# SYNTHESIS OF SUPERABSORBENT POLYMERS BY DIFFERENT TECHNIQUES AND THEIR CHARACTERISATIONS

A thesis submitted in partial fulfillment of the requirements for the Degree of

**MASTER OF ENGINEERING**
**IN**
**POLYMER TECHNOLOGY**

Submitted by

**NAND KISHOR**
**(University Roll No -12732)**

Under the Guidance of

**Prof. Dr. G.L. Verma**
**(Head of the Department )**
**Dept. of Applied Chemistry and polymer chemistry,**
**Delhi College of Engineering, Delhi -110007**

**DEPARTMENT OF APPLIED CHEMISTRY AND POLYMER TECHNOLOGY**
**DELHI COLLEGE OF ENGINEERING**
**BAWANA ROAD, DELHI -110042**
**(UNIVERSITY OF DELHI)**

**2006-2009**

# CERTIFICATE

This is to declare that the major project *entitled* ***"SYNTHESIS OF SUPERABSORBENT POLYMERS BY DIFFERENT TECHNIQUES AND THEIR CHARACTERISATIONS "*** is being by Mr. Nandkishor, is a bonafide record of student's own work a carried by him under our guidance and supervision in partial fulfillment of the award of the degree of Master of Engineering in Polymer Technology from Delhi College of Engineering. University of Delhi, Delhi, during the session of 2006-2009

This result contained in this project is original and have not been submitted to any University or Institute for the award of any degree.

**Prof. Dr. G.L. Verma**
**(Internal Guide)**
(HOD)
Dept. of Applied Chemistry and
Polymer Technology
Delhi College of Engineering
New Delhi-110042

**Dr. Amita Malik**
**(External Guide)**
(Asstt. Director & Chief )
Shriram Institute for Industrial Research
19, University Road, Delhi - 110007

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***Nand Kishor***
*College Roll no 06/POLY/09*
*University Roll no. 10295*
*M.E. (Polymer Technology)*
*Dept. of Applied Chemistry and Polymer Technology*
*Delhi College of Engineering*
*New Delhi-110042*

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# Abstract

Super absorbent polymers are used in the different hygienic and medical applications. In this work we have developed superabsorbent polymers by different methods such as thermal and radiation methods. SAP was synthesized by using two different monomers synthetic one i.e. Acrylic Acid

and natural one i.e. Gum Arabic. SAP developed by different technique were characterized for water absorption, water retention and gel content. IR Study has been carried out for structural analysis . TGA has been carried out to study thermal behaviour of developed SAP.Such studies can be used to specifies can be used which technique is suitable for specific purposes

# *Chapter – 1:* Objectives

- Synthesis of super absorbent polymer using different technique of polymerizations :
  1. Thermal (Bulk , Suspension and Emulsion) and
  2. Radiation techniques ( $\gamma$-radiations).

- Characterization of SAP for water absorption, water retention and gel contents.
- Study of swelling behaviour by carrying out gel content of SAP
- FTIR characterization for structural study.
- Study the thermal behaviour of SAPs by using TGA
- Behaviour of developed SAP towards different pH solution

# *Chapter – 2: INTRODUCTION*

## 2.1 Superabsorbent Polymers :

Superabsorbent polymers (SAPs) (also called **slush powder**) are polymers that can absorb and retain extremely large amounts of a liquid relative to its own mass. These are cross linked networks of flexible polymer chain in which water absorption takes place by dissociated,ionic functional groups.

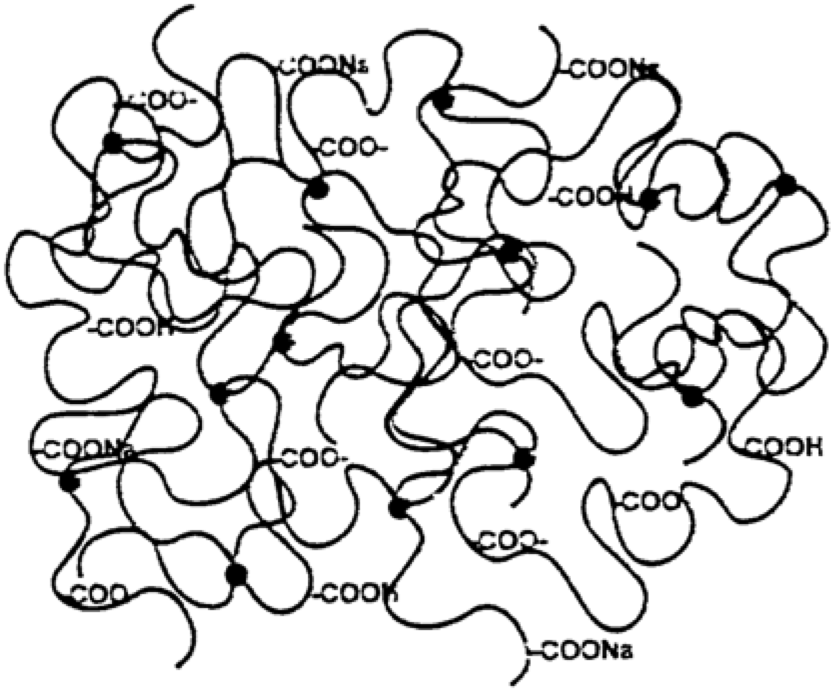

Figure 1. Superabsorbent Polymer Network

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**SAPs are hydrophilic and insoluble in water, and they swell in its presence (or in the presence of any aqueous fluid), increasing in volume and becoming soft and elastics, but keeping their shape, until reaching a physical-chemical balance. These characteristics are a consequence of diverse factors :**

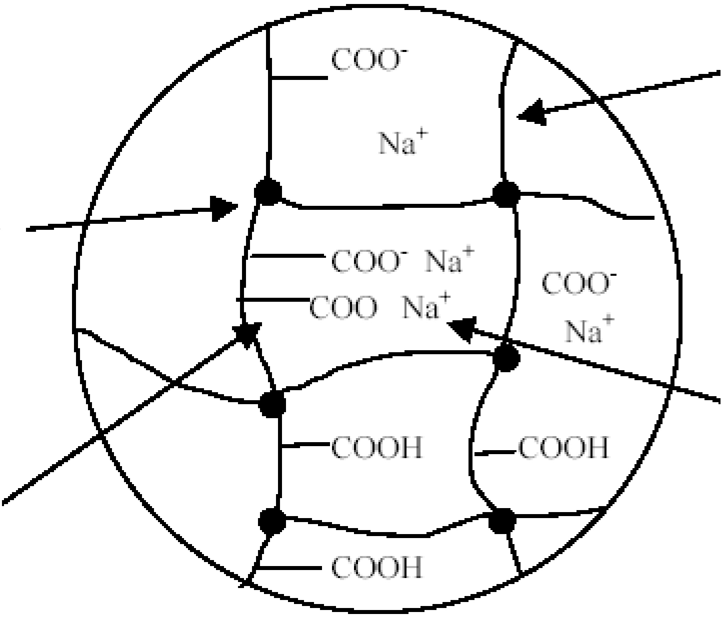
- Their hydrophilic nature is due to the presence of polar grops, such s –OH, -COOH, -CONH2, HSO3 along the polymer chains

- Their insolubility in water is due to the existence of a three-dimensional cross-linked network in their structure. This cross-linking can be due to weak cohesive forces and due to covalent or ionic bonds.

- Their elastic consistency is determined by the hydrophilic monomer used and the low density of the cross-linking of the polymer.

- The conservation of the shape is a result of the balance between the osmotic forces originated by the water upon entering the polymer and the cohesive forces exerted by the polymeric chains that resist that expansion

There are several mechanisms to the process of swelling, all of which contribute to the swelling capacity (or centrifuge retention capacity CRC – which is the amount of 0.9 wt% saline solution that a SAP can retain under free swelling conditions when surface water has been removed in a cenrifuge). Figure below is a diagrammatic representation of part of the polymer network.



Hydrophilic Polymer chains

Cross-links between chains prevent 'infinite' swelling.

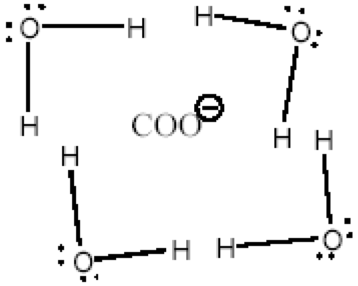
The dissociated sodium carboxylate groups increase osmotic pressure in the gel. Electrical neutrality is maintained because $Na^+$ are trapped in the gel.

Repulsion between negative charges expands polymer coils

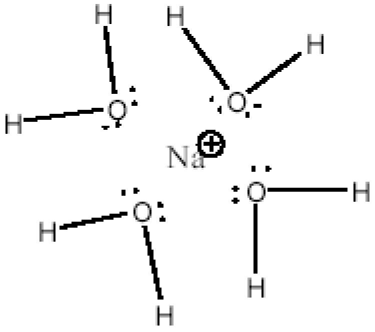
The polymer backbone in SAP is hydrophilic i.e. 'water loving' due to the presence of carboxylic acid groups (-COOH). When water is added to SAP there is a polymer/solvent interaction; hydration and the formation of hydrogen bonds are two of these interactions.

**Hydration :**

This is the interaction of ions of a solute with molecules of a solvent i.e. $COO^-$ and $Na^+$ ions attract the polar water molecules.



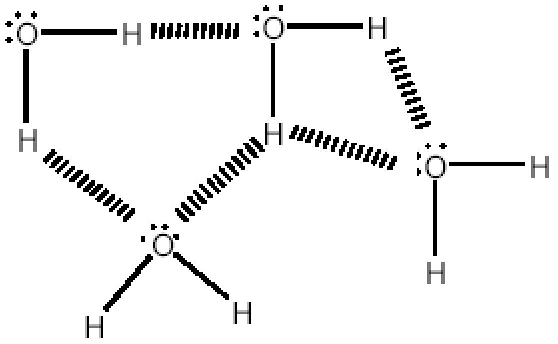
**a**



**b**

**Hydrogen Bonds :**

Hydrogen bonds are electrostatics interactions between molecules, occurring in molecules that have hydrogen atoms attached to small electronegative atoms such a N, F and O. The hydrogen atoms are attracted to the non-bonding electron pairs (lone paris) on other neighbouring electronegative atoms.



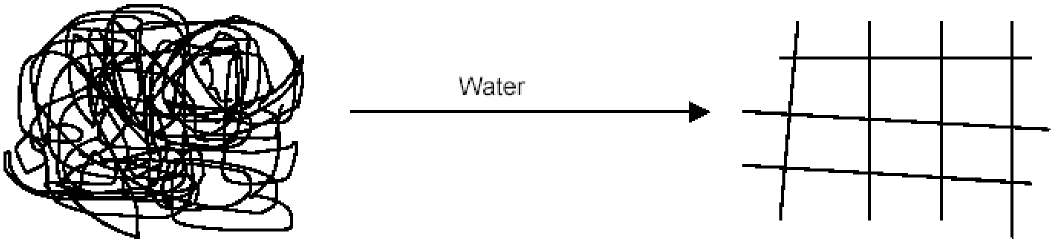
In water the electronegative atom is oxygen which pulls the hydrogen’s electrons towards itself setting up a dipole in the molecule. The positive hydrogen atoms are attracted to the oxygen lone pairs on other water molecules. Oxygen has two lone pairs of electrons and each is capable of hydrogen bonding to two other water molecules.

These effects decrease the energy and increase the entropy of the system. Due to the hydrophilic nature of SAP the polymer chains have a tendency to disperse in a given amount of water (i.e. they are trying to dissolve in the water), which leads to a higher number of configurations for the system and also increases entropy.

For ionic polymers there is another solvent/polymer interaction beyond simple mixing. The neutralised chains contain charges that repel each other. Overall electrical neutrality is maintained as the negative carboxylate groups are balanced by the positive sodium ions. Upon contact with water the sodium ions are hydrated which reduces their attracdtion to the carboxylate ions (due to the high dielectric constant of water). This allows the sodium ions to move freely within the network, which contributes to the osmotic pressure within the gel. The mobile positive sodium ions however, cannot leave the gel because they are trapped by a semi-permeable membrane. So the driving force for swelling is the difference between the osmotic pressure inside and outside the gel. Increasing the level of sodium outside of the gel will lower the osmotic pressure and reduce the swelling capacity of the gel. The maximum swelling of the gel will occur in deionized water.

### Why doesn't SAP dissolve in water :

Cross-links between vhains form a three-dimensional network and prevent the polymer swelling to infinity i.e. dissolving. This is due to the elastic retraction forces of the network, and is accompanied by a decrease in entropy of the chains, as they become stiffer from their originally coiled state.



Coiled cross-linked chains

Hydrated chains

There is a balance now between the forces of retraction and the tendency for the chains to swell to infinite dilution. The degree of cross-linking has a direct effect on the level of swelling of the polymer and the strength of the network i.e. Increased cross-link density = decreased swelling capacity = incrased gel strength.

## 2.2 Classification of Superabsorbents :

Superabsorbents can be classified based on :

**A. Monomeric composition:**

1. Homopolymeric Superabsorbents
2. Copolymeric Superabsorbents
3. Interpenetrating Polymer Network (IPM) Superabsorbents

**B. Ionic charges on the monomer:**

1. Non-Ionic or neutral
2. Ionic Superabsorbents
    - i. Anionic
    - ii. Cationic
    - iii. Polyampholytic

**C. Physical nature (Network Structures):**

1. Amorphous structures
2. Semicrystalline Structures
3. Hydrogen Bonded Structures

**Homopolymeric Superabsorbents :**

Homopolymers are formally referred to as a polymer network in which a single species of the monomer is the basic structural unit. Homopolymers could have crosslinked or uncrosslinked skeletal structure depending on the nature of the monomer and polymerisation technique.

