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Synthesis and biodegradability of starch-g-ethyl methacrylate/sodium acrylate/sodium silicate superabsorbing composite

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Abstract A new superabsorbent composite polymer (SAP) has been prepared by graft copolymerization reaction using starch, ethyl methacrylate (EMA), benzoyl peroxide (BPO) as initiator and sodium acrylate as crosslinking agent. Further, it is observed that the composite doped with sodium silicate exhibits higher waterabsorbency as the silicate can well disperse in the water and enter into the network structure of the composite, thereby increasing the porosity of the composite. Sodium acrylate plays an important role as the crosslinker forming a network structure of the superabsorbent composite. The composite was characterized by IR, TGA, and XRD methods. The biodegradability of these valuable novel materials was evaluated for their industrial and commercial importance. The surface morphology was compared by scanning electron microscopy (SEM) before and after biodegradation of the composite.

Introduction

The polymers that can swell or absorb water more than thousand times of its original weight are generally known as superabsorbent polymers (SAPs). Due to the excellent characteristics, the SAPs has raised a considerable interests and researches and has been used in health, agriculture [1, 2]. About 90% of all superabsorbent materials are used in disposable articles. As most of them are disposed of landfills or by incineration, there is a perceived environmental problem and thus it is currently an active area of research.

Pollution due to non-biodegradable polymers causes many environmental problems i.e., plastic wastes originate from packaging materials such as rubbish bags, agricultural mulch films, food wrappers, and containers with their disposal. The biodegradable polymers generally constitute a loosely defined family of polymers that are designed to degrade through the action of living organisms. Since last decades, many attempts have been focused on grafting or blending of plastic materials with cheap and biodegradable natural biopolymers, such as starch, cellulose, and chitin etc. to create new materials with desired properties [3–12]. These biopolymers, especially starch, are abundant, inexpensive, renewable, and also degradable.

In this article, we have synthesized a new starch based superabsorbent material with systematic investigation of the influence of crosslinking agent and additive on the capacity for absorbing water and the novelty of this paper is the study on their biodegradation through soil burial, sludge water and microorganisms, i.e., *Bacillus cereus* (gram positive) which has not been attempted/ reported.

Experimental

Ethyl methacrylate (EMA) and Na_2CO_3 were purchased from E merck, Germany and acrylic acid, benzoyl peroxide (BPO), hydroquinone were from E merck, India Ltd. Sodium silicate (SS) was a gift sample from PQ Corporation, The Netherlands.

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Graft copolymerization

The graft copolymers were prepared by free radical polymerization. EMA was taken in a three-necked flask equipped with a mechanical stirrer, condenser and N_2 line in deionized water via stirring with sodium acrylate (SA) – a crosslinker. The solution was stirred at 400–500 rpm for 15 min. The silicate solution was prepared by weight percentage basis. The mixture was slowly heated upto 80 °C and BPO initiator was added at this temperature. After 2 h of reaction the above prepared silicate solution was added to it. Then after 1 h of reaction polymerization was completed by addition of 0.1 M solution of hydroquinone. The coagulated products were first purified by washing with distilled water and dried in oven at 40 °C, then refluxed with methyl alcohol for 8 h, for the removal of PEMA.

Preparation of sodium acrylate (SA)

Sodium acrylate (0.5 M) solution was prepared [13] in distilled water and titrated against acrylic acid (0.1 M) placed in a conical flask in dry ether. The white solid separated out was filtered under vacuum and dried in a vacuum desiccator. The reaction is,

$$\underset{\text{acrylic acid}}{2CH_2{=}CHCOOH} + Na_2CO_3 \rightarrow \underset{\text{sodium acrylate}}{2CH_2{=}CHCOONa} + H_2O + CO_2 \uparrow$$

Characterization

The crystallinity [14] was confirmed by using X-ray diffraction (XRD) at a scan speed of 2 °/min on a Philips PW-1847 X-ray crystallographic unit equipped with a Guinier focusing camera.

IR spectra of starch, PEMA, St-g-PEMA and St-g-PEMA/SS samples in the form of (0.5 g) KBr pellets were recorded in the Perkin Elmer Paragon 500 FTIR spectrophotometer in the range of 400–4000 cm^{-1}.

The thermal properties were measured by using a Shimadzu DTA-500 system. It was carried out in room temperature to 600 °C at a heating rate of 10 °C/min using dry nitrogen at a flow rate 50 mL/min.

