

Polyacrylamide (PAA) Copolymer as a Super Absorbent Polymer

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Abstract: *This work is devoted to the study of the synthesis, properties and practical applications of the class of superabsorbent polymers based on the acrylate Polyacrylamide (PAA). Solution, emulsion/gel polymerization techniques were used for the synthesis. Each absorbent was characterized primarily by its equilibrium water absorption capacity and absorption rate. The swelling characteristics of the polymers were evaluated in terms of changes in polymerization variables, which include the type and amount of crosslinker, monomer composition and polymerization process, temperature, initiator concentration, monomer concentration, mixing speed, and product particle size. The rapidly growing nanotechnology has led to further exploration of SAP and SAPC for biomedical, biotechnology, and advanced technology applications. Examples of SAP and SAPC research work published in peer-reviewed, peer-reviewed articles are listed..*

Keywords: PAA superabsorbent polymers; swelling properties of SAP. Superabsorbent polycomposites; Water absorption capacity; cross-linking reaction;

I. INTRODUCTION

1.1 Definitions

In our daily life, cotton, paper and sponges are commonly used to absorb water. These materials only absorb several times their weight in water and have rather poor water retention properties. However, some types of polymers and copolymers act as highly water absorbent, have very good water retention properties and a high affinity for water. These polymers are called superabsorbent polymers As mentioned above, a superabsorbent polymer can absorb water up to several thousand times its own weight and hold that water under pressure. Absorbed water can be slowly released when the SAP is placed in dry air to maintain ambient humidity.

Superabsorbent polymers (SAPs) are materials that have the ability to absorb and retain large volumes of water and aqueous solutions. This makes them ideal for use in water absorbent applications such as baby diapers and adult incontinence pads to absorbent medical dressings and controlled release media.

1.2 Classification of Superabsorbent Polymers

SAP can be classified using different methods. From the morphological point of view, they can be divided into particle, powder, spherical, fibrous, membrane and emulsion types, etc.

There are two primary types of superabsorbent polymers:

Starch grafted polymers and polymers based on crosslinked polyacrylates. Although starch graft polymers were the first to be developed, these polymers suffer from the disadvantage of salt instability. Polyacrylate polymers initially had difficulty achieving high absorption under load (AUL) characteristics at moderate pressures because the materials partially dissolved. However, this problem was solved by partially cross-linking the polyacrylate to form a network structure. Sodium acrylate and starch graft polymers account for virtually all of the commercial volume of superabsorbent polymers. Although other chemistries such as polyacrylamide, poly(ethylene oxide), poly(vinyl alcohol), polysuccinimides, and hydrolyzed polymers of polyacrylonitrile have been explored, they have yet to gain widespread commercial acceptance.

1.3 Polyacrylamide

Polyacrylamide (abbreviated PAA) is a polymer with the formula (-CH₂CHCONH₂-). It has a linear chain structure. PAM is highly water absorbent and forms a soft gel after hydration. An estimated 750,000,000 kg was produced in 2008, mainly for water treatment and the paper and mineral industries.

IUPAC name: poly(2-propenamide)

Other names: poly(2-propenamide), poly(1-carbamoylethylene)

Polyacrylamide is used in pulp and paper production, agriculture, food processing, mining and as a flocculant in wastewater treatment.

Very low molecular weight polyacrylamide was synthesized by radical polymerization using thioglycolic acid as an initiator at moderate temperature (40 °C). The ratio of thioglycolic acid to acrylamide monomer was approximately 0.02 (g/g) and a polyacrylamide with a molecular weight of approximately 20,000 g/mol was produced.

III. CHEMICALS AND DEVICES:

Acrylamide (99%), potassium persulfate (98%) and (CH₃)₂NCH₂CH₂N(CH₃)₂. (tetramethylethylenediamine) (TMEDA) (98%) were purchased from Nice Chemical Distributors. Thioglycolic acid, hydrogen peroxide, acetone, ethanol, and methanol were also purchased from the same distributors.

2.1 Equipment and Instrumentation

The polymerization reaction was carried out in a Memmert water bath (thermostatically controlled, heating capacity up to 100 °C). A 1 liter five-necked Pyrex glass reactor was suitably placed in the Memmert water bath. The reactor was equipped with a mechanical stirrer, a condenser equipped with a water collector, a thermometer and an inlet tube of gaseous nitrogen (Oxygen Free Nitrogen).

2.2 Recrystallization of Chemicals

Acrylamide (AA) was dissolved in acetone at 56 °C (the boiling point of acetone) to form a saturated solution, the solution was then filtered to remove insoluble particles and allowed to cool to crystallize the solute, the solid crystals were separated from acetone by suction filtration using a Büchner funnel, washed with cold acetone and then dried under vacuum for 24 h at 60 °C. This method was repeated twice. Potassium persulfate was recrystallized twice from distilled water at 100 °C (boiling point of distilled water) using the same procedure described above. The rest of the chemicals were used without further purification.

