

Preparation of a superabsorbent polymer and exploration of its properties

*A Dissertation
Submitted in partial fulfillment*

**FOR THE DEGREE OF
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**NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA**

By
Amrita Jagdev

Under the guidance of
Dr R.K.Patel



Department of Chemistry
NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA-769008(ORISSA)

GUIDE CERTIFICATE

Dr. R.K.PATEL
M.Sc., PhD.FIC (INDIA)
Sr. Lecturer of Chemistry Department
National Institute Of Technology
Rourkela-769008
Orissa



This is to certify that the dissertation entitled “**PREPARTION OF SUPERABSORBENT POLYMER AND EXPLORATION OF ITS PROPERTIES**” submitted by **Amrita Jagdev** to the department of chemistry, National Institute of Technology, Rourkela for the degree of Master of Science in Chemistry is based on the result obtain in the bonafide project work carried out by her under my Guidance and supervision.

I further certify that to the best of my knowledge **Amrita Jagdev** bears a good moral character.

N.I.T, Rourkela
Date:

Dr. R. K. Patel

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1. INTRODUCTION

Natural polymers (from the Greek *poly* meaning “many” and *meros* meaning “parts”) are found in many forms such as horns of animals, tortoise shell, shellac (from the *lac* beetle), rosin (from pine trees), asphalt, and tar from distillation of organic materials. One of the most useful of the natural polymers was rubber, obtained from the sap of the hevea *tree*. (Rubber was named by the chemist Joseph Priestley who found that a piece of solidified latex gum was good for rubbing out pencil marks on paper. In Great Britain, erasers are still called “rubbers”.) Natural rubber had only limited use as it became brittle in the cold and melted when warmed. In 1839, **Charles Goodyear** discovered, through a lucky accident, that by heating the latex with sulfur, the properties were changed making the rubber more flexible and temperature stable. That process became known as **vulcanization**.

The simplest definition of a polymer is something made of many units. Think of a polymer as a chain. Each link of the chain is the “mer” or basic unit that is made of carbon, hydrogen, oxygen, and/or silicon. To make the chain, many links or “mers” are hooked or polymerized together. Polymerization can be demonstrated by linking strips of construction paper together to make paper garlands or hooking together hundreds of paper clips to form chains.

The first synthetic polymer, a phenol-formaldehyde polymer, was introduced under the name “**Bakelite**”, by **Leo Baekeland in 1909**. Its original use was to make billiard balls. Rayon, the first synthetic fiber was developed as a replacement for silk in 1911.

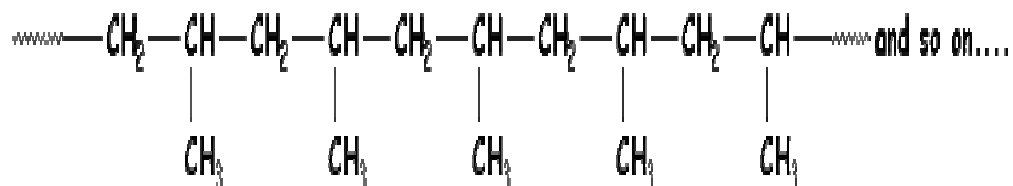
Polymers have been with us since the beginning of time. Natural polymers include such things as tar and shellac, tortoise shell and horns, as well as tree saps that produce amber and latex. These polymers were processed with heat and pressure into useful articles like hair ornaments and jewelry. Natural polymers began to be chemically modified during the 1800s to produce many materials. The most famous of these were vulcanized rubber, gun cotton, and celluloid. The first synthetic polymer produced was Bakelite in 1909 and was soon followed by the first semi-synthetic fiber, rayon, which was developed in 1911.

Even with these developments, it was not until World War II that significant changes took place in the polymer industry. Prior to World War II, natural substances were generally available; therefore, synthetics that were being developed were not a necessity. Once the world went to war, our natural sources of latex, wool, silk, and other materials were cut off, making the use of synthetics critical. During this time period, we saw the use of nylon; acrylic, neoprene, SBR, polyethylene, and many more polymers take the place of natural materials that were no longer available. Since then, the polymer industry has continued to grow and has evolved into one of the fastest growing industries in the U.S. and in the world.

Although many polymers were made in the following years, the technology to mass produce them was not developed until World War II, when there was a need to develop synthetic rubber for tires and other wartime applications and nylon for parachutes. Since that time, the polymer industry has grown and diversified into one of the fastest growing industries in the world. Today, polymers are commonly used in thousands of products as Plastics, elastomers, coatings, and adhesives. They make up about **80%** of the organic chemical industry with products produced at approximately **150 kg of polymers per person annually in the United States.**

The Structure of Polymers:

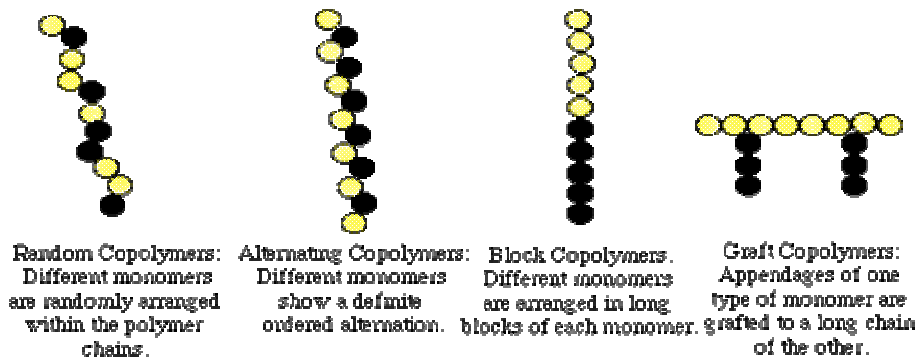
Many common classes of polymers are composed of hydrocarbons. These polymers are specifically made of small units bonded into long chains. Carbon makes up the backbone of the molecule and hydrogen atoms are bonded along the backbone. Below is a diagram of polypropylene, the simplest polymer structure.



There are polymers that contain only carbon and hydrogen (for example, polypropylene, polybutylene, polystyrene, and polymethylpentene). Even though the basic makeup of many polymers is carbon and hydrogen, other elements can also be involved. Oxygen, chlorine, fluorine, nitrogen, silicon, phosphorous, and sulfur are other elements that are found in the molecular makeup of polymers. Polyvinyl chloride (PVC) contains chlorine. Nylon contains nitrogen and oxygen. Teflon contains fluorine. Polyesters and polycarbonates contain oxygen. Vulcanized rubber and Thiokol contain sulfur. There are also some polymers that, instead of having carbon backbones, have silicon or phosphorous backbones. These are considered inorganic polymers. One of the most famous silicon-based polymers is Silly Putty.