The surface morphology of St-g-PEMA/SS before and after biodegradation was recorded by Jeol Ltd., Japan Model 5200 scanning electron microscope (SEM) with magnifications of ×1000.

Properties

Waterabsorbency measurement

One gram of the grafted composite was immersed in water at room temperature until equilibrium was reached. The water absorption was determined by weighing the swollen samples after it had been allowed to drain on a sieve for 10 min. The water absorbency [13] Q (g H_2O/g sample) was calculated using the following equation:

$$Q(\text{g}\,H_2O/\text{g}\,\text{sample}) = (m - m_0)/m_0,$$

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

Biodegradation

Biodegradation of the samples i.e., starch, PEMA and St-g-PEMA/SS was studied on three different methods mentioned as follows:

Degradation in activated sludge The activated sludge water was collected from septic tank receiving toilet and domestic wastewater. The sludge water was collected [15] in a polypropylene container, which was filled completely and then closed perfectly. Then the wastewater was transferred to the lab immediately. After settling for about 1 h the total solid concentration was increased to 5000 mg/L. The activated sludge and a polymer sample (0.2 g) were incubated together in a sterilized vessel at room temperature (28 ± 2 °C). Duplicate samples were removed at time intervals for biodegradation study through weight loss. Vessels containing polymer sample in distilled water in absence of sludge were treated as control.

Soil burial degradation Biodegradability [16] of the samples in soil was studied by weight loss. Samples of 30 × 30 × 1 mm were weighed and then buried in boxes containing alluvial soil, collected from farmland topsoil at monsoon. Samples were buried at a depth of

20 cm. A controlled box containing only sample without soil was also taken. The burial samples were dug out in certain time intervals, washed with distilled water, dried in a vacuum oven at 40 ± 2 °C for 24 h, then equilibrated in a descicator for at least 24 h and evaluated by measuring their dry weight. The same procedure described above was adopted prior to burial to obtain the starting weight.

Degradation in cultured medium A cultured medium was prepared by taking nutrient broth. In that medium *B. cereus* (gram positive stain) bacteria were inoculated. The pure cultures were maintained separately in the incubator. The nutrient broth so prepared was sterilized for 45 min at a pressure of 15 lb/in.^{2} at 80 °C. Then to 10 mL of sterilized broth 0.1 g each of the samples i.e., starch, PEMA and St-g-PEMA composites were added asceptically in separate test tubes and each tube of samples were supplemented with inoculome of different bacterial strains separately.

The degradation of samples by *B. cereus* gram positive was monitored in time intervals of 8, 15, 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.

Results and discussion

IR spectra

Grafting onto starch were studied by FTIR spectroscopy as shown in Fig. 1. The transmission bands in the region 2900–3000 cm^{-1}, namely at 2980, 2940 and 2910 cm^{-1} are due to C–H stretching vibrations or the methylene, (C) CH_3 and ethylene $O(C_2H_5)$ groups [17]. The OH-bond stretching of starch shows at 2900–3400 cm^{-1}, but for St-g-PEMA it appears at 3200–3700 cm^{-1} [18]. The carbonyl group peak for PEMA appears at 1725 cm^{-1} but for St-g-PEMA it appears at 1680 cm^{-1}. For St-g-PEMA/SS composite, the Si–O–Si bond stretching shows peak at 900–1050 cm^{-1}.

X-ray diffraction

X-ray diffraction method [19] is a very useful and powerful analytical technique for understanding the crystallinity of polymers. From the different peaks in Fig. 2, it has been found that the crystalline region increases on grafting of homopolymer (PEMA) onto starch with crosslinker, SA and additive, SS, although starch, SS are semicrystalline [20] St-g-PEMA/SS is crystalline in nature. Applying Brag's formula, d-spacings were calculated at their peak positions, for PEMA, it was 15.235 Å and for St-g-PEMA/SS it was 12.973 Å. Thus it is predicted that St-g-PEMA/SS with higher