Homopolymers, which are generally crosslinked, find important applications such as slow drug delivery devices and contact lenses

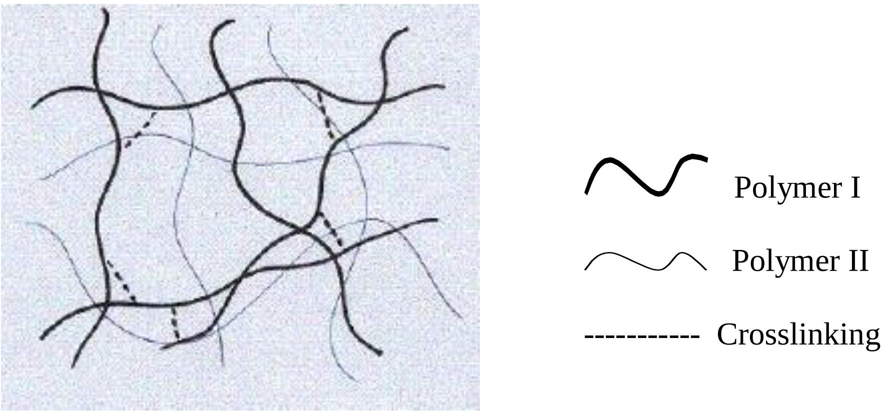
**Copolymeric Superabsorbents:**

Copolymeric hydrogel networks are comprised of two or more diferent monomer species with at least one hydrophilic component, arranged in a random, block or alternating configuration along the chain of the polymer network. The copolymeric hydrogel networks are generally covalently or ionically crosslinked structurals, which are not water-soluble.

A wide range of important copolymeric SAPs are prepared by vast combinations of compatible monomers some of which include poly(NVP-co-HEMA), poly(HEMA-co-MMA) and poly(HEMA-co-AA).

**Interpenetrating Polymer Network (IPN) superabsorbents :**

IPN, as important class of SAPs materials, are defined as two independent crosslinked synthetic and/or natural polymer components contained in a network form as shown in Figure. A semi-IPN is an IPN where one of the components is a crosslinked polymer while the other component is a non-crosslinked polymers



**Structure of IPN**

The two basic synthetic routes to form IPNs are sequential and simultaneous polymerisation methods. The formation of an IPN increases the compatibility of the polymer components thus preventing phase separation and allows access to properties that may be hybrids of those of the component macromolecules.

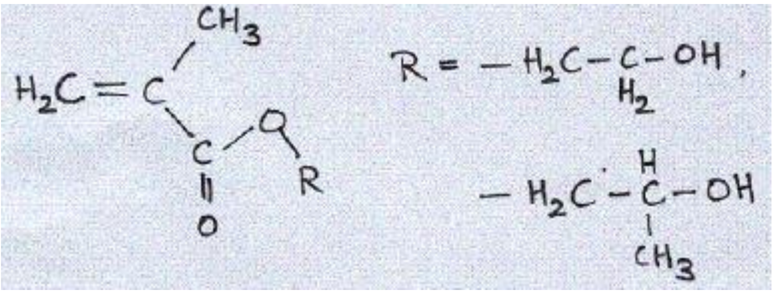
Since there is no chemical bonding between the two polymeric components, each component may retain its own property while the proportion of each network can be varied independently thus obtaining the desired combinations of the properties of the two macromolecule components.

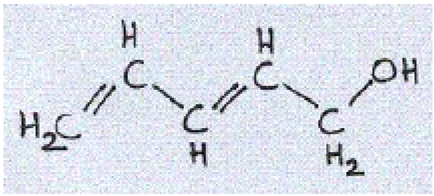
Furthermore, one or both of the macromolecular networks of the IPN cound be made biodegradable with potential bio-applications A number of IPNs and semi-IPNs based on polysaccharides such as chitosan and its derivatives, PNVP, PVA, poly(ethylene oxide) (PEO) , poly(N-Isopropyl acrylamide) (PNIPAM) with potential bio-applications have been reported

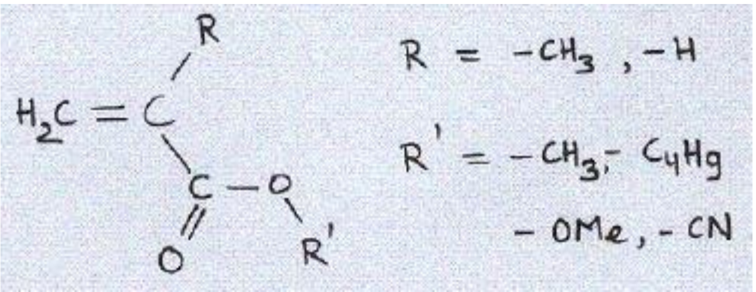
**Non-Ionic Superabsorbent:**

Non-ionic superabsorbents, often referred to as neutral superabsorbents, are homopolymeric or copolymeric networks, which do not bear any charged groups in their structure. Neutral SAPs may be prepared by various polymerisation techniques or by conversion of existing polymers\
Some neutral monomers commonly utilized to prepare superabsorbents are

**Hydroxyalkyl methacrylates** **2, 4 Pentadiene-1-ol**







**Hydrophobic acrylics**

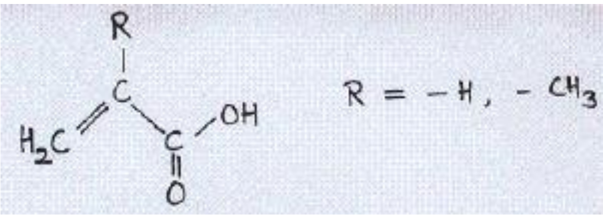
**Ionic Superabsorbents:`**

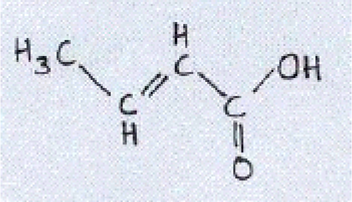
Ionic superabsorbents also known as polyelectrolytes are prepared from monomer/s accompanying ionic charges. Inclusion of charged species in the olymer backbone enhances the stimuli responsive properties, which could be controlled, depending on the nature of the pendent group thus widening its scope of bioapplications. Based on the charges present in the polymeric back bone, ionic suerabsorbents can be categorises as :

**Anionic Superabsorbents:**

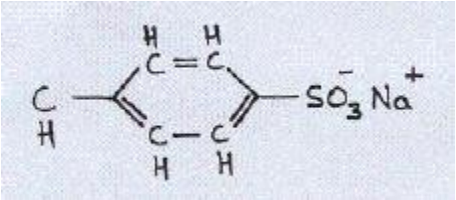
Anionic SAPs networks are usually referred to as either homopolymers of negatively charged acidic or anionic monomers or copolymers of an anionic monomer and a neutral monomer. However, anionic SAPs could also be prepared through modification of existing polymeric non-ionic SAPs such as by the partial hydrolysis of poly(hydroxy alkyl methacrylates) or by the addition of excess polyanions in the case of polyelectrolyte complexes to form anionic superabsorbents.

Anionic monomers commonly utilized to form anionic SAPs are shown as :





**Acrylic acid derivatives** **Crotonic acid**

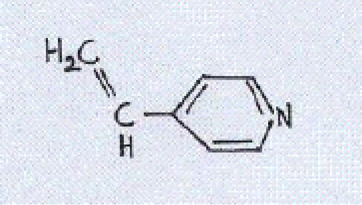


**Sodium Styrene sulfonate**

Anionic SAPs are known to exhibit a marked increase in the swelling ratio with increase in the environmental pH.

**Cationic Superabsorbents:**

Homopolymers of positively charged basic or cationic monomers or copolymers of cationic and neutral monomers are commonly referred to as cationic superabsorbents networks.



**Vinyl pyridine**

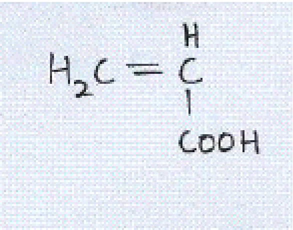
Cationic polymeric networks could also be derived through modifications such as partial hydrolysis of the existing non-ionic pre-formed polymer networks. It is also possible to synthesize cationic hydrogels through polyelectrolytes complexation reactions by addition of excess polycations. Cationic pendant groups in polymer network in contrary to anionic pendant give rise to superabsorbents, which remain collapsed in the basic environment and swollen in the acidic environment due to the electrostatic repulsion between the positively charged groups.

## Polyampholytic Superabsorbents:

Polyampholytic networks are referred to as macromolecules capable of possessing both positively and negatively charged moeties in the polymer network. The presence of ionic species along the polymer chain has a distinct effect on the solution and solid-state properties of the polyampholytes. The columbic attractions between the oppositely charged sides afford inter- and intramolecular ionic interactions that are stronger than Van der Waals forces, yet weaker than covalent bonds.

Some common acidic and basic monomer combinations used to prepare polyampholytes are illustrated as :

**1**



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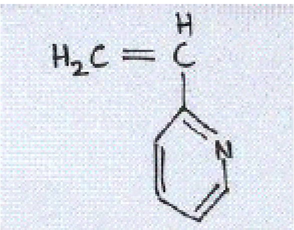
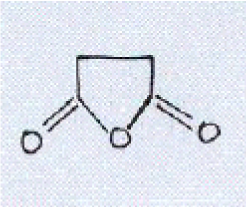


**Acrylic acid**

**2-Vinylpyridine**

**2**



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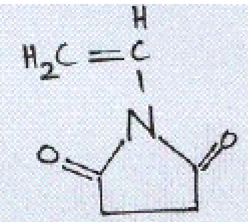


**N-vinylsuccinimide** **Maleic anhydride**

## Superabsorbent Network Structures:

Flory states that the polymeric Superabsorbent network structure may have several roles. In aqueous medium the network may dissociate and take the role the solute as in the case of some water – soluble superabsorbent networks or swell to equilibrium by imbibing the medium in its structure. As the network expands in an aqueous medium, a force resisting the expansion occurs due to the elongation of the chain into a lesser entropically desirable conformation. When the osmotic pressure driving the medium into the superabsorbent network is matched by the exerted expansion resistance force, equilibrium degree of swelling is achieved.

The physical and other properties of the hydrogels depend on the structures of the polymeric networks. Based on the polymer structure, SAPs are classified in three types :

The extent of crosslinking in the superabsorbents network is referred to as crosslinking density. Increased crosslinking density will increase the resistance force to chain elongation consequently reducing the degree of equilibrium swelling in contrast to superabsorbent with low crosslinking density.

### Amorphous SAP Structures :

The term ‘amorphous’ also known as non-crystalline is usually attributed to optically transparent isotropic polymeric networks that contain randomly arranged macromolecular chains. The amorphous SAPs network often contains localized ordered structures or non-homogeneous structures that are not suggested by the common Flory definition of amorphous polymers. Thus the most acceptable definition of such networks is a collection of Gaussian chains between crosslinks.

The temperature at which the polymeric network undergoes the transformation from a glassy to a rubbery state is referred to as the glass transition temperature (Tg). The characteristic feature of amorphous polymeric networks is that when exposed to temperature conditions below its Tg value, they pass successfully through the transformation from a rubbery to glassy state without any clear demarcation between the two phases. The glassy, transparent nature, and important characteristics of amorphous SAP networks, has widened their scope as bio-applicable materials requiring optical transmittance.

**Semi crystalline SAPs Structures:**

Semicrystalline SAPs networks are complex mixtures of amorphous and crystalline phases, which contain dense regions of ordered macromolecular chains (crystallites). The lack of mechanical strength in some conventional crosslinked SAPs network structures for certain biomedical applications has led the development of an-isotropic semi-crystalline polymeric networks which are characterized by the presence of strong covalent bonds along the polymer chain.

Semicrystalline hydrogel networks are produced by heat treatment of non-crystalline hydrogels above their Tg. Crystallization of polymers in polymer-diluent systems is the typical method of preparing semicrystalline hydrogel networks. In the crystallization process the short chains that are not able to fold are rejected from the crystalline phase and thus they participate in the amorphous phase hence the resultant polymer network contains continuous composition of amorphous and crystalline regions. The tendency of the polymers to crystallize is enhanced by its regularity and polarity. Peppas (1977) suggests that when semicrystalline polymer networks are placed in aqueous medium, only the amorphous regions swell and the crystalline regions are not affected by the medium thus they play the role of crosslinks in the polymer network.

**Hydrogen Bonded Hydrogel Structures:**

Hydrogen bonding is referred to as an electrostatic interaction between electronegative atoms such as oxygen, nitrogen, fluorine and chlorine and hydrogen atoms that are covalently bound to similar electronegative atoms. The strength of the hydrogen bonding (<10Kcal/mol), however, is far weaker than covalent bonding (>100Kcal/mol) but still stronger than the Vander-Walls interactions (≈1Kcal/mol).

The formation of multiple hydrogen bonds between two water-soluble macromolecules may result in strong intermolecular structures, which are physically crosslinked three-dimentional polymeric networks such as IPNs and semi-IPNs. The driving force behind the formation of the multiple simultaneous hydrogen bond between the macromolecules is the co-operative interaction between the macromolecules, which is restricted to the chain length of macromolecules.

## 2.3 Materials Used : The Common Monomers Used for Synthesizing Superabsorbents :

Superabsorbent polymers (SAPs) can be prepared from materials of i.e.:

1. Natural origin i.e. material obtained from plants and animals and their modification.
2. Synthetic origin based on polymeric materials.