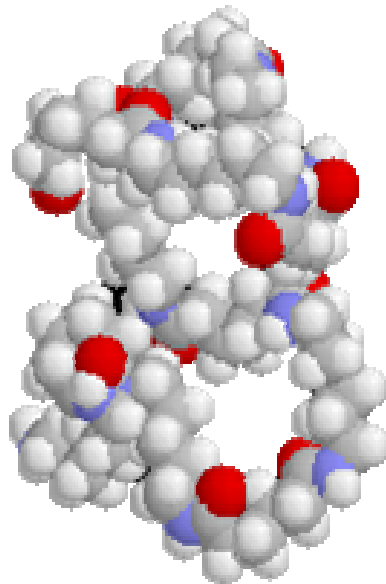
The monomers in a polymer can be arranged in a number of different ways. As indicated above, both addition and condensation polymers can be linear, branched, or cross-linked. **Linear** polymers are made up of one long continuous chain, without any excess appendages or attachments. **Branched** polymers have a chain structure that consists of one main chain of molecules with smaller molecular chains branching from it. A branched chain-structure tends to lower the degree of crystallinity and density of a polymer. **Cross-linking** in polymers occurs when primary valence bonds are formed between separate polymer chain molecules.

Chains with only one type of monomer are known as **homopolymers**. If two or more different type monomers are involved, the resulting **copolymer** can have several **configurations** or arrangements of the monomers along the chain. The four main configurations are depicted below:



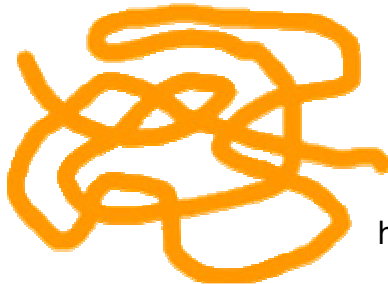
polymers are made up of many molecules all strung together to form really long chains (and sometimes more complicated structures, too). What makes polymers so fun is that how they act depends on what kinds of molecules they're made up of and how they're put together. The properties of anything made out of polymers really reflect what's going on at the ultra-tiny (molecular) level. So, things that are made of polymers look, feel, and act depending on how their atoms and molecules are connected, as well as which ones we use to begin with! Some are rubbery, like a bouncy ball, some are sticky and gooey, and some are hard and tough, like a skateboard.

Below is a diagrammatic representation of a long polymer of a very large molecule. It is made up off thousands and thousands of monomers. Here it is clearly seen that many functional groups are closely imbedded with each other. Here the different functional groups are shown by different colors.



Most of the polymers we'll talk about here are linear polymers. A linear polymer is made up of one molecule after another, hooked together in a long chain. This chain is called the backbone.

Now, linear polymers don't have to be in a straight, rigid line. Those single bonds between atoms in the backbone can swivel around a bit, kind

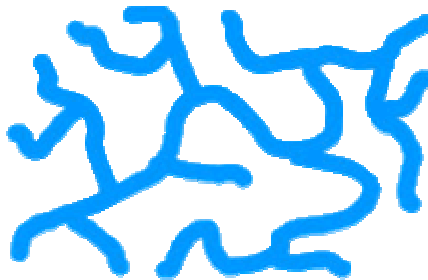


like paper clips hooked together end-to-end.

A **LINEAR** polymer chain starts at the beginning and goes straight to the end. You can take your finger and trace the curvy path from one end to the other.

To the rest of the world, "linear" means "straight and not curved" but for polymers, linear means "straight and not branched".

Branch Out!



A **BRANCHED** polymer chain has extra beginnings (branches!) along the chain and so it has lots of ends. No matter where you start, you can't trace the entire polymer without backtracking.

Characteristics of Polymers:

The two major groups of polymers are thermoplastics and thermosets. Thermoplastic and thermosetting nature is based on the heat response of polymers. The light transmittance of polymers includes the description of materials as being transparent, translucent, or opaque. Transparent polymers are

those that you can see through, translucent are those that you cannot see through but allow light to pass through, and opaque polymers are those that you can neither see through nor allow light to pass through. Light penetration qualities are dependent on the degree of crystallization of the polymer and the presence of additives.

Every polymer has very distinct characteristics but most polymers have the following general attributes.

1. Polymers can be very resistant to chemicals. Consider all the cleaning fluids in your home that are packaged in plastic. Reading the warning labels that describe what happens when the chemical comes in contact with skin or eyes or is ingested will emphasize the chemical resistance of these materials.

2. Polymers can be both thermal and electrical insulators. A brief trip through your house will reinforce this concept, as you consider all the appliances, cords, electrical outlets, and general wiring that are made of or covered with polymeric materials. Thermal resistance is evident in the kitchen with pot and pan handles made of polymers, with the foam core of refrigerators and freezers, and with insulated cups, coolers, and microwave cookware. The thermal underwear that many skiers wear is made of polypropylene, and the fiberfill in a winter jacket can be made from polypropylene or polyester fiber.

3. Generally, polymers are very light in mass with varying degrees of strength. Consider the range of applications from a dime store toy to the frame structure of space stations, or from delicate nylon fiber used to make pantyhose to Kevla which is used in bulletproof vests.

4. Polymers can be processed in various ways to produce thin fibers or very intricate parts. Plastics can be molded into bottles or the body of a car, or can be mixed with solvents to become an adhesive or paint. Elastomers and some plastics stretch and are very flexible. Other polymers can be foamed, like polystyrene) and urethane, to give just two examples.

Polymers are materials with a seemingly limitless range of possible characteristics, and colors. Polymers have many inherent properties that can be enhanced by a wide range of additives to broaden their use and application. The ability to design or engineer the polymer for each specific application makes plastics unique among basic material types.

Each polymer resin can be identified by fundamental identification tests. Melting point, burning properties, solubility, relative density, and halogen tests can identify resins in a lab. When testing the resins, be sure to use safety goggles and perform the tests in a lab fume hood.

Of the most common resins, polyethylene (PE) and polypropylene (PP) both have a translucent, waxy texture, and are the only non-foam plastics that float in water. The burning properties will discriminate between these two resins. PE burns rapidly, drips flames, smells like candle wax and, when extinguished, will produce a white smoke. PP, on the other hand, burns more slowly, smells like burning fuel, and does not drip flames while burning.

PE is impervious to chemical solvents while PP will dissolve in hot toluene. Other common plastics can be identified by their burning properties. Polyvinyl chloride (PVC) can be ignited but will self-extinguish as soon as the fire source is removed. PVC has a very acidic odor when burning because hydrogen chloride

is a burning by-product. (A halogen test can be performed to identify the presence of chlorine in PVC. A copper wire is heated in a laboratory burner flame to incandescence and then touched to the PVC. When the wire is returned to the burner, a brilliant green flame is produced.) Rigid PVC will become rubbery in the presence of benzene or will dissolve in methyl ethyl ketone. Polystyrene (PS), on the other hand, burns rapidly, has a strong gas odor, and produces tremendous amounts of soot. PS will swell readily in acetone.

