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Synthesis and characterization of poly (acrylic acid) / Starch / Bentonite superabsorbent polymer composite

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ABSTRACT

A novel poly (acrylic acid)/Bentonite/Starch superabsorbent polymer (SAP) composite was synthesized by solution polymerization of acrylic acid (AA) on bentonite and starch using N, N-methylene bis acrylamide (MBA) as a crosslinker and potassium per sulfate (KPS) as an initiator in aqueous solution. The effects of various parameters such as initial monomer concentration, degree of neutralization of AA, amount of crosslinker, amount of initiator and amount of bentonite clay on water absorbency were investigated. The synthesized polymer was characterized by Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction (XRD) & scanning electron microscope (SEM). The water absorbencies for these superabsorbent composites in water and saline solutions were investigated. The synthesized superabsorbent polymer has potential applications in hygienic, agricultural, medical and pharmaceutical applications.

KEYWORDS

Acrylic acid;
Superabsorbent;
Crosslinking;
Water absorbency;
Clay;
Starch.

INTRODUCTION

Superabsorbent polymers are moderately cross linked hydrophilic polymer networks that can absorb and retain large quantities of water in swollen state. Superabsorbent have received significant attention because of their considerable applications in many areas such as sanitary goods[1-3] agriculture and horticulture[4], wastewater treatment[5], medicine for drug delivery system[6] and so on. Despite of a wide range of applications, most of superabsorbents used as disposable particles are based on fully petroleum-based polymers with high production cost and having serious environment impact and therefore it possess certain limitations. SAP are usually synthesized by free-radically-initiated polymerization of acrylics monomers (such as acrylic acid), its sodium or potassium salts, and acrylamide (AM) with crosslinkers via solution or inverse suspension polymerization techniques[2,7]. The solution polymerization of AA and/or its salts with a water-soluble cross-linker in an aqueous solution is a straight forward process with short time period[7,8]. Superabsorbent polymer composites synthesized by aqueous solution polymerization with low monomer concentration[8] gives more efficient preparation method and is especially valuable in industry. However, this method suffers from the necessity to handle a rubbery/solid reaction product, lack of a sufficient reaction control, non-exact particle size distribution and increasing the sol content mainly due to undesired effects of hydrolytic and thermal cleavage[7,9]. In an inverse suspension method the monomers are well-dispersed which is an advantage since the products are obtained as powder or microspheres (beads), and thus grinding is not required[7,10]. The inverse-suspension is a highly flexible and versatile technique to produce SAPs with high swelling ability and fast absorption kinetics[7,9,11]. Considering the above environmental and synthesis issues, the development of new types of multi-component superabsorbent polymers derived from the naturally available raw materials is desired. In recent years, the preparation of organic–inorganic superabsorbent composites[7] have attracted great attention because of their relatively low production cost, high water absorbency and their considerable range of applications in agriculture and horticulture. Synthesis and swelling behavior of superabsorbent composites through polymerization of diluted solution of monomers by using Bentonite clay and modified Bentonite clay have been recently investigated. Because of their hydrophilic nature, clays have been more suitable for use in water absorbents as additives.

In the present research study we have focused on studying the synthesis and characterization of Starch-acrylic-based superabsorbents through solution method. Starch is low cost materials. In-situ polymerization of Starch with acrylic acid and clay will produce a low cost superabsorbent composite.

EXPERIMENTAL

Materials

Potato Starch was obtained from Loba Chemie Pvt Ltd. (India), Acrylic acid (AA) monomer was supplied by S.D.Fine- Chemical Ltd, Mumbai (India). Potassium persulfate (KPS, initiator) was procured from Qualigens Fine Chemicals (India). N, N- methylene bisacrylamide (MBA) as a crosslinking agent was supplied by Chemika Biochemika Reagents, Mumbai, (India). All reagents used were of analytical *grade*. Bentonite Clay was procured from Kolkata (India) and was used as received. All solutions used in this study were prepared in distilled water. The polymerization temperature was kept constant at 70 ± 0.10°C, using a thermostat.

