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Development of Superabsorbents from Agro-Wastes: Microwave-Assisted Synthesis of Green Composite Superabsorbent, Sugarcane Bagasse Fibre (Scbf-G-Phema)/Mmt

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RESEARCH ARTICLE

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ABSTRACT

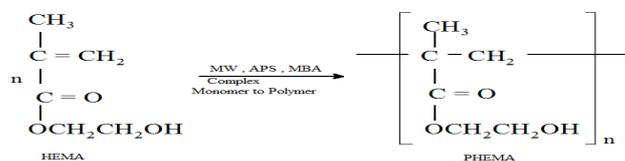
Agrowaste sugarcane bagasse fibre (SCBF) based green composites were prepared by a series of experiments such as bleaching and grafting with 2-Hydroxyethyl methacrylate (HEMA) together with N,N'-methylenebis-acrylamide (MBA) and ammonium persulfate (APS) as crosslinker and initiator respectively using hexaamminecobalt(III)chloride complex as catalyst and montmorillonite (MMT) as additive in a microwave oven. UV-Visible spectral analysis revealed various interactions between the developed complexes with other reacting components. The synthesized (SCBF-g-PHEMA)/MMT composites were characterised by FT-IR, and their morphology was imaged by scanning electron microscopy (SEM). Water absorbency and biodegradability of these composites in soil and sludge water were evaluated for their novel commercial importance as superabsorbent. The water absorption of the grafted composites with MMT was more than that of the virgin and the copolymer fibre. The results of this work can be used in designing novel structural materials like superabsorbents which could have immense application in the field of horticulture in developing green garden in desert, medical devices in diapers, sanitary napkins, etc.

INTRODUCTION

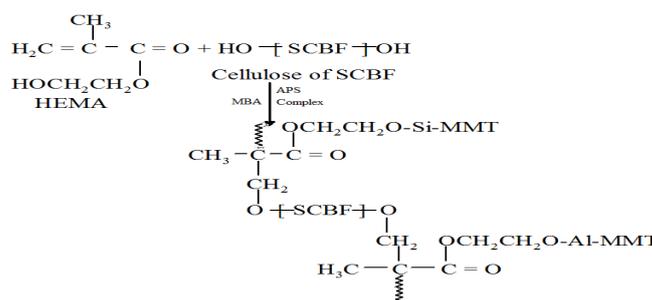
To minimise the use of expensive synthetic polymers and fibres of petrochemical and mineral origin cellulose-based natural fibres are used for low-cost composite materials and use in textile fields to enhance many needed properties such as tensile strength, drying rates ability, insect resistance ^[1], and many other properties. There is growing awareness about the environment protection and new standards have been legislated and applied. There is a great interest in developing sustainable and environmentally friendly systems through enhanced performances, by including suitable bio-based composites. The use of cellulose – based bio-fibres include sisal, flax, hemp, cotton, jute, etc. are used to reinforce both synthetic polymeric matrixes and natural polymers because of their relative high strength, improved thermal properties and high stiffness ^[2,3]. Utilising bio fibres from renewable resources not only contributes to a healthy ecosystem, but also makes them economically feasible for industrial application. Also polymer layered silicate composites exhibit properties dramatically different from their more conventional counterparts. The objectives of this study are to investigate the use of bio-composites as superabsorbent which gives maximum sustainable substances.

Sugarcane (*Saccharum officinarum*) bagasse is a waste residue obtained after extraction of juice from sugarcane. One ton of sugarcane generates 270 kg of sugarcane bagasse ^[4]. The utilization of sugarcane bagasse is still limited and is used mainly as a fuel to power the sugar mill which causes pollution. So it is a challenge to synthesize novel biodegradable substances using these waste materials. We have already investigated swelling behaviour, mechanical properties of grafted samples of various vinyl

monomers on the backbone of jute [5,6], pineapple leaf fibres [7], sugarcane bagasse (SCBF-g-PAM)/MMT [8] and flame-retardancy properties of rice straw (RS-g-PMMA)/SS [9]. There is no report about composites of SCBF taking vinyl/acrylic monomer and MMT-clay as filler. Therefore, we have synthesized novel composite and characterized it by infrared (IR) spectroscopy, scanning electron microscopy (SEM) and studied the properties like water absorbency and biodegradability to be used as economically viable superabsorbent materials in industries. The prime objective of the report is to develop novel materials from agro-wastes by increasing its water absorbency via composite formation using acrylic monomer and nano fillers like MMT (**Schemes 1a and 1b**).



