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Studies on poly (acrylamide)/Starch/Bentonite superabsorbent composites: Synthesis and characterization

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ABSTRACT

A polyacrylamide/Bentonite/Starch superabsorbent composite was synthesized by solution polymerization of acrylamide (AAM) on Bentonite and Starch using *N,N*-methylene bis acrylamide (MBA) as a cross linker and potassium persulphate (KPS) as an initiator in aqueous solution followed by hydrolysis with sodium hydroxide. The effects of variable factors such as initial monomer concentration, amount of cross linker, initiator, and bentonite clay on water absorbency were investigated. The graft copolymerization reaction of AAM on Bentonite and Starch was characterized by FTIR. The morphology of prepared superabsorbent composites was characterized by scanning electron microscopy (SEM). The water absorbencies for these superabsorbent composites in water and saline solutions were investigated. The super absorbent composite synthesized under optimal conditions with Bentonite exhibits absorption of 980g/g in distilled water and 163g /g in saline solution. © 2014 Trade Science Inc. - INDIA

KEYWORDS

Acrylamide;
Superabsorbent;
Solution polymerization;
Water absorbency;
Bentonite;
Starch.

INTRODUCTION

Superabsorbent polymers are moderately cross linked hydrophilic three dimensional polymer networks exhibit the ability to swell in water, saline or biological fluids.^[1] They retain significant fraction of them within their structure but they do not dissolve in water. Superabsorbent polymers (SAPs) are polymers that can absorb and retain water, saline solutions or physiological fluids up to several thousand times their dry weight. Superabsorbent can be applied to many industrial applications, such as baby diapers, personal hygiene products, controlled drug release, horticulture, heavy metal ions removal and agriculture.^[2-7] Superabsorbent made from synthetic polymers possess excellent characteris-

tics, the limitations of these materials in comparison to the natural based ones seem to be worth nothing. The toxicity and non biodegradability may create environmental problems and limit their uses. At present, materials biodegradability is an important focus of the research in this field because of the renewed attention towards environmental protection issues.^[8] So the new types of multi-component superabsorbent derived from naturally available raw materials are desired, and the organic-inorganic composites of natural polysaccharides with inorganic clays undoubtedly become promising materials because they showed both excellent performance and environmental friendly characteristics.^[9,10]

In past, the preparation of organic-inorganic superabsorbent composites have attracted great atten-

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tion because of their relatively low production cost and high water absorbency.^[11-15] they used Bentonite as a clay material because of its natural large abundance and low cost. Synthesis and swelling behaviour of superabsorbent composites through polymerization of diluted solution of monomers by using clay and modified clay have been recently investigated.^[12] Because of their hydrophilic nature; clays have been more suitable for use in water absorbents as additives. In the present research work, we have focused on studying the synthesis and characterization of starch-acrylamide-based superabsorbent through solution polymerization method. Starch is low cost materials. In-situ polymerization of starch with acrylamide and clay will produce a low cost superabsorbent composite.

