Preparation of Superabsorbent Polymer (Rice Straw-*g*-Polyacrylamide) from Renewable Biowaste

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A new class of technologically advanced material like superabsorbent polymers involved multidisciplinary research started when its potential is recognized. Rice straw-graft-polyacrylamide (RS-*g*-PAM) superabsorbent polymers was synthesized *via* simultaneous cross linking and graft copolymerization of acrylamide monomer onto backbone of rice straw using complex initiating system [CuSO₄/glycine/ ammonium persulfate] in an aqueous medium without and with N,N-methylene*bis*acrylamide as crosslinker. The chemically modified rice straw, RS-*g*-PAM have been characterized by FT-IR and their morphology was studied by scanning electron microscopy. Systematically, variables that affect the water absorbance behaviours of RS-*g*-PAM SAPs were optimized with the effects of solvent, degree of neutralization and crosslinker concentrations. The tensile and dyeing properties of RS-*g*-PAM superabsorbent polymers were also studied. A mechanistic pathway in synthesizing RS-*g*-PAM SAPs was suggested. The biodegradation and water absorbency have been carried out for its ecofriendly nature and better commercialization.

Keywords: Rice straw, Polyacrylamide, Graftcopolymers, Superabsorbent polymers, Biodegradation.

INTRODUCTION

Superabsorbent polymers (SAPs) are hydrophilic and three dimensional networks that exhibit the ability to highly swell in water, saline or biological fluids and retain significant fraction of the fluids within their structure but they do not dissolve in water[1]. Superabsorbent polymers have great advantages over traditional water absorbing materials such as cotton, pulp and sponge. They are widely used in sanitary goods such as disposable diapers and hygiene napkins. Besides, these materials can help conserve water in a variety of agricultural and horticultural applications by improving the water holding capacity of sandy soil.

Although superabsorbent polymers made from synthetic polymers exhibit excellent characteristics, the limitations of these materials in comparison to natural based, one seems to be worth noting. In fact, their toxicity and non-biodegradability might pose long term environmental problems and limit their uses. Therefore, modifications of natural materials such as starch[2,3], cellulose[4,5] and carrageenan[6] have been utilized to prepare superabsorbent polymers.

The desired features of superabsorbent polymers are high swelling capacity, high swelling rate and high absorbency under load. The majority of reported superabsorbent polymers posses only the first and second feature despite many efforts to synthesize superabsorbent polymers in recent years which focused on improving other parameters superabsorbent polymers.

Rice is one of the major crops in the world. Global rice production was projected above 395.9 million tons. Associated with rice production is a corresponding annual production of rice straw. In a day basis rice straw contains 43 to 49 % cellulose, 25 to 28 % hemicellulose, 15.8 % lignin, 12.5 % silica, resins, gums, proteins and mineral compounds.

Rice straw is a low-cost multi cellular lignocellulosic fiber and has become attractive as a renewable resource because it is available in large quantities and routinely cultivated in the developing countries, especially in India and South Asia which is used as an animal food and for burning purpose[7,8]. The conventional method of burning of rice straw for disposal purpose often creates environmental problems in that it generates carbon dioxide, carbon monoxide and other gases contributing to the green house effect. So, it is important to explore that how high performance material can be prepared from these low cost biowaste.

Thus, economic utilization of rice straw in turning its abundant supply into value-added products will be beneficial. Grafting of vinyl monomer such as acrylamide onto rice straw

backbone may be used to modify and improve various properties in the original vinyl polymer[9]. However, synthetic polymer based superabsorbent polymers are poor in degradability especially for applications in agriculture and horticulture, though, they alone do have large fluid absorbing capacities[10]. Therefore, extensive attention has been directed towards superabsorbent polymers being prepared through graft copolymerization of monomers onto the chain of such natural fibres to render the superabsorbent polymers to be biodegradable and hence producing environmentally friendly superabsorbent polymers, which may offer advantages for such applications.