Preparation of superabsorbent composites

A series of samples with varying amounts of Bentonite clay, crosslinker, initiator, Starch and acrylic acid with different degrees of neutralization were prepared in distilled water and then neutralized with sodium hydroxide procedure. In a typical method of preparation, acrylic acid was dissolved in solution. In a four-neck glass reactor equipped with a stirrer, a condenser, a thermometer, 10 % Starch solution was heated at 95°C for 30 min. The temperature was further lowered down to 30°C. The monomer, acrylic acid was added in the reactor under Nitrogen atmosphere with continuous stirring. Under above conditions, Bentonite clay powder and the crosslinker MBA were dispersed in the above mixture. The temperature of the reaction medium was then brought slowly to 60°C with vigorous stirring and the radical initiator KPS was charged to the mixed solution. The reaction was carried out for 3 hrs at 70 ± 0.10°C. After 3 hr of the reaction, the resulting product was washed several times with ethanol and distilled water and then dried in oven at 60°C to a constant weight resulting into the formation of the superabsorbent composite. Crosslinked Starch graft poly (acrylic acid) superabsorbent polymer was prepared by similar method as mentioned above except Bentonite clay. Whereas uncrosslinked poly (acrylic acid) was prepared by above similar method except without Starch, clay and crosslinker.

Water-absorbency measurement

A weighted 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_{H2O}, grams of water per gram of sample) of the superabsorbent composite was determined by weighing the swelled samples, and the Q_{H2O} of the samples was calculated using equation 1. Where m_1 and m_2 are the weights of the dry sample and the water-swollen sample, respectively.

$$Q_{H_2O} = \frac{m_2 - m_1}{m_1} \tag{1}$$

Characterizations

Particle size analysis of Bentonite clay was determined using a Beckman Coulter particle size analyzer.

The results of particle size analysis were confirmed using particle size distribution in the clay by dispersing it in water and then ultrasonicating. Specific surface area was measured by BET surface area analyzer. The Bentonite clay was also characterized by Rigaku Miniflex, X-ray diffraction instrument, Japan. A normal focus copper X-ray tube was operated at 30 kV and 15 mA. Sample scanning was done from 2.00° to 80.00° at the rate of 3.00°/min. For reliability of data, each sample was scanned several times. The IR spectrum of the Bentonite clay, Starch, super absorbent polymer composite was recorded on a JASCO FTIR-4100 spectrometer using KBr pellets. Morphology of superabsorbent composite was studied by Scanning Electron Microscope (SEM) with JEOL 6380 LA (Japan) and coated with gold before imaging.

RESULTS AND DISCUSSIONS

Characterization of Bentonite clay

Particle size distribution graph of Bentonite clay is shown in Figure 1; the graph was plotted volume in % vs. particle diameter in μm. The mean particle size was found to be 3±1 μm. Surface area of the clay measured by BET surface area analyzer was found to be 17137 cm^2/gm. The X-ray diffraction pattern of the Bentonite clay is shown in Figure 2. XRD plots of such clay shows the presence of montmorillonite (M) as a major phase & monoclinic structure and other minor phases are kaolinite (K), quartz (Q) and illite (I)[13,14].

Characterization of superabsorbent composite

Infrared spectroscopy

The IR spectra of Bentonite clay and Starch-graft-poly (acrylic acid)/Bentonite SAP (with 40% neutralization degree, 0.5% clay) are shown in Figure 3 The characteristic peaks at 3621cm^{-1} attributed to the –OH groups on Bentonite (Figure 3, a) disappeared after reaction (Figure 3, d) for the PAA/Bentonite/Starch superabsorbent composite. The absorbance peak at 2358 cm^{-1} (Figure 3, b), due to the stretching vibration of the hydroxyl from —COOH in Starch is also shortened for the PAA/Bentonite/Starch superabsorbent composite (Figure 3, d). The absorbance peak at 1641cm^{-1}, attributed to the intramolecular hydrogen bond of carboxyl (Figure 3, c) also disappeared for the PAA/Bentonite/Starch superabsorbent composite (Figure 3, d).

Scanning electron microscopy

One of the most important properties that must be considered is hydrogel microstructure morphologies. Figure 4 verifies that the synthesized polymer have a microporous structure. The micrographs of crosslinked PAA and PAA superabsorbent composites are shown in Figure 4 (a) and (b) respectively. The SEM micrograph of crosslinked PAA (Figure 4, a), which has water absorbency of 681.6 g/g, is porous. In addition,