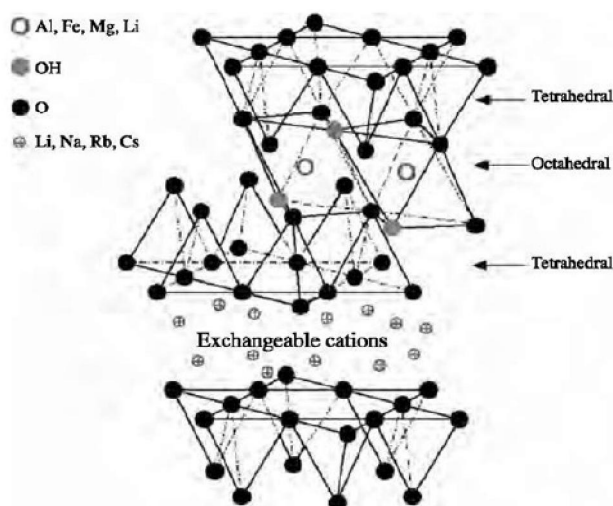


Figure 1 : Schematic structure of Bentonite clay

EXPERIMENTAL

Materials

Potato Starch was obtained from Loba Chemie Pvt Ltd, Acrylamide (AAm) monomer was supplied by Loba Chemie Pvt Ltd., Mumbai, Potassium persulfate (KPS, initiator) was procured from Qualigens Fine Chemicals, N,N2 -methylene bisacrylamide (MBA) as a crosslinking agent was supplied by Chemika Biochemika Reagents, Mumbai. Bentonite Clay was purchased from S D Fine chemicals, Mumbai. All solutions were prepared in distilled water. The schematic illustration (Figure 1) of Bentonite clay is presented as below.

The polymerization temperature was kept constant

at $70 \pm 0.1^\circ\text{C}$, using a thermostat.

Preparation of superabsorbent composites

A series of samples with different amounts of Bentonite, cross-linker, initiator, starch and acrylamide were prepared by the following procedure.

In a four-neck glass reactor equipped with a stirrer, a condenser, a thermometer, 10 % Starch solution was prepared by heating at 95°C for 30 mins under nitrogen atmosphere. A mixed solution of acrylamide monomer, cross-linker, bentonite clay and initiator were added in the flask at room temperature under Nitrogen atmosphere with continuous stirring.

The temperature of the reaction was then brought slowly to 70°C with vigorous stirring. The reaction was carried out for 3 hrs at $70 \pm 0.1^\circ\text{C}$. After 3 h of the reaction, the resulting product was transferred to a sodium hydroxide solution and allowed saponification reaction for 2 h at 90°C . The saponified product was filtered and washed several times with distilled water to remove ungrafted molecules, unreacted monomer and base until the neutral solution was obtained then dried in a oven at 70°C to a constant weight. The superabsorbent composite was then milled to get fine powder.

Water-absorbency measurement

A weighed quantity of the superabsorbent composite was immersed in distilled water at room temperature to reach the swelling equilibrium. Swollen samples were then separated from unabsorbed water by filtering. The water absorbency ($Q_{\text{H}_2\text{O}}$) of the superabsorbent composite was determined by weighing the swelled samples, and the $Q_{\text{H}_2\text{O}}$ of the samples was calculated using the following equation:

$$Q_{\text{H}_2\text{O}} = (m_2 - m_1) / m_1 \quad (1)$$

where m_1 and m_2 are the weights of the dry sample and the water-swollen sample, respectively. $Q_{\text{H}_2\text{O}}$ was calculated as grams of water per gram of sample (g/g).

Characterization of clay

Particle size analysis of Bentonite clay was carried out in a Beckman Coulter particle size analyser and the results confirmed the particle size distribution in the clay. The particle size distribution of clay was obtained by dispersing the clay in water and then ultrasonating the clay. The Bentonite clay was characterized by X-ray

diffraction using PANalytical X-pert Pro diffraction unit which had a CuK α radiation source operated at a generator voltage 40 kV and current 30 mA. The instrument was run at the step scan mode within 2 θ angle 0 $^\circ$ to 10 $^\circ$. For reliability of data, each sample was scanned several times.

Characterization of clay and superabsorbent composites

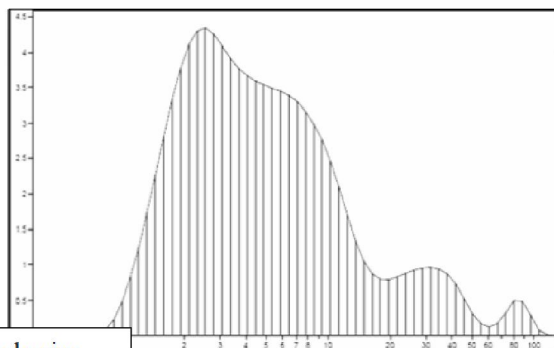


Figure 2 : Particle size distribution curve for Bentonite clay

sorption bands corresponding to the functional groups attached to the monomeric units.