These identification tests are not conclusive determinations for polymer content, but are a solid guideline. Polymers with colorants, additives, and stabilizers will naturally have somewhat altered behaviors. Infrared spectrophotometry, gas chromatography, and X-ray are some of the analytical identification tests that can be performed to positively identify polymeric materials. Elastomers are unique polymers, which include rubber, synthetic rubber, and thermoplastic elastomers, and are characterized by their elasticity and flexibility. Elastomeric materials stretch and have the ability to recover with limited permanent set or distortion. These materials are generally thermosetting and can be distinguished by similar basic identification tests like the plastics previously mentioned. However, commercial products are usually compounded with more than one base elastomer, making identification by analytical instrumentation a necessity.

Molecular Arrangement of Polymers:

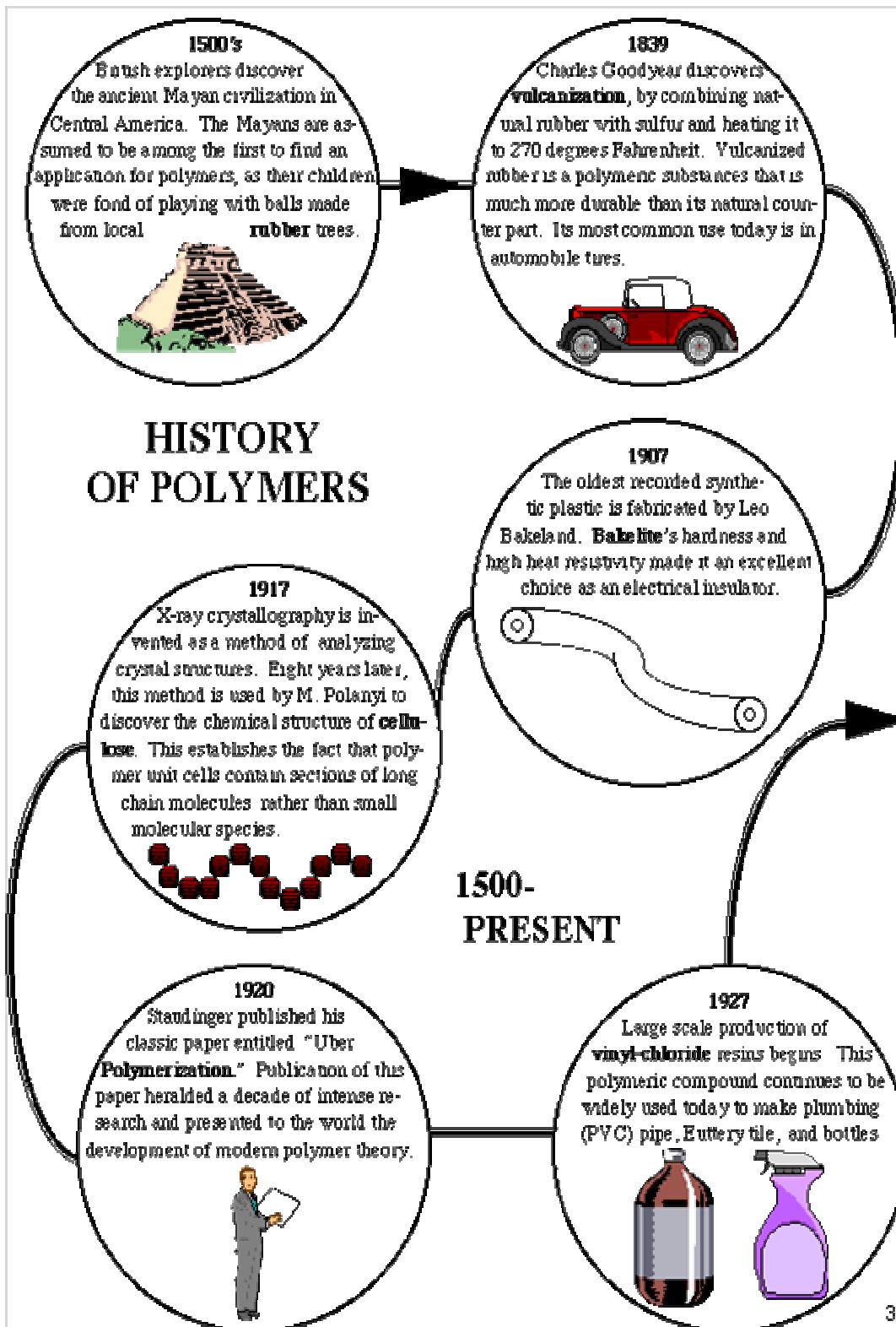
Think how noodles look on a plate. This is similar to how polymers can be arranged if they are amorphous. An amorphous arrangement of molecules has no long-range order or form in which the polymer chains arrange themselves.

Amorphous polymers are generally transparent. This is an important characteristic for many applications such as food wrap, Plexiglas, headlights, and contact lenses. Controlling and quenching the polymerization process can result in amorphous organization.

Obviously, not all polymers are transparent. The polymer chains in objects that are translucent and opaque are in a crystalline arrangement. By definition, a crystalline arrangement has atoms, ions, or, in this case, molecules in a distinct pattern. You generally think of crystalline structures in salt and gemstones, but not in plastics. Just as quenching can produce amorphous arrangements, processing can be controlled to produce the degree of crystallinity desired. The higher the degree of crystallinity, the less light can pass through the polymer. Therefore, the degree of translucence or opaqueness of the polymer is directly affected by its crystallinity. Crystallinity also affects the melting point of a polymer. The more crystalline the pattern of the molecules, the more energy is needed to cause the molecules to separate, melt, and flow. Amorphous polymers, on the other hand, will have lower melting points. Care must be taken to retain the degree of crystallinity in a polymer. Reprocessing, recycling, overheating, fabricating, machining, UV light, or heat in service use or storage can potentially affect the crystallinity of a plastic. As a polymer becomes more crystalline, its melting point and strength increase. However, its strength can increase to the point that the polymer becomes brittle and loses characteristics it was originally made to have.

By manipulating factors on the molecular level that affect the final polymer produced, engineers continually are challenged to produce better-suited materials for a wide variety of old and new applications.