(a)



(b)

Scheme 1: Formation of (a) PolyHEMA, and (b) Grafted Composite (SCBF-g-PHEMA)/MMT.

MATERIALS AND METHODS

2-Hydroxyethyl methacrylate (HEMA) (Merck, Darmstadt, Germany), ammonium persulfate (APS) and N,N'-methylenebisacrylamide (MBA) were purchased from Fluka (Buchs, Switzerland). Methanol, benzene and cobalt (II) chloride were from E. Merck, India. Montmorillonite (MMT) clay with cation exchange capacity of 90 meqiv/100 g was from Himedia and was used without further purification. All other chemicals were also of analytical grade. Milli-Q grade deionised water was used for preparing the solution. HEMA was vacuum distilled at 50 °C/50 mm Hg prior to use in order to remove the inhibitor. In HEMA vacuum distillation, hydroquinone was added to prevent polymerization. The sugarcane bagasse fibre studied was a waste residue of the sugarcane milling process obtained from traditional sugar juice maker around the Bhubaneswar and Cuttack town of Odisha State, India.

Modification of Sugarcane Bagasse Fibre (Scbf)

The raw material obtained from juice maker was sun-dried for four days and the samples had moisture content of about 10 g/100 g. Initially, the dried bagasse was cut into 3-4 cm length. It was immersed in 1:1 benzene and methanol solution for 12 hours to remove waxes and resins. Then it was washed with distilled water for three times and air dried till a constant mass was obtained. The dried materials were bleached with sodium hypochlorite (3%) solution for 24 hours to remove the lignin content. Then, it was washed with double distilled water three times and dried in vacuum-evaporated oven at 50 °C for 24 hours. The bleached fibre was then reduced in size by a blender and screened with a sieve of mesh size number 200. The modified material was stored in a plastic bag for synthesizing copolymer and composite.

Preparation and Interaction of Complex $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

The $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ complex was prepared using the method available in literature [10]. 4.8 g of cobalt(II)chloride hexahydrate, 3.2 g of ammonium chloride and 4 ml of water were taken in a beaker and shaken vigorously till it completely dissolved. 0.5 g of activated charcoal and 10 ml of concentrated NH_3 were added to it. Cobalt was oxidized by bubbling a vigorous stream of air through the solution for seven hours. Then it was converted into yellowish brown coloured precipitate which was filtered and 1 ml of conc. HCl was added to it. Then 30 ml of distilled water was added. The mixture was heated to completely dissolve the precipitate and filtered hot. 8 ml of conc. HCl was added to get precipitate and it was cooled to 0 °C in ice bath. The precipitate was filtered and washed with 60% alcohol and then washed with 95% alcohol. It was dried at 100 °C and the formation of the complex hexamminecobalt (III) chloride was confirmed by UV-Visible spectral analysis (**Figure 1 (b)**). Further the catalytic activity of the complex was ascertained by studying the interaction of the reacting components, monomer, HEMA, initiator, APS before and after polymerization as shown in **Figure 1**.

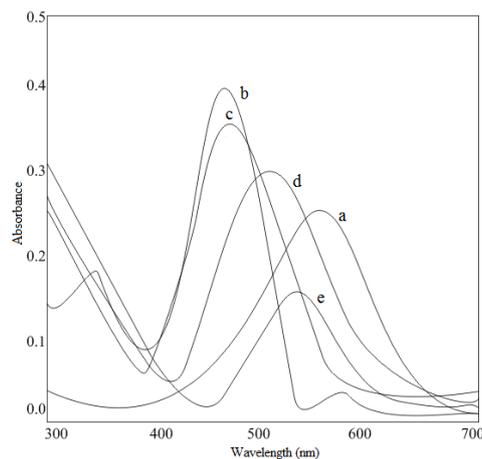


Figure 1. UV-Visible spectra of (a) CoCl_3 (b) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, (c) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ + HEMA, (d) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ + HEMA+APS before reaction and (e) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ +HEMA+APS after reaction.

