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STARCH-G-POLY(ACRYLIC ACID)/MICA BIONANOCOMPOSITE SUPERABSORBENT: BIODERADABILITY AND SWELLING BEHAVIOUR STUDIES

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ABSTRACT

A novel Starch-g-Poly(acrylic acid)/mica superabsorbent bionanocomposite was synthesized by graft copolymerization reaction of starch with acrylic acid (AA) and addition of fine mica powder via emulsion polymerization using ammonium persulfate (APS) as initiator at 50^0C. The reaction parameters such as initiator and monomer concentrations were optimized to get the maximum percentage grafting. The grafted samples were characterized by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and thermo gravimetric analysis (TGA) techniques and evaluated for properties like swelling behavior, biodegradability and thermal stability. The swelling behavior and biodegradability were found to be higher with higher starch and lower mica content. Thermal stability of the synthesized bionanocomposite was higher for the increased mica content specimens. The novelty of this synthesized bionanocomposite is that it can be used as a superabsorbent having potential thermal stability in probable biomedical as well as engineering applications.

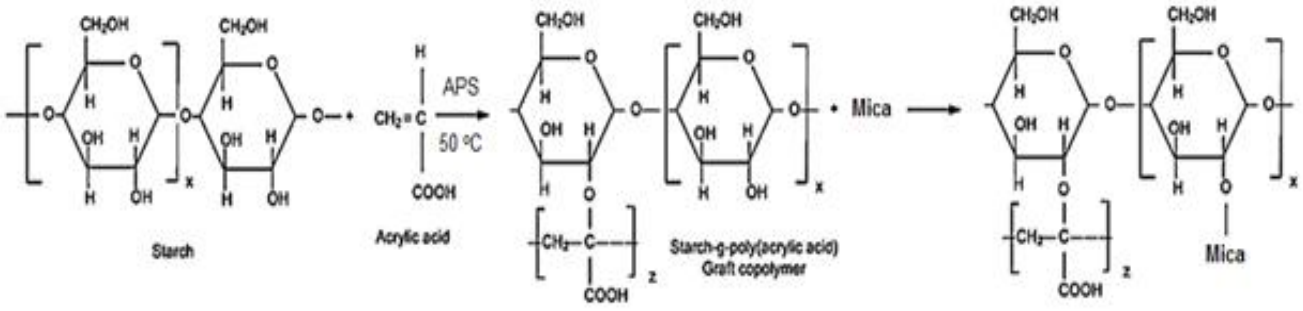
KEYWORDS: Starch, acrylic acid, mica, bionanocomposite, superabsorbent, Biodegradation.

INTRODUCTION

Starch is a renewable and biodegradable natural polymer, found to be useful in a variety of commercial applications due to its property of swelling irreversibly by absorbing large quantities of water. This property has been useful in the textile and paper industries by incorporating starch as a thickener and sizing agent. The combination of the hydrophilic acrylic polymer with the starch-based blends lead to interesting hydrogels with important applications, especially as hydrogels for personal care products, food packages, and agricultural purposes. [1] Graft co-polymerization is a method of addition of new and desirable properties to starch without affecting the basic properties of starch. Grafting of vinyl monomers onto the polysaccharides, especially starch improves their properties like biodegradation, thermal stability and metal ion binding ability and therefore their industrial utility. [2] A large number of studies have been reported for the graft copolymerization of different vinyl monomers onto starch obtained from different sources. [3,4] The Acrylic Acid (AA) forms a three-dimensional polymeric network like structure upon polymerization which can be used as a hydrogel for various absorbing purposes in agricultural and personal care fields. Polyacrylic acid(PAA) gives enhanced stability to starch when grafted onto it due to the hydrogen bonding between its carboxylic groups and the hydroxyl groups of starch. [5,6] The polyacrylic acid (PAA) and starch copolymer exhibits different properties depending on the type of interactions within the network, due to chemical cross-linking and hydrogen bonding. Mica is a layered aluminum silicate with reactive groups on its surface. It is an environmental friendly mineral nano filler and physiologically harmless and odorless. It can be used as reinforcement additive for polymer. Applications of mica as nano filler in the polymer biocomposites help in (a) improving mechanical performance of the composite (b) increasing dimensional stability (c) increasing heat deflection temperature (d) increasing UV stability. The above properties of the bionanocomposite will be reflected in the future communications.