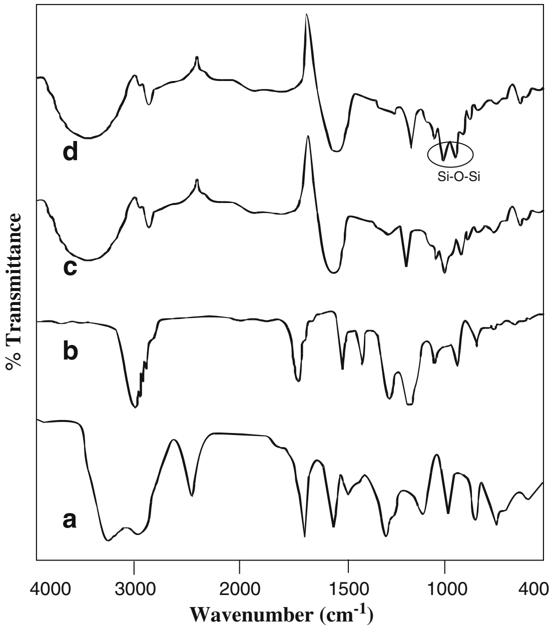

Fig. 1 IR spectra of (**a**) starch, (**b**) PEMA, (**c**) St-g-PEMA, and (**d**) St-g-PEMA/SS X-ray diffraction

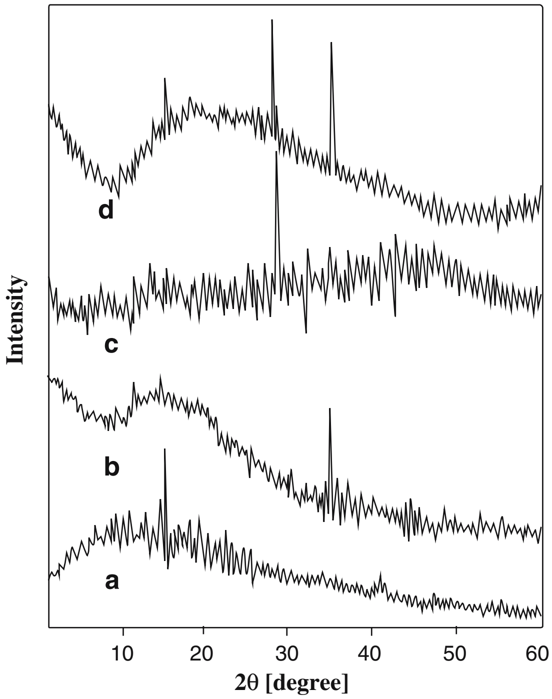

Fig. 2 XRD curves of (**a**) starch, (**b**) PEMA, (**c**) sodium silicate, and (**d**) St-g-PEMA/SS TGA

Table 1 Waterabsorbency with respect to variation of [Monomer], [Initiator], [SA] and [SS] at 80 °C

Polymer code	Starch in g	[EMA] mol dm^{-3}	[BPO] mol dm^{-3}	[SA] mol dm^{-3}	[SS] mol dm^{-3}	Q (H_2O/g sample)
S_1	1	0.326	0.01	13.3	0.1	1337
S_2	**1**	**0.653**	**0.01**	**13.3**	**0.1**	**2857**
S_3	1	0.978	0.01	13.3	0.1	2416
S_4	1	1.304	0.01	13.3	0.1	1910
S_5	1	1.63	0.01	13.3	0.1	1308
S_6	1	0.653	0.005	13.3	0.1	1215
S_7	1	0.653	0.015	13.3	0.1	1734
S_8	1	0.653	0.02	13.3	0.1	1567
S_9	1	0.653	0.025	13.3	0.1	1481
S_{10}	1	0.653	0.01	3.3	0.1	431
S_{11}	1	0.653	0.01	6.6	0.1	753
S_{12}	1	0.653	0.01	10.0	0.1	1694
S_{13}	1	0.653	0.01	16.5	0.1	2387
S_{14}	1	0.653	0.01	13.3	0.01	551
S_{15}	1	0.653	0.01	13.3	0.05	1156
S_{16}	1	0.653	0.01	13.3	0.5	1812
S_{17}	1	0.653	0.01	13.3	1.0	2119

crystallinity and higher porosity shows maximum water absorption capacity as shown in Table 1.

TGA

The thermal behavior of starch, PEMA, St-g-PEMA and St-g-PEMA/SS were studied at room temperature at (28 ± 2 °C) by comparing their thermogram curves as shown in Fig. 3. From the curves the temperature of decomposition (T_D) were found to be 210 °C for starch, 230 °C for PEMA and 285 °C for St-g-PEMA/SS. As the sample St-g-PEMA/SS decomposes at high temperature so it has high thermal stability than other mentioned samples.