Preparation of SCBF-g- PHEMA

The polymerization reactions ^[11] were carried out in a Kenstar (Model No MOW9811, 1200W) domestic microwave oven. The average bulk temperature at end of the reaction was measured by inserting a thermometer in the reaction mixture. All the experiments were done with deionised water as solvent and the temperature less than 100°C . The polymerization experiment was carried out in two steps. In the first step 0.1 g of modified SCBF and different proportion of HEMA was taken in the reaction vessels and N_2 gas was bubbled for 30 minutes with constant stirring at 600-700 rpm at room temperature. In the second step, requisite amount of initiator APS solution was carefully injected to the reaction mixture with complex solution and MBA. Then, reaction mixture was heated with microwave oven for 180-240 seconds. The reaction vessel was removed and kept in the ice bath for 30 minutes to stop the polymerization process. The samples formed were dissolved in methanol for 24 hours to remove homopolymers **Scheme 1 (a)**. The product was filtered and washed with methanol again, then with deionised water and dried at 50°C till getting a constant mass.

Synthesis of (SCBF-g-PHEMA)/MMT Composite

The green composite was synthesised in the microwave oven (Kenstar, Model No MOW9811, 1200W) in two steps. In the first step 0.1 g of modified SCBF and different proportion of HEMA was taken in the reaction vessels and N_2 gas was passed for 30 minutes with constant stirring at 600-700 rpm at room temperature. In the second step, initiator APS solution was carefully injected to the reaction mixture with 1% (w/v) complex solution, MBA and also 1% (w/v) MMT solution was added to the reaction mixture. Then, reaction mixture was heated with microwave oven for 180-240 second. The reaction vessel was removed and kept in the ice bath for 30 minutes to stop the polymerization process. The composite formed **Scheme 1 (b)** was dissolved in methanol for 24 hours to remove homopolymers **Scheme 1 (a)**. The product was filtered and washed with methanol, then deionised water and dried at 50°C till a constant mass was obtained.

CHARACTERIZATION

UV Spectroscopy

The UV-Visible spectra of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ complex and its interaction with reacting components were studied using a Perkin Elmer UV-Visible spectrophotometer model Lambda-20 to show its catalytic activity.

FTIR Spectroscopy

The FT-IR spectra were used to analyse composition of the samples that gave information about grafting behaviour and functional groups present in the composite structure in the range of $400\text{-}4000\text{ cm}^{-1}$ by a Perkin Elmer Paragon 500 FTIR (Boston, MA) Spectrophotometer using KBr pellets to prepare the samples.

Scanning Electron Microscopy

The morphological characteristics of modified SCBF, copolymer, and composite were observed by using a scanning electron microscope (Hitachi S4800, Japan.)

PROPERTY STUDY

Water absorbency

1 g of the sample was immersed in water at room temperature until equilibrium was reached. The water absorption was determined by weighing the swollen sample after it had been allowed to drain on a sieve for 10 min. The water absorbency ^[12] %Q was calculated using the following equation:

$$\%Q = (m - m_0) / m_0 \times 100$$

Where m and m_0 denote weight of the sample swollen by water and weight of the absorbent respectively

Biodegradation

Biodegradation of the samples were studied on two different methods mentioned as follows:

Degradation by sludge water: The activated sludge water was collected from septic tank receiving toilet and domestic waste water. The sludge water was collected ^[12] in a polypropylene container, which was filled completely and then closed perfectly. Then the waste water was transferred to the lab immediately. After settling for 1 h the total solid concentration was increased to 5000 mg/l. Then activated sludge water and sample (0.2 g) were incubated together in a sterilized vessel at room temperature ($28 \pm 2^\circ\text{C}$). Duplicate samples were removed at time intervals for biodegradation study through weight loss. Vessels containing polymer sample without sludge water were treated as control.