Grafting of starch-g-acrylic acid copolymer onto mica and to synthesize a bionanocomposite is significant for its cost effectiveness and improved water-absorbing property of the superabsorbent materials [7] as well as biodegradability and thermal stability. Because of their improved characteristics of water absorption and retention, super absorbents are widely used in health, agriculture and horticulture fields, which have stimulated immense interest and research in this field. For conserving the petrochemical resources and reducing environmental pollution, efforts have been exerted to develop starch-based polymers as alternatives of

petroleum based polymers.[8] The current work is aimed at preparing starch-g-PAA/mica bionanocomposites using ammonium persulfate (APS) as initiator. Optimum conditions for graft polymerization of AA onto starch and mica were investigated, as shown in scheme 1. Characterization and probable applications of the prepared bionanocomposites in the fields of biomedical and engineering such as in sanitary napkins, drug delivery and cosmetics were discussed.



Scheme 1- Reaction scheme of Starch, Acrylic acid and Mica

EXPERIMENTAL

Materials

Monomer, acrylic acid (AA) was purchased from SRL INDIA LTD. (Mumbai, India) and was partially neutralized at ambient temperature with aqueous solution of NaOH to achieve desired degree of neutralization. The potato starch (from QUALIGENS) was dissolved in different volumes of water to prepare starch slurry of desired concentration. 0.5% sorbitol solution was prepared with distilled water. Mica was a gift solid sample from WALKO PURE CHEMICAL INDUSTRIES, Osaka, Japan and was used in powdered form having average particle size below $2x10^{-7}$m.

Preparation of Poly(Acrylic Acid)

A suitable amount of partially neutralized acrylic acid (AA) solution and definite amount of initiator ammonium persulfate solution (APS) were degassed under reduced pressure for about 30 minutes. Under a nitrogen atmosphere the reaction mixture was stirred and heated up to 50 °C in a water bath for 3 hours. The polymerization reaction was terminated by adding 0.1M ferrous ammonium sulfate solution. The homopolymer obtained was purified by washing with distilled water and vacuum dried at 65 °C.

Preparation of bionanocomposites

A suitable amount of AA was dispersed in different wt. of starch slurry via stirring with the sorbitol 0.5% (w/v) as shown in Table 1. The mica powder was added on a weight percentage basis individually. The mixture (starch, AA, sorbitol and mica) was first degassed with N_2 for 10 mins and slowly heated to 50°C with stirring and radical initiator ammonium persulfate (APS) dissolved in distilled water was added to initiate polymerization. After 3h of polymerization, reaction was terminated by the addition of a 0.1moi/ litre ferrous ammonium sulfate solution.

Table 1. Samples Preparation

Sl No	Sample code	Name of Sample	[AA] $mol.dm^{-3}$	[APS] $mol.dm^{-3}$	Starch, % (w/v)	Mica,% (w/v)	Sorbitol, % (w/v)
1	S1	PAA	1.75	0.1			
2	S2	Starch-g-PAA	1.75	0.1	10		
3	S3	Starch-g-PAA/mica	0.5	0.1	10	30	0.5
4	S4	Starch-g-PAA/mica	1.0	0.1	10	30	0.5
5	S5	Starch-g-PAA/mica	1.5	0.1	10	30	0.5
6	S6	Starch-g-PAA/mica	1.75	0.1	10	30	0.5
7	S7	Starch-g-PAA/mica	2.0	0.1	10	30	0.5
8	S8	Starch-g-PAA/mica	1.75	0.1	3	30	0.5
9	S9	Starch-g-PAA/mica	1.75	0.1	6	30	0.5
10	S10	Starch-g-PAA/mica	1.75	0.1	9	30	0.5
11	S11	Starch-g-PAA/mica	1.75	0.1	12	30	0.5
12	S12	Starch-g-PAA/mica	1.75	0.1	10	10	0.5
13	S13	Starch-g-PAA/mica	1.75	0.1	10	20	0.5
14	S14	Starch-g-PAA/mica	1.75	0.1	10	40	0.5
15	S15	Starch-g-PAA/mica	1.75	0.1	10	50	0.5