HISTORY OF POLYMERS (CHART REPRESENTATION)



SUPERABSORBENT POLYMERS:

Super-absorbent polymers are lightly cross-linked networks of hydrophilic polymer chains. The most efficient water absorbers are polymer networks that carry dissociated, ionic functional groups. These are essentially hydrophilic non-toxic and partially cross-linked polymers that can absorb several hundreds their weight in water, but cannot dissolve of their three dimensional polymeric network structure. The network can swell in water and hold a large amount of water while maintaining the physical dimension structure. The product swells and forms a tight gel that holds water molecules, even under pressure. One kg of these materials can absorb over 300 liters of water.

They are widely used in sanitary products, such as sanitary napkins and disposable diapers, and also in a variety of other fields. It was known that commercially used water-absorbent polymeric materials employed in such applications including partial neutralization products of cross-linked polyacrylic acids, partial hydrolysis products of starch–acrylonitrile copolymers, starch–acrylic acid graft copolymers and so on. These polymers are poor in degradability and remain semi permanently in water or soil. At present, material's biodegradability is an important focus of the research in this field because of the renewed attention towards environmental protection issues.

On the other hand, biodegradable polymers have attracted interest as 'globe-compatible materials' in recent years. Their use as super-absorbent polymers has also been proposed. Known examples of biodegradable super-absorbent polymers employed in such applications include cross-linked polyethylene oxide, cross-linked polyvinyl alcohol, and cross-linked carboxymethylcellulose, cross-linked alginic acid, cross-linked starches, and cross-linked polyamino acids. Among these, the cross-linked polyethylene oxide and cross-linked polyvinyl alcohol have low water absorption ability and are not particularly suited for use as materials in products requiring high water-

absorbency such as sanitary products, disposable diapers, disposable dust cloths and paper towels.

A multi-layer structure containing an evenly dispersed super absorbing polymer to be used for fabric covered cooling, wetting, and fire deterrent applications. Such multi-layer structure incorporates a laminate super-absorbing polymer within various layers and pockets to maintain an even distribution of super-absorbing polymer within the fabric layers. Various applications such as cooling neckbands, fever reducing suits, house-covering fire deterrent blankets and other personal cooling devices are disclosed.

Further, these compounds can be biodegraded only by certain particular bacteria, so that under general conditions, their biodegradation will be slow or will not take place at all. Moreover, the biodegradability will be reduced extremely when the molecular weight was high. In addition, cross-linked saccharides such as cross-linked carboxy-methylcellulose, cross-linked alginic acid and cross-linked starches contain many firm hydrogen bonds in their molecules, thereby exhibiting strong interaction between water molecules and polymers. Accordingly, molecular chains cannot be opened widely indicating that their water-absorbency was low and. However, a high demand has remained for super-absorbent polymers having high saline-absorbency and excellent water-absorbency, resulting in a large demand for polymers with high performance.

PROPERTIES OF SUPERABSORBENT POLYMERS:

- It's a **non-biodegradable** polymer.
- **Freeze-Thaw Tested-** Superabsorbent Polymer Will Not Release Liquids after Freezing And Subsequent Heating to 160° F.
- Will Not Release Entrapped Ionic Contaminants If Soluble Evaporation Occurs.
- Expands In Volume By Less Than 1% - **Reduces Waste Disposal Costs.**
- **Passes The Paint Filter Test (EPA 9095).**
 - Approved For Use At Hanford & EnviroCare Of Utah.
 - SEG Certified Incinerable Material.
 - Incinerable Polymer with a Heat Value of 5560 BTU/lbs.

Typical absorptive properties:-

(All figures expressed on a gram/gram basis)

- Free Swell In D.I. Water.....330
- In 1% AlCl₃24
- Free Swell In 1% NaCl.....48
- 6N NaOH.....26
- Free Swell In 2% NaCl.....37
- 8N NaOH.....25
- Free Swell In 10% NaCl.....21

USES OF SUPERABSORBENT POLYMERS:

Due to excellent properties to traditional water absorbing materials (such as sponge, cotton and pulp, etc.) super absorbents are widely used in many fields,

such as hygienic products, horticulture, gel actuators, drug-delivery systems, as well as water-blocking tapes and coal dewatering. Various methods has been tried to improve absorbing properties and to expand application fields of super absorbents, since US Department of Agriculture reported the first superabsorbent polymer.

Recently, much attention has been paid to inorganic materials for the preparation of superabsorbent composites, such as montmorillonite, attapulgite, kaolin, mica and, bentonite and sercite. The incorporation of these clays not only reduce production cost, but also improve the properties (such as swelling ability, gel strength, mechanical and thermal stability) of superabsorbent and accelerate the generation of new materials for special applications .For example- Attapulgite, a kind of hydrated octahedral layered magnesium aluminum silicate absorbent mineral with reactive –OH groups on its surface, is less sensitive to salts comparing with other clays (such as smectite),with high absorbing capacity.

The most common dry form of super absorbents is a white/off-white powder that looks like table salt or sugar. However, some dry SAP granules are as large as rock salt, or as small as talcum powder. Absorbent polymers can vary in their absorption capacity, and even in their speed of absorption some are fast and some are slow. In deionized water, most super absorbents will absorb at least 200 times their weight

Practical Uses of Superabsorbent polymers:

- **Baby diapers and napkins:** specially for thin superabsorbent diapers & napkin.

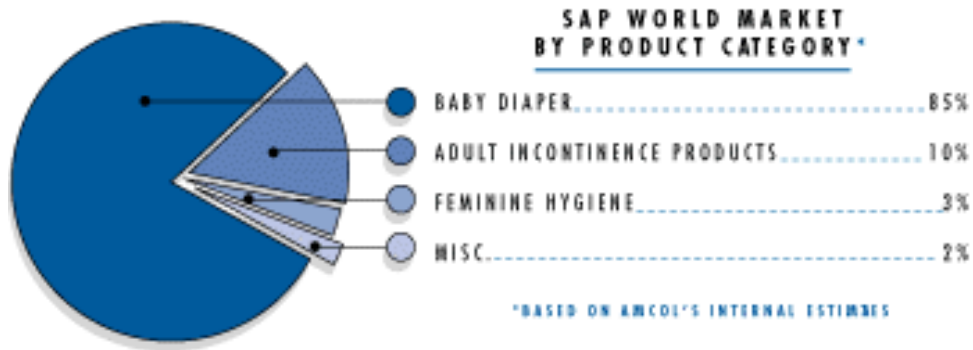
DIAPER CONSTRUCTION

Overall Construction:

Disposable diapers have changed greatly during the past 30 years, but three basic design components are used in any diaper. A diaper consists of an absorbent core between a porous top-sheet and an impermeable back sheet. The top-sheet must do three things: it must allow the urine to flow through it, keep the liquid away from the baby's skin, and retain the structural integrity of the absorbent core. Usually it is made of a porous, hydrophobic substance, for example, polyester or polypropylene non-woven fabric. The back sheet helps keep the baby's clothing dry and is a nonporous, hydrophobic substance, such as a polyethylene film. The absorbent core takes in the liquid, distributes it to all regions of the core, and holds the liquid under pressure from the baby.