Soil burial degradation: Biodegradability ^[13] of the samples in soil was studied by weight loss. Samples of $30 \times 30 \times 1$ mm were weighed and then buried in boxes containing alluvial soil, collected from farmland topsoil before planting. Samples were buried at a depth of 20 cm. A controlled box containing only sample without soil was also taken as control. The burial samples were dug in certain time intervals, washed with distilled water, dried in a vacuum oven at 40°C for 24 h, equilibrated in a desiccator for at least 24 h and evaluated by measuring their dry weight.

RESULTS AND DISCUSSION

UV Spectroscopy

The UV-Visible Spectra of various solutions like CoCl_2 , $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3/\text{HEMA}$, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3/\text{HEMA}/\text{APS}$ before reaction and after reaction were measured in an aqueous solution to obtain an idea of the interaction between the reacting species (**Figure 1**). The central metal ion, Co(III) is coordinated with monomer (HEMA) as revealed from the sharp change in absorbance from 0.4 (b) to 0.35 (c) in **Figure 1**. On the addition of the initiator (APS), to the above mixture, the absorbance reduces from 0.35 (c) to 0.3 (d) showing the initiation of polymerization. The polymerization in complex medium is evident by sharp change in absorbance from 0.4 (b) to 0.14 (e) in **Figure 1**. Further, the formation of complex and initiation of polymerization are evidenced from the gradual fading of purple colour of CoCl_2 with reaction time by the addition of monomer and initiator. The high conversion values were due to the high rate of production of initiating radicals generated by heterolysis of initiator bounded by complex $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ where the internal energy is transferred to the monomer.

FTIR spectroscopy

The FTIR spectra (**Figure 2**) of modified SCBF show the removal of pectins, lignin and hemicelluloses resulting from the vanishing of the characteristic band at 1733.5 cm^{-1} for carboxylate groups, 1605.5 cm^{-1} for acetyl groups, 1252.4 cm^{-1} for methyl ester groups, 1513.8 and 1426.6 cm^{-1} for aromatic C=C stretching ^[2,14]. So modification had removed large amount of pectin, lignin, and hemicelluloses. It was confirmed by a prominent band at 1735 cm^{-1} due to C=O stretching of HEMA, that poly (HEMA) was incorporated on the cellulose backbone which was further confirmed by SEM micrograph (**Figure 3 (b)**) and also by greater swelling ratio of copolymer. For composite (SCBF-g-PHEMA)/MMT and copolymer (SCBF-g-PHEMA) (a,b), the characteristic peaks are present with little shifting of the position. The peaks at 1162 and 1080 cm^{-1} corresponding to C-O-C stretching also confirms the presence of ester group of polyHEMA. Presence of MMT in the composite is confirmed by the new peaks at 517 and 514 cm^{-1} respectively due to the Al-O stretching and Si-O bending of MMT. Similar results were reported in the literature ^[15,16]. This is also confirmed by SEM micrograph (**Figure 3 (c)**) and tremendous increase in water absorption ratio of synthesized composite (SCBF-g-PHEMA)/MMT.

Scanning Electron Microscopy

SEM of modified SCBF, SCBF-g-PHEMA copolymer and (SCBF-g-PHEMA)/MMT green composite were shown in **Figure 3**. Grafting of PolyHEMA on the backbone of modified SCBF was confirmed in **Figure 3 (b)** with white deposition which is further confirmed by more water absorbency of copolymer than that of modified SCBF. From the **Figure 3 (c)** it was confirmed that the MMT particles were dispersed into the polymer matrix thereby forming a network- like structure which retains a large amount of water in its cavities. This results in higher water absorbency of the green composites which can be confirmed from its greater water absorbency ratio than the grafted copolymer and virgin SCBF.

