrile. The formation of insulative carbonaceous char barrier on the surface due to the formation of crosslinked type of network by the grafted polymer inhibited the degradation rate.

**Durability of polymer grafted rice straw**

The durability of lignocellulosic biomass is determined by biodegradability index. It has been observed that the value

| Table 2b | EDAX result of the relative percentage of elements in polymer grafted rice straw sample. |
|----------|------------------------------------------------------------------------------------------|
| **Element** | **Weight%** | **Atomic%** |
| C K       | 40.32      | 47.11       |
| N K       | 7.10       | 7.12        |
| O K       | 51.87      | 45.51       |
| Na K      | 0.12       | 0.07        |
| Si K      | 0.01       | 0.01        |
| Cl K      | 0.24       | 0.10        |
| K K       | 0.03       | 0.01        |
| Mn K      | 0.31       | 0.08        |
| **Total** | **100.00** |             |

![EDAX spectrum of (a) delignified rice straw and (b) polymer grafted rice straw.](image)
of BOD decreases while that of COD considerably rises after polymer grafting. One of the simplest ways to compute biodegradability is to compare the BOD with the COD value [37]. Generally if the ratio of BOD to COD is more than 0.6, the sample is said to be bio-degradable. If the ratio is found to be within 0.3–0.6, the sample cannot be subjected to biological treatment. The ratio of less than 0.3 would imply that the rate of biodegradability is too slow due to the presence of one or more non-biodegradable components in the sample under experimental conditions. The aim was also to make the rice straw non-biodegradable to prevent its decomposition and enhance its durability. In the present analysis, the BOD and COD were found to be 3.73 mg/L and 248 mg/L respectively. The BOD/COD ratio obtained in this case is 0.02 which confirms appreciable durability of the sample corroborated with the results shown in Table 3.

Flame retardancy

Limiting oxygen index is a numerical tool to evaluate the flammability of fire-retardant polymeric materials. Air contains about 21% of oxygen. Therefore materials having LOI more than 21% are said to be self-extinguishing polymer as they require an external energy source for combustion whereas materials with LOI less than 21% are categorized as combustible polymer [32]. These substances exhibit good flame retardant properties. In the current investigation, the acrylonitrile is found to possess a LOI of 27%. The sample was subjected to the cone-calorimetry test where the combustion gases produced were captured by means of an exhaust duct system with a centrifugal fan and a hood after passing through the heating cone. Certain measurements such as gas flow, concentrations of oxygen, CO, CO2 and smoke density were used for the estimation of the quantity of heat released per unit surface area and time.

Effect of different parameters on polymer grafting

The success and extent of grafting onto polymer matrix is greatly influenced by several parameters viz. salt concentration, dosage of monomer, reaction time and temperature at which reaction occurs. The grafting percentage obtained in any process strongly depends upon the pre-treatment methodology that has been undertaken for the work. In the present study, the variation of reaction time, monomer concentration and reaction temperature was considered keeping salt concentration constant.

Effect of reaction time

Reaction time serves as one of the most important parameters to determine the grafting efficiency. In this case, the extent of grafting with the progress of the reaction has been represented in Fig. 6. The total grafting procedure was completed in 120 min. This duration was divided into 6 individual batches.

| Days | Weight of raw straw (g) | Percentage weight loss/gain (%) | Weight of polymer grafted straw (g) | Percentage weight loss/gain (%) |
|------|-------------------------|--------------------------------|-----------------------------------|--------------------------------|
| 0 day| 5.85                    | –                              | 8.62                              | –                              |
| 15 days| 5.37                    | 8.14                           | 8.35                              | 3.13                           |
| 30 days| 5.17                    | 3.86                           | 8.02                              | 0.39                           |
| 45 days| 5.06                    | 2.02                           | 7.07                              | 0.12                           |
| 60 days| 5.00                    | 1.18                           | 6.05                              | 0.10                           |
of 20 min. 100 g of the rice straw was taken for the analysis. The process occurred at a temperature of around 50 °C. Porous structure of rice straw was obtained through delignification. The extent of grafting initially increased as shown in the curve and with the progress of reaction the grafting percentage increased. So the grafting percentage increased with the progress of the reaction. However with the advancement of time, the increase in the graft percentage became more gradual as the active sites came to be occupied by chemicals used for grafting. Finally, after attaining 57% of grafting, no more change was observed even with further allowance of reaction time. Fig. 6a shows the time-grafting curve during the reaction of rice straw with polyacrylonitrile at 50 °C. Graft percentage increased with the increase in reaction time but no longer increased after 80 min, i.e., a limit was attained. The time dependence on the grafting percentage increased rapidly in the first 60 min of the process. Longer durations did not significantly improve the percentage of grafting. During the grafting process initially the extent of grafting increases resulting in initial rise of grafting yield whereas it was observed to fall after 80 min indicating the formation of more homopolymers with respect to copolymer resulting from the used up acrylonitrile thereby depleting the initial radicals generated on the hollow cellulose backbone. Thus the optimum grafting time is 80 min and a longer reaction time would not result in higher graft yield.