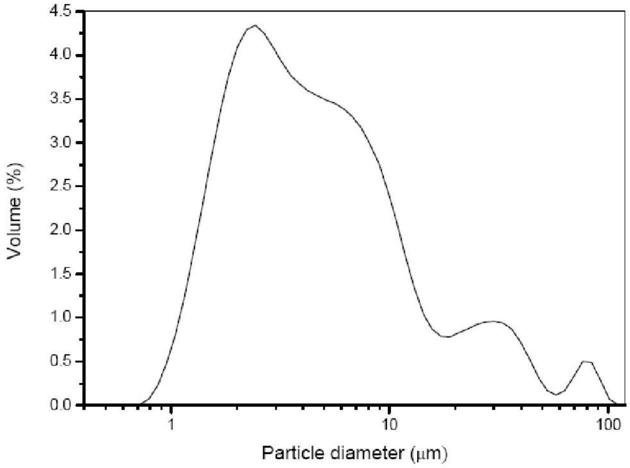

Figure 1 : Particle size distribution curve for Bentonite clay

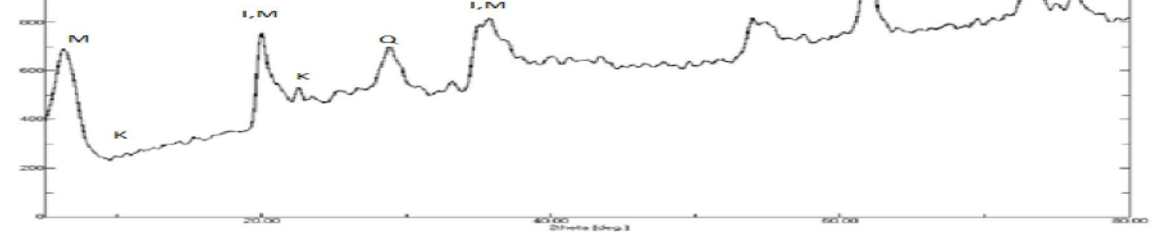

Figure 2 : X-ray diffraction pattern of Bentonite clay

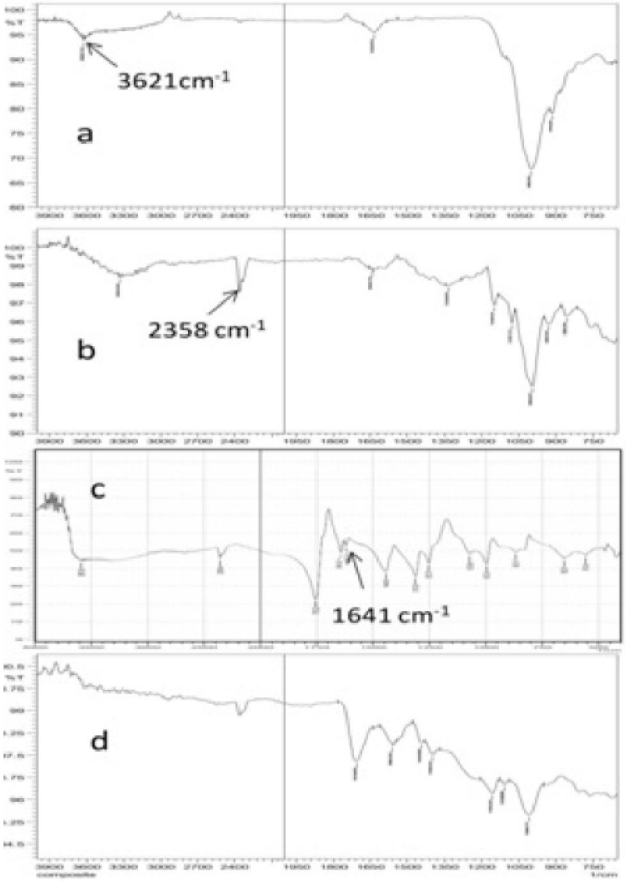

Figure 3 : Infrared spectra of (a) Bentonite, (b) Starch (c) AA and (d) PAA/Starch/Bentonite superabsorbent composite

PAA superabsorbent has a greater absorbency and is shown in Figure 4 (b), where Starch and clay agglomerate can be seen which was absent in crosslinked PAA (Figure 4, a). These observations are in good agreement with water-absorbency observations as discussed in the subsequent text.

Effect of weight ratio of AA to Starch

TABLE 1 show that the water absorbency of superabsorbent composite. It is observed that the water absorbency increases with increasing content of AA. The maximum water absorbency was reached when the superabsorbent composite was synthesized with the weight ratio of AA to Starch of 3:1. It could be due to the fact that grafting and the molecular weight of the grafted PAA chain increased with an increase in AA content.