Early superabsorbents were made from chemically modified starch and cellulose and other polymers like poly(vinyl alcohol) PVA, poly(ethylene oxide) PEO all of which are hydrophilic and have a high affinity for wate. When lightly cross-linked, chemically or physically, these polymers became water swellable but not water-soluble.

Superabsorbent polymers are now commonly made from the polymerization of acrylic acid blended with sodium hydroxide in the presence of an intiator to form a poly-acrylic acid, sodium salt (sometimes referred to as cross-linked sodium polyacrylate). whch has been proven to give the best performance versus cost ratio. This polymer is the most common type of SAP made in the world today. The polymers are manufactured at low solids levels for quality and economica reasons, and are dried and milled in to granular white solids. Other materials are also used to make a superabsorbent polymer, such as polyacrylamide copolymer, ethylene maleic anhydride copolymer, cross-linked carboxy-methyl-cellulose, polyvinyl alcohol copolymers, cross-linked polyethylene oxide, and starch grafted copolymer of polyacrylonitrile. The latter is one of the oldest SAP forms created.

Table 1. Monomers used in the synthesis of superabsorbents

| Monomer abbreviation | Monomer |
|---|---|
| HEMA | Hydroxyethyl methacrylate |
| HEEMA | Hydroxyethoxyethyl Methacrylate |
| HDEEMA | Hydroxydiethoxyethyl Methacrylate |
| MEMA | Methoxyethyl methacrylate |
| MEEMA | Methoxyethoxyethyl Methacrylate |
| EGDMA | Ethylene glycol dimethacrylate |
| NVP | *N*-vinyl-2-pyrrolidone |
| NIPAAm | *N*-isopropyl AAm |
| Vac | Vinyl acetate |
| AA | MAA |
| HPMA | *N*-(2-hydroxypropyl) Methacrylamide |
| EG | Ethylene glycol |
| PEGA | PEG acrylate |
| PEGMA | PEG methacrylate |
| PEGDA | PEG diacrylate |
| PEGDMA | PEG dimethacrylate |

For synthesizing of superabsorbents the polymerization usually is carried out using heat (with thermal-initiators), light (with photoinitiators), $\gamma$ radiation, or an electron beam. Radiation polymerization does not require initiators and can be used with almost any monomer. Initiators provide free radicals that initiate a chain reaction among the monomer and cross-linker molecules. Thermal initiators include peroxides and azo compounds that undergo cleavage at a rate that is markedly terperature dependent, and redox systems comprised of reducing agents such as ferrous salts, sodium metabisulfite, or tetramethylene (TEMED), plus oxidizing agents ammonium persulfate or hydrogen peroxide. Radiation sources include Co-60, Ce-137, or electron beams

## 2.4 Applications of Superabsorbents

Water- swollen crosslinked superabsorbents polymers have varied applications in fields such as food additives  pharmaceutical as well as biomedicine. The pioneering work on crosslinked HEMA SAPs was done by Wichterle and Lim in 1954. From their research, and discovery of the hydrophilic and biocompatible properties of superabsorbents, there emerged a new class of SAPs technologies based on biomaterial application. Later natural polymers such as collagen, and shark cartilage were incorporated into superabsorbents as wound dressings. Natural and synthetic polymers are used for encapsulation of 13 cells, as well as encapsulation of islets in a semipermeable membrane. Superabsorbents have been used to prevent adhesions and prevent thrombosis after surgery, and as cell adhesion resistant surfaces.

Among these applications, hydrogel-based drug delivery devices have become a major area of study, and several commercially available products are already in the market [1.36]. Proteins, peptides, DNA based drugs can all be delivered via hydrogel carrier devices. The various properties of hydrogels such as biocompatibility, hydrophilicity, flexibility all make it ideal for use as drug delivery matrix.

## 1. Drug Delivery :

Proteins, peptides, and other materials have been identified as “drugs” which can be used to treat physiological life processes, pain, and discomfort. These can all be delivered via hydrogel as superabsorbent carrier devices. An increasing understanding of cellular biology at the molecular level and breakthroughs in proteomics have led to the concept of gene delivery. Drugs have to reach the site of action following administration (oral intravenous, transdermal etc) in a specific manner and in specific quantity. This is the basis of the drug delivery field. Drug delivery aims at delivering the right drug at the right place, at right concentration for the right period of time.

Sometimes direct delivery of such drugs is difficult, due to the treacherous route of delivery or discomfort caused to the patient. For such cases, strategies have been developed for delivering drug with a carrier. The drug carrier, whether it be an implantable device, or long chain polymer must be biocompatible with the drug and the body. Drug delivery systems alter the biodistribution and pharmokinetics of the drug. Therefore one must take into account obstacles such as drug solubility, enzyme degradation, toxicity, inability to cross biological barriers as well as adverse environmental conditions. In order to make the delivery of the drug effective without causing an immune response in the body, proper design and engineering of the drug delivery system is essential.

SAPs based delivery devices can be used for oral, ocular, epidermal and subcutaneous application. The Fig 2 below indicates various sites that are available for the application of hydrogels for drug delivery.

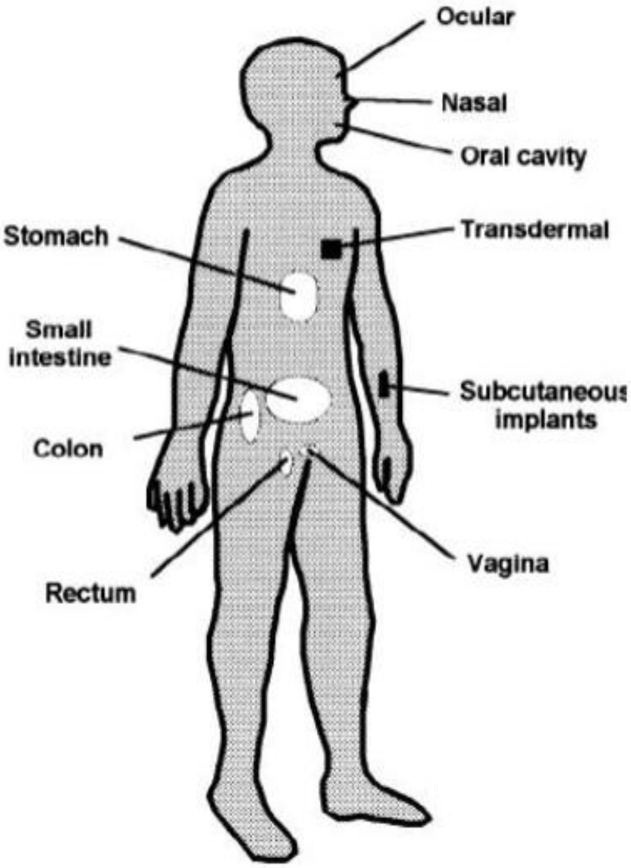


**Figure 2. Tissue locations applicable for SAPs based drug delivery syestems**

**2. Superabsorbents as Fire Protection Materials :**

It is well known that moist fire protection materials have good fire resistance characteristics. Due to its high water content, SAPs can be used as burn free materials for fire protection. A commercial fire protection product Burnfree Fire/Trauma Blankets is made of pure virgin wool, woven with a unique interlinking cell construction. Burnfree blankets reduces physiological and psychological trauma by providing immediate cooling, soothing, and moistening of the burn. It also reduces the pain and trauma of wounds from fires, flames, scalds, chemical, and electrical injuries. Superabsorbents are also used as dry fire extinguishing agent or mixed with water as aqueous extinguishing agent.

**3. Superabsorbent as Absorbing Materials :**

In the past 20 years, superabsorbent polymers (SAPs) have achieved a worldwide market.

The largest use of SAP is found in personal disposable hygiene products, such as baby diapers, adult protective underwear and sanitary napkins. The first commercial production of superabsorbent polymer was began in Japan in 1978, as feminine napkins, using cross-linked starch-grafted polyacrylate. In 1980, superabsorbent polymer was used in baby diapers in Germany and France. At first, the diapers used only a small amount of superabsorbent polymer as a supplement to fluff pulp that furnished most of the absorbenty. Gradually, the superabsorbent polymers become the major component of the diapers. The commercial diaper products are packed with poly(acrylic acid) resins. Superabsorbent polymers are added to baby diapers in basically two ways ; layered or blended. In the layered application, powered polymers first is scattered onto a layer of fluff pulp, then the fluff is folded, making the polymer located in a centralized layer in the absorbent structure. This structure is covered with a nonwoven fabric layer.

## 4. Superabsorbents as Agricultural Applications :

Superabsorbent polymers have also found limited utility as additives to soil to improve the water-holding ability. The Superabsorbents (hydrogels) absorbs the water and controls its release back into the soil as conditions become drier. Poly(ammonium acrylate) and poly(acrylamide) SAPs have been studied for spray application to the soil and plants. The gels are prepared for spraying by adding water to provide a readily deformable polymer that will pass through a spray apparatus. Such SAPs may be sprayed into the soil by use of a plow with special attachments for spraying below the surface of the soil that allows the gel to be placed at a definite depth and concentration. Modified PAM SAPs are also used for conserving irrigation water and increasing the agricultural potentialities of sandy soils.

Biodegradable SAPs based on polysaccharide or polyester-polyurea-polyurethane are used as an artificial soil for plant material capable of growth (eg, embedding plant materials in biodegradable SAPs for use an an artificial seed). The cross-linked PEO has been shown to substantially reduce the sensitivity of plants to water shortage, to promote their growth under condition of water shortage, and to improve the seeding survival and final crop. Beside a direct addition to growth media, polymer SAPs can also been used as coatings for seeds and bare roots.

## How are superabsorbents helping the environment :

Many environmental applications for superabsorbents have been found for agriculture, as well as the the construction and horticulture industries. superabsorbents help reduce water runoff and soil erosion, thus improving the quality of lakes, streams, and rivers. superabsorbents also help with moisture retention and water conservation by helping soil increase water holding capacity, allowing plants to survive during droughts. Erosion control, soil management, and environmental clean-ups are also ways superabsorbents can help the environment. Many scientists continue to study the effect of superabsorbents on the environment.

## 5. Superabsorbents for Tissue Engineering :

The use of biocompatible SAPs for tissue engineering is one area of intense research activity. The candidate materials include both natural polymers ( such as fibrin, collagen, and gelatin) and Synthetic polymers. The use of SAPs matrices for tissue repair and regeneration in the Central Nervous system (CNS) is based on two complementary aspects:

**The first is concerned** with the healing process in the injured CNS as a potential mechanism for Tissue repair and axonal regeneration in mammals as observed in the lamprey, amphibians, and Fish.

**The second is concerned** with the process of organ repair and regeneration. Restoration of organ continuity and some degree of tissue repair in the CNS can be achieved using collagen gels that exactly moulds the lesion. Porous matrices prepared from synthetic SAPs are more stable, allowing it to sustain tissue growth and organisation over long periods. But the potential toxicity with biological tissue of the synthetics SAPs is a concern for tissue repairing.

Natural hydrogel materials are being investigated for tissue engineering, these materials include agarose, methylcellulose, hylaronan, gum arabic and other naturally derived polymers.

## 6. Superabsorbents as Wound Dressings :

Throughout the healing process, wounds produce a variety of fluids, generally known as wound exudate. The exudate contents may vary consisting primarily of blood and serum fluids to highly concentrated protein solutions. The amount of wound exudates must be controlled because overproduction can provide a media for bacterial proliferation or lead to maceraton of the surrounding healthy tissue. Wound dressing can help control the wound. There are two types of dressings : wet and dry. It has been reported that healing with a wet environment is faster than that with the dry environment, due to the fact that renewed skin, without the formation of eschar, forms during healing in a wet environment. Hydrogel as superabsorbent dressings were originally invented as wound burn dressings. SAPs wound dressings have many interesting properties including immediate pain control, easy replacement, transparency to allow healing follow up, absorption and loss prevention of boly fluids, barrier against bacteria, good adhesion, good handling, oxygen permeability, and control of drug release. Hydrogel produced by radiation polymerization are fully sterile. The hydrogel allows permeation of drug and oxygen to the wound being healed and sticks to healthy skin surrounding the wound but not to the newly forming dermis. Superabsorbents wound dressings are made in sheets with an impermeable polymeric backing sheet. The backing sheet prevents the partially hydrated hydrogel from dehydrating and drying onto the wound bed. Superabsorbents based on collagen, PVA, PVP, PVA/PVP, and PEO/PVA have been investigated for wound dressings. These superabsorbents can be produced in a variety of forms such as sheets, tubes, sponges and powder. It shows some properties that can meet the requirements of an ideal wound dressing. e.g. effective fluid absorption, pleasant in touch and painless on removal, exhibit a high elasticity but also good mechanical strength, good Transparency, and can act as an efficient barrier against the microbes.

### 7. Superabsorbents as Artifical Organs :

Physical properties of Superabsorbents resemble living tissue more than any other kind of synthetic biomaterials. In particular, the high water content and the soft, rubbery consistency give them a strong, superfical resemblance to living soft tissue. PHEMA and its copolymers have been used as hemodialysis membranes that act as an artificial kidney, methacrylate-co MMA), and PHEMA hydrogels. The artificial kidney works like outside the body. Some artificial kidneys incorporate living kidney cells into its design, so that it can produce important hormones, process metabolites, and provide immune functions that dialysis can not.