In our previous works we have already prepared grafted sample of various vinyl monomers on the backbone of natural fiber like jute[11-13], rice straw[14] and pineapple leaf fibers (PALF)[15]. In our knowledge, few articles on rice straw grafted materials where the mechanical, water absorbency, crystallography properties, *etc.* have been studied along with their composite applications.

The objective of this paper is to synthesize RS-*g*-PAM superabsorbent polymers and to study the characteristic and swelling behaviour. The synthesized superabsorbent polymer has benefited the system in enhancing the swelling ability while reducing the production cost and accelerates the generation of new materials for special applications.

EXPERIMENTAL

Acrylamide monomer was purchased from E. Merck, Germany and was purified by recrystallization from acetone and dried at room temperature in vacuum. All other reagents were from E. Merck, India and used after purification by standard techniques. A local product rice straw was cut into 3-4 cm then extracted by a mixture of methanol and benzene (1:1) for 6 h to remove waxes and resins. The residual materials were air-dried till a constant mass was obtained. The dried materials were dipped for 24 h at 35 °C in sodium chlorite (3 %) solution for bleaching and to remove the lignin content. Then it was washed with 3 to 4 times in deionised water and dried in a vacuum oven at 50 °C for 12 h.

Preparation of graft copolymer: Rice straw (0.1 g) was presoaked in appropriate quantity of monomer acrylamide for 24 h at room temperature[15]. The requisite $CuSO_4$, glycine, N,N-methylene*bis*acrylamide, NaOH (2M) solution and distilled water as solvent with different degrees of neutralization were prepared at nitrogen atmosphere. Rice straw was first presoaked in monomer acrylamide for 12 h at room temperature. Then it was transferred to reaction vessel containing water. The requisite amount (0.1 M) each of Cu(II) SO_4, 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 (ammonium persulfate) was injected carefully in to the reaction system. Turbidity appears within 15 min of the reaction time. After 3 h, the reaction was arrested by addition of ammonium ferrous sulfate solution in ice cold water to consume unreacted ammonium persulfate and dried it under room temperature as described elsewhere[12]. Then the grafted copolymer was washed in deionized water for 2-3 times to

remove the excess water soluble substances present. The copolymer was dried in air till a constant mass. Similarly, numbers of samples were prepared. The percentage graft yield (G %) and rate of grafting (R_g) were calculated from the initial weight of rice straw (W_i) and weight of RS-*g*-PAM (W_g) using the following relationships:

$$G \% = [(W_g - W_i)/W_i] \times 100$$
$$R_g = (w \times 1000)/V \times t \times M)$$

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.

FT-IR spectra: The IR spectra of unbleached, bleached rice straw and RS-*g*-PAM, in the form of KBr pellets, were taken using the Perkin-Elmer model Paragon-500 FTIR spectrophotometer.

Tensile strength: The tensile properties of the rice straw and RS-*g*-PAM before and after biodegradation were evaluated by measuring stiffness at break (tensile strength) following the methods of Haque and Habibuddowla[16]. The stiffness at break was determined from the value of tenacity (g/den) and elongation at break by using the following relationship:

Tensile strength = (Tenacity at break/elongation at break) × 100

After conditioning the samples, they were combed and fiber aggregates of uniform length were taken. Their weight and length were determined and their mechanical properties were measured by means of a Dutrons tensile tester (Brand-20 Kgf capacity).

Scanning electron microscopy: The scanning electron microscopy micrographs of rice straw and cross linked RS-*g*-PAM were recorded by using scanning electron microscope (Model 5200) of Jeol Ltd, Japan, after coating it with gold at different magnifications.