CHARACTERIZATION

The synthesized graft polymers were investigated by FTIR, TGA, TEM and SEM techniques in order to know the grafting pattern, thermal stability, nano structure and morphology respectively. The FTIR spectra of Starch, Starch-g-PAA, starch-g-PAA/mica, in the form of KBr pellets, were recorded with a Perkin–Elmer model Paragon-500 FTIR spectrophotometer. Thermal properties were measured by using a Shimadzu DTA-500 system in air from room temperature to 800°C at a heating rate of 10°C/ min. Nanoscale structure of Starch-g- PAA /mica was studied by means of TEM (H- 700, Hitachi Co.), operated at an accelerating voltage of 100 kV. The ultrathin section with a thickness of 100 nm was microtomed at -80 ^{o}C. The morphology of graft polymers were examined with a JEOL JSM-5400 scanning electron microscope (SEM).

PHYSICO-CHEMICAL PROPERTIES

Swelling behavior

Certain amount of the accurately weighed dried sample was put in tea bags and put into the distilled water at room temperature for 24 hrs. After swelling up to saturation the tea-bags were suspended to drain excess water, and weighed. The swelling rate [9] Wa (g/g) was calculated by using the following equation:

$Wa = (Ws - Wd)/Wd$,

Where, Ws and W_d denote weight of the swollen sample and weight of the dry sample, respectively.

Biodegradation by activated sludge

The sludge water which contains many microorganisms (bacteria, fungi, yeast, etc.) responsible for biodegradation was collected [10] in a polypropylene container from a tank area receiving wastewater. After settling for about 1h, the total solid concentration was increased to around 5000 mg/L by adding more sludge, as this environment is suitable for the decomposition of bionanocomposites. The activated sludge water and a polymer sample (0.2 g) were incubated together in a sterilized vessel at room temperature (26±2°C). Duplicate samples were removed at time intervals for biodegradation study via weight loss. Vessels containing polymer samples without sludge water were treated as controls for comparison.

RESULTS AND DISCUSSION

Fourier Transform Infra-Red Spectroscopy

The FTIR spectra of pure starch, starch-g-PAA and starch-g-PAA/mica (Figure 1) show a broad absorption band characteristic of the glucosidic ring of starch, in the range of 3200–3450 cm^{-1}. Bands those at 2931 and 2927 cm^{-1} are due to C-H stretching and peaks around 1157.2 cm^{-1} are due to C-OH stretching of hydroxyl groups of starch. A strong peak of Si-O stretching at 972 $cm^{-1}$and a sharp peak of Al-O stretching at 694 cm^{-1}were due to mica. [11] The spectrum of starch/PAA showed a new band at 1708.8 cm^{-1} (C=O stretching) for the PAA grafted chains. The absorption peaks at 1647 cm^{-1} are due to O-H bending vibrations in original sample. The additional peak was observed in spectra of grafted sample at 1427cm^{-1} due to C-H bending. These additional peaks confirmed the grafting of PAA sample onto potato starch backbone. [12]