Water Absorbency

The water absorption of various samples were studied in deionised water (**Figure 4a**) and water of the Mahanadi river (**Figure 4b**), the biggest river of Odisha state in India. It was found that the water absorption of SCBF is low in both cases, because of the absence of lignin and binding materials. The water absorbency of SCBF-g-PHEMA copolymer shows higher value than SCBF in both cases because of the increasing hydrophilic nature of PHEMA grafted onto the backbone of SCBF. The further increase in water absorbency of (SCBF-g-PHEMA)/MMT composite in both cases due to increasing hydrophilic nature of PHEMA, porosity of MMT and formation of network- like structure of the green composite. Results indicate the synergistic effect of the MMT with copolymer in increasing water absorption capacity. The exfoliation of the MMT could be a benefice factor in increasing the specific surface, and therefore increasing water absorbency of the composites.

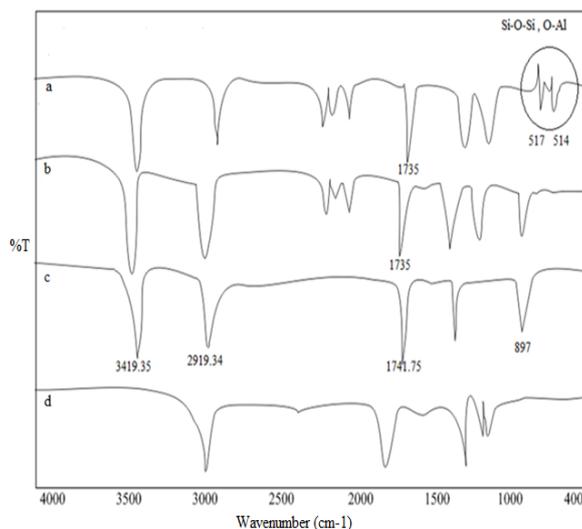


Figure 2. FTIR Spectra of (a) (SCBF-g-PHEMA)/MMT, (b) SCBF-g-PHEMA, (c) SCBF and (d) PHEMA.

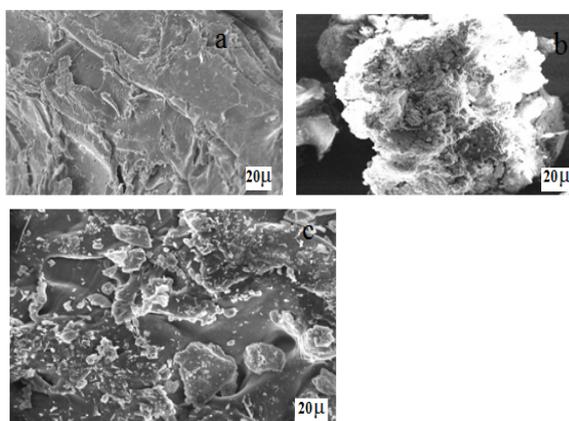


Figure 3. SEM of (a) Modified SCBF, (b) Copolymer SCBF-g-PHEMA and (d) Composite (SCBF-g-PHEMA)/MMT.

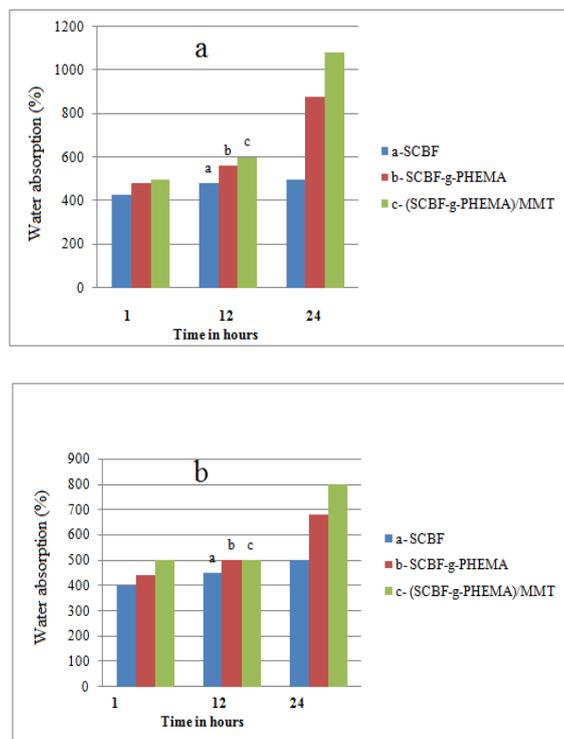


Figure 4. Water absorbency in (a) Distilled water and (b) Mahanadi water.