RESULTS AND DISCUSSIONS

Infra red spectra

The infrared spectra of Acrylamide, starch, Bentonite clay and starch-graft-poly (acrylamide)/bentonite

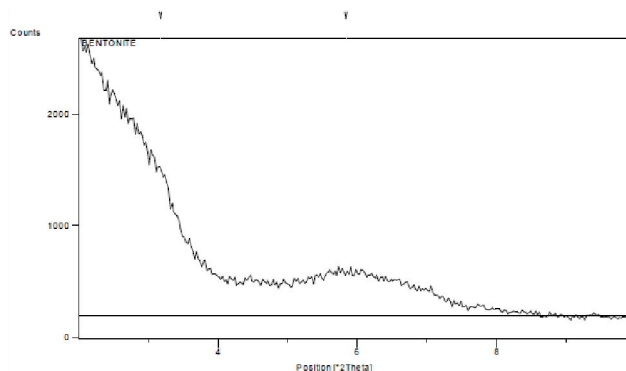


Figure 3 : XRD pattern of Bentonite clay

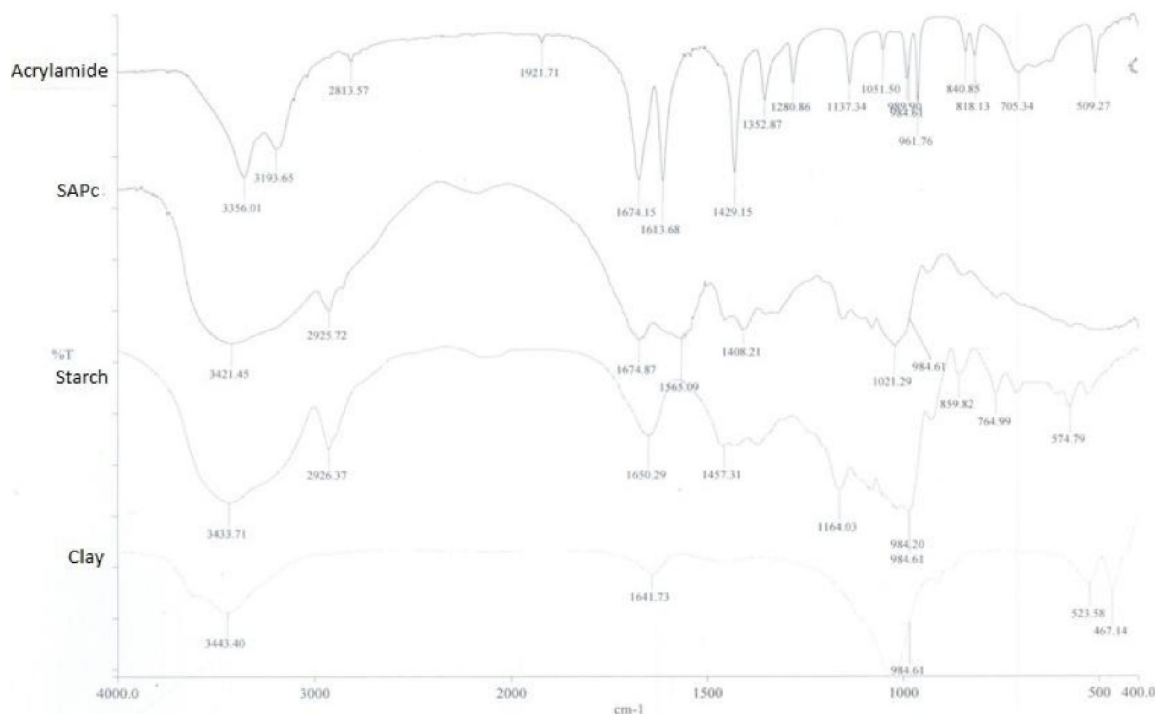


Figure 4 : Infrared spectra of Bentonite clay, Starch, Acrylamide and PAAm/Starch/Bentonite clay superabsorbent composite.