Recently, hydrogel membranes have been used for cell microencapsulation. Microfiltration membranes (0.5μm pore size) with neutral PAM hydrogels have been used for the separation of ribonuclease A (RNAse, 13.5 kD) and BSA (67 kD)

### 8. As Water Sealing Construction materials :

Superabsorbent polymer can be used as a water-locking construction filler with cement and asphalt emulsion. The main benifit of the fill material is its high ductility compared to conventional construction backfills such as gravel or san . These fillers can be delivered in low viscosity, which aids int the complete filling of the space. Similar principles are employed in making and using sealing compounds for electrical and optical cables.

### 9. Superabsorbents as Molecular Separation :

Temperature sensitive superabsorbents have been used to separate large molecules (eg proteins) from small molecules (eg, water). In the separation, collapsed superabsorbent (ie, below LCST) is added to the aqueous solution that is to be concentrated. Superabsorbents swells by absorbing water, and small molecular solutes, leaving larger molecules behind. After equilibrium swelling is reached, the solid Superabsorbents is physically removed from the solution. The superabsorbents is re-activated for another de-swelling use by raising the temperature a little over the LCST.

Adjusting the cross-linking density can control the pore size of the hydrogels. The technology has been studied for the separation of soy proteins, enzymes, celluloses, nonionic surfactants, lignin, and bacteria dispersions. Since most thermo-sensitive SAPs have LCST<50 °C, they require low energy to operate.

Although smart SAPs have several advantages in the separation of biomolecules over conventional methods, a number of properties (swelling rate, mechanical strength, and surface adsorption) of SAPs need to be considered or improved before large scale use.

### Other Applications :

Superabsorbents have been commonly utilized commercially in other important industrial areas such as cosmetics, food industry, photography and instrumentation. A list of some important industrial applications of polymeric superabsorbent systems are summarised as :

- Superabsorbents are used as thickening agents (e.g., starch and gelatin) in foods.
- The addition of hydrogel-forming agents to incontinence products increases the fluid uptake and ensures improved retention capacity.
- Technical and electronic instruments can be protected from corrosion and short-circuit exposure of , or sheathing with highly absorbent hydrogel-forming agents.
- Superabsorbents are used in photograpic technology because they are light permeable and can also store light sensitive substances.
- as sustained-release delivery systems

- In electrophoresis and chromatorgraphy, the separation and diffusion characteristics of the gel structure are exploited. Superabsorbents, thus applied, operate within only a very limited range of swelling.
- Currently used as scaffolds in tissue engineering. When used as scaffolds, hydrogels may contain human cells in order to repair tissue.
- Environmentally sensitive superabsorbents. These hydrogels have the ability to sense changes of pH, temperature, or the concentration of metabolite and release their load as result of such a change.
- provide absorption, desloughing and debriding capacities of necrotics and fibrotic tissue.
- hydrogels (superabsorbents) that are responsive to specific molecules, such as glucose or antigens can be used as biosensors as well as in DDS.
- used in disposable diapers where they "capture" urine, or in sanitary napkins
- contact lenses (silicone hydrogels, polyacrylamides)
- medical electrodes using hydrogels composed of cross linked polymers (polyethylene oxide, polyAMPS and polyvinylpyrrolidone)
- Water gel explosives
- hydrogel as breast implants
- granules for holding soil moisture in arid areas
- dressings for healing of burn or other hard-to-heal wounds. Wound gels are excellent for helping to create or maintain a moist environment.
- reservoirs in topical drug delivery; particularly ionic drugs, delivered by iontophoresis (see ion exchange resin)

# *Chapter – 3:* Literature Survey

## 3.3 Polymerisation Techniques :

The polymerisation techniques could be carried out using a variety of curing processes such as thermal, redox and radiation methods. Thermal polymerisation techniques involves the use of heat in the presence of a suitable initiator while the redox method simply involves reduction-oxidation reaction between the participating species. Radiation sources commonly utilized by researchers to synthesize polymeric hydrogels include low energy ultraviolet (UV) radiation technique and high-energy ionisation techniques such as gamma radiation and electron beam radiation. The use of UV curing is a field of growing interest. However, the only drawback in this curing method is the use of chemical initiators. Gamma radiation technique does not require the inclusion of chemical initiator of any sort. To minimize use of chemical it is important to develop technology based on gamma radiation.

Poly(acrylic acid) is prepared by all techniques. Crosslinked Poly(acrylic acid), PAA is produced in abundance because this polymer can absorb a large quantity of water this remarkable property has found applications in different domains such as medicine, agriculture, the construction industry, optical fibers for communication cables, humidity control, and fire fighting agents. It was only in the early 1980s that this polymer with superabsorbent properties was introduced into the Japanese market and used in the manufacturing of baby diapers. The final form of the polymer and its field of application determine the method used for its production. These techniques differ from each other in their processing.

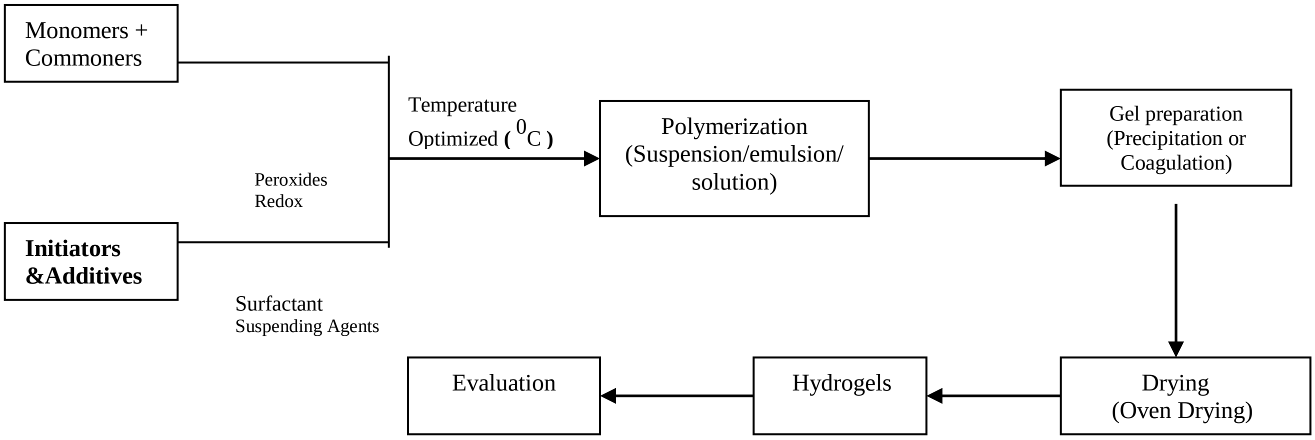
In this research work we have carried out the following polymerisation techniques :

- Thermal polymerization :
    1. Suspension Polymerisation
    2. Emulsion Polymerisation
    3. Bulk Polymerisation

- Radiation Polymerisation :
    1. Gamma radiation polymerization

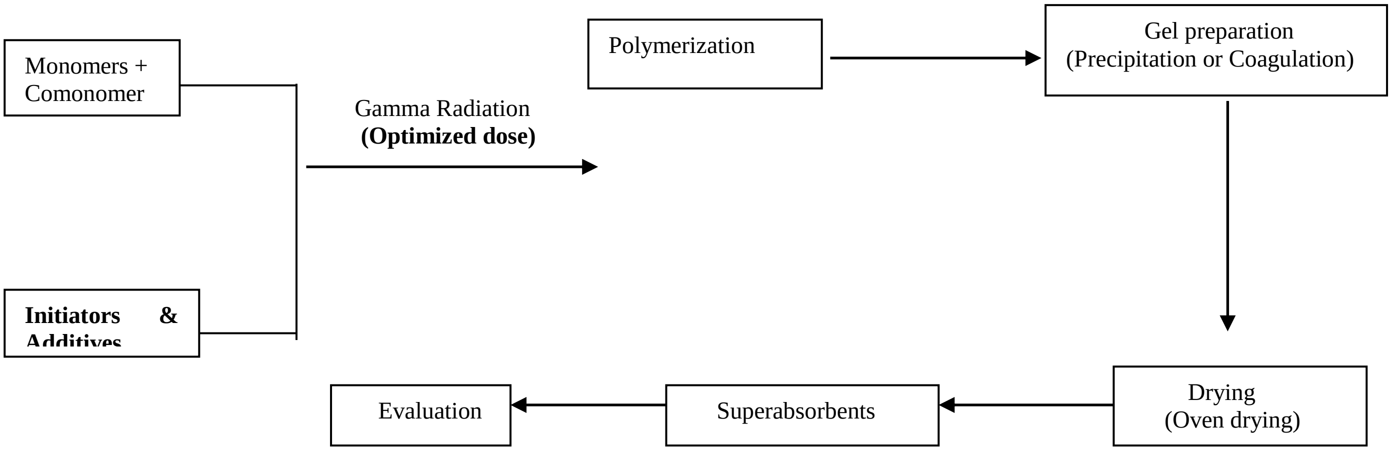
### Thermal Polymerization Process

Thermal polymerization will be carried out using heat with thermal initiators :



### Gamma radiation polymerization

This polymerization is carried out by using Gamma radiation without using initiators. The sources of Gamma radiation will be Co $^{60}$



These techniques are being explained as :

### 3.3.1 Radiation Polymerisation:

It is important for synthetic materials, to be biocompatible and nontoxic in order for it to be a useful biomedical polymer. Most polymers used for biomedical application must pass a cytotoxicity and in-vivo toxicity tests. Most toxicity problems associated with hydrogels as superabsorbents arise due to unreacted monomers, oligomers and initiators that leach out during application. Thus an assessment of the potential toxicity of all materials used for fabrication of gel is an integral part of determining suitability of the gel for biological applications. To lower chances of toxic effects, the use of initiators is being eliminated, with the advent of gamma irradiation as polymerization technique. Radiation polymerization need not to eliminate contaminants from SAP, by repeated washing and treatment. This polymerization technique results in higher conversion rates, and avoid unreacted monomers

Radiation, is energy in the form of waves or moving subatomic particles. Electromagnetic (EM) radiation, also called light, even though it is not always visible, is a self-propagating wave in space with electric and magnetic components. These components oscillate at right angles to each other and to the direction of propagation, and are in phase with each other. Electromagnetic radiation is classified according to the frequency of the wave. These include, in order of increasing frequency, radio waves, microwaves, terahertz radiation, infrared radiation, visible light, ultraviolet radiation, X-rays and gamma rays.

Electromagnetic waves can be imagined as a self-propagating transverse oscillating wave of electric and magnetic fields.

*Table 1 Electromagnetic radiations.*

| Serial No. | Type | Wavelength Range | Generation | Detection |
|---|---|---|---|---|
| 1. | X-Rays | 0.006-1019 | Emitted by sudden stopge of fast moving electrons | • Photographic<br>• Phosphorescence<br>• Chemical action<br>• Ionization |

|  |  |  |  |  |
|---|---|---|---|---|
|  |  |  |  | • Photoelectric action<br>• Diffraction by crystals |
| 2. | Gamma rays | 0.001-1.4 | Emitted when atomic nuclei disintegrate ( Radioactivity) | As for X-Rays but more penetrating |
| 3. | UV-Rays | 136-3900 | Radiation from very hot bodies and emitted by ionized radiation | Same as X-Rays as reflected refracted by final grating |
| 4. | Visible rays | 3900-7700 | Radiation from hot bodies and emitted by ionized gases | Sensation of light same as ultraviolet |
| 5. | IR-Rays | 7700 - 4x10 ^ 6 | Heat radiation | Heating effect on thermocouple .bolometer etc. Rise in temperature of receiving body . |
| 6. | Solar radiation | 2960-53000 |  | Limited wavelength Reaching earth |
| 7. | Radio wave | 1x10^11-3x10^14 | Spark gas discharge Oscillation triode valve | Coherer ,spark across minute gaps in resonant receiving circuit. Reflected ,refracted ,diffraction |
| 8. | Electric waves | 3x10^14-3.5x10^16 | Coil rotating in magnetic field | Mechanical, Electrical, Thermal effect of alternating current |
| 9. | Broadcasting band | 2x10^12-5.5x10^12 | Same as radio waves | Same as radio waves |

**Gamma Rays:**

Gamma rays (denoted as $\gamma$) are one of the three types of natural radioactivity. Gamma rays are electromagnetic radiation, like X-rays. The other two types of natural radioactivity are alpha and beta radiation, which are in the form of particles.

Gamma rays are the most energetic form of electromagnetic radiation , these are generally characterized as electromagnetic radiation having the highest frequency and energy, and also the shortest wavelength less than one-tenth of a nanometer. Gamma radiation is the product of radioactive atoms.

**Gamma Rays production:**

A nucleus which is in an excited state may emit one or more photons (packets of electromagnetic radiation) of discrete energies. The emission of gamma rays does not alter the number of protons or neutrons in the nucleus but instead has the effect of moving the nucleus from a higher to a lower energy state (unstable to stable).

Gamma rays are often produced alongside other forms of radiation such as alpha or beta. When a nucleus emits an α or β particle, the daughter nucleus is sometimes left in an excited state. It can then jump down to a lower level by emitting a gamma ray in much the same way that an atomic electron can jump to a lower level by emitting visible light or ultraviolet radiation.

Gamma rays, x-rays, visible light, and radio waves are all forms of electromagnetic radiation. The only difference is the frequency and hence the energy of the photons. Gamma rays are the most energetic. An example of gamma ray production follows.

First $^{60}$Co decays to excited $^{60}$Ni by beta decay:

$$^{60}\mathrm{Co} \rightarrow {}^{60}\mathrm{Ni}^{*} + e + V\mathrm{e}$$

Then the $^{60}$Ni drops down to the ground state (see nuclear shell model) by emitting two gamma rays in succession:

$$^{60}\mathrm{Ni}^{*} \rightarrow {}^{60}\mathrm{Ni} + \gamma$$

Gamma rays of 1.17 MeV and 1.33 MeV are produced.