Biodegradation

Figure 5 (a) and 5 (b) show the biodegradation of SCBF, SCBF-g-PHEMA copolymer, (SCBF-g-PHEMA)/MMT composite by soil

burial method and in activated sludge water respectively. Biodegradation is more in sludge water than in soil burial test. In both the cases it is observed that biodegradation is more in green composite (SCBF-g-PHEMA)/MMT than copolymer (SCBF-g-PHEMA) and that of SCBF. This was due to the addition of hydrophilic PHEMA in SCBF backbone which increases the water absorbency of the SCBF-g-PHEMA copolymer and hence the biodegradation of copolymer than that of SCBF. Biodegradation of (SCBF-g-PHEMA)/MMT composite is further increased in both cases due to addition of hydrophilic MMT and network-like structure of the composites. The increased biodegradation of the composites was due to higher water absorbency providing conducive atmosphere for the growth of micro-organism.

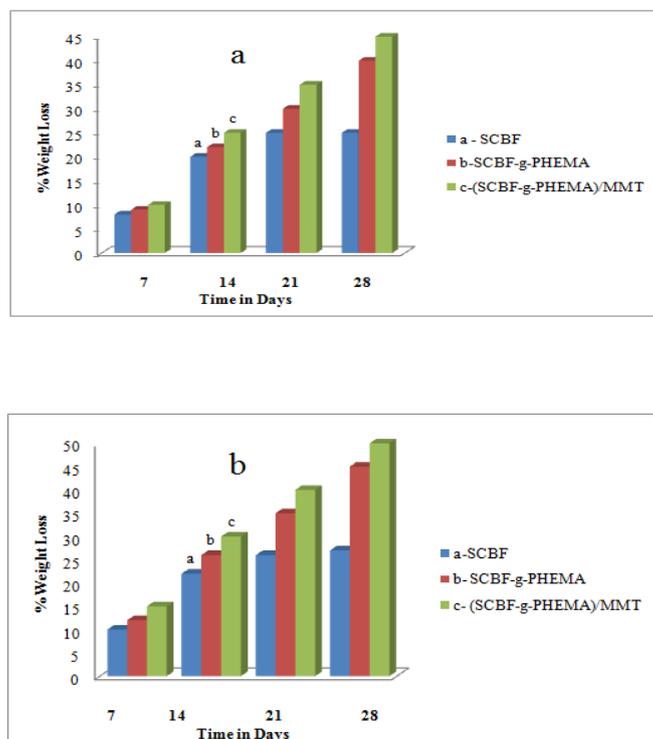


Figure 5. Biodegradation by (a) Soil Burial Methods and (b) Sludge Water Test.

CONCLUSION

Green composites (SCBF-g-PHEMA)/MMT were successfully synthesized by using ammonium persulfate (APS) as an initiator and MBA as a crosslinker and hexaamminecobalt(III)chloride complex as catalyst with a microwave oven. The UV-Visible spectra revealed the fast polymerization reactions occurred by fast decomposition of initiator due to the complex. The FTIR analysis confirms the grafting of PHEMA on SCBF backbone as well as MMT. The SEM micrographs of the (SCBF-g-PHEMA) and (SCBF-g-PHEMA)/MMT confirms the network-like structures of the green composites which accounts for enhanced water absorbency. The composite (SCBF-g-PHEMA)/MMT can be used as a superabsorbent due to its high water absorbing capacity and is eco-friendly due to higher biodegradability which have potential application in the field of medicines, agriculture and in consumer good sectors.

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