Water absorbency: The water absorption (% Q_{H_2O}) of the rice straw, RS-*g*-PAM superabsorbent polymers were determined by immersing the dry samples (W_0 = 1 g each) in deionized water at room temperature for 24 h. After the required time period, the samples were drained for 0.5 h for the elimination of excess nonabsorbed water and then the weight of the swollen samples (W_s) was recorded. The water absorbency was calculated[17] using the following equation:

$$\% Q_{H_2O} \text{ (g } H_2O\text{/g sample)} = [(W_s - W_0)/W_0] \times 100$$

Absorbency under load (AUL): A macroporous sintered glass filter plate was placed in a petri dish and a weighted dried sample was placed uniformly on the surface of polyester gauze located on the sintered glass. A cylindrical solid load was put on the dry sample while it can be freely slipped in a glass cylinder. The desired load (applied load 5, 10 and 15 N) was placed on the dry sample (Fig. 1). Then, 0.9 wt. % saline solution was added so that the liquid level was equal to the height of the sintered glass filter.

The set was covered to prevent surface evaporation and probable change in the saline concentration. After 60 min, the swollen sample was weighted again and AUL was Calculated using following equation[18].

$$AUL \text{ (g/g)} = \frac{W_1 - W_2}{W_1}$$

where, W_1 and W_2 denote the weight of dry and swollen superabsorbent polymers, respectively. The AUL is taken as a
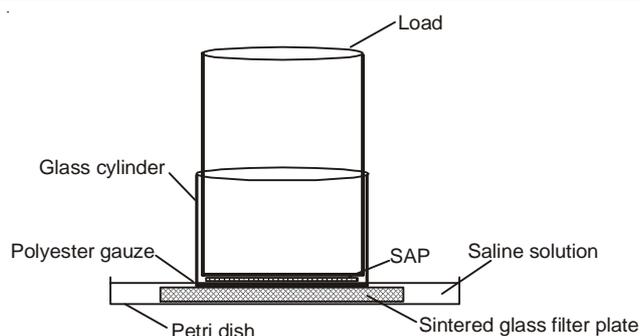
Fig. 1. A typical AUL tester picture (a) and various parts. (b) [Ref. 20]

measure of the swollen gel strength of superabsorbent polymers materials[18-20].

Biodegradation: Biodegradation of rice straw and RS-*g*-PAM (SAPs) studied under sludge water, soil burial and a bacteria culture medium at different conditions in order to compare the extent of degradation under these conditions.

Sludge water degradation: A series of above-mentioned samples (0.1 g) were immersed and incubated at 40 °C in the supernatant liquid taken from standard activated sludge water collected from waste dump areas where both solid and liquid wastes from different departments of the university were collected. It was centrifuged and the supernatant liquids were taken for detailed study.

Soil burial degradation: Soil burial is a traditional way to test samples for degradation because of its similarity to actual conditions of waste disposal. For this test, the samples were buried laterite soil for up to one year and at predetermined intervals, they were recovered from the soil, cleaned with a buffer/ethanol solution and dried in a vacuum oven. The dried samples were weighed to determine the weight loss.

Cultured medium degradation: A cultured medium was prepared using agar nutrient in which *Bacillus cereus* gram positive bacteria was cultured. The degradation of samples by *B. cereus via* weight loss was monitored in time intervals of 7, 14, 21 and 28 days. After the required time period the samples were washed repeatedly with deionized water, oven dried at 40 ± 1 °C for 24 h. Then the samples were weighed to determine the weight loss. Biodegradation by *B. cereus* was also studied by the amount of CO_2 evolved[21] during the incubation periods of 7, 14, 21 and 28 days.

Chemicals requirement: Na_2CO_3, phenolphthalein indicator.

Procedure: The cultured sample ('X' mL) and blank tube was titrated against Na_2CO_3(N/50) ('Y' mL) using phenolphthalein indicator until the pink colour persists for at least 30 sec. This was continued till getting a concordant reading.