2.3 Synthesis of PAA of Different Molecular Weights

Polyacrylamide Acrylamide monomer is crystalline. It is relatively stable and is soluble in water and many organic solvents (acetone, ethanol, methanol, etc.). Acrylamide readily polymerizes by conventional free radical methods. Solutions of acrylamide in water polymerize at 40 °C under the influence of almost all sources of free radicals, including persulfates, peroxides, azo compounds and redox couples. The synthesis of polyacrylamides with different molecular weights is strongly influenced by temperature, solvent, initiator type, initiator concentration, and monomer concentration. Synthesis of Very Low Molecular Weight Polyacrylamide Under a nitrogen atmosphere, a mixture of acrylamide monomer (10 g), thioglycolic acid (0.20 g) and tetrahydrofuran (THF) (20 mL) was placed in a 500 mL five-neck Pyrex glass reactor equipped with a reflux condenser. and a mechanical stirrer placed in a bath with a constant temperature of 40 °C. The polymerization took place for 2 hours with stirring. Polyacrylamide was isolated and reprecipitated by pouring its solution into acetone. It was then dried under vacuum at 60°C for 24 hours. Synthesis of low molecular weight polyacrylamide

Acrylamide monomer was polymerized in distilled water using hydrogen peroxide as an initiator. Nitrogen gas was bubbled inside a five-neck Pyrex glass reactor containing acrylamide monomer (20 g), distilled water (200 mL) as solvent, and hydrogen peroxide (0.5 mL) as initiator. The reactor was placed in a bath with a constant temperature of 90 °C for 3 hours with stirring. Polyacrylamide was isolated and reprecipitated by pouring its solution into acetone. It was then dried under vacuum at 60°C for 24 hours. Synthesis of medium, high and very high molecular weight polyacrylamide High purity of monomer and initiators and the absence of oxygen are essential in the polymerization

process. High monomer concentrations and low initiator concentrations are required for synthesized high and very high molecular weight polyacrylamides. Polyacrylamides of different molecular weights (medium, high, and very high) were synthesized using potassium persulfate and the (CH₃)₂NCH₂CH₂N(CH₃)₂ (tetramethylethylenediamine) (TMEDA) system as an initiator. Increasing the concentration of acrylamide monomer will increase the molecular weight of the resulting polyacrylamide. Thus, under a nitrogen atmosphere, 15, 30 and 50 g of acrylamide monomer were polymerized in (500 ml) distilled water as a solvent and a (0.135 g) potassium persulfate/(180 μl) TEMDA system as an initiator to form medium, high and very high molecular weight polyacrylamides, respectively. The mixture was placed in a 500 mL five-neck Pyrex glass reactor equipped with a reflux condenser and a mechanical stirrer placed in a constant temperature bath of 40 °C. The polymerization was carried out for 2 hours with stirring. Polyacrylamide was isolated and reprecipitated by pouring its solution into acetone. It was then dried under vacuum at 60°C for 24 hours.

2.4 Viscosity Average Molecular Weight of Polyacrylamide

The viscosity average molecular weight of polyacrylamides was determined by determining the internal viscosities of polyacrylamides using an Ubbelohede viscometer, no. 4809 ASTM at 25 ± 0.1°C. Polyacrylamide solutions were prepared in distilled water. Intrinsic viscosity calculations were performed for the polyacrylamide after filtration through a 250 micron sieve to remove any undissolved "gel" lumps. The dilute solution viscosity method was used to determine the viscosity average molecular weight of polyacrylamide samples by determining their intrinsic viscosities. The test sample was prepared by dissolving 0.5 g of polyacrylamide in 100 ml of distilled water at room temperature using a magnetic stirrer. The resulting solution was filtered through a 250 micron sieve to remove any undissolved "gel" lumps. By suitably diluting the tested sample with distilled water, a series of polyacrylamide working solutions with concentrations in the range of 5 x 10⁻³ and 1 x 10⁻³ g/ml were prepared. Approximate amounts of the solution were transferred to an Ubbelohde viscometer and the viscometer was placed in a water bath set at 25 ± 0.1 °C and allowed to equilibrate. The outflow time (ie, the time required for the liquid inside the viscometer to pass from the upper meniscus to the lower meniscus) was determined. For each sample, the average of three measurements (which did not differ by more than 3 seconds) was taken. Thermal Gravimetric Analysis (TGA) Samples were prepared for TGA measurement by weighing 5.0 to 10.0 g of dry polyacrylamide into an aluminum dish. The pan was then sealed with an aluminum cap. Thermal gravimetric analysis (TGA) of polyacrylamides with different molecular weights was performed in the temperature range of 30-600 °C at a heating rate of 10 °C/min under nitrogen using a Perkin-Elmer.