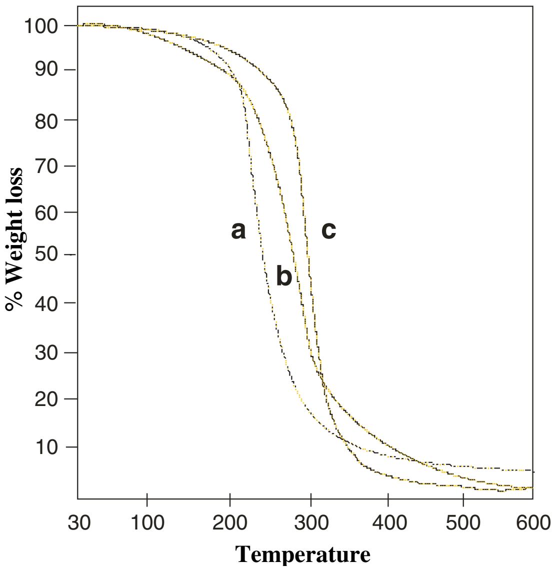

Fig. 3 TGA thermograms of (**a**) PEMA, (**b**) starch, and (**c**) St-g-PEMA/SS

Scanning electron microscopy

Figure 4 shows the surface morphology of St-g-PEMA/SS before and after cultured media biodegradation. The SEM of St-g-PEMA/SS shows more networking surface and a regular grafting on starch but, after biodegradation, the surface seems to be rough and unclear, which confirm the microorganisms mediated degradation of the St-g-PEMA/SS.

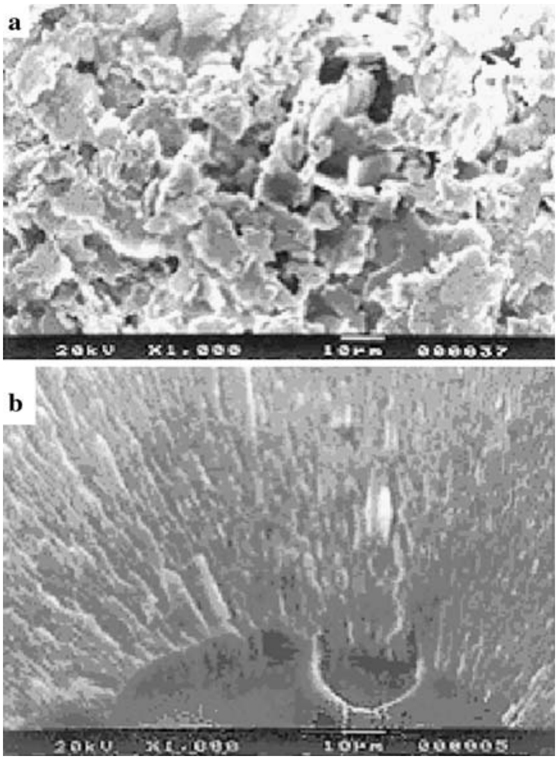

Fig. 4 Scanning electron micrographs of St-g-PEMA (**a**) before, and (**b**) after biodegradation superabsorbency

Superabsorbency

Effect of [initiator, BPO]

The effect of initiator concentration was studied as presented in Table 1. The swelling amount increases as BPO concentration rises from 0.005 mol dm^{-3} to 0.01 mol dm^{-3} and then decreases slowly due to increase in number of radicals produced as the concentration of BPO increases. The increase in the production of radicals at higher initiator concentration increases the rate of polymerization; thereby lessening the crosslinking density and this factor is responsible for the decrease in the swelling capacity of the polymer.

Effect of [crosslinker, SA]

The relation between crosslinker concentration and waterabsorbency (Q (H_2O)) for the samples are shown in Table 1. The waterabsorbency increases as SA concentration increases from 3.3 to 13.5 × 0^{-3} mol dm^{-3} and then decreases considerably with higher SA concentration. This is explained based on the fact that as the concentration of crosslinker increases, the number of crosslinks increases and as a result the porous nature of the copolymer decreases, which, in turn, is responsible for the less waterabsorbency.

Effect of [Additive, SS]

Sodium silicate has an important role in superabsorbent property. The waterabsorbency (Q (H_2O)) of the additive based composite i.e., St-g-PEMA/SA/SS was measured and shown in Table 1. The composite showed highest water absorption at [EMA] = 0.653 mol dm^{-3}, [BPO] = 0.01 mol dm^{-3}, [SA] = 13.3 mol dm^{-3} and [SS] = 0.1 mol dm^{-3}. It is due to that, as SS is completely soluble in water it may form weak bond with the polymer, which enhances the hydrophilicity of the polymer and facilitates to increase the water absorbing capacity in the network. At higher concentration of SS the water absorbency decreases, because at higher concentration there may be more Si–O–Si linkage of the composite and may not be enough space for water molecules to enter into the network.