Calculation:

$$N_1V_1 = N_2V_2$$
$$(CO_2)\ (Na_2CO_3)$$

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

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

$\Rightarrow$ Free CO_2 = $[(Y \times 22 \times 1000)/(50 \times X)]$ mg/L

$\Rightarrow$ Free CO_2 = $[(440 \times Y)/X]$ ppm

Dying properties: The dyeability of the alkali treated rice straw, RS-*g*-PAM copolymer were studied using 1 % (w/v) ethanolic solution of erichrome black T. Then, 5 % (w/v) NaOH

solution was added to the dye as described in earlier report[22]. Copper complexes are suitable for mordanting cellulosic fibres such as cotton, linen, ramie and pineapple[23]. To mordant the fibre, it was first treated with a boiling solution of $CuSO_4$ in the presence of a reducing agent (oxalic acid) and then dipped in the solution of dye (as prepared above) so as to precipitate the insoluble coloured lake on the fibre. After dying the fibres were rinsed sequentially with cold-hot-cold water, stored at 40 °C for 12 h and then dipped in 10 % (w/v) NaCl solution.

RESULTS AND DISCUSSION

Graft copolymerization of acrylamide onto chemically modified rice straw was done with a view to increase grafting % given in Table-1. The results indicated that, how grafting % changed in different concentration of variables. The schematic representation of proposed mechanism for crosslinking graft polymerization of acrylamide onto rice straw backbones in the presence of ammonium persulfate and N,N-methylene*bis*-acrylamide is shown in Fig. 1. In the first step, the thermally dissociating initiator, *i.e.* Ammonium persulfate, sulfate ion radicals, are well known chain carriers. Polymeric materials containing cellulose, -OH and C-H sites are the active centers for grafting of polymeric chains onto the natural fibres back-bone. Thus, the radical abstracts hydrogen from one of the existing hydroxyl groups in the rice straw backbone to form the corresponding macro-initiator, implying to the formation of alkoxy (C-O$^\bullet$) radicals on the substrate as shown in Fig. 2.

These macro-radicals initiate a radical polymerization of acrylamide grafting onto the rice straw backbone, which results the graft copolymerization. Now PAM was believed to be grafted on the rice straw surfaces. On the other hand, the hydrolyzed amide groups in PAM which were converted into carboxylate groups during neutralization are carrying negative charges. These negatively charged groups are susceptible to the
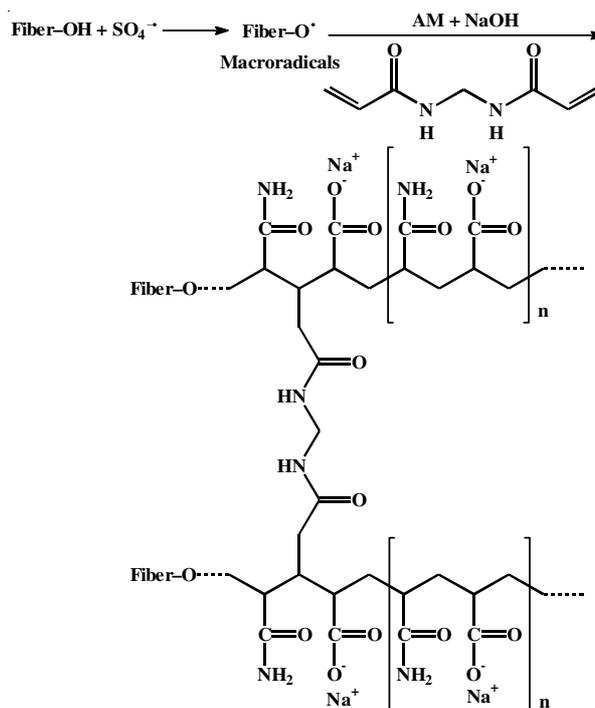
Fig. 2. Schematic mechanism pathway for synthesis of RS-*g*-PAM superabsorbent polymers

TABLE-1
EFFECT ON CHANGE AMOUNT OF RS, ACRYLAMIDE, AMMONIUM PERSULFATE, TIME AND
TEMPERATURE AT CONSTANT [CuSO₄], GLYCINE AND N,N-METHYLENEBISACRYLAMIDE