III. RESULTS AND DISCUSSION

The molecular weight of polyacrylamide can be varied by several techniques, including monomer concentration, initiator concentration and initiator type, and polymerization temperature. The monomer concentration can be increased to 50% or more for high molecular weight polyacrylamide because the molecular weight of the viscous polymer is the internal phase. The high purity of the monomer and initiators and the absence of oxygen are essential in the polymerization process. Polymerization reaction at different temperatures of acrylamide monomer with different initiators, i.e. thioglycolic acid (40 °C), hydrogen peroxide (90 °C) and potassium persulfate/(CH₃)₂ NCH₂CH₂ N(CH₃)₂ -(tetramethylethylenediamine) (TMEDA)), polyacrylamide very low, low, medium, high and very high molecular weight products (listed in Table 1). The synthesis of high and very high molecular weight polyacrylamide was achieved by increasing the concentration of acrylamide monomer using potassium persulfate/TMEDA as initiator at mild temperature. The synthesis method for the preparation of polyacrylamide is shown in Table 1. The choice of initiators and the concentration of monomers were also studied.

Table 1: Type of initiator used and resulting polyacrylamide with molecular weight

The type of initiator used

Type of initiator used	Resultant molecular weight
polyacrylamide Thioglycolicacid	Very low
Hydrogen peroxide	Low
Potassium persulfate/ (TMEDA)	Medium, high and very high

3.1 Synthesis of very low molecular weight polyacrylamide

Very low molecular weight polyacrylamide was synthesized by radical polymerization using thioglycolic acid as an initiator at moderate temperature (40 °C). The ratio of thioglycolic acid to acrylamide monomer was about 0.02 (g/g), and polyacrylamide with a molecular weight of about 20,000 g/mol was produced. The use of thioglycolic acid as a chain transfer agent has been shown to be a very efficient method of producing very low molecular weight polyacrylamide (7). Thioglycolic acid is used as a chain transfer agent where it is desired to lower the molecular weight in radical polymerization. Thioglycolic acid enters the propagation scheme by donating a proton to the growing radical chain, terminating it but possibly initiating a new chain. Thioglycolic acid was found to be an acceptable initiator for the production of very low molecular weight polyacrylamide at moderate temperature and maximum yield was achieved without any undesirable side products. The product was a white colored liquid with very low viscosity. Acetone was used to isolate and reprecipitate the polyacrylamide product from its liquid solution and dried under vacuum at 60°C for 24 hours to give a 70-75% yield of very low molecular weight polyacrylamide.

3.2 Synthesis of low molecular weight polyacrylamide

A low molecular weight polyacrylamide was synthesized using hydrogen peroxide as an initiator and the reaction was carried out at high temperature (90 °C) to produce polyacrylamide without contaminants detected by FTIR spectroscopy. The product was a white liquid with low viscosity. The polyacrylamide product was precipitated from its liquid solution using acetone and then dried under vacuum at 60°C for 24 hours to obtain a 70-75% yield of low molecular weight polyacrylamide. The molecular weight was found to be 170×10^3 g/mol by viscosity measurement, which is considered low.

3.3 Synthesis of medium, high and very high molecular weight polyacrylamide

The potassium persulfate/TMEDA initiator system was used for the synthesis of medium, high and very high molecular weight polyacrylamides. TMEDA has a high promoting effect on radical polymerization initiated by potassium persulfate. The rate of polymerization increases about threefold in the presence of TMEDA. The potassium persulfate/TMEDA system can shorten the reaction time and react at moderate temperature (40°C). The potassium persulfate/TMEDA system was found to be an acceptable redox initiator for the production of medium, high and very high molecular weight polyacrylamides at moderate temperature and a maximum yield of 90-95% was achieved without any unwanted by-products. The product was a white highly viscous liquid. The polyacrylamide was precipitated from the solution using acetone and then dried under vacuum at 60 °C for 24 h. Figure 1 shows the effect of monomer concentration on the molecular weight of polyacrylamide. As shown, the concentration of acrylamide monomer strongly affects the molecular weight of polyacrylamide. An increase in the concentration of acrylamide monomer caused an increase in the molecular weights of polyacrylamide. The fact that high monomer concentration initiates many sites, resulting in longer polyacrylamide chains, on the other hand, shorter polyacrylamide chains at lower monomer concentration. This is reflected in their corresponding intrinsic viscosity values. The intrinsic viscosity of a polymer is a measure of its hydrodynamic volume in solution, which in turn depends on its molecular weight, the nature of the solvent, and the temperature of the medium (8).