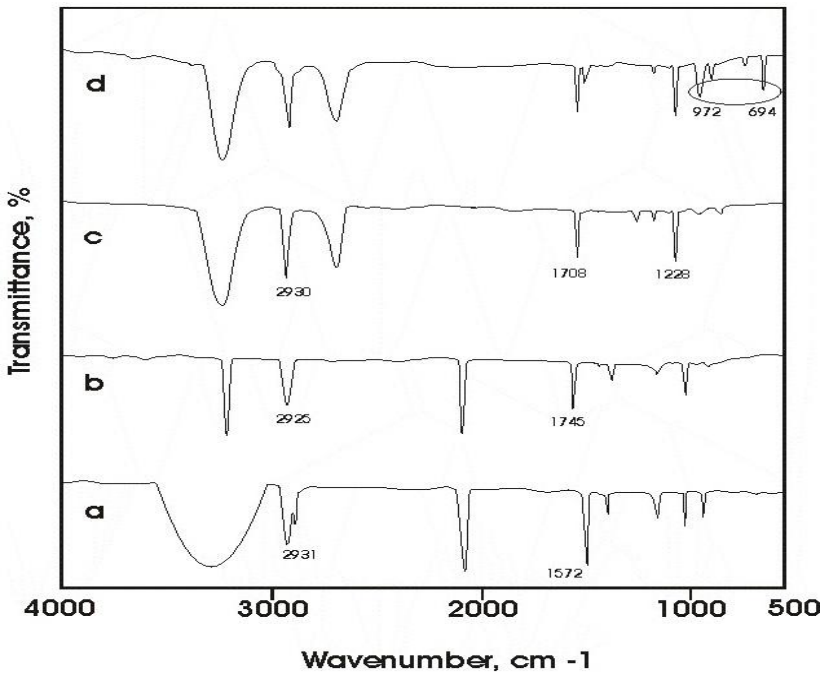


Fig- 1 FTIR spectra of (a) pure starch, (b) PAA, (c) starch-g-PAA and (d) starch-g-PAA/mica

Thermo-Gravimetric Analysis

TGA of starch, starch-g-PAA, Starch-g-PAA/mica nanocomposites are shown in Figure 2. Starch shows two stages of decomposition with a major weight loss of 66%, at the second stage at T_{max}= 300 ^{0} C and the first stage shows weight loss about 12%, within the temperature range of 40–140 ^{0}C is due to the loss of absorbed moisture. Starch-g-PAA biocomposite shows three characteristic peaks with T_{max} equals 193, 276 and 407 ^{0}C, respectively due to the breaking of PAA from the backbone of starch, the breaking of ungrafted starch which may be present in the sample and the degradation of the total bionanocomposite respectively where as starch-g-PAA/mica shows T_{max} at 209, 297 and 432 ^{0}C . The increase in three characteristics T_{max} values of starch-g-PAA / mica in comparison to starch-g-PAA are due to the insertion of mica which prevents the degradation and increases the thermal stability of the prepared bionanocomposite. Thus it is concluded that grafting of synthetic polymer onto natural polymer can lead to the formation of more thermally stable biocomposite (i.e. starch-g-PAA) than pure starch. The onset of decomposition for starch-g-PAA/mica bionanocomposites is shifted toward a higher temperature, indicating an enhancement of the thermal stability upon insertion of mica.

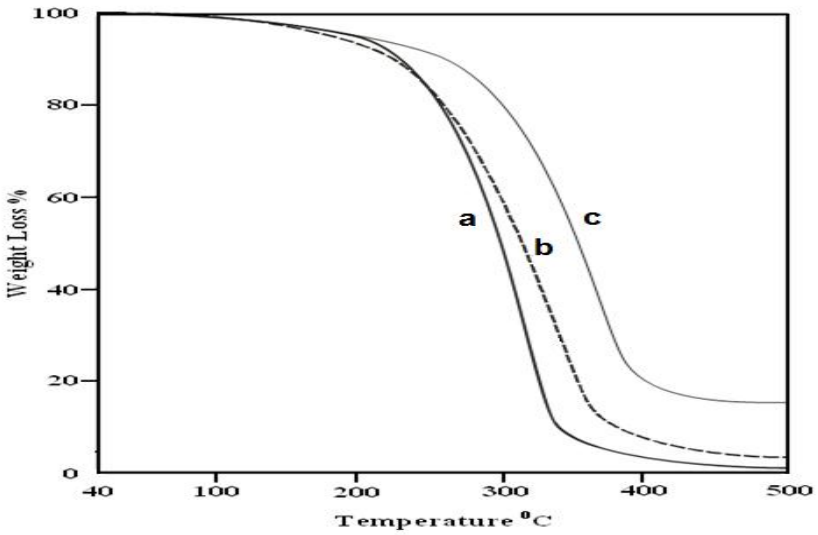


Fig-2 TGA of (a) Starch,(b) Starch-g-PAA,(c) Starch-g-PAA/mica

Transmission Electron Microscopy

The insertion of polymer into the layered structure of mica was confirmed by TEM study as shown in Figure 3. The high magnification (50nm) and also the low magnification (200nm) TEM images of starch-g-PAA/mica demonstrates that the dark bands of the silicate layers of mica are structured in good order, where it is well dispersed perfectly in the polymer matrix indicating exfoliation.