Effect of temperature

The kinetics of graft co-polymerization is controlled by one of the important factors known as temperature. Graft percentage generally increases with temperature unless a limit is reached. The increase in temperature is accountable for the large number of active sites created by the removal of moisture and volatile matter from rice straw. Thus the extent of grafting accelerated with temperature reaching a maximum of 35% corresponding to a temperature of 75 °C as shown in the Fig. 6b. This is also because the diffusion rate of monomer in the backbone of the polymer significantly rises due to an elevation in temperature, thus facilitating the process of grafting [38]. The yield of MMA grafting on silk is reported to increase substantially with increase in temperature resulted from greater swelling of silk and a corresponding diffusion rate of the monomers in the area of the silk [39]. Sun et al. have explained this behaviour as a consequence of increased rate of thermal decomposition of initiator that improved the initiator efficiency in producing free-radicals on base polymer to obtain good polymer macro-radical concentration, thus enabling graft polymerization [40]. The rate of chemical reactions could be regulated with variation of temperature. Experiments indicated that an increase in the temperature had a very strong effect on grafting percentage as it dramatically improved the percentage of grafting. However after 75 °C, the percentage of grafting decreased which could be explained by the low boiling point (77 °C) of the monomer. A temperature of 75 °C can be thus proposed for the grafting temperature of this system.
Effect of monomer concentration

The reactivity of the monomer plays a dominant role in successful grafting and is affected by various factors viz. steric and polar nature, monomer concentration and swell-ability of backbone in the presence of the monomers. It is very clear from Fig. 6c that increase in monomer concentration increases the graft yield due to larger amount of acrylonitrile available for copolymerization. However, it was observed that the excess monomer concentration (above 9 mL) did not result in graft copolymerization product. The increase in acrylonitrile concentration leads to the creation of an excess of monomer molecules relative to available sites for graft formation and they compete for the limited sites for grafting as the available number of active sites remains constant at a given initiator concentration thereby leading to homopolymerization of acrylonitrile molecules decreasing its grafting percentage. This may be explained by the following factors: (a) preferential homopolymerization over graft copolymerization, (b) increase in the chance of chain transfer to monomer molecules increase in the viscosity of reaction medium, which hindered the movement of free radicals and (c) increase in the viscosity of reaction medium, which hindered the movement of free radicals. The preceding observations are found to nicely tally with the results reported for the grafting of methyl acrylate onto starch [41] and of ethyl acrylate onto cellulose [42]. Statistical analysis was done to analyse the main effects of factors namely time, temperature and monomer concentration on polymer loading. The results are described in Table 4. There is a significant difference ($P < 0.001$) in the mean values among the different levels of time, temperature and concentration.

Conclusions

The present research work highlights the contrivance of a polymer grafting technology to enhance the durability and flame retardancy of rice straw towards its exploitation as an efficient roofing material. A pre-treatment process consisting of delignification and dispersion of inorganic salts was successfully implemented onto rice straw to make it suitable for efficient polymer grafting with acrylonitrile. Delignification has been done to open the porous fibril structure of rice straw which enables the binding and dispersion of the inorganic chemicals in the hay matrix which limits radiation heat transfer to the adjacent layers. The restrictions associated with the usage of rice straw were overcome by determining their biodegradability and flame retardant properties. The grafting extent can be altered by tuning the reaction variables such as reaction time (120 min), reaction temperature (55–75 °C), monomer dose (7–12 mL) and salt concentration 2% by weight (of water added). A maximum grafting efficiency of 57% and graft yield percentage of 136.67% were obtained under these parametric conditions. Biodegradability was inferred as a ratio of BOD to COD which was found to be 0.02. The flame retardant properties were ensured by LOI index of 27%. The EDAX and FTIR analyses show that the chemical groups have been effectively grafted into the rice straw matrix thus altering its undesirable characteristics to benefit its utilization as a roofing material.