- **Farms & garden soil additive:** to retain moisture in soil for longer periods.
- **Water blocking taps:** to keep moisture from degrading delicate fiber-optic and power cables, especially underwater cables.
- **Oil /Water separation:** removes water from fuel tanks & filters of tractors, trucks, boats etc.
- **Fire fighting gels:** keeps water on the fire surface-forest fires, structure coatings etc.
- **Heat packs:** for ease & control of heat pads, body, heat packs, foods etc.
- **Pesticide gels:** makes liquid pesticides manageable and remains effective for a much long period of time.
- **Fragrance gels:** reduces evaporation of perfumes and deodorizers.
- **Bed pans and portable urinals:** with a fragrance additive converts liquid to solid or gel and reduces odor.
- **Spill control:** picks up any aqueous liquid spills quickly.
- **Autopsy absorbents:** stops leakage of body fluids from corpses. Used in lining of caskets.
- **Supermarket meat and fish:** lining to keep the packing dry.
- **Cat litter additive:** holds litter and reduces odor.

- **Liquid human waste solidifier:** used in dry toilets of modern buses and camping vehicles.



HISTORY OF SAP:

Super absorbent polymers were first introduced by union carbide in the mid 60's. Then they were developed in the 70's to grow plants in deserts. However, they were used very little by commercial growers due to their relatively high cost in comparison to their swell capacity. In the early 80's superabsorbent began to be widely developed for the baby diaper market (hundreds of millions of thousands) which led to newer, higher swell polymers, some with long lasting life that were suitable for agriculture in the later periods. Polymers like water-keep have been recommended by various cooperative extension services as a beneficial soil amendment. The fine powders have also been used by nurseries for bare root dipping. Now a growing use has been seen in nursery container mix, landscaping (especially), vegetables and flower gardens and Orchards.

Superabsorbent polymers are primarily used as an absorbent for water and aqueous solutions for diapers, adult incontinence products, feminine hygiene

products, and similar applications. Undoubtedly, in these applications, superabsorbent materials will replace traditional absorbent materials such as cloth, cotton, paper wadding, and cellulose fiber.

Commercial production of superabsorbent polymers began in Japan in 1978, for use in feminine napkins. This early superabsorbent was a cross linked starch-g-polyacrylate. Polyacrylic acids eventually replaced earlier super absorbents, and are the primary polymer employed for superabsorbent polymers today. In 1980, European countries further developed the superabsorbent polymer for use in baby diapers. This first diapers employing this technology used only a small amount of polymer, approximately 1-2 g. In 1983, a thinner diaper using 4-5 grams of polymer and less fluff was marketed in Japan.

The use of superabsorbent polymers revolutionized the diaper industry. Diaper manufacturers began to design diapers to take advantage of the amazing liquid retention ability of the polymer. Superabsorbent polymers absorb, and retain under a slight mechanical pressure, about 30 times their weight in urine. The swollen gel holds the liquid in a solid, rubbery state and prevents the liquid from leaking onto the baby's skin and clothing.

Superabsorbent polymers are prepared from acrylic acid and a cross linker by solution or suspension polymerization. The type and quantity of cross linker control both the swelling capacity and gel modulus. The synthesis and use of cross linked polyacrylate super absorbents have been a popular topic in the polymer literature. However, very little information about manufacturing processes has been given due to its proprietary content.

The properties of superabsorbent polymers can be employed in many different applications. The largest use of superabsorbent polymers is in personal hygiene

products. These consumer products include, in order of volume of superabsorbent used, disposable infant diapers, children's training pants, adult incontinence articles, and feminine sanitary napkins.

Demand:

Since the introduction of superabsorbent diapers in Japan in 1983, the global market for superabsorbent polymers has grown and changed dramatically in the last ten years as super absorbents have replaced fluff pulp in diapers and other personal hygiene articles. Worldwide superabsorbent polymer production capacity grew from only a few million metric tons in 1985 to greater than 700 million tons in 1995 with the United States accounting for 30% of this superabsorbent polymer demand.

Superabsorbent Polymer Manufacturers:

In just twenty years, worldwide production of superabsorbent polymers is in full swing. Many industrial leading countries have companies producing some type of superabsorbent polymer. In the U.S., current manufacturers of acrylate-based super absorbents include The Dow Chemical Company, Sanyo Chemical Industries, Nippon Shokubai Company, and the Chemdal Corporation, which is a subsidiary of AMCOL International.

Other manufacturers located in Europe include AMCOL, Stockhausen GMBH, Dow Chemical, Hoechst Casella, Allied Colloids, and Nippon Shokubai. Superabsorbent polymer production in Japan comes from companies such as Nippon Shokubai, Sanyo, Mitsubishi Petrochemical Company, and Sumitomo Seika.

The leading producers of SAP consist of Stockhausen GMBH, Nippon Shokubai, Chemdal Corporation, Hoechst Casella, Dow Chemical, and Sanyo. These companies manufacture eighty percent of the worldwide production of super absorbents.

Information regarding manufacturing processes of SAP is hard to attain. The majority of manufacturing processes producing SAP employ solution polymerization, in which the monomer acrylic acid is dissolved in a solvent with free radical initiators. Another process used to produce SAP is suspension polymerization, although in much smaller quantities. In 1996, there were three commercial superabsorbent polymer manufacturers using a suspension process. These were Kao Soap Co. and Sumitomo Seika in Japan and Elf Atochem S.A. in France. Suspension polymerization is a process in which droplets of monomer or monomer solution are dispersed in an immiscible continuous phase. The polymerization is carried out independently in these dispersed droplets. Sumitomo Seika and has been the most prominent users of a suspension process to make superabsorbent polymers.

The following table shows SAP production for these industry leaders:-

Stockhausen GMBH	162,000
Nippon Shokubai	137000
Chemdal Corporation	120,000
Hoechst Casella	94,000
Dow Chemical	90,000
Sanyo	47,000

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2. REVIEW OF THE PREVIOUS WORK:

❖ In the past, water absorbent crystals, more commonly known as super absorbent polymer, has been utilized in baby diapers, feminine napkins and other materials, because the super absorbent polymer crystals (are known to hold from about 20 to about 2,000 times its weight of water). Prior art attempts to utilize this for cooling an individual have included the use of the SAP for holding water against the skin.