**Irradiator Used :**

a) The radiation source is housed in a pool of demineralised water of capacity 25000, lts. In the cell area around the wall of 1.6 meter thick concrete.

b) Product movement

An automatic system which conveys the samples into the irradiation cell through labyrinth where boxes are exposed to the radiation for a specific time and are brought out automatically.

The products to be sterilized are packed in standard corrugated card board cartoons . these cartoons are loaded in carriers ,having five shelves .each carrier travels at a controlled speed on an over head mono rail ,enters the irradiation cell through a labyrinth, passes each side of the source twice and return through the labyrinth ,passes each side of the source twice; ensuring exposure of the samples to a required dose .

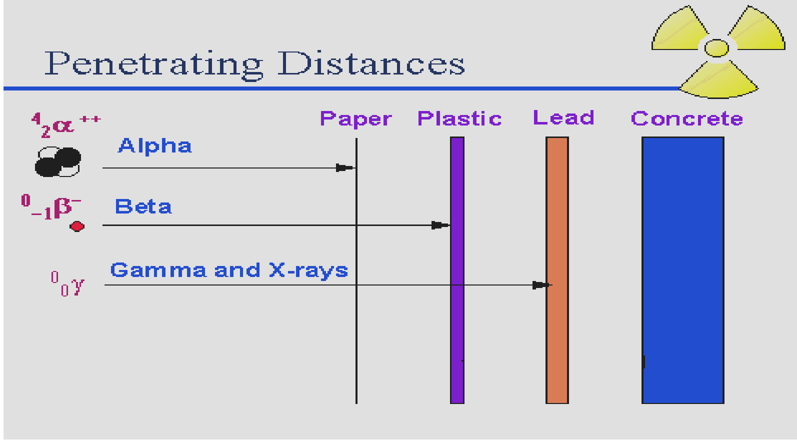


*Figure 3. Penetration power of different particles.*

**Advantages of Radiation Polymerisation** :

- Radiation-induced polymerization has advantages in easy process control, speed of cure, reversibility, simplicity of operation, high purity, sterilization, no necessity of initiators and/or crosslinkers
- An important advantage of radiation processing in immobilization of bioactive materials is that the substrated are not exposed to high temperatures; most bioactive materials are heat-sensitive
- Applications of the technique include the formation of protective coatings on materials, an alternative method of laminating paper materials, methods of consolidating fragile surfaces, plus several other uses in painting conservation.

**Disadvantages of Radiation Polymerisation :**

- Radiation Polymerisation is not easy due to unavailability of radiation plant everywhere.
- Radiation techniques are expansive

## 3.3.2 Thermal Polymerisations :

Thermal polymerisation techniques involves the use of heat in the presence of a suitable initiator. Different thermal polymerization techniques are being described below :

### 3.3.2.1 Suspension Polymerisation:

Suspension polymerisation ( also known as pearl polymerization, bead polymerization and granular polymerisation) is a polymerization process that uses mechanical agitation to mix the monomer or mixture of monomers in a liquid phase such as water, polymerizing the monomer droplets while they are dispersed by continuous agitation. This process is used in the production of most PVC, a widely used plastic, as well as Sodium polyacrylate, a superabsorbent polymer used in disposable nappies (diapers).

In suspension polymerisation a monomer or mixture of monomers is dispersed by strong mechanical agitation into droplets suspended in a second liquid phase in which both monomer and polymer are essentially insoluble. The monomer droplets, which are larger than those in a true emulsion, are then polymerized while dispersion is maintained by continuous agitation.

**Inverse Suspension Polymerisation :**

Crosslinked poly(acrylic acid) was synthesized by inverse suspension plymerization.. An aqueous phase containing partially neutralized acrylic acid, crosslinking agent, and initiator agent was dispersed in an organic phase and stablized by a surfactant. The inverse suspension polymerisation was carried out in heptane as the organic phase with a partially neutralized monomer as aqueous phase, and several stirring speeds. The polymerization was initiated by potassium persulfate ($K_2S_2O_8$) as the crosslinker with N-N'-methylenebisacrylamide (MBAc) as the crosslinker and SPAN-80 as the surfactant. The kinetics results obtained by differential scanning calorimetry showed that conversion and polymerization rates are a function of the solution pH, and they fell when the concentration of the crosslinking agent was higher than 7.5% in the mass of MBAc.

In this process, the aqueous phase containing the monomer and the crosslinking agent is dispersed in oil containing initiator and surfactant to produced spherical particles. This form is particularly attractive for industrial applications.

**Advantages of Suspension Polymerisation :**

- Easy heat removal and control
- The polymer is obtained in a convenient, easily handled and often directly useful form

**Disadvantages of Suspension Polymerisation** :

- Surfactants and other polymerization adjuvants remain in the polymer or are difficult to remove
- Low yield per reactor volume
- Somewhat less pure polymer than bulk polymerisation, since there are bound to be remnants of the suspending agent(s) absorbed on the particle surface
- For dry (isolated) polymers, water removal is an energy-intensive process
- It cannot be used to make condensation polymers or for ionic or Zieler-Natta polymerisation (anything which reacts with water). Some exceptions are known

### 3.3.2.2 Emulsion Polymerisation :

As in the case of suspension polymerisation, in emulsion polymerisation also, the monomer is dispersed in the aqueous phase not as discrete droplets, but as a uniform emulsion. The emulsion is stabilised by surface active agents (surfactants), protective colloids. The surfactants can be anionic (alkali salts of fatty acids and of aryl and alkyl sulfonic acids), cationic (alkyl amine hydrochlorides and alkyl ammonium halides) or non-ionic (alkyl glycosides and saccharose esters of fatty acids). Surfactants serve the purpose of lowering the surface tension at the monomer-water interface and facilitate emulsification of the monomer in water.

Monomer solubility in water : Only slightly soluble

Initiators : Water soluble persulphates and per-oxides;

Place of initiation of polymerisation : In aqueous solution or in miscelle surfaces.

Emulsion Polymerisation is a type of radical polymerization that usually starts with an emulsion incorporating water, monomer, and surfactant. The most common type of emulsion polymerization is an oil-in-water emulsion, in which droplets of monomer (the oil) are emulsified (with surfactants) in a continous phase of water. Water-soluble polymers, such as certain polyvinyl alcohols or hydroxyethyl celluloses, can also be used to act as emulsifiers/stablizers. Here, in the emulsion polymerisation technique, the monomer is only slightly soluble, e.g. styrene, acrylic and methacrylic esters, vinyl chloride.

But acrylic acid is water-soluble, this means here an oil in water emulsion is not possible. Thus emulsion polymerisation is not feasible.

### Inverse Emulsion Polymerisation :

An aqueous solution of the hydrophilic monomer such as acrylic acid is dispersed in a continuous lipophilic medium using surfactants, which promote the formation of a water-in-oil (W/O) emulsion. The water-in-oil (W/O) emulsion polymerisation process has superior characteristics such as the low viscosity of the dispersion, easy removal of the reaction heat and the high molecular wight of the obtained polymer *etc*. And it is attractive to investigate the reaction system because the polymerization process is also prospective to prepare particles in nano-scale.

### Advantages of Emulsion Polymerisation :

- High molecular weight polymers can be made at fast polymerization rates. By contrast, in bulk and solution free radical polymerization, there is a tradeoff between molecular weight and polymerization rate.
- Easy to heat removal and control.
- The continuous water phase is an excellent conductor of heat and allows the heat to be removed from the system, allowing many reaction methods to increase their rate.
- Since polymer molecules are contained within the particles, viscosity remains close to that of water and is not dependent on molecular weight.
- The final product is obtained in a convenient, easily handled and can be used as is and does not generally need to be altered or processed.
- Inverse phase (water in oil) emulsion is possible

### Disadvantages of Emulsion Polymerisation :

- Surfactants and other polymerization adjuvants remain in the polymer or are difficult to remove
- Low yield per reactor volume

- Somewhat less pure polymer than bulk polymerisation, since there are bound to be remnants of the suspending agent(s) absorbed on the particle surface
- For dry (isolated) polymers, water removal is an energy-intensive process
- It cannot be used to make condensation polymers or for ionic or Zieler-Natta polymerisation (anything which reacts with water). Some exceptions are known

## 3.3.2.3 Bulk Polymerisation :

Here, the monomer is taken in the liquid state and the initiator is dissolved in the monomer. The chain transfer agent, whenever used to control the molecular weight, is also dissolved in the monomer itself. The whole system is heated for initiating the polymerisation and is kept under agitation for proper mass and heat transfers.

**Advantages of Bulk Polymerisation :**

1. Bulk polymerisation is quite simple and the product obtained has a high purity since, except the Initiatior and the chain transfer agent, no other additive that could contaminate the product is used.

2. The polymer obtained can also be used as such since no isolation from other components is involved.

**Disadvantages of Bulk Polymerisation :**

1. As the polymerisation proceeds, the viscosity of the medium increased and mixing becomes progressively difficult, leading to products with very broad molecular weight distribution.

2. As the medium gets viscous, the diffusibility for the growing polymer chains becomes restricted, the probability of chain collision becomes less, termination becomes difficult, active radical sites accumulate and the rate of polymerisation increased enormously. This whole phenomenon is called ‘autoacceleration’ and sometimes, the uncontrolled exothermic reaction can lead to an explosion.

# *Chapter – 3: Material Uesd*

During the past decade, we focused on special types of SAPs i.e. lightly crosslinked networks with high water absorption capacity (Superabsorbent polymers). Recently, we modified SAPs via incorporating natural materials to improve the cost of the product and biodegradable.

In our study we used two types of material in the synthesis of superabsorbent polymers – synthetic one (Acrylic acid) and natural one (Gum Arabic)

## 3.1 Acrylic Acid:

Acrylic Acid is known as propenoic acid in IUPAC nomenclature , it is a simple vinylformic acid. It is an important industrial chemical chiefly used to produce its polymer, polyacrylic acid (PAA).

$$CH_2 = CH - COOH$$

**Acrylic acid** or **prop-2-enoic acid** is a chemical compound (formula $C_3H_4O_2$) and it is the simplest unsaturated carboxylic acid with a vinyl group at the α-carbon position and a carboxylic acid terminus. In its pure form, acrylic acid is a clear, colorless liquid with a characteristic acrid odor. It is miscible with water, alcohols, ethers and chloroform. Acrylic acid is produced from propene, a gaseous product of oil refineries.

Acrylic acid and its esters readily combine with themselves or other monomers (e.g amides, acrylonitrile, vinyl, styrene and butadiene) by reacting at their double bond, forming homopolymers or copolymers which are used in the manufacture of various plastics, coatings, adhesives, elastomers as well as floor polishes and paints. It is now mostly used for the production of superabsorbents

### 3.1.1 Safety

Acrylic acid is severely irritating and corrosive to the skin. Eye contact can result in severe corneal burns and may result in irreversible injury. Inhalation of vapors may cause irritation to the respiratory tract, drowsiness or headache, although simply smelling the monomers does not mean you are being exposed to a hazard (air monitoring is necessary to determine exposure). The odor is described as pungent and acrid. Low exposure will cause minimal or no health effects, while high exposure could result in pulmonary edema.

### 3.1.3 Properties of acrylic acid

Acrylic acid have the different physical properties :

| | |
|---|---|
| Molecular formula | $CH_2$=CHCOOH |
| Molar mass | 72.06 g/mol |
| Appearance | Clear, colorless liquid |
| Density | 1.051 g/mL, liquid |
| Melting point | 12 °C (285 K; 54 °F |
| Boiling point | 139 °C (412 K; 282 °F) |
| Solubility in water | Soluble |

## 3.2 Gum Arabic

Gum Arabic is a water-soluble gum obtained from several species of the acacia tree, especially Acacia senegal and A. arabica, in the bark of the tree. Gum arabic is a complex and variable mixture of arabinogalactan oligosaccharides, polysaccharides and glycoproteins

Gum arabic consists of a mixture of lower molecular weight polysaccharide (M.Wt.. ~$0.25x10^6$; major component) and higher molecular weight hydroxyproline-rich glycoprotein (M.Wt. ~$2.5x10^6$ minor component)but with wide variability between commercial samples. Because it is a mixture and the material varies significantly with source, the exact molecular structures are still rather uncertain.

### 3.2.2 Safety

Gum Arabic is the amber, amorphous, odorless, colorless, tasteless and nontoxic to health. Although gum arabic function is based primarily on its properties as a protective colloid and emulsifier, its unique characteristics is usually due to its comparatively very low viscosity.

### 3.2.3 Application :

- Gum Arabic, naturally originated polysaccaride is used for synthesizing hybrid SAPs which are biodegradable. Such biodegradable SAPs are widely used for drug delivery, tissue engineering and other medical purposes

- The simultaneous presence of hydrophilic carbohydrate and hydrophobic protein enables its emulsification and stabilization properties.
- As a food additive, it is a useful if rather expensive hydrocolloid emulsifier, texturizer and film-former, widely used in the drinks industry to stabilize flavors and essential oils, for example in soft drink concentrates. .
- Gum arabic is used in confectionery such as traditional hard (wine) gums, pastilles and as a foam stabilizer in marshmallows.used in the manufacture of adhesives and ink, and as a binding medium for marbling colors.