Conflict of Interest

The authors have declared no conflict of interest.

Compliance with Ethics Requirements

This article does not contain any studies with human or animal subjects.

Acknowledgement

Authors express their indebtedness to Anoar Ali Khan, PhD research fellow, Department of Chemical Engineering, NIT Durgapur, for his technical help during experimentation. The financial aid from Ministry of Science and Technology, Government of West Bengal, India through research project ST/P/S&T/1G-9/2011 is sincerely acknowledged.

References

[1] Wu C. Characterization and biodegradability of polyester bioplastic-based green renewable composites from agricultural residues. Polym Degrad Stab 2012;97:2388–95.
[2] Thompson A, Walker P. Durability characteristics of straw bales in building envelopes. Constr Build Mater 2014;68:135–41.
[3] Goodhew S, Griffiths R, Wooley T. An investigation of the moisture content in the walls of a straw-bale building. Build Environ 2004;39:1443–51.
[4] Kim JS, Manan ZA, Alwi SRW, Hashim H. A review on utilization of biomass from rice industry as a source of renewable energy. Renew Sust Energy Rev 2012;16:3084–94.
[5] Binod P, Sindhu R, Singhania RR, Vikram S, Devi L, Nagalakshmi S, et al. Bioethanol production from rice straw: an overview. Biores Tech 2010;101:4767–74.
[6] He Y, Pang Y, Liu Y, Li X, Wang K. Physiochemical characterization of rice straw pre-treated with sodium hydroxide in solid state for enhancing biogas production. Energy Fuels 2008;22:2775–81.
[7] The Catholic Media Network News. Philrice to study rice straw as power source; 2012.
Researchers eye rice straw as renewable energy source. Yahoo News: Philippines; 2012.

Guoliang C, Xiao YZ, Yaqiang W, Fangcheng Z. Estimation of emissions from field burning of crop straw in China. Chin Sci Bull 2008;53:784–90.

Gadde B, Bonnet S, Menke C, Garivait S. Air Pollutant Emissions from rice straw open field burning in India, Thailand and the Philippines. Env Poll 2009;157:1554–8.

Ferrous K, Ahmad SR. Graft copolymerization reaction of water-emulsified methyl methacrylate with preirradiated jute fiber. J Appl Polym Sci 1998;65:459–68.

Mohanty AK, Tripathy PC, Misra M, Parija S, Sahoo S. Chemical modification of pineapple leaf fiber: Graft copolymerization of acrylonitrile onto defatted pineapple leaf fibers. J Appl Polym Sci 2000;77:3035–43.

Focher B, Marzetti A, Marsano E, Conio G, Tealdi A, Cosani as an initiator. J Appl Polym Sci 1998;66:961–74.

Farag S, Al-Afaleq Eljazi I. Preparation and characterization of polyacrylamide-graft starch—graft copolymer. Carbohy Polym 2002;48:1–5.

Das A, Saikia CN. Graft copolymerization of methyl methacrylate onto non-mulberry silk-Antheraea assama using potassium permanganate-oxalic acid redox pair. J Appl Polym Sci 1996;59:1987–93.

Ibrahim NA, WanYunus WMZ, Abu-Ihaiwi FAF, Rahman MZA, Ahmad MB, Dahlan KZM. Optimized condition for grafting reaction of poly(butyl acrylate) onto oil palm empty fruit bunch fibre. Polym Int 2003;52:1119–24.

Ghosh P, Bandyopadhyay AR. (Photo) graft copolymerization of methylmethacrylate (MMA) on polyamine-modified oxycellulose in a limited aqueous system. J Appl Polym Sci 1986;31:1499–507.

Farag S, Al-Afaleq Eljazi I. Preparation and characterization of saponified delignified cellulose polyacrylonitrile-graft copolymer. Carbohy Polym 2002;48:1–5.

Housni E, Atif BH, Ahmed WI, El-Hady OA, Dewiny CEY, Abo-Sedera SA. Evaluating the grafting approaches for utilizing the rice straw as environmental friendly and potential low cost hydrogels. Emir J Food Agric 2013;25:211–24.