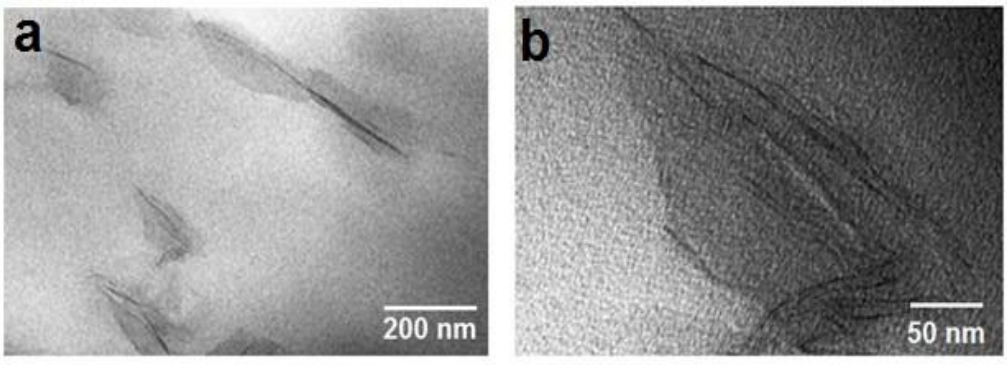


Fig-3 TEM images of Starch-g-PAA/mica at (a) 200 nm and (b) 50 nm

Scanning Electron Microscopy

The surface morphologies of the starch-g-PAA and starch-g-PAA/mica were studied by scanning electron microscope as shown in Fig 4. Starch-g-PAA had coarse surface [Fig 4(d)] rather than smooth surface of starch, which was due to grafting of PAA onto starch. Fig 4 (c) reveals the dispersion of nano sized mica into polymer matrix which enhances the thermal properties of the biohybrid materials.

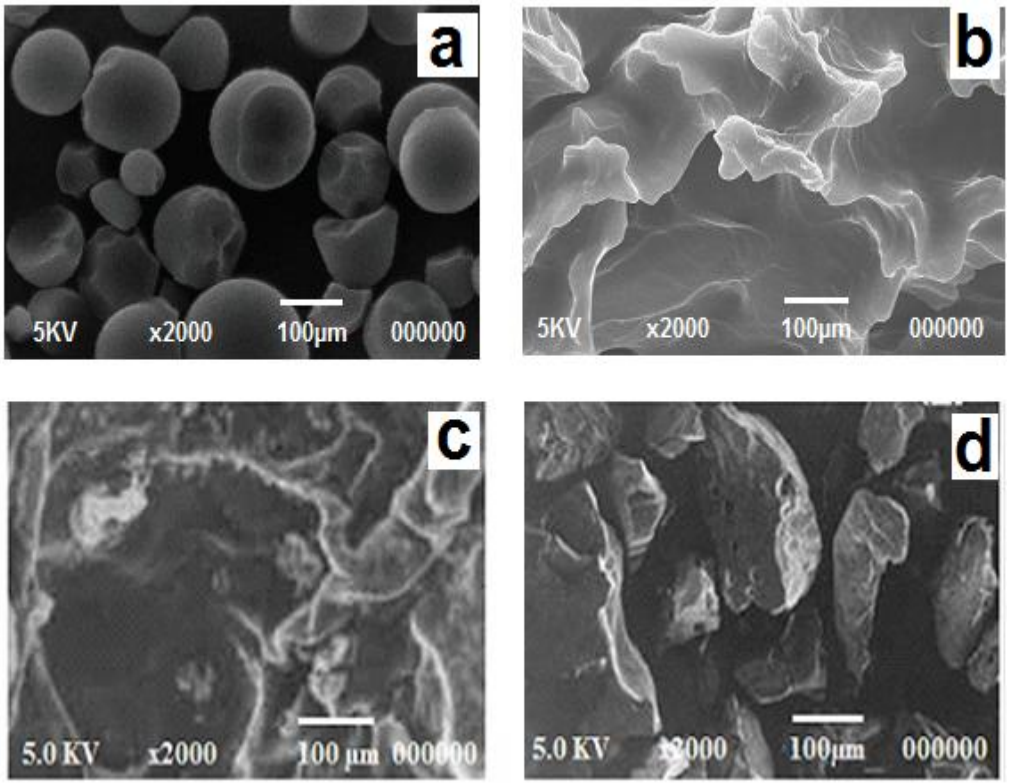


Fig- 4 SEM micrograph of (a) Starch, (b) PAA, (c) Starch-g-PAA/mica (S6) and (d) Starch-g-PAA (S2)