# *Chapter – 4:* EXPERIMENTAL WORK

Acrylic acid is synthetic material. Thus, the developed Na-polyacrylate as SAP is purely synthetic which is not of vital importance. There has been always been research over for making SAPs which are biodegradable in nature and thus biocompatible and nontoxic in order to be a useful biomedical polymer with human body for drug delivery, tissue engineering etc. Here keeping this in mind, we have prepared SAP as copolymer by using Gum Arabic as natural monomer and acrylic acid as synthetic materal for making biodegradable SAP, by using Thermal polymerization techniques

Most polymers used for biomedical application must pass a cytotoxicity and in-vivo toxicity tests. Most toxicity problems associated with hydrogels as superabsorbents arise due to unreacted monomers, oligomers and initiators that leach out during application. Thus an assessment of the potential toxicity of all materials used for fabrication of gel is an integral part of determining suitability of the gel for biological applications. To lower chances of toxic effects, the use of initiators should be eliminated. This is possible by using gamma irradiation as polymerization technique. Radiation polymerization need not to eliminate contaminants from SAP, by repeated washing and treatment. This polymerization technique results in higher conversion rates, and avoid unreacted monomers

## Thermal Polymerisation :

### 4.1 Synthesis of SAPs by Suspension Polymerisation:

**Chemicals used :**

i ) Acrylic Acid as synthetic monomer (AA)
ii) Gum Arabic as natural monomer
iii) NaOH solution
iv) N,N'methylene bis acrylamide as Crosslinker (MBAc)
v) $K_2S_2O_8$ as Initiator
vi ) SPAN-80 as Surfactant

**Equipment used :**

i ) Five necked round bottom flask
ii) $N_2$ gas Cylinder

## Polymerisation Procedure:

Polyacrylic acid has been prepared by free radical polymerisation of acrylic acid. Polymerisation of acrylic acid was carried out in a 500 ml five necked round bottom flask fitted with a gas inlet tube, dropping funnel, thermometer pocket, reflux condenser and a mechanical stirrer, Figure 4.

## Aqueous Phase

29 ml of acrylic acid was partially neutralized drop by drop by adding aqueous NaOH, the reaction is kept cool to prevent an exothermic reaction and from acrylic acid precipitation. The partial neutralization degree is defined as

$$\alpha = n_b / n_a,$$

where na and nb are the number of moles of AA and of NaOH, respectively. A defined amount

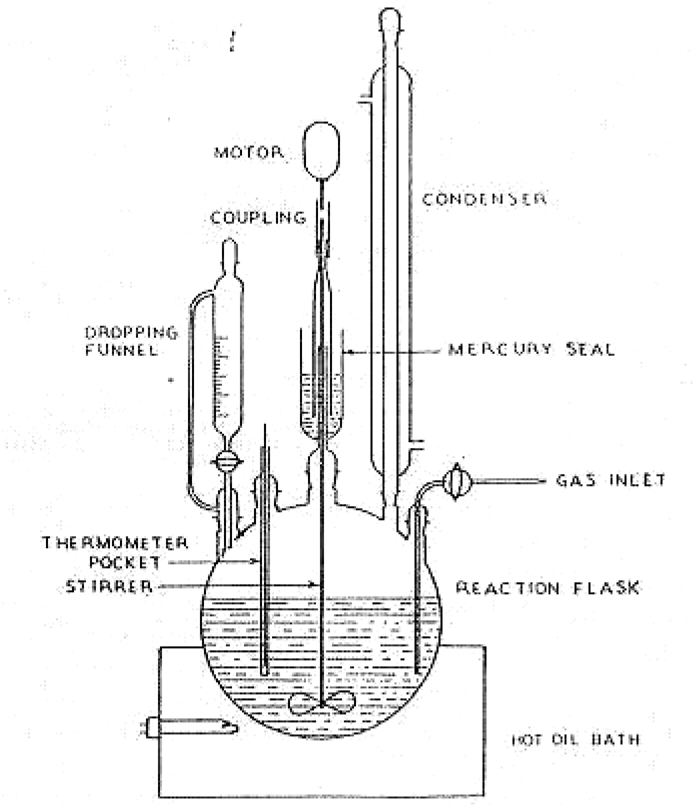


**Figure 4. Lab Scale Polymerisation Assembly** (Synthesis of Sodium Polyacrylates)

MBAc (0.2% mass of the aqueous phase, Aldrich) was dissolved in the solution and the clear mixture obtained was degased by nitrogen bubbling for about 30 min.

**Organic Phase**

The surfactant SPAN 80 (Aldrich) was dissolved in heptane in five necked round bottom flask. A defined amount of $K_2S_2O_8$ (1% mass of the aqueous phase, Aldrich) was added after 15 min of nitrogen bubbling, this phase was heated to 65 °C and reactor stirred at 600 rpm.

Now the aqueous phase was added drop wise and the agitation was constantly agitated for 30 min. At the end the temperature was increased to 78 °C and maintained for 2-3 hr to consume all the monomer. During the reaction the viscosity of the medium increased and the color changed from opaque to milky. At this temperature, probably, a phase inversion occurs and the aqueous phase becomes the continuous phase. At the end of the reaction stirring was stopped and two phases were observed.

The liquid constituted of heptane was at the top of the reactor and the aqueous suspension of PAA particles was at the bottom.

The particles were recovered by methanol precipitation. After drying under a primary vacuum at 40 °C, a powder was obtained, then characterized this by different parameter i.e. % water absorbance, retention capacity, pH behavior, gel content and TGA .

## 4.2 Synthesis of SAPs by Emulsion Polymerisation :

An aqueous phase of the hydrophilic monomer such as acrylic acid is dispersed in a continuous lipophilic medium using surfactants, which promote the formation of a water-in-oil (W/O) emulsion. The water-in-oil (W/O) emulsion polymerisation process has superior characteristics such as the low viscosity of the dispersion, easy removal of the reaction heat and the high molecular wight of the obtained polymer *etc*. And it is attractive to investigate the reaction system because the polymerization process is also prospective to prepare particles in nano-scale.

**Procedure :**

The continuous lipophilic phase consisted of $CCl_4$ and co-emulsifiers of Span 80 (sorbitan monooleate)-Tween 80 ( polyethyleneglycolsorbitan monooleate) with AIBN as initiator was used. For the aqueous phase acrylic acid neutralized with sodium hydroxde (the degree of neutralization was 90%) is mixed with definite amount of Gum Arabic. 1% crosslinking agent N,N'-methylene-bis acrylamide is also added. Then both phases are mixed yielding a W/O emulsion with 70% lipophilic and 30% hydrophilic phase. Stirred the reaction at 600 rpm at 65 °C for 2 hrs. After completion of the reaction it is cooled to room temperature for 15 min, the particles were isolated by centrifugation, washed several times with methanol, and then dried in a vacuum oven at 45 °C to remove residual water.

## 4.3 Synthesis of SAPs by Bulk Polymerisation :

In bulk polymerization technique partially firstly neutralized acrylic acid monomer is mixed with aqueous solution of Gum Arabic and then initiator is dissolved in the monomers. The cross-linking agenti i.e. MBA is also dissolved in the monomer system itself. The system is purged with $N_2$ gas for 15 minutes. The whole system is then heated at 65 °C with continuous agitation for initiating the polymerisation. At the end of polymerisation the mixture gets viscous At this stage it is transferred to the container and is dried in vaccum oven for 2 hrs.

The SAP thus obtained is grind for homogeneous size distribution and sieved through 200 microns sieve. Finally, synthesized SAPs are kept in dessicator till their characterisations.

## 4.4 Synthesis of SAPs by Gamma radiation polymerization :

Radiation polymerization was carried out by using Gamma radiation without using initiators. The sources of Gamma radiation used was, cobalt-60, $Co^{60}$.

In this synthetic monomer, Acrylic acid (29 ml) neutralized with 52ml aqueous solution of NaOH (10gm in 52ml of distilled water) and natural monomer, Gum Arabic in different proportions ( 2.5gm to 10.0gm in 29 ml of acrylic acid) are mixed properly and filled in 100 ml capacity glass bottles. The samples are packed in standard corrugated card board cartoons . These cartoons are loaded in carriers having shelves, each carrier travels at a controlled speed on an over head mono rail ,enters the irradiation cell through a labyrinth, passes each side of the source twice and return through the labyrinth, ensuring exposure of the samples to a required dose.

Then these bottles are then sent to radiation plant. An automatic system conveys the samples into the irradiation cell through labyrinth where bottles are exposed to the radiation for a specific time and are brought out automatically.

After irradiation, the samples get converted into gel like product. The gel are are removed from the bottles and the product is dried in oven at 60 °C for 2 hrs. These are then grinded and sieved through 200 mesh size. And the samples are stored in desiccator.

# *Chapter – 5:* CHARACTERISATION OF SUPERABSORBENTS

Synthesis of SAPs by different techniques, thermal and radiation polymerization have been carried out. But their synthesis should not be only be the ultimate aim of the project work. synthesis of SAPs by different techniques should not be the ultimate aim of the project. Thus, here we have characterized the synthesized SAPs by studying different parameters for carrying out the comparative study.

There are some characterization parameters which have been carried out in SAPs as :

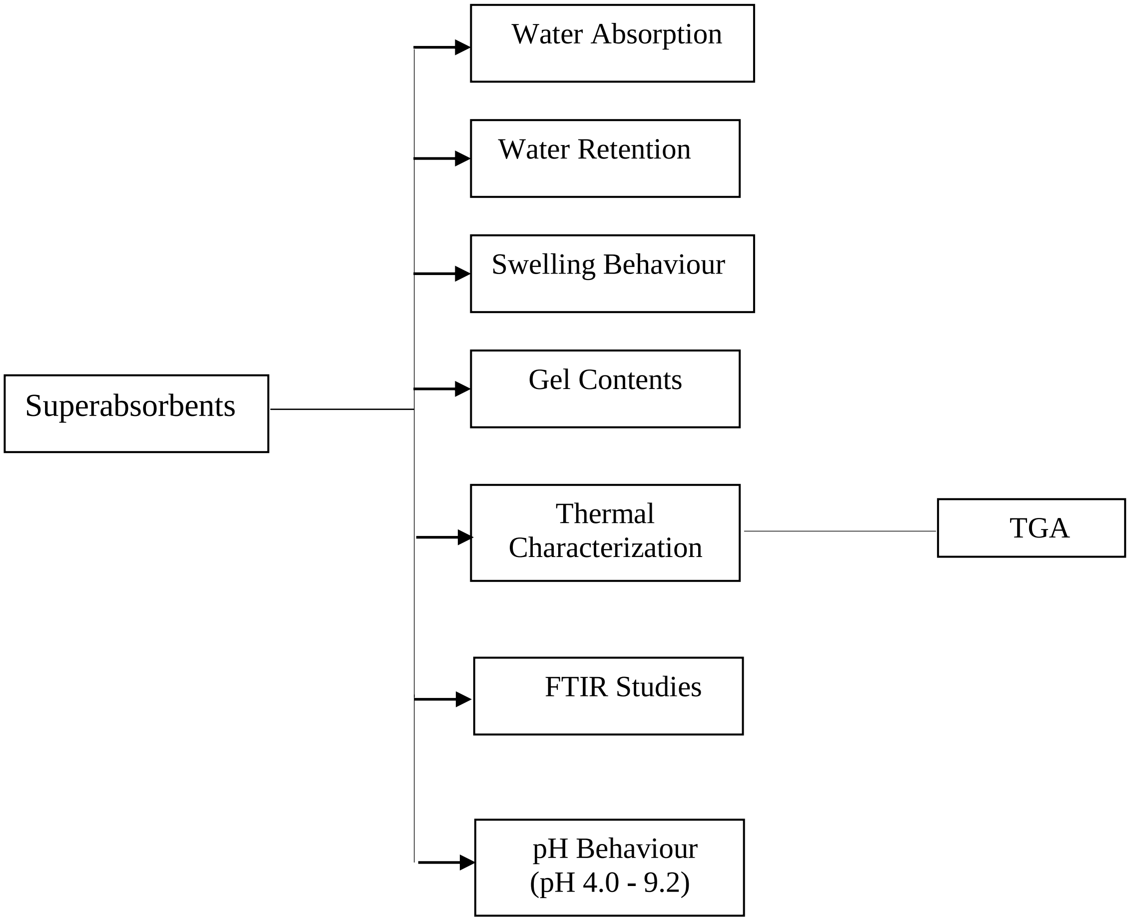


**Figure - Characterisation Chart**

### 5.1 Percentage Absorption :

The most important property of superabsorbents is the ability to imbibe water i.e. swelling. This is the internal property of the SAPs. A high water content is generally considered favorable for being used as biocompatible. In case of hydrogels as superabsorbent, diffusion is the main mechanism of transport of the solute and this mass transfer is achieved by the swelling of the gel. As the gel swells, the cross linked chains widen, thus increasing the mesh size and allowing solute transfer to take place from the gel. Increased swelling means larger mesh size and vice-versa. Thus increased swelling results in better drug transfer in the blood. Swelling can be measured in terms of percentage absorption.

**Procedure**

Approximately 0.2gm of sample is weighed to an accuracy of not less 0.01g in tea bags. The sample is then submerged horizontally in distilled water and other solutions maintained at the same temperature, 25 °C for approx. 30 minutes. Then after the swelled samples are taken out from the solutions carefully without touching the tea bags from the swollen sample side and excess water shall be wiped of with tissue paper. Each specimen is then reweighed to an accuracy of 0.01g.

$$\text{Water absorption (\%)} = \frac{(M_2\text{-}M_1)}{W_1} \times 100$$

Where $M_1$ is the mass of test sample before immersion, in gms and $M_2$ is the mass of test sample after immersion, in gms.