Biodegradation

Degradation by activated sludge

From the comparative biodegradation study of starch, PEMA and St-g-PEMA/SS, it was found that St-g-PEMA/SS showed accelerated rate of degradation (by weight loss). But starch showed less amount of weight loss and there was very negligible amount of weight loss found in case of PEMA as shown in Fig. 5. As St-g-PEMA/SS has more net like space than others, it holds up more water than others, as a result of which it is more biodegradable.

Degradation by soil burial test

In this test, there was very low increase in the rate of weight loss in PEMA, for its hydrophobic nature. But in case of starch, there was slow rate of degradation up to 28 days and then gradually up to 1 year some improvement in weight loss was found as shown in Fig. 6. For St-g-PEMA/SS, as it is a superporous material and having networks in it, it can hold up more water which helps microorganisms to grow easily.

Degradation by Bacillus cereus

From the experiment it was confirmed that St-g-PEMA/SS degraded at a faster rate than PEMA and starch by *B. cereus* as shown in Fig. 7. It may be attributed to the fact that the growth of bacteria is

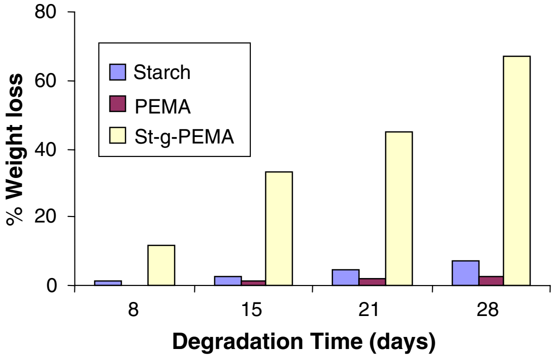

Fig. 5 Degradation in activated sludge at [EMA] = 0.563 mol dm^{-3}

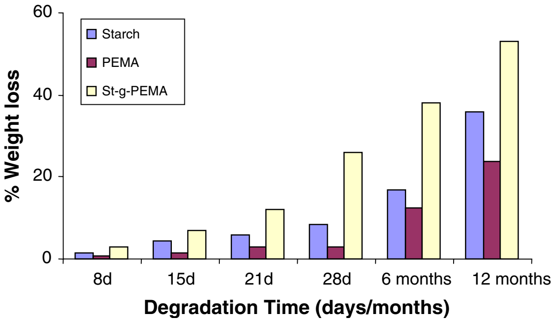

Fig. 6 Degradation in soil burial test at [EMA] = 0.563 mol dm^{-3}

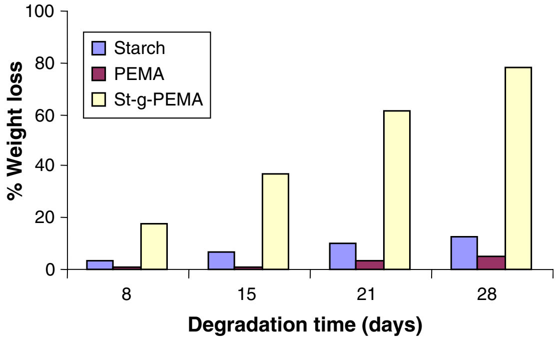

Fig. 7 Degradation by bacteria (*B. cereus*) at [EMA] = 0.563 mol dm^{-3}

more in the system containing St-g-PEMA/SS than others only due to the increase of hydrophilicity nature.

Conclusion

The novel modified starch composite consisting of the system: (St-g-PEMA)/SA/SS exhibits high superabsorbency for which SAPs can be used as bioplastic materials and in agricultural and horticulture fields for their efficient retention of water in dry and desert regions to transform them into green and fertile lands. The potential SAP composites were fully characterized by IR, XRD, TGA and were found to exhibit higher thermal stability and crystallinity than the substrate starch. The degradability of the composite was also studied by the SEM micrograms. Further, the biodegradation studies of the SAP composites so synthesized, termed as bioplastics of starch were done by different methods of activated sludge, soil burial and cultured media. The slow degree of degradation in case of soil burial condition in comparison to other methods could make the SAPs available for their novel commercial uses.

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