S no.	RS amount 'g'	[AM] (mol dm^{-3})	[APS] × 10^{-3} mol (dm^{-3})	Time (min)	Temperature (°C)	Grafting (%)
S$_0$	0.2	00	0	0	0	0
S$_1$	0.05	0.4	10	180	50	62.4
S$_2$	0.10	0.4	10	180	50	76.8
S$_3$	0.15	0.4	10	180	50	86.7
S$_4$	0.20	0.4	10	180	50	92.8
S$_5$	0.25	0.4	10	180	50	88.5
S$_6$	0.30	0.4	10	180	50	78.8
S$_7$	0.35	0.4	10	180	50	71.5
S$_8$	0.20	0.1	10	180	50	59.9
S$_9$	0.20	0.2	10	180	50	71.3
S$_{10}$	0.20	0.3	10	180	50	84.2
S$_{11}$	0.20	0.5	10	180	50	87.4
S$_{12}$	0.20	0.6	10	180	50	82.4
S$_{13}$	0.20	0.7	10	180	50	78.2
S$_{14}$	0.20	0.4	2.5	180	50	54.9
S$_{15}$	0.20	0.4	5.0	180	50	71.8
S$_{16}$	0.20	0.4	7.5	180	50	83.8
S$_{17}$	0.20	0.4	12.5	180	50	86.3
S$_{18}$	0.20	0.4	15	180	50	79.5
S$_{19}$	0.20	0.4	17.5	180	50	72.5
S$_{20}$	0.20	0.4	10	60	50	48.8
S$_{21}$	0.20	0.4	10	90	50	69.5
S$_{22}$	0.20	0.4	10	120	50	78.4
S$_{23}$	0.20	0.4	10	150	50	89.9
S$_{24}$	0.20	0.4	10	210	50	92.9
S$_{25}$	0.20	0.4	10	240	50	93.0
S$_{26}$	0.20	0.4	10	180	35	44.0
S$_{27}$	0.20	0.4	10	180	40	67.5
S$_{28}$	0.20	0.4	10	180	45	85.8
S$_{29}$	0.20	0.4	10	180	55	82.9
S$_{30}$	0.20	0.4	10	180	60	69.6
S$_{31}$	0.20	0.4	10	180	65	42.6

crosslinker; *i.e.* N,N-methylene*bis*acrylamide. Thus, cross-linking occurs and finally a three-dimensional network of superabsorbent polymers was obtained, which may possess characteristics for both rice straw and PAM.

FT-IR spectra: From the FT-IR spectra of the grafted superabsorbent polymers (Fig. 2) a strong broad peak at 3447 cm^{-1} show the characteristic H-bond (OH) stretching vibration as observed in the spectra of rice straw reported earlier[14]. The presence of sharp bands near 1734 and 1647cm^{-1} indicates the presence of carbonyl group (> C=O) stretching acquired from the monomer and the sharp band at 1590 cm^{-1} indicates the aromatic rings. As compared to rice straw, in the case of RS-*g*-AM, the new peak obtained at 1755 cm^{-1} is the stretching vibration of carbonyl group present in acrylamide.