### 5.2 Centrifuge Retention Capacity (CRC) :

Centrifuge retention capacity is the amount of 0.9 wt% saline solution that a SAP can retain under free swelling conditions when surface water has been removed in a cenrifuge. Centrifuge retention capacity tells us about the % of saline water that can be retained in the SAPs after being pressurized by certain force as in baby diapers, under soil as agricultural applications

**Equipment and materials :**

1. Analytical balance accurate to 0.001 grams (with cover)
2. Paper tea bag (60mm × 85mm)

3. Large pan, approx 15cm deep and large enough to hold several tea bags, volume approx 5L
4. Weighing boat or equivalent
5. Household centrifuge or laboratory centrifuge capable to deliver a centrifugal force of 250g (1400 rpm).
6. 0.9% NaCl saline prepared with distilled or deionized water.
7. Loose superabsorbent sample

**Procedure**

1. Prepare two identical tea bags or use two pre-sealed tea bags.
2. Rotate the sample container end-over-end several times in order to obtain a representative sample.
3. Weigh 0.200 ± 0.005 g loose superabsorbent (record as $W_1$) in a weighing boat and transfer into the tea bag. Heat-seal the open end of the tea bag.

   Repeat step 3 for the second tea bag.

   Note : If it takes longer than 5 minutes to prepare the superabsorbent-containing tea bags and start the test, place the tea bags in a dessicator.

4. Fill the pan with 0.9% saline. The temperature of the saline should be consistent at about 22 ± 2 °C (this is not required if the test is being completed in a temperature and humidity controlled room).

   Note : The saline in the pan should be changed after every 6 tea bags per one liter.

5. Hold the superabsorbent-containing tea bags horizontally and distribute the superabsorbent throughout the tea bag.

6. Lay the tea bags on the surface of the saline. Allow the tea bags to hydrate for one minute before submerging completely. Assure that entrapped air bubbles are eliminated.

   Note : Plastic mesh, placed above the tea bags, may help keep the samples submerged.

7. After a soaking period of 30 minutes ( ±1 minute ), remove the bags.
8. Place the superabsorbent-containing tea bags in the centrifuge basket, in pairs. Position the tea bags in the centrifuge with each tea bag “sticking” to the outer wall of the centrifuge basket. Be

careful to evenly space the bags for proper balance when spinning ( especially important if more than two tea bags are being are being placed inside the centrifuge).

9. Close the lid to activate the centrifuge and start the timer after the first revolution. Centrifuge the tea bags for 0.3 minutes ( ± 10 seconds ) at 1400 rpm (250 g).

10. Remove the tea bags, weigh each one, and record the weights as $W_3$.
11. For each batch of tea bags that were used in the sample analysis, determine the average wet blank weigh by taking ten dry, sealed tea bags and performing steps 7-11. Record the weight of each wet tea bag and calculate the average wet blank weight ( record as $W_2$).

    **Note** : Step 12 should only be completed every time a new batch of tea bags is prepared by hand or each time a new box of pre-cut, pre-sealed tea bags is opened. The average wet blank weight can be used for all samples prepared within a given batch of tea bags.

**Calculation :**

Centrifuge Retention Capacity is calculated by formula as :

$$\text{Centrifuge Retention Capacity, ( g/g )} = \frac{(W_3 - W_2) - W_1}{W_1}$$

$W_1$ = Weight of dry sample, in grams

$W_2$ = Weight of wet blank tea bag ( after centrifugation), in grams

$W_3$ = Weight of wet superabsorbent-containing tea bag (after centrifugation), in grams

The final result is the arithmetic mean of the two measurements, provided that the difference between them is not greater than 5% of their mean value.

Reported the results with  no decimal place.

## 5.3 Gel Content % Analysis :

Gel is nothing but high molar mass polymer absorbing large percentage of water i.e. Gel is somewhat losely-bound crosslinking among chains but not too highly crosslinked, otherwise it leads to less % water absorbence.

**Procedure :**

For determining the gel content values, approx. 0.50gm of sample is taken in tea bags and dispersed in 0.90 wt % NaCl solution to swell for 72 hr. Then after it is taken out and dried at 65 °C for 5 hrs and weighed. Gel content (Gel, %) is calculated as :

$$\text{Gel content, \%} = \frac{m_f - 0.009A}{m_i} \times \mathbf{100}$$

Where, $m_i$, $m_f$ and A stand for initial weight of sample, final weight of sample, and the equilibrium swelling of the sample in the saline solution, respectively.

## 5.4 Fourier transform infrared spectroscopy (FTIR) Study :

FTIR stands for Fourier Transform Infra Red , the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through. The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. (The specimen's transmittance and reflectance of the infrared rays at different frequencies is translated into an IR absorption plot consisting of reverse peaks. The resulting FTIR spectral pattern is then analyzed and matched with known signatures of identified materials in the FTIR library). Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis. The Infrared Fourier-Transform transform (FTIR) spectrophotometry facility serves as the measurement facility for characterization of the optical properties of materials in the infrared spectral range of 1 µm to 100 µm, with particular emphasis on the 2 µm to 20 µm region.

FTIR (Fourier Transform Infrared) Spectroscopy, or simply FTIR Analysis, is a failure analysis technique that provides information about the chemical bonding or molecular structure of materials, whether organic or inorganic. It is used in failure analysis to identify unknown materials present in a specimen, and is usually conducted to complement EDX analysis.

FTIR spectroscopy does not require a vacuum, since neither oxygen nor nitrogen absorb infrared rays. FTIR analysis can be applied to minute quantities of materials, whether solid, liquid , or gaseous. When the library of FTIR spectral patterns does not provide an acceptable match, individual peaks in the FTIR plot may be used to yield partial information about the specimen.

**Applications of FTIR :**

- It can identify unknown materials
- It can determine the quality or consistency of a sample
- It can determine the amount of components in a mixture

## 5.5 Differential Scanning Calorimetry Analalysis (DSC):

Thermal characteristics are the ways of characterizing the meterials. Differential scanning calorimetry (DSC) is used to characterize materials by studying a wide range of thermal transitions in their system. More often than not DSC is used to determine melting and crystallization temperatures and thermodynamic parameters associated with these changes.

DSC measures the temperatures and heat flows associated with phase transitions in substances as a function of time and temperature. Such measurements provide important information about physical and chemical changes that involve endothermic or exothermic effects, or heat capacity changes.

In the power compensated DSC instrument used in this research, the temperatures of a sample and an inert reference material are controlled independently using two separate, identical furnaces. The temperatures of the sample and the inert reference are made identical by varying the power input of the furnaces. The instrument measures the energy needed to approaching zero temperature difference between the sample and the reference material. The heat capacity changes in the sample relative to the reference is measured by the energy required to complete the above job, as the two specimens are within the identical temperature system that changed at a controlled rate.

Since $T_{sample} = T_{reference}$, $\Delta H = k(\Delta W)$, where $\Delta H$ is the heat capacity change, k is a constant, and $\Delta W$ is the change in energy needed to keep $T_{sample}$ equal to $_{Treference}$. DSC is primarily used to characterize polymers and other organic materials, but it is also applicable for testing some inorganic materials. The table below lists the main applications of DSC :

**Main applications of DSC :**

| | |
|---|---|
| Glass transition measurements | Oxidative stability |
| Degree of Crystallinity | Specific Heat measurement |
| Melting Point | Purity measurement |
| Reaction kinetics | Quality control of raw materials |

The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more or less heat will need to flow to it than the reference to maintain both at the same temperature. Whether more or less heat must flow to the sample depends on whether the process is exothermic or endothermic. For example, as a solid sample melts to a liquid it will require more heat flowing to the sample to increase its temperature at the same rate as the reference. This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid. Like wise, as the sample undergoes exothermic processes (such as crystallization) less heat is required to raise the sample temperature. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transition. DSC may also be used to observe more subtle phase changes, such as glass transition. DSC is widely used in industrial settings as quality control instrument due to its applicability in evaluating sample purity and for studying polymer curing.

### 5.6 Thermogravimetry Analysis (TGA):

Being one of the oldest thermal analytical procedures used for the study polymeric systems, the thermogravimetry analysis is a technique of evaluating the thermal decomposition kinetics of materials by monitoring the weight loss of the sample in a chosen atmosphere (usually nitrogen or air) as a function of temperature. Not all thermal events result in a change of the sample mass: melting, crystallization, and glass transition do not exhibit a mass change, whereas desorption, absorption, sublimation, vaporization, oxidation, reduction and decomposition do. TGA is the best known for its ability to provide information on the bulk composition of compounds. The usefulness of TGA for analyzing complex systems is greatly enhanced by the ability to record simultaneously the first derivative of the weight loss, that is, the derivative of the thermo-gravimetric curve.

TGA measures the weight change in materials as a function of time and temperature. The measurements provide basic information about the thermal stability of a chemical and its composition. TGA is one of the most commonly requested thermal techniques and it is used to characterize both inorganic and organic materials, including polymers. The measurement is typically carried out on milligram size samples with a constant heating rate from 20°C to 800 °C in a nitrogen atmosphere.

**Procedure:**

A sample (2-4mg) is placed into a tarred TGA sample pan, which is attached to a sensitve micro-balance assembly. The sample holder portion of the TGA balance assembly is subsequently placed into a high temperature furnace. The balance assembly measures the initial sample weight at room temperature and then continuously monitor changes in sample weight (losses or gains) as heat is applied to the sample. TGA tests may be run in a heating mode at some controlled heating rate (5°C), or isothermally. Typical weight loss profiles are analysed for the amount or percent of weight loss at any given temperature, the amount or percent or non-combusted residue at some final temperature, and the temperatures of various sample degradation processes.

# Chapter – 6 Results and Discussion – Thermal Polymerisation:

## 6.1. Absorption % Data of SAPs (Prepared by different techniques) in different absorbing solutions :

### i. % Absorption in Distilled Water :

The variations in % water absorption of SAPs are shown in table no. 3. The values show the two trends.

Trend 1:- The % water absorption decreases with the increasing concentration of gum arabic in case of bulk polymerisation. A constant decrease has been observed when the concentrate increase for 2.5gm to 7.5gm. But the decrease is less in case of 10.0gm of gum arabic.

Trend 2:- The % water absorption increases with increase in concentration of gum arabic in case of SAP prepared by suspension and emulsion technique. Better results have been obtained in case of emulsion techniques.

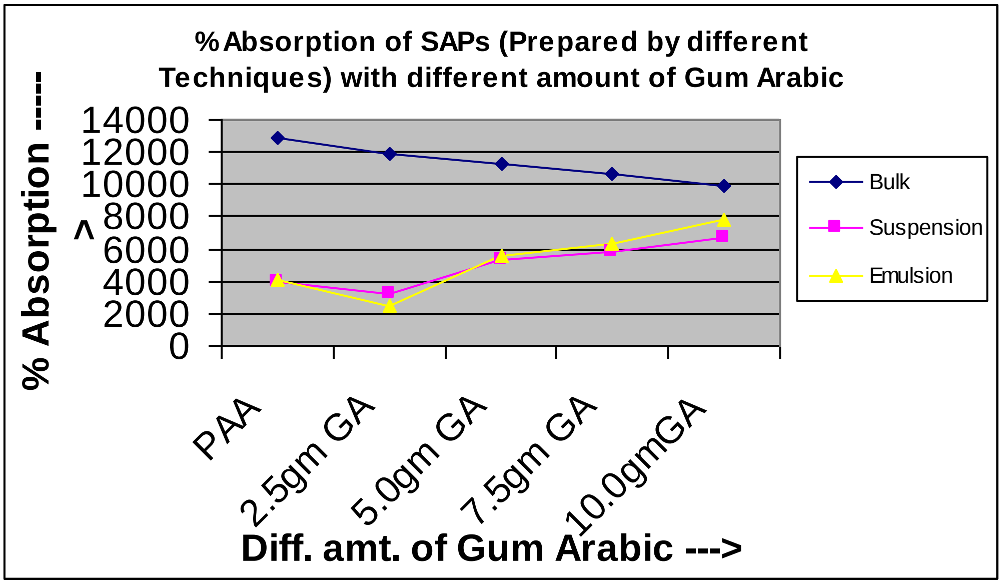
*Table No. 3 :Variation in % Absorption data of SAPs in Distilled Water prepared by Thermal Polymerisation with different amount of Gum Arabic :*

| SNo | Techniques<br>Systems | % ABSORPTIONS | | |
|---|---|---|---|---|
| | | Bulk | Suspension | Emulsion |

|  |  |  |  |  |
|---|---|---|---|---|
| 1 | PAA | 12917 | 3947 | 4128 |
| 2 | PAA (29ml) + 2.5gm GA | 11916 | 3269 | 2516 |
| 3 | PAA (29ml) + 5.0gm GA | 11266 | 5287 | 5564 |
| 4 | PAA (29ml) + 7.5gm GA | 10679 | 5852 | 6328 |
| 5 | PAA (29ml) + 10.0gmGA | 9918 | 6659 | 7847 |

These trends depicted in the table are clearly shown in the figure-5 shown below.

*Fig 5: Variation in % Absorption data of SAPs in Distilled Water prepared by Thermal Polymerisation with different amount of Gum Arabic :*

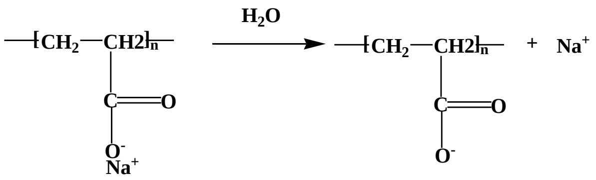


## Interpretation of Results:

The figure shows that the % absorption is highest at all concentrations of Gum Arabic in case of Bulk polymerization as compared to Suspension and Emulsion Polymerisation Techniques, this is because of the use of surfactants in emulsions and suspension polymerizations techniques.