The IR spectra of the Bentonite Clay and superabsorbent composites were recorded on a Perkin Elmer Spectrum One FTIR using KBr pellets. The IR spectrum of the superabsorbent composite shows ab-

superabsorbent composites are shown in Figure 4. According to the IR spectra of the product peak observed at 3421cm $^{-1}$ is attributed to the -NH stretching of acrylamide unit, 1674 cm $^{-1}$ is attributed for the

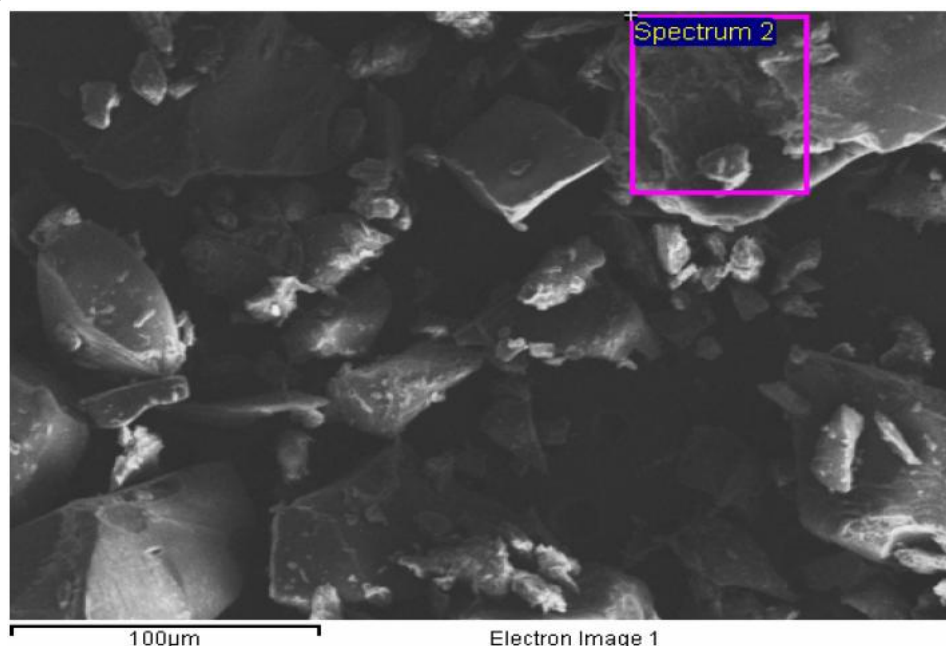


Figure 5 : SEM micrograph of SAPc having 2wt% clay.

TABLE 1: Effect of weight ratio of AAm to Starch, Initiator, Crosslinker percentage in the feed on the water absorbency of the superabsorbent composite

AAm: Starch	Water Absorbency (g/g)
1:1	594
2:1	668
3:1	629
4:1	547

Reaction conditions: Reaction Temperature, 70°C, 0.5wt% KPS, 0.5wt% MBA and 0.5wt % Clay

C=O stretching in the acrylamide unit in the superabsorbent. The absorption peak attributed to OH of Bentonite group (3443cm^{-1}) has changed after reaction. Absorption peak at 574cm^{-1} attributed to OH of starch became changed, indicated that OH group on starch changed during reaction. The absorption peaks at 3356 , 1673 and 1613cm^{-1} attributed to the $-\text{CONH}_2$ group on the acrylamide also change during the reaction and a new peak at 1408cm^{-1} attributed to $-\text{CO}_2$ group appeared. The above results showed that the characteristic absorption peak for OH groups on Bentonite and starch and $-\text{CONH}_2$ group has changed after copolymerisation reaction. It may be due to the fact that there was the reaction between Bentonite, Starch and Acrylamide leading to the formation of network structure.

The existence of clay particles in the SAPc was confirmed by SEM micrograph (See Figure 5). The

SEM micrograph indicate that uniformly distribution of clay particles within polymer matrix. The copolymers have rough morphology with clay particles trapped on the rough surface of polymer matrix.