❖ The most common use has been a tube of fabric being somewhat filled with the dried SAP crystals, and soaking in water for approximately 15 to 20 minutes to allow the crystals to expand and fill the tube. Manual manipulation is then required in order to squish the swollen SAP crystals into place. Problems with that technology have included rashes on the necks of people who have utilized

the neckband for cooling purposes due to the SAP oozing through the fabric and contacting their skin. The inventors believed that the thickened tube, after wetting, appeared as a kielbasa sausage around the neck of the wearer. Furthermore, the contact point of the "sausage" around the neck is a single point, and did not provide much cooling.

❖ In yet another application for the materials having super absorbent polymers contained therein includes fire deterrent devices and methods. 3M Corporation of Minnesota has utilized some of the SAP technology for making fire ponchos for firemen and firefighters. In this application, it is the water holding properties of the SAP that is used to prevent fire from contacting a firefighter. Consequently, although the super absorbent polymer may also be used to deter fire damage, it also acts as a cooling material by evaporating it, as described herein above.

❖ Surgical and other medical procedures routinely leave a patient with an incision to heal over the weeks and months following a surgery. During the healing process, the incision may become itchy, painful, and may exhibit burning and other uncomfortable side effects. Conventional treatments include the use of a bandage over the incision, but this does not alleviate the itching, burning and pain. Furthermore, other medical procedures, including the use of poultices, casts, stints and other bandage type devices, further produce uncomfortable situations for itching, burning and other discomforts experienced. In an attempt to solve this problem, most hospitals and doctors cover the device with a piece of gauze and tape the gauze over the incision. Normally, there is nothing generally proposed to stop the burning, itching, and discomfort. Rather the bandage that is placed over the incision is utilized to prevent infection from attacking the incision site. The present invention utilizes a multi-layer wet type bandage which incorporates super-absorbing polymeric materials for holding cool-to-the-touch material and moisture against the incision during the healing process. Personal experience has shown us that such a covering for an incision helps to remove

the burning, itching and pain associated with the healing of such an incision. Therefore, the present invention is being promoted in order to help post-surgery recovery.

❖ To prevent water ingress into fibre optic, copper data/telecom and energy cables, these polymers are used. When water enters a cable protected by Megotape water-swelling tapes, the super absorbent powder within the tape instantly forms a water blocking gel. The gel is then held in place, preventing further damage, by the strength of the non-woven material. The water is therefore practically stopped where it starts, avoiding more costly damage to the cable. When a gap in the cable is encountered, the combination of powder and tapes fills the hole more thoroughly than traditional water-swelling materials. This can prevent water vapour and high humidity from penetrating the cable even further. The secret of Megotape water-blocking efficiency in tapes is a superior water-swelling powder commonly referred to as a SAP.

A PREVIOUS WORK AT CALIFORNIA:

Nick R. Ennis, observed the effects of time and weather on the application of crystalline and amorphous superabsorbent Polymers in domestic fire prevention. Also, he studied the configuration and conformation of cross-linked polyelectrolyte.

To demonstrate how super absorbent polymers protect household exteriors. For that he constructed small models using common household building materials. In choosing these materials he used stucco as the most common form of household siding in that area (California) coated with common exterior paint and primer. The most common roofing materials include high definition laminated roofing tiles, and Spanish clay roofing tiles. He applied multiple varying polymer mixtures to the surfaces. After super absorbent Polymers membrane formation, He tested their resistance toward direct heat over time, and charted the results.

Results:

Due to the drastic temperature changes throughout the winter months of November and December, the membrane formed by the super absorbent Polymers became brittle and began to break down. The burn ring increased over the six-week period, indicating that the polymer mixture was not tolerating the environmental elements. Based on the presented data, the super absorbent Polymers mixtures absorbed water as expected, swelled in mass, and transformed to a gel like state. The polymer gel created a protective barrier for the stucco.

Conclusions:

The barrier was effective in protecting the stucco from heat and fire damage initially, however with exposure to a variety of climate changes, the super absorbent Polymers began to break down and lose effectiveness. The semi-permeable membrane began to deteriorate and lose effectiveness as a barrier. The combination of amorphous and crystalline polymers created a protective membrane with properties from both types contributing to the effectiveness of the barrier gel.

2. OBJECTIVE OF THE PRESENT WORK:

Superabsorbent polymers are cross-linked polyelectrolyte. Because of their ionic nature and interconnected structure, they absorb large quantities of water and other aqueous solutions without dissolving. This makes them ideally suited as absorbents of body fluids in various products. Keeping in view the above, present research work has been undertaken with the following objectives.

- a) To prepare a new super absorbent polymer by the simplest method.
- b) To characterize the material obtained and to study its various properties.
- c) To access the absorption capacity of the material.
- d) To study the change in properties in presence of various salts.

3. MATERIALS AND METHODS:

a) Chemicals Required:

Acrylic acid is used as a monomer to make some specific polymers. They can be either homopolymerised or be copolymerized with other of monomers capable of being polymerized. Here it is used as a monomer for the polymerization reaction. Ammonium persulfate is a strong oxidizing agent and generates free radicals which are good active oxidizing agent. Sorbitan Oleate is used as a surfactant. Tetramethylethylenediamine (TMEDA) used as the water soluble free radical initiator. N-N'-methylenebisacrylamide (MBAA) used as a soluble cross linking agent. Safranin-O is used as a coloring agent as it has high color stability in comparison to other dyes. Acetone and Xylene are used as reagents.

b) Procedure:

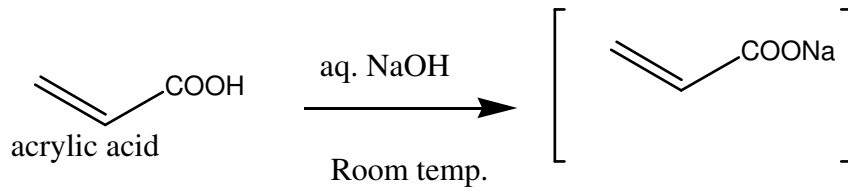
About 1.07 gm of NaOH was dissolved in water (10 ml) in a conical flask (250 ml). Then the above conical flask was inserted in a crushed ice bath of (500 ml) beaker and was allowed to attain 0°C. Then the above whole arrangement was placed on a magnetic stirrer along with a magnetic pallet in the NaOH solution. To the above stirred solution about 2.7 ml of acrylic acid was added slowly, using a dropper. Then the ice bath was removed from the magnetic stirrer and was placed directly on the stirrer, allowing the solution to reach room temperature. Then about 5.2 mg of MBAA and 0.1 gm of ammonium persulfate was added to the above solution (increasing the amount of persulfate to 0.18 gm can result in a more viscous polymer). A solution of 0.01 gm of Safranin-O and 0.2 gm of sorbitan Oleate was made in 40 ml of Xylene and was added to the stirred solution in the conical flask. A suspension was formed, to which again 0.8

ml of TMEDA was added at room temperature while constant stirring was continued. An exothermic polymerization reaction was resulted that was felt by touching the conical flask. The formed viscous layer was stirred till the end of the exothermic reaction.