Effect of solvent: The effect on the volume of water used as solvent in synthesizing the superabsorbent polymers was studied by varying the volume from 5 to 25 mL. In Fig. 3 (a), the maximum water absorbency of RS-*g*-PAM SAPs of 609.05 g/g, was achieved when the volume of solvent in the reaction system was around 20 mL. Basically, the volume of solvent affects the reactants concentration which directly affected the water absorption capacity of the polymer. At low water volume, *i.e.* below 20 mL, the solvent was insufficient to completely dissolve the required amount of acrylamide. Therefore, the concentrations of the reactants were very high which actually has increased the rate of polymerization and crosslinking
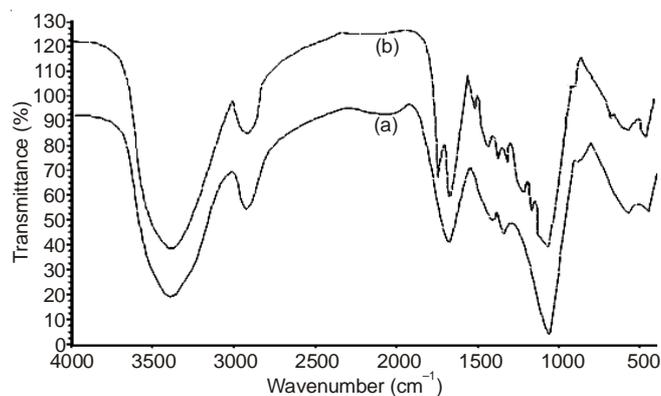
Fig. 3. FTIR spectra of (a) rice straw, (b) RS-*g*-PAM copolymer

reaction and mean kinetic chain length became shorter and polymer network space became smaller. Consequently, the water absorbency of the RS-*g*-PAM copolymer obtained at low solvent volume was decreased which was correlated with the results of Chen *et al.*[24].

Effect of degree of neutralization: The effect of degree of neutralization on water absorbency of the synthesized superabsorbent polymers in distilled water is shown in Fig. 3 (b). The water absorbency increased with the increase of degree of neutralization from 10 to 20 % and decreased with further increase up to 40 %. Once the monomer acrylamide was neutralized with NaOH, the amide groups on the side chains

of grafted PAM SAPs has turned into carboxylate group, which possess higher hydrophilicity than the amide group[25-27]. In a certain range of molar ratio, the electrostatic repulsion, ionic hydrophilic property and osmotic pressure difference increased with the increase of degree of neutralization, resulting in the increase of water absorbency[28].

Further increase in the degree of neutralization results in the generation of more sodium ions in the polymeric network, which reduces the electrostatic repulsion and increases the chain stiffness by screening the negative charges of the carboxyl groups, thus resulting in a decrease of water absorbency. The chains could expand to such an extent that the distance between neighboring charges became too high for optimum cooperation effects between the charges[26].

Effect of crosslinker: The amount of N,N-methylene*bis*-acrylamide was varied from 0.10 to 0.30 wt. %. It is obvious that crosslinker loading at 0.15 wt. % resulted in the maximum water absorbency of 589.06 g/g for the synthesized SAP. When the crosslinker amount was over 0.15 wt. %, the water absorbency was sharply decreased. It is noted that a higher concentration of crosslinker will develop a larger number of growing polymer chains by the generation of more crosslink points that caused the formation of an additional network[27]. Thereby, water absorbency decreased with the increase in crosslinker concentration due to the available free volume within the superabsor-bent polymers system which gets diminished and less water molecules can enter the superabsorbent polymers network structure. Clarification has also been supported by Wu *et al*.[29] and others[27,28].

However, when the volume of water in the reaction system was increased, the concentrations of the crosslinking agent, the initiator and the monomer were all decreased. As a result, the rates of polymerization and crosslinking reaction were slowed down and hence, less polymer network. In addition, when the amount of the solvent increases, the percentage of grafting was also decreased due to the free movement of the monomer molecules in the relative large volume of reaction mixture, hence, the interaction between the monomer was reduced.

Biodegradation

Degradation by soil burial test: In this test, there was very low increase in the rate of weight loss up to 28 days, but the rate increased remarkably beyond 28 days up to one year. In case of PAM, the biodegradation was greater than that of either rice straw or RS-*g*-PAM as shown in Fig. 4(a). The homopolymer PAM being highly hydrophilic is very suscep-tible to microbial attack in the soil, whereas the grafting of acrylamide homopolymer onto the rice straw backbones causes the degradation of RS-*g*-PAM composites to be greater than that of the substrate, rice straw and less than that of PAM.