Effect of weight ratio of AAm to Starch

It can be seen from TABLE 1 that the water absorbency of superabsorbent composite increased with increasing ration of AAm to starch. The maximum water absorbency was reached when the superabsorbent composite having weight ratio of AAm to Starch of 2:1 with 0.5wt% of KPS, MBA and clay respectively. This is due to fact that both grafting and molecular weight of grafted polymer chain increased with increasing AAm content but with further increasing AAm content beyond 2:1, the water absorbency decreases. This could be because of increase in homopolymer percentage of PolyAAm, which causes in an increase in soluble materials at fixed cross linking density.

Effect of initiator content

The effect of initiator concentration in the composite on water absorbency is shown in Figure 6. The Water absorbency increases when initiator KPS content increases from 0.5% to 1.25% and highest water absorbency 750 g/g was found at 1.25 wt% initiator concentration. Water absorbency was decreased with further increase in the concentration of KPS. This could be

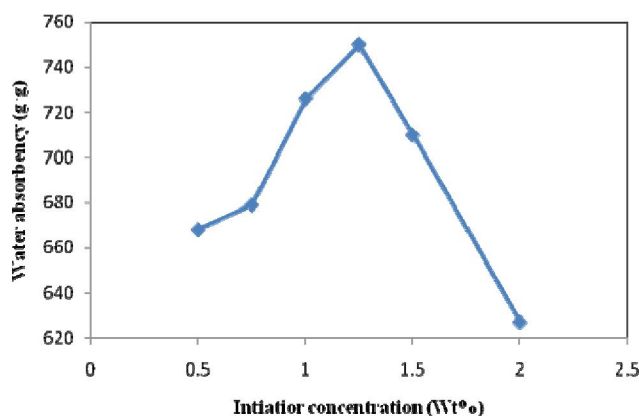


Figure 6 : Effect of initiator content on distilled water absorbency of the superabsorbent

Reaction conditions: Reaction Temperature, 70°C, Starch: Am 2:1, 0.5wt% MBA and 0.5wt % clay

because of increase in the number of free radicals with the increase in concentration of initiator. As the number of free radicals increases, the rate of polymerization is also increases, which reduces the polymer network space thereby decreasing water absorbency of composites. On the other hand when the concentration of initiator is lower than 1.25 wt%, the graft copolymerization reaction is slower, results in fewer network spaces and thus water absorbency is decreases under the same condition.

Effect of cross linker content

The effect of cross-linker content on water absorbency is shown in the Figure 7. Water absorbency increases as cross-linker content increases from 0.5wt% to 1 wt% and was found to be 794 g/g at 1 wt% cross-linker. Further increase in cross linker content from 1wt % to 1.5wt % decreases the water absorbency due to the fact that increase in the cross linker content creates more cross linking, leads to additional networks and decreases free volume that water can occupy resulting in less water absorbency value. On the other hand when cross-linker content is lower than 0.75 wt%, the copolymerization reaction between starch molecules and acrylamide does not occur effectively. Therefore the cross-linkage network does not form and starch and acrylamide exist as monomer or low molecular weight polymers.

Effect of clay content

The influence of the amount of Bentonite powder in composites on the water absorbency is shown in Fig-

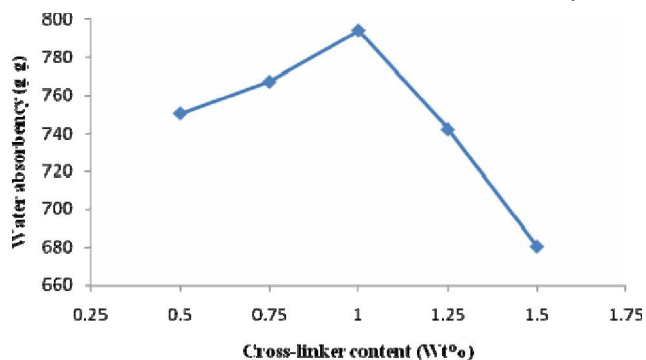


Figure 7 : Effect of crosslinker content on distilled water absorbency of the superabsorbent

Reaction conditions: Reaction Temperature, 70°C, AAm:Starch 2:1, 1.25wt% initiator, 0.5wt% clay