Effect of initiator content

The effect of initiator content and ratio of acrylic acid and starch on water absorbency are shown in Figure 5. It is observed that water absorbency increases with increasing the initiator KPS content from 0.3% to 1.25% and reaches maximum of 110.32 g/g.

Effect of cross linker content

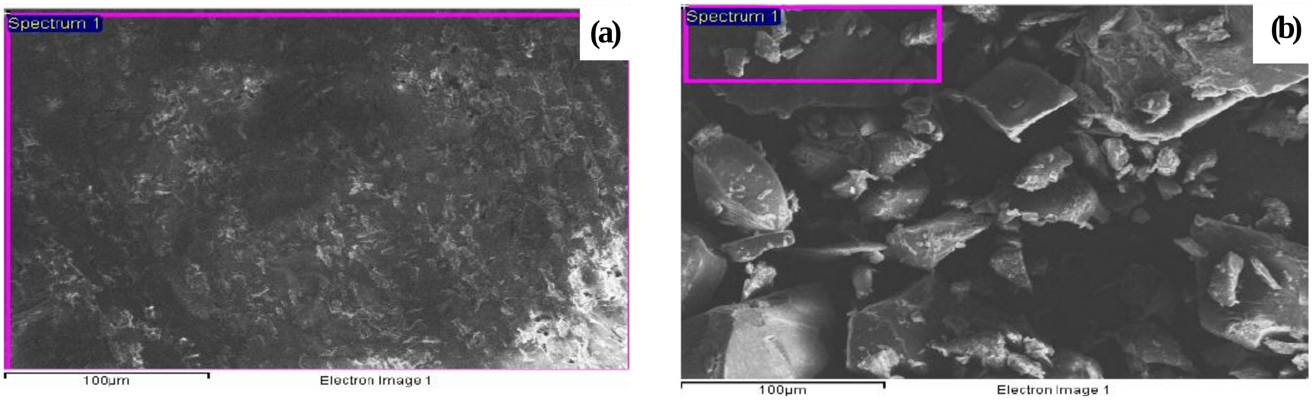

Figure 4 : Scanning electron micrograph of (a) crosslinked PAA & (b) PAA superabsorbent composite

The effect of crosslinker content on water absorbency is also studied and the results are shown in the Figure 6. It is observed that water absorbency decreases with increase amount of cross linker. Higher cross linker creates more cross linking which in turns causes additional network & decrease free volume, hence the water absorbency decrease[15].

Effect of clay content and effect of saline solution

Figure 7 shows the effect of the amount of Clay on the distilled water absorbency of the superabsorbent composite. It is observed that with increasing amount of clay from 0.5% to 1.0%, the water absorbency gradually increases. Further addition of clay from 1.0% to 1.5% results in decrease in the water absorbency. The inorganic clay material can act as additional cross linking point additionally it results in increased

TABLE 1 : Effect of weight ratio of AA to Starch in the feed on the water absorbency of the superabsorbent composite (Reaction conditions: temperature: 70oC, 40 % neutralization degree of AA and 0.5 % clay in all compositions. Initiator and crosslinker were added as 0.75%, 0.375% and 1.25% in the compositions 1, 2 and 3, respectively.)

	AA:Starch	Water Absorbency (g/g)
Composition 1	1:1	698.3
Composition 2	1:3	687.5
Composition 3	3:1	710.32

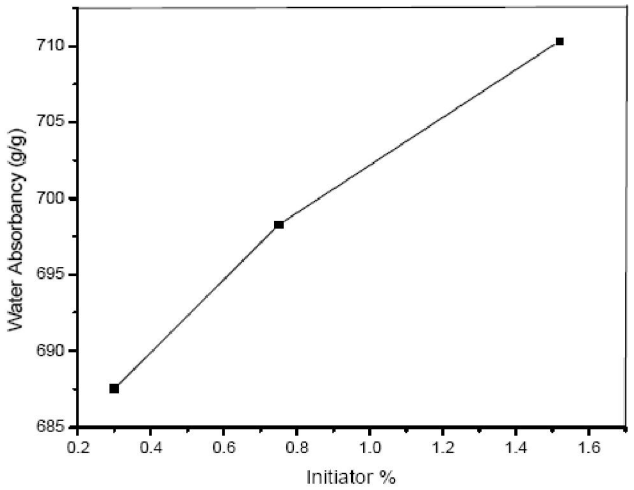

Figure 5 : Effect of initiator content on distilled water absorbency of the superabsorbent