IV. SPECTRAL INFORMATION

4.1 Fourier Transform Infrared (FTIR) Spectral Analysis

Fourier transform infrared (FTIR) spectroscopy of polyacrylamide showed a strong absorption at wavenumber 1655 cm^{-1} due to the presence of a primary amide band, which is used to distinguish true polyacrylamide from the alternative polymerization product poly(β -alanine) which has a secondary amide band instead band at 1555 cm^{-1} (4). The band for (N—H) stretching vibrations appears at 3448 cm^{-1} of the NH_2 group. Furthermore, the absence of the (C=C) band, which usually appears at 1610 cm^{-1} , proved that the acrylamide monomer has been completely converted to polyacrylamide and no monomer residue is present in the polymer (9) studied the FTIR spectra of polyacrylamide, their finding is in in good agreement with our results.



4.2 Measurement of Glass Transition Temperature (T_g)

The glass transition is the physical change from the glassy to the liquid state that occurs in amorphous solids when they are heated. This point is characterized by the glass transition temperature determined by differential scanning calorimetry (DSC). The glass transition temperature, T_g, of very low, low, medium, high, and very high molecular weight polyacrylamide appeared at 100.944, 109.077, 120.811, 148.727, and 154.461 °C, respectively. This indicates that up to these relatively high temperatures the polyacrylamide was in a glassy state and thus relatively resistant to ingress (path in) or exit (path out) of small molecules, and it is necessary to use higher temperatures to insert the polymer. In the rubbery state, when the adsorbed solvent molecules are mobile enough to be desorbed. Molecular weight significantly affects T_g. At lower molecular weights where the excess free volume associated with the chain ends is significant. As the molecular weight increases, the concentration of chain ends decreases until their contribution to the free volume becomes negligible.

4.3 Thermal Gravimetric Analysis (TGA)

TGA is mainly used to determine the thermal stability of polymers. The TGA method is based on continuous weight measurement on sensitive balances while increasing the temperature of the sample in an inert atmosphere. The data is recorded as a thermogram of the dependence of weight on temperature. Initially, the weight loss may result from evaporation of residual moisture or solvent, but at higher temperatures it results from polymer decomposition (11). The thermal stability of polyacrylamides of different molecular weights was studied by TGA from 50°C to about 600°C. Very high molecular weight polyacrylamide showed the highest stability in the series, indicating the importance of molecular weight for thermal stability. On the other hand, very low molecular weight polyacrylamide showed the lowest stability. An increase in molecular weight caused a decrease in % weight loss. The residue at 600 °C is 11.67%, 14.68%, 17.83%, 19.45% and 22.55% for the cases of very low, low, medium, high and very high molecular weight polyacrylamides, respectively. Activation energy values for different degrees of decomposition were calculated from thermal gravimetric analysis (TGA). TGA of polyacrylamide was three-step as previously observed by Ismail et al. First, there is a loss of water, which is non-stoichiometric. This is followed by the subsequent loss of ammonia and other gaseous products from the structure of polyacrylonitrile formed during the decomposition of polyacrylamide and partly from the remaining polyacrylamide when heated to 600 °C.

V. USE OF PAA

In the 1970s and 1980s, the proportionally greatest use of these polymers was in water treatment.[2] Another major application by weight is additives for pulp processing and papermaking. About 30% of polyacrylamide is used in the oil and mineral industry.[13]

5.1 Flocculation (precipitation from solution in the form of a wavy mass)

One of the biggest uses of polyacrylamide is the flocculation of solids in a liquid. This process applies to water treatment and processes such as papermaking and screen printing. Polyacrylamide can be supplied in powder or liquid form, with liquid form subcategorized as solution and emulsion polymer.

Although these products are often called "polyacrylamide," many are actually copolymers of acrylamide and one or more other species, such as acrylic acid or its salt. These copolymers have modified wettability and swellability.

Ionic forms of polyacrylamide have found an important role in the drinking water treatment industry. Trivalent metal salts such as ferric chloride and aluminum chloride are bridged by long polyacrylamide polymer chains. This results in a significant increase in the flocculation rate. This allows water treatment plants to significantly improve the removal of total organic content (TOC) from raw water.

5.2 The Fossil Fuel Industry

In the oil and gas industry, polyacrylamide derivatives, especially copolymers, have a significant impact on production as they increase oil recovery by increasing viscosity. High viscosity aqueous solutions can be generated with low concentrations of polyacrylamide polymers injected to improve the economics of conventional waterflooding. In a separate application, hydraulic fracturing benefits from the reduction in drag resulting from the injection of these solutions. These applications use large volumes of polymer solutions at a concentration of 30–3000 mg/l.[15]

5.3 Land Preparation

The primary function of polyacrylamide soil conditioners is to increase soil slope, aeration and porosity and to reduce compaction, dustiness and water runoff. Typical applications are 10 mg/L, which is still expensive for many applications.[15] A secondary function is to increase plant vigor, color, appearance, rooting depth and seed emergence while reducing water requirements, disease, erosion and maintenance costs. FC 2712 is used for this purpose.

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