PHYSICO-CHEMICAL PROPERTIES

Swelling Behavior

The swelling behavior is due to the presence of polar and hydrophilic nature of the Starch, AA respectively.

a) Variation with monomer concentration

The swelling behavior of bionanocomposites increases with increasing concentration of monomer upto concentration 1.75M (keeping other variables constant) and further increase in concentration results in decrease of swelling behavior (Fig 5). This is due to the increase in grafting percentage of the monomer up to the said concentration and then decreases due to predominance of homopolymerization over graft copolymerization. With homopolymerization, the system becomes heterogeneous and prevents free radicals in reaching active sites on the backbone of polymer. [12-14]

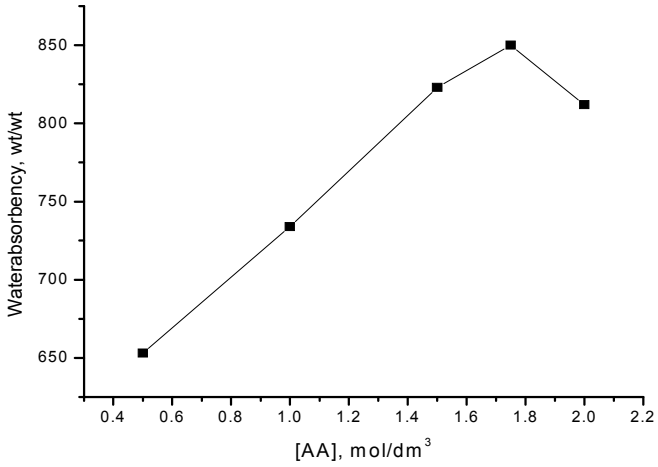


Fig-5 Variation of swelling behavior with [AA] (at optimum Starch and mica conc.)

b) Variation with amount of starch

The swelling behavior of superabsorbent bionanocomposites increases with increasing the amount of starch up to concentration 10 % (w/v) (keeping other variables constant) after which swelling behavior decreases (Fig 6). This is due to the increase in grafting percentage of the starch up to the said concentration and the decrease of swelling behavior may be due to non-availability of other reagents which decrease the number of active sites for grafting and the rate of termination of grafting exceeds the rate of initiation.

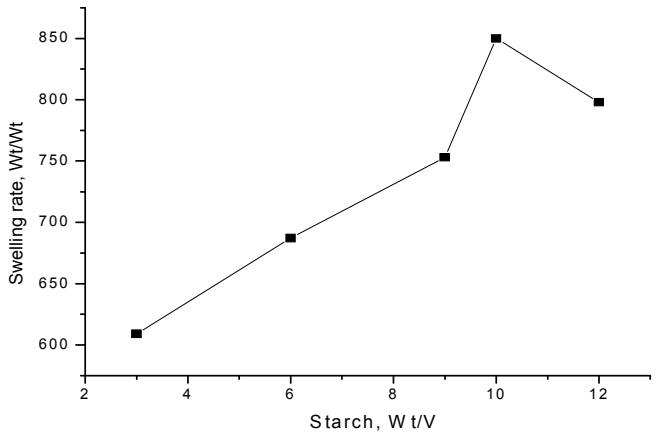


Fig-6 Variation of swelling behavior with [Starch] (at optimum AA and mica conc.)

c) Variation with amount of mica

The relationship between swelling behavior and the amount of mica present in the superabsorbent bionanocomposite is shown in Fig7. It can be seen that the swelling behavior

was optimum (943g/g) at 10% (w/v) of mica and gradually decreases with increasing amounts of mica. The swelling behavior of the bionanocomposites was found to be 850g/g at mica 30 % (w/v) and when the amount of mica reaches 50% (w/v), it is close to 687 g /g. This decrease in swelling behavior with increasing amounts of mica may be due to the fact that the mica powder acts as an additional network point. The higher the amount of mica powder, the larger is the crosslink density of the composite. Therefore, the space network available for water molecules to enter becomes smaller and the swelling behavior gradually decreases.