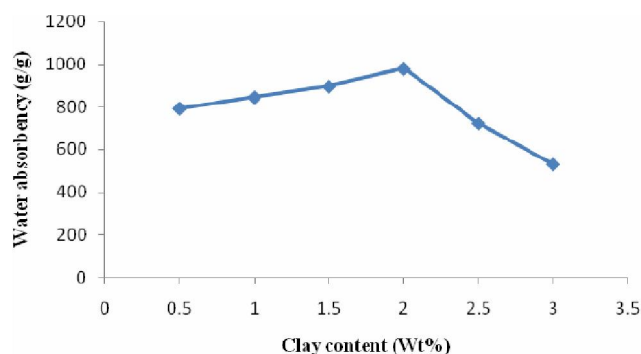


Figure 8 : Effect of clay content on water absorbencies of the superabsorbent composites

Reaction conditions: Reaction Temperature, 70°C, AAm: Starch 2:1, 1.25wt % Initiator, 1wt% Crosslinker.

ure 8. It can be seen that the water absorbency increases the most in the range of 0.5-2 wt% and highest water absorbency 980 g/g was found at 2 wt% of Bentonite clay. Beyond this concentration the water absorbency decreases because this inorganic clay material can act as cross linking point in superabsorbent composite. With larger amount of Bentonite more than 2 wt%, composites with higher cross linking density are formed making water difficult to permeate through the composite thereby decreasing water absorbency.

Effect of salt solutions

Figure 9, shows the effect of concentration of aqueous Sodium chloride, Calcium Chloride and Sodium Sulphate on water absorbency of superabsorbent composite. The water absorbency decreases with increase in concentration of saline solution. According to Hermans the water absorbency of superabsorbent decreased with increase of ionic strength of external solution^[15] This decreases water absorbency with increas-

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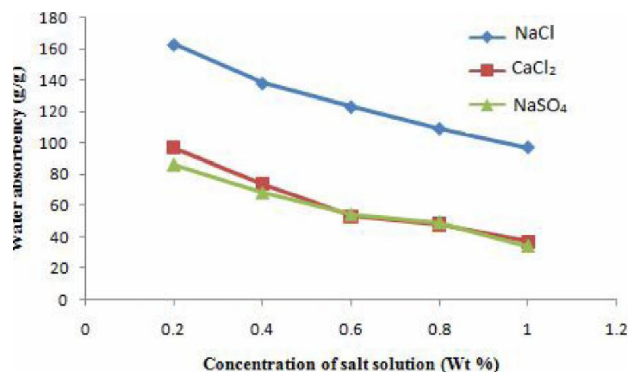


Figure 9 : Water absorbency of SAPc in NaCl, CaCl₂, and NaSO₄ aqueous solutions with various concentrations

Reaction conditions: Reaction Temperature, 70°C, AAm:Starch 2:1, 1.25wt% KPS, 1wt% MBA, and 2 wt% Clay

ing ionic strength of solution which results in decreasing osmotic pressure difference between the superabsorbent composite and the external saline solutions. Figure 8 also shows that for a given concentration of saline solution, the water absorbency in NaCl was far higher than CaCl₂ and NaSO₄ aqueous solutions. This drastic decrease of water absorbency in multivalent cationic solutions might be due the complexing ability of carboxylate groups. This induces the formation of intramolecular and intermolecular complexes which in turn results increased cross-linking density of network. The water absorbency in 2 N NaCl solution was 163g/g.

CONCLUSIONS

A starch-graft-poly (acrylamide)/bentonite superabsorbent composite with water absorbency of 980g/g was synthesized by graft copolymerization reaction among acrylamide and potato starch in the ratio of 2:1, 1.25wt% potassium persulfate, 1wt% methylene bis-acrylamide, and 2wt% Bentonite clay in aqueous solution. FTIR characterization confirmed the polymerization reaction mechanism. The uniform distribution of Bentonite clay was confirmed with SEM micrograph. With the addition of clay the water absorbency increases and is helpful in the formation of network structure. This approach of preparation of superabsorbent composites utilizing natural resources like starch, clay would certainly reduce the production cost as well as make the material environment friendly.

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