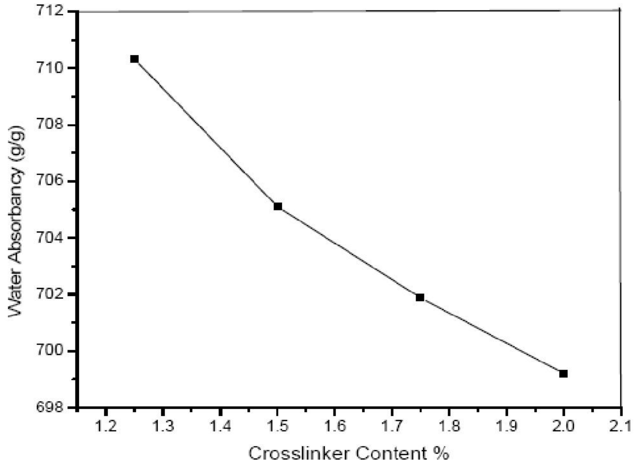

Figure 6 : Effect of crosslinker content on distilled water absorbency of the superabsorbent (Reaction conditions: Reaction Temperature, 70°C, 40 % neutralization degree of AA, 0.5% clay, 1.25% initiator, AA:Starch 3:1)

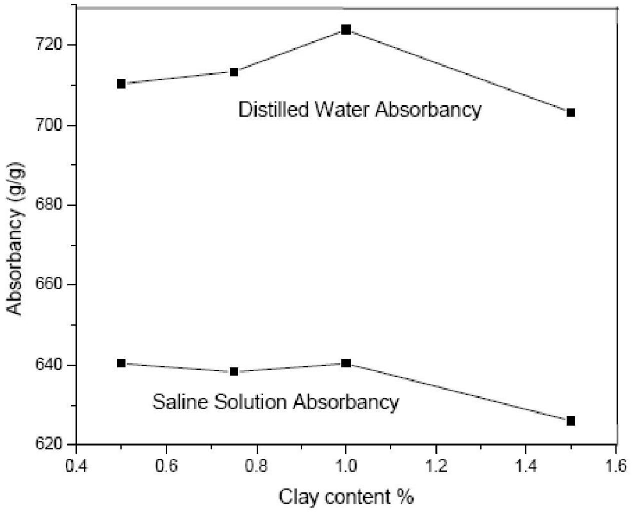

Figure 7 : Effect of Clay Content on water absorbencies of the superabsorbent composites (Reaction conditions: Temperature: 70°C, 40 % degree of neutralization of AA, 1.25% Initiator and 1.25% Crosslinker, AA:Starch 3:1)

crosslinking density of superabsorbent composite and therefore, increased water absorbency is observed. The phenomenon can be explained by two reactions between Bentonite and AA. In one case, Bentonite may act as an additional network point in the composite after the polymerization[16]. The additional crosslinking points can improve the hydrophilic network because it can increase the length of the polymeric chain. The other reaction, means the carboxyl of PAA reacts with —OH on the surface of layers of Bentonite[17]. Thus, the carboxyl, as the far end of the polymer chain has been adequately use to form a more efficient water absorbent network, can hold up more water in it. However, a greater amount of Bentonite results in the generation of more crosslinker points, which increased the crosslinking density of the superabsorbent composite and leaves less space for water to enter.

Figure 7 also shows the effect of concentration of aqueous Sodium chloride on water absorbency of superabsorbent composite. SAP composites with variable clay content ranging from 0.5% to 2% were used for the above studies. It is observed that the saline solution absorbency decreased as compared to distilled water with increasing amount of the clay content. The water absorbency of superabsorbent composites decreases with increase the ionic strength of external solutions. This may be attributed to the decrease in the osmotic pressure difference between the superabsorbent composite and the external saline solution[18].

CONCLUSIONS

A novel starch-graft-poly (acrylic acid/Bentonite superabsorbent composite was synthesized by graft copolymerization reaction of starch and AA in presence of Bentonite clay powder in aqueous solution. The optimum synthesizing conditions were as follows: weight ration of AA to starch 3:1, initiator content 1.25%, crosslinker 1.25%. The superabsorbent composite prepared under optimum condition exhibited absorption of 123.83 and 40.41 g H_2O/g sample in distilled water and in 0.2% NaCl solution, respectively. This approach of preparation of superabsorbent utilizing natural resources like starch, clay would certainly reduce the production cost as well as make the material environment friendly. These types of materials also find applications in agriculture and horticulture.

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