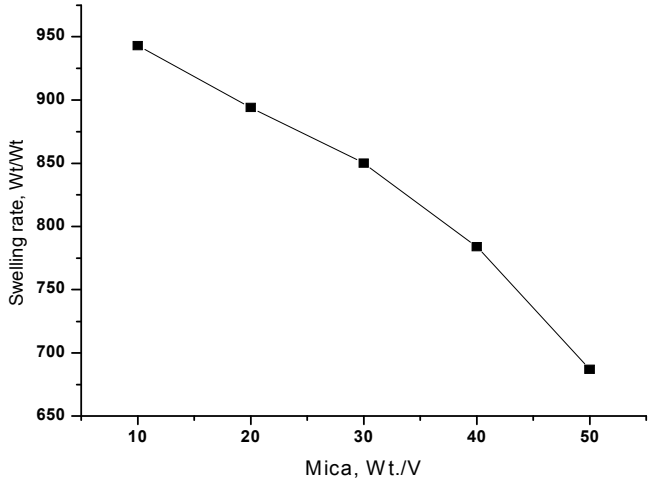


Fig-7 Variation of swelling behavior with [mica] (at optimum AA and Starch conc.)

Biodegradation by activated sludge

Biodegradation by activated sludge was found less in the case of starch-g-PAA/mica than that of Starch-g-PAA and PAA. The biodegradation was found to be lesser with increasing amount of mica and more with increasing swelling behavior as shown in Fig 8. This may be due to the conducive environment for the growth of microorganisms with increasing water retention capacity in superabsorbent bionanocomposites.

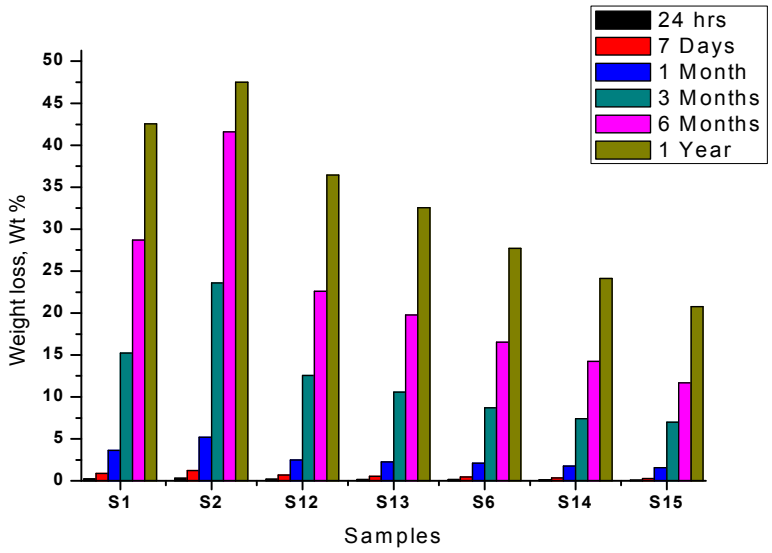


Fig-8 Biodegradation of samples at different time intervals

CONCLUSION

The starch-g-PAA/mica superabsorbent bionanocomposites were prepared by graft copolymerization of acrylic acid (AA), starch and mica in aqueous medium with emulsion polymerization. The results showed that monomer concentration, amount of starch and mica influence the swelling behavior of the obtained hydrogel and alter their thermal stability and biodegradation. The maximum water absorption obtained for starch-g-PAA/mica super absorbent bionanocomposites in distilled water was 943g/g at optimum monomer concentration of 1.75M, starch=100g/l and mica of 10 wt.%. The starch-g-PAA/mica super absorbent bionanocomposites are thermally stable than starch and starch-g-PAA. This was found to be more eco-friendly due to its biodegradability and its property of being thermally stable, and this could be used in biomedical and agricultural engineering fields and other areas of commercial importance.

ACKNOWLEDGEMENT

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