Degradation by active sludge: From the biodegradation study of rice straw, PAM, RS-*g*-PAM it is found that of the degradation rate accelerated (by weight loss) at first but after 21 days the biodegradation slowed down, as (RS-*g*-PAM) copolymer has more space due to net like structure than others. It holds up more water than others as a result of which it is more biodegradable as shown in Fig. 4(b) and further confor-med by its scanning electron microscopy Fig. 4 (c) and (d).
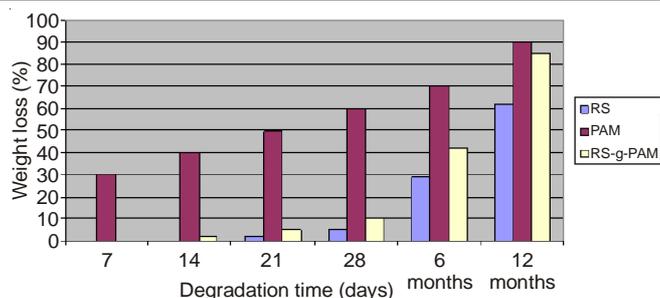
Fig. 4. (a) Degradation by soil burial method
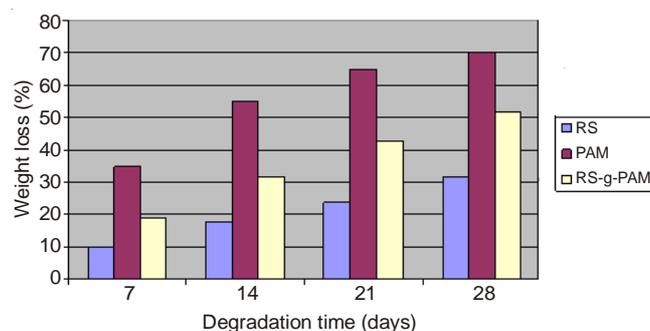
Fig. 4. (b) Biodegradation by activated sludge
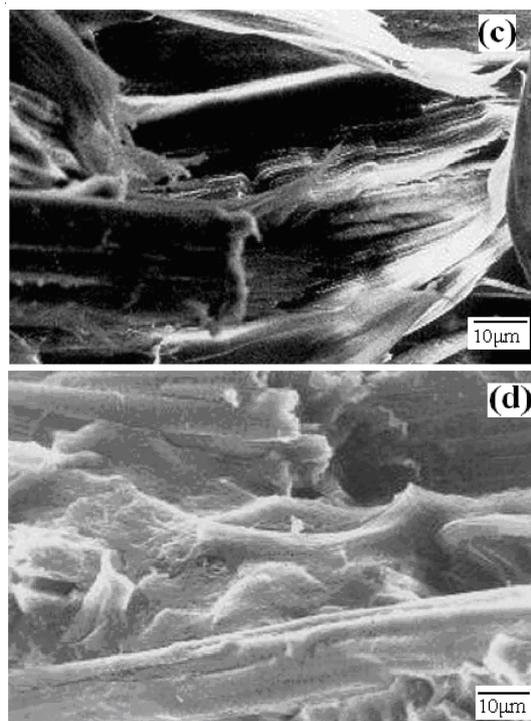
Fig. 4. (c) before and (d) after degradation by sludge water; Scanning electron microscopy figure of RS-*g*-PAM

Degradation by *B. cereus*: For its commercialization, ecologically friendly nature was tested through biodegradation testing of the copolymer which is shown in Fig. 5. The weight loss data revealed that rice straw or RS-*g*-PAM degraded under the influence of *B. cereus* at a faster rate than rice straw. The degradation value was least in case of rice straw due to its hydro-phobic nature. Due to the hydrophilic nature of PAM, the water absorbency and the growth of microorganisms have been incre-ased in the RS-*g*-PAM. The rate of water absorbency in case of rice straw and RS-*g*-PAM justified the biodegradability data.