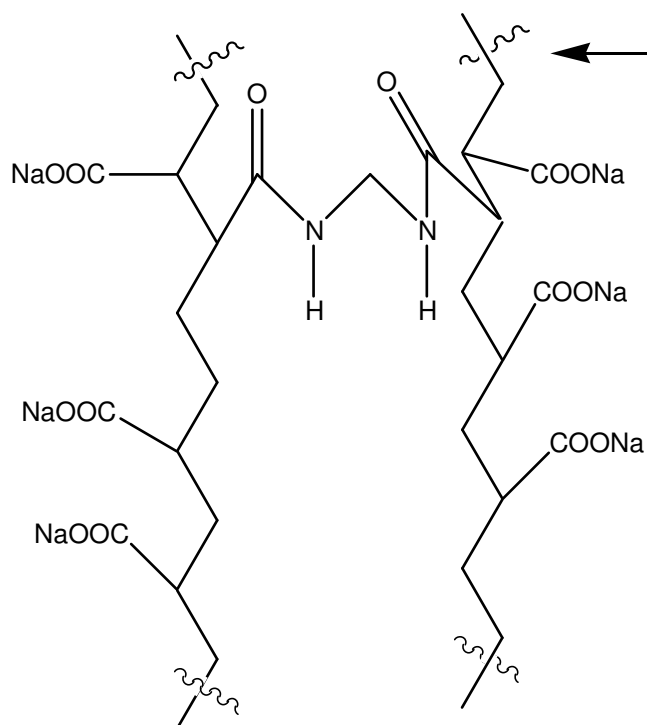
Then the solution was cooled and the upper liquid portion was decanted off (which is meant for waste). Then the gel was transferred to a dish and washed many times with acetone. Finally moist wine red colored polymeric gel was obtained. A dry powder of the obtained polymer can be made by heating it in oven at 70°C.

After one hour of drying, the big pieces were cut into small ones using a good pair of scissors. To obtain powder, heating was continued for three hours or may be overnight. After drying they were cut into small pieces and stored in a desiccators.

THE OVERALL REACTION:



1. MBAA
2. Safranin-O
3. $(\text{NH}_4)_2\text{S}_2\text{O}_8$
4. TMEDA



Cross linked colored polymer made in this experiment

4. RESULTS AND DISCUSSIONS:

In this present experiment, a colored superabsorbent polymer was prepared by free radical emulsion polymerization and cross-linking mechanism.

a) MECHANISM OF PREPARATION:

All polymerization reactions involve basically three steps namely initiation, propagation and termination. Free radical polymerizations are initiated by free radicals, which are produced mostly by the mild thermal decomposition of free radical initiators. The water soluble initiator used here is **ammonium peroxydisulfate**. Mild thermal activation of that is needed, that results in generation of the sulfate free radical, ($\text{SO}_4^{\cdot-}$) which is also an active oxidizing agent.

Free radical polymerization can again be carried out by three methods, namely bulk, solutions or emulsion polymerization. The best for making acrylate polymer is by emulsion polymerization. Here water acts as a moderator and a solvent for the initiator.

A soap or surfactant as it is referred to in emulsion polymerizations, has two ends of different solubility. One end termed as tail, is a long chain hydrocarbon, which is hydrophobic. The other end is often a sodium or potassium salt, which is water soluble. Here **sorbitan Oleate** is the surfactant. At a certain concentration in water called the critical micelle concentration (CMC) soap molecules congregate micelles. In an emulsion the surface is dissolved in water until CMC is reached. The interior of the micelle provides for the site for polymerization. A monomer and a water soluble free initiator are added and stirred. The monomer will enter the micelle.

Initiation takes place when an initiator fragment migrates into a micelle and reacts with a monomer molecule. As the micelle prevents the aggregation of the

monomeric units, there will be more uniform polymerization and polymer particles can grow to extremely high molecular weights, especially if the initiator concentration is very low. The monomer migrates from the larger monomer droplets to the micelles to sustain polymerization. On an average, there is one radical per micelle. As a result, there is not much competition for the monomer between the growing chains in the particles, and they grow to nearly identical molecular weights.

The polymerization of acrylic acid proceeds by a free radical mechanism and therefore requires a free radical initiator. In this experiment, a mixture of ammonium peroxydisulfate and tetramethylethylenediamine will be used as the water soluble free radical initiator. We also require a light cross-linking. Each polymer chain should be as long as possible and cross linked at a few places. A very small amount of the water soluble cross-linker, N, N'-methylenebisacrylamide will be used.

Coloring the gel makes it more attractive for the experiment. In this experiment, a wine red colored organic indicator dye, namely Safranin-O will be used. Although one can try using other dyes, this dye has been tested and found to have color stability in comparison to all.

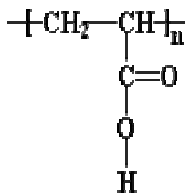
A surface-active agent, sorbitan Oleate is also added to blend in the organic dye. The polymer obtained is washed with acetone and dried at 70°C and can be powdered afterwards.

b) STUDY OF THEIR PROPERTIES:

1) CHEMICAL PROPERTIES

Structure – Property Relationship:

The structure of Polyacrylic acid is as follows, and contains an ionizable group on each repeat unit (-COOH). These polymer chains are then cross linked at the -OH.



The mechanism of swelling of ionized, cross linked polymer networks is based upon the concept of osmotic pressure and hydrogen bonding. The water absorbing action of the material is due to the high ionic strength inside the polymer matrix. The polymer acts as a semi permeable membrane, which does not allow charge substituents to exit out of the polymer into the surrounding solutions. The difference in the sodium ion concentration between the inside of the polymer and the solution in which it is immersed, causes water to flow in rapidly. Sodium ions have high affinity for water (the reason why people with high blood pressure and those who are obese are advised to go for low sodium containing food). Also, the polymer chains are lined with carboxyl groups with about 50-70 % of these in the sodium salt form. In contact with water, carboxyl groups dissociate into negatively charged carboxylate ions. These form hydrogen bonds with water molecules.

In addition these carboxylate sites repel each other, which widen the polymer network, thus allowing more water to be absorbed. However, the cross linked

Polymer molecules can only stretch to a limit. Therefore the amount of water absorbed is in part determined by the balance between the widening of the polymer network as hydrogen bonds form, and the elastic pressure of the cross

linked molecules. The electrolyte concentration in the water being absorbed greatly affects the amount of fluid that can be absorbed by the polymer. The ions of the electrolyte, acts as contaminator ions and decrease the imbalance, which drives the osmotic pressure.