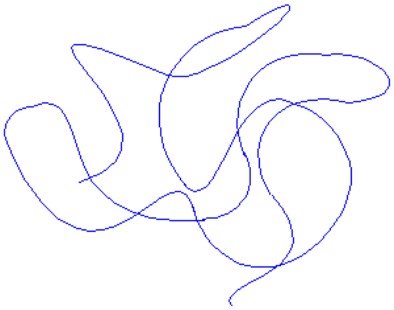
And also % absorption decreases with increase in Gum Arabic in Bulk but follows reverse trend in case of Suspension and Emulsion. This trend can be expained in terms of Gel content % achieved in SAPs with additional amount of Gum Arabic ( Gel % increases with increase in Gum Arabic % in Suspension and Emulsion Techniques while it decreases in case of Bulk Techniques and Absorption increases with increase in Gel content %). In case of emulsion and suspension the polymerisation is carried out in droplets of micelles formed. Gum arabic being polysaccharide the reaction between Gum Arabic (viscous solution in water) and acrylic acid may not be the compatible due to the less free space available for reaction accomplishment as in case of emulsion and suspension polymerization which is being carried out using solvents as a media for reaction, helping in proper alignment of monomers for gel formation easily.

But why does it swell so much in distilled water, can be explained as : Sodium polyacryalte is a type of polyelectrolyte. When it is put into water, it just breaks apart into positive and negative ions as sodium chloride.

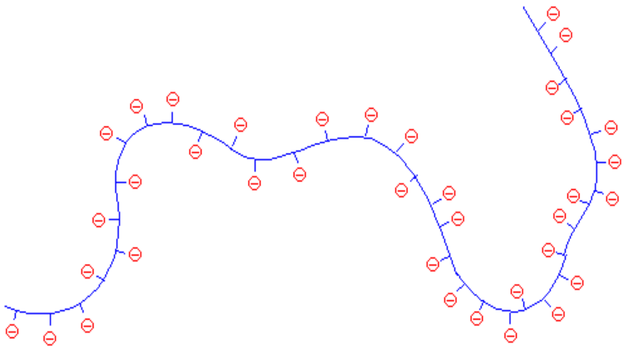


$$-[CH_2-\underset{\underset{\underset{Na^+}{O^-}}{|}}{\underset{|}{C}{=}O}{CH2}]_n- \xrightarrow{H_2O} -[CH_2-\underset{\underset{O^-}{|}}{\underset{|}{C}{=}O}{CH2}]_n- + Na^+$$

Normal uncharged polymer molecules, when they're in solution tend to be tangled up in what big shot scientists call a *random coil*,



A polymer molecule tangled in a random coil.



A polyelectrolyte expands because it's like charges repel each other

All those negative charges are going to repel each other. But when the polymer chain is covered with negative charges (which repel each other), the polymer can't be bunched in on itself. So the chain stretches out. This makes the solution (remember we're talking about polyelectrolytes *in solution*) more viscous. When the polyelectrolyte chain stretches out it takes up more space, and is more effective at resisting the flow of the solvent molecules around it. So the solution becomes thick and syrupy.

## ii. % Absorption in Saline Water :

The variations in % absorption of SAPs in saline are shown in table no. 4. The values show the two trends.

Trend 1:- The % absorption is highest in SAPs prepared by Bulk Polymerisation Technique as compared to SAPs prepared by Suspension and Emulsion Polymerisation Techniques.

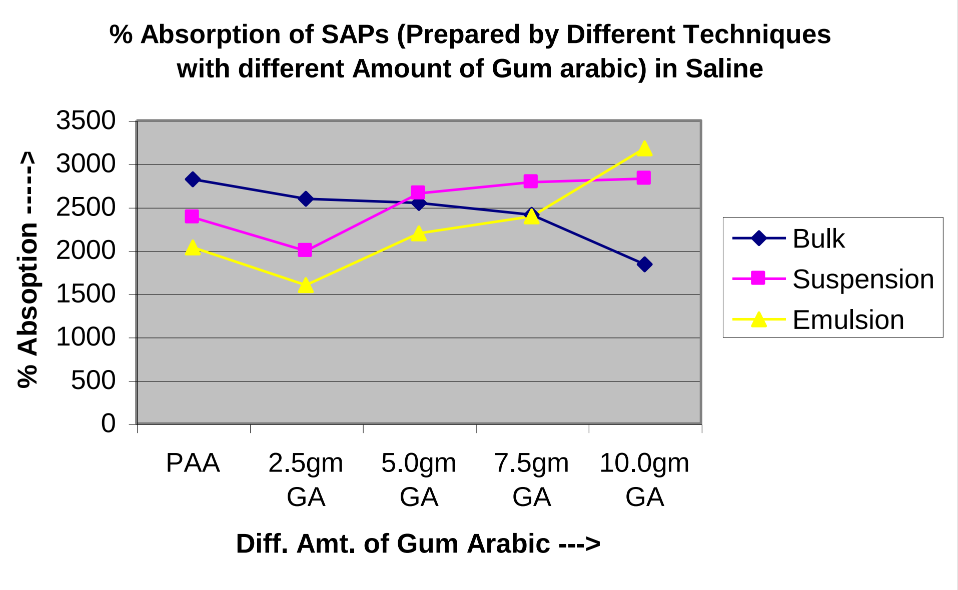
Trend 2:- The % absorption decreases in Bulk technique while it increases in case of suspension and Emulsion Polymerisation Techniques as we goes on increasing the % of Gum Arabic (from 2.5gm to 10.0gm) in SAPs

*Table No. 4 :Variation in % Absorption data of SAPs in Saline prepared by Different Techniques with different Amount of Gum Arabic :*

| SNo | Techniques / Systems | % ABSORPTIONS | | |
|---|---|---|---|---|
| | | Bulk | Suspension | Emulsion |
| 1 | PAA | 2820 | 2380 | 2035 |
| 2 | PAA + 2.5gm GA | 2596 | 1994 | 1598 |
| 3 | PAA + 5.0gm GA | 2549 | 2657 | 2197 |
| 4 | PAA + 7.5gm GA | 2411 | 2786 | 2393 |
| 5 | PAA + 10.0gmGA | 1837 | 2828 | 3179 |

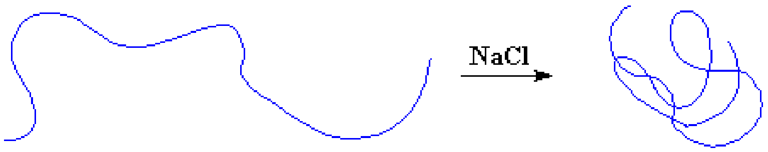
This trend can be expained in terms of Gel content % achieved in SAPs with additional amount of Gum Arabic ( Gel % increases with increase in Gum Arabic % in Suspension and Emulsion Techniques while it decreases in case of Bulk Techniques and Absorption increases with increase in Gel content %, as discussed later)

*Fig 6: Variation in % Absorption data of SAPs in Saline, prepared by Thermal Polymerisation with different amount of Gum Arabic :*



## Interpretation of Results:

If we compare the results of % absorbency in saline solution with % absorbency in distilled water, we find thd value of % absorbance is much lower in saline. This can be explained as if one take a solution of a polyelectrolyte in water, and throws in a lot of salt. The NaCl will separate into $Na^+$ and $Cl^-$ ions. In the case of a negatively charged polyelectrolyte, the positively charged $Na^+$ ions will get in between the negative charges on the polymer, and cancel them out in effect. When this happens, the polymer chain collapses back into random coil again.



Salt makes polyelectrolytes in solution collapse into random coils.

The figure again shows the % absorption is overall highest at all conc. of  Gum Arabic in case of Bulk polymerization as compared to Suspension and Emulsion Polymerisation Techniques. And also % absorption decreases with increase in Gum Arabic in Bulk but follows reverse trend in Suspension and Emulsion. This trend can be expained in terms of Gel content % achieved in SAPs with additional amount of Gum Arabic ( Gel % increases with increase in Gum Arabic % in Suspension and Emulsion Techniques while it decreases in case of Bulk Techniques and Absorption increases with increase in Gel content %, as discussed later)

### iii. % Absorption in Different pH Solutions :

The variations in % absorption of SAPs in different pH solutions are shown in table no. 5. The values show the two trends.

Trend 1:- In case of semisynthetic SAPs with gum arabic the results have shown that % absorbency decreases in case of polymer obtained by bulk technique. Better absorbency can be achieved by suspension and emulsion.

Trend 2:- Better absorbency can be achieved in alkaline medium than in acidic media in case of polymer obtained by all the techniques. Bulk polymerisation technique gives better polymer than emulsion and superior even in alkaline medium. This observation can be used for preparing drug delivery system.

*Table No. 5 :Variation in  % Absorption data of SAPs in Distilled Water prepared by Thermal Polymerisation with different amount of Gum Arabic :*

| SNo | Techniques with pH / Systems | % ABSORPTIONS | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Bulk | | | Suspension | | | Emulsion | | |
| | | pH=4 | pH=7 | pH=9.2 | pH=4 | pH=7 | pH=9.2 | pH=4 | pH=7 | pH=9.2 |
| 1 | PAA | 3904 | 4385 | 5949 | 2776 | 2853 | 2964 | 2266 | 2355 | 2421 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 2 | PAA + 2.5gm GA | 3683 | 4180 | 5668 | 2146 | 2319 | 2354 | 1755 | 1875 | 1895 |
| 3 | PAA + 5.0gm GA | 3437 | 3932 | 5370 | 2694 | 2954 | 3107 | 2482 | 2476 | 2693 |
| 4 | PAA + 7.5gm GA | 3301 | 3736 | 4220 | 2753 | 3225 | 3300 | 2632 | 2752 | 2966 |
| 5 | PAA + 10.0gmGA | 2758 | 3187 | 3770 | 2788 | 3375 | 3438 | 3460 | 3422 | 3767 |

In all pH solutions the % absorption decreases in case of polymer obtained in bulk polymerization techniques, but it decreases in bulk polymerized SAPs.

| SNo | Techniques with pH<br>Systems | % ABSORPTIONS | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | pH=4 | | | pH=7 | | | pH=9.2 | | |
| | | Bulk | Suspension | Emulsion | Bulk | Suspension | Emulsion | Bulk | Suspension | Emulsion |
| 1 | PAA | 3904 | 2776 | 2266 | 4385 | 2853 | 2355 | 5949 | 2964 | 2421 |
| 2 | PAA + 2.5gm GA | 3683 | 2146 | 1755 | 4180 | 2319 | 1875 | 5668 | 2354 | 1895 |
| 3 | PAA + 5.0gm GA | 3437 | 2694 | 2482 | 3932 | 2954 | 2476 | 5370 | 3107 | 2693 |
| 4 | PAA + 7.5gm GA | 3301 | 2753 | 2632 | 3736 | 3225 | 2752 | 4220 | 3300 | 2966 |
| 5 | PAA + 10.0gmGA | 2758 | 2788 | 3460 | 3187 | 3375 | 3422 | 3970 | 3438 | 3767 |

The figure-7 shows that in the starting the % absorption is maximum in SAPs prepared by Bulk polymerization as compared to Suspension and Emulsion Polymerisation Techniques in all pH solutions. As we go on increasing the amount of Gum Arabic in SAPs, % absorption goes on decreasing in case of Bulk polymerized SAPs and increasing in case of Suspension and Emulsion polymerized SAPs i.e. suspension and emulsion polymerization techniques show better results when Semisynthetic SAPs are synthesized with higher concentration of Gum Arabic This trend can be interrelated with Gel content % achieved in SAPs ( % Absoption increases with increase in Gel content %, as discussed later)

*Figure no – 7a : Variation in % Absorption data of SAPs in pH= 4 Solutions, prepared by Thermal Polymerisations with different amount of Gum Arabic :*

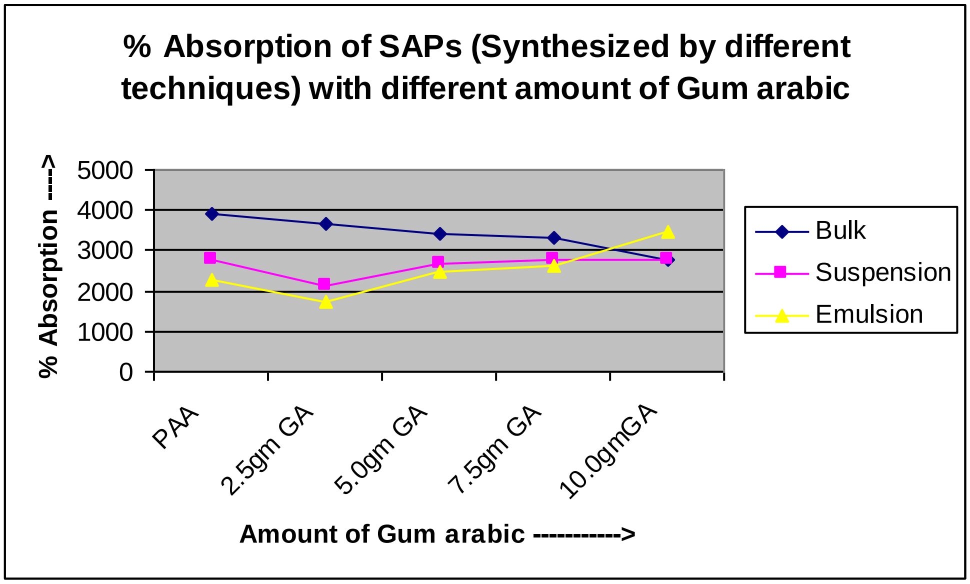