Sample	Elongation at break (BL %)	Tenacity (g/den)	Tensile strength (N/m²)	Tensile strength after 6 months (N/m²)	Strength retained (%)
Raw RS	24.5	0.084	35.8	4.13	11.54
Bleached RS	28.9	0.108	39.9	5.16	12.93
RS-*g*-PAM	36.6	0.212	48.4	7.16	14.79

TABLE-2
TENSILE STRENGTH OF RS, RS-*g*-PAM
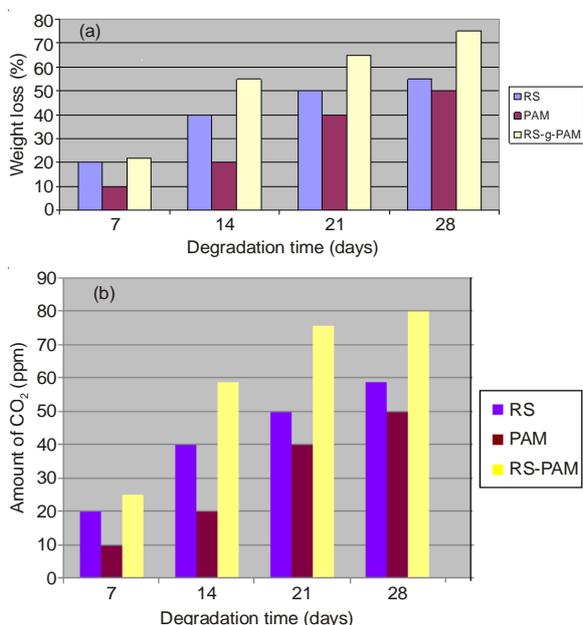
Fig. 5.   (a) Biodegradation by *B. cereus* bacteria of rice straw (RS), PAM and RS-g-PAM *via* weight loss and (b) Biodegradation by *B. cereus* bacteria of rice straw (RS), PAM and RS-g-PAM *via* CO_2 release method

Again, the rate of degradation was also measured by calculating the amount of CO_2 evolved from the cultured medium at various intervals of time. The results showed similar trend of degradation exhibiting more biodegradability of the copolymer than the virgin fiber. On comparison of both weight loss method and the CO_2 release method for the study of degradation of the copolymer, it was inferred that the rate of degradation of rice straw or RS-*g*-PAM was equivalent in both methods and it was further concluded that the copolymer was biodegradable in nature.

Tensile behaviour: The strength of the raw, chemically modified and grafted copolymer was calculated and is presented in Table-2. The decrease in tensile strength due to alkali treatment was not only compensated but enhanced by the grafting of PAM onto the fiber backbone, which imparted 10-50 % improvement in tensile strength. Similar effects were observed for the elongation and tenacity of the grafted copolymers and the raw fibers.

Conclusion

In this work, RS-*g*-PAM superabsorbent copolymer was prepared by graft copolymerization of acrylamide onto rice straw backbones with or without a cross linking agent N,N-methylene*bis*acrylamide (MBA). The chemical structure of the RS-*g*-PAM superabsorbent polymers was characterized by means of FTIR spectroscopy. Swelling measurements of the synthesized superabsorbent in different salt solutions showed appreciable swelling capacity especially in sodium chloride solution. Thermal stability of the grafted rice straw is better than that of the original fiber.

The effects of initiator, crosslinker and filler concentration as well as solvent quantity and the degree of neutralization on water absorbency of RS-*g*-PAM SAP were studied. Maximum absorbency of RS-*g*-PAM SAP was achieved at 489.06 g/g when the amount initiator and N,N-methylene-*bis*acrylamide were 1.5 and 0.15 wt. %, respectively and the rice straw loading was 10 wt. %. This is a novel natural-based superabsorbent polymer (SAP) had a large degree of water absorbency.

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