2) Swelling Capacity:

Certainly the first property and arguably the most important in a commercial superabsorbent used in the personal care market is the extent of swelling (this is true not only because swelling is related to the properties of the network, but also because the principal performance criterion for diapers is the amount of liquid contained per unit cost of diaper. In which case, the swelling capacity is approximately 20-40 mL of urine per gram of polymer). If the superabsorbent polymer is more highly cross linked, it is more rigid in the swollen state. Improving the rigidity of the particles enables the swelling particles actually to push aside the fiber component of the composite, thereby maintaining the porosity and permeability during subsequent contacts with liquid. However, this must be optimized, as particles which are too rigid will cause leaks by tearing the surrounding fiber.

Absorbency under load and stability of the gel against shear are important properties of superabsorbent polymers and relate strongly to their performance. Diaper leakage was closely correlated to the stability of gel to shearing. More rigid superabsorbent particles, created by increasing the cross linking, allows for a higher gel modulus and helps the particle withstand the shearing (mainly when used in baby's diaper).

3) Granules:

The most commonly available superabsorbent polymers are hard, dry, granular powders that look much like clean white sand or granular table sugar. When these polymer particles are placed in water, slurry of water and the particles is formed. Gradually the superabsorbent polymer absorbs the water, turning into a soft, rubbery gel. On average, fluffed cellulose pulp fibers will absorb about 12 g of water per gram of dry fiber, whereas superabsorbent polymers will absorb up to 1,000 g of water per gram of polymer.

4) Crosslinkers :

Small amounts of crosslinkers play a major role in modifying the properties of superabsorbent polymers. In addition to modifying the swelling and mechanical properties, the crosslinkers affects the amount of soluble polymer found during the polymerization as result of its relative reactivity with acrylic acid or sodium acrylate. Efficiency of cross linking will also depend on steric hindrance and reduced mobility at the site of pendant double bonds, the tendency of a given crosslinkers to undergo intermolecular addition reactions, and the solubility of the crosslinkers in the monomer mixture.

5) Surface Tension:

Actually capillaries may exist between fluff pulp fibers, polymer particles, or the two in combination. Distribution of liquid will be affected by the surface tension of the liquid that is flowing in these capillaries. In use, impurities may be extracted from a swollen superabsorbent polymer into the solution external to it. Through the surface tension of the solution, the movement of fluid through the capillaries may be affected by these impurities.

6) Temperature Change:

Superabsorbent polymers are used under conditions in which the system temperature may change over time. For example, in a diaper, the superabsorbent polymer will first be bathed in a salt and urea solution that is at the internal temperature of the human body, but the resulting gel will cool slowly in contact with the external environment. The extent and rate of cooling will depend on the climate and other environmental factors. The diffusion coefficient of polymers in solution is temperature dependent, and this should be reflected in the absorption rate of superabsorbent polymers.

c) THE ABSORPTION CAPACITY:

The water absorbing property of polyacrylic acid is very much dependent upon the extent of cross linking that is with more cross linking the water absorption gets reduced.

If a colorless polymer is prepared, then the extent of water absorbing capability can be measured quantitatively. A water solution of a high molecular weight, colored organic compound (eg. blue dextran) can be taken and a weighed amount of a dry polymer powder can be added. Here we can determine the increase in concentration of the color of the water solution after addition of the polymer by a UV-visible spectrometer. The compound with high molecular weight will remain outside the gel while water alone will be absorbed, thus increasing the concentration of the colored species in the solution.

How Absorption Works:

Superabsorbent polymers are cross linked networks of flexible polymer chains. The most efficient water absorbers are polymer networks that carry dissociated ionic functional groups. Except for the molecular-sized chains that make up the network, this picture of a network is remarkably similar looking to the mass of cotton fibers. The difference is that cotton takes up water by convection – water is "sucked" up, wetting the dry fibers; super absorbent polymers work by diffusion on the molecular level, since their "fibers" are actually

long chained molecules. Water diffuses into a particle of superabsorbent polymer when the concentration of water is initially lower in the interior of the particle. As water travels into the particle, it swells to accommodate the additional molecules. Because the polymer molecules are cross linked, they do not dissolve in the absorbing liquid.

d) To study the changes in presence of salts:

SWELLING IN SALT SOLUTIONS:

The behaviour of this polymer is also sensitive to the presence of salts such as NaCl and CaCl₂. Water absorbance is roughly ten times lesser in a 0.02% sodium chloride solution. A block of the water absorbed gel will melt down completely when a small amount of table salt is sprinkled on it.

Polyacrylic acid super absorbents are lightly crossed polymers which are partially neutralized and therefore possess a buffer property. This polymer works efficiently and can absorb 700-800 times of its weight of water. But the water holding capacity much depends on the extent of cross linking. The swelling of superabsorbent polymers in saline solutions was appreciably reduced with increase in the percentage of presence of salt solutions. This well known phenomenon commonly observed in the swelling of ionic hydrogels often results from a charge screening effect of the additional cations causing a non-perfect anion-anion electrostatic repulsions, led to a decrease osmotic pressure (ionic pressure) difference between the polymer network and the external solutions.

6. CONCLUSION:

From the above studies it is concluded that superabsorbent polymer that has been formed has excellent water absorbing capacity. The yield of the product obtained was about 80%. When the reaction conditions were changed there was not much change in the yield. From the characteristics study it was inferred that it has a cross linked structure and the water absorbing property is dependent on the extent of cross linking. The change in property was not very high in presence of different salt solutions. Due to lack of time all the properties could not be studied, however future study in this field will definitely lead to a better product which can be useful for many purposes.

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8. FUTURISTIC STUDY:



a) Nanoparticles, super-absorbent gel clean radioactivity from porous structures.

Researchers are using engineered nanoparticles and a super-absorbent gel to design a clean-up system for buildings and monuments exposed to radioactive materials. Having this system available will allow the nation to be more prepared in case of a terrorist attack with a “dirty bomb” or other radioactive dispersal device.

“If a radioactive device were activated in public, the primary concern would be widespread contamination,” said **Michael Kaminski**, lead scientist of the project. “This contamination is particularly hard to remove in buildings made from brick or concrete, where the pores, or holes, in those materials make it easy for radioactive materials to become trapped.” Enter **Kaminski** and his team of **Argonne** scientists, whose decontamination system could safely capture and dispose of radioactive elements in porous structures in an outdoor environment. Using a simple, three-step procedure, the system operates much like an automated car wash, where remote spray washers apply a wetting agent and a super-absorbent gel onto the contaminated surface. The wetting agent causes the bound radioactivity to resuspend in the pores. The super-absorbent polymer gel then draws the radioactivity out of the pores, and fixes it in the engineered

nanoparticles that sit in the gel. Finally, the gel is vacuumed and recycled, leaving only a small amount of radioactive waste.