El Hady O, Abo Sedera SA, Basta AH, Saied HE. The role of rice straw-based hydrogels on some soil microorganisms strains. BIO 2011:1:78–84.

Fanta GF, Burr RC, Doane WM. Graft polymerization of acrylonitrile onto wheat straw. J Appl Polym Sci 1987;33:899–906.

Ibrahim SM, El Salmawi KM, Zahran AH. Synthesis of cross linked superabsorbent carbomethoxy cellulose/acrylamide hydrogels through electron beam irradiation. Carbohy Polym 2008;71:334–41.

Bhattacharya A, Misra BN. Grafting: a versatile means to modify polymers techniques, factors and application. Prog Polym Sci 2004;29:767–814.

Kislenko V, Berlin A. Kinetics of interaction between water-soluble derivatives of lignin and hydrogen peroxide. Euro Polym J 1996;32:1023–9.

Kislenko V, Olinyk L. Kinetics of hydrogen peroxide decomposition inuaicil solution, catalyzed by hexacyanoferrate (II). Russ J Gen Chem 2003;73:114–8.

Zheng G, He S, Qi Q, Gao J. Fe2+/H2O2 initiated grafting of lignocellulose with methyl methacrylate and its mechanism. J Macro Sci Part A: Pure App Chem 1995;32:287–99.

Chen RL, Kota BV, Daneault C, Valade JL. Some watersoluble copolymers from lignin. J Appl Polym Sci 1986;32:4815–26.

Kahar P. Synergistic effects of pretreatment process on enzymatic digestion of rice straw for efficient ethanol fermentation. Int J Bioauto 2013;17:199–200.

Ehraman T. Chemical analysis & testing task: standard method for determination of total solids in biomass (LAP-001). Gold Co. USA; NREL; 1994.

Ehraman T. Chemical analysis & testing task: standard method for determination of ash in biomass (LAP-005). Gold Co. USA; NREL; 1994.

Cooke NE, Fuller OM, Gaikwad RP. FTIR spectroscopic analysis of coal and coal extracts. Fuel 1986;65:1254–60.

Laoutid F, Bonnaud L, Alexandre M, Lopez-Cuesta JM, Dubois P. New prospects in flame retardant polymer materials: From fundamentals to nanocomposites. Mat Sci Eng R: Rep 2009;63:100–25.

Enright PA, Fleischmann CM. Uncertainty of heat release rate calculation of the ISO5660-1. Cone calorimeter standard test method. Fire Technol 1999;35(2):153–69.

Wei G, Saitoh S, Saitoh H, Fujiki K, Yamauchi T, Tsubokawa N. Grafting of polymers onto vapor grown carbon fiber surface by ligand-exchange reaction of ferrocene moieties of polymer with polycondensed aromatic rings of the wall-surface. Polymer 2004;45:8723–30.

Mostafa KM, Samarkandy AR, Sanabary AA. Synthesis and characterization of (poly (N-vinyl formamide)—pregelled starch)—graft copolymer. J Polym Res 2010;17:789–800.

Liu Z, Xu A, Zhao T. Energy from combustion of rice straw: status and challenges to China. Ener Pow Eng 2011;3:325–31.

Ghosal SK, Sanyal SK, Datta S. Introduction to chemical engineering. New Delhi: Tata McGraw Hill Publishing Company Limited; 2011.

Dilli S, Garnett JL, Martin EC, Phuc PH. The role of additives in the radiation induced copolymerization of monomers to cellulose. J Polym Sci 1972;37:57–118.

Sasmal S, Sahu G, Lenka S, Nayak PL. Graft copolymerization of methyl methacrylate onto silk using isoquionoline-sulphurdioxide charge transfer complex as the initiator. J Appl Polym Sci 1978;33:1853–8.

Sun T, Xu P, Liu Q, Xue J, Xie W. Graft copolymerization of methacrylic acid onto carboxymethyl chitosan. Eur Polym J 2003;39:189–92.

Doyle CD. Estimating thermal stability of experimental polymers by empirical thermogravimetric analysis. Anal Chem 1996;3:77–9.

Pourjavadi A, Mohammad J, Zohuriaan M. Modification of carbohydrate polymers via grafting in air ceric-initiated graft copolymerization of acrylonitrile onto natural and modified polysaccharides. Starch 2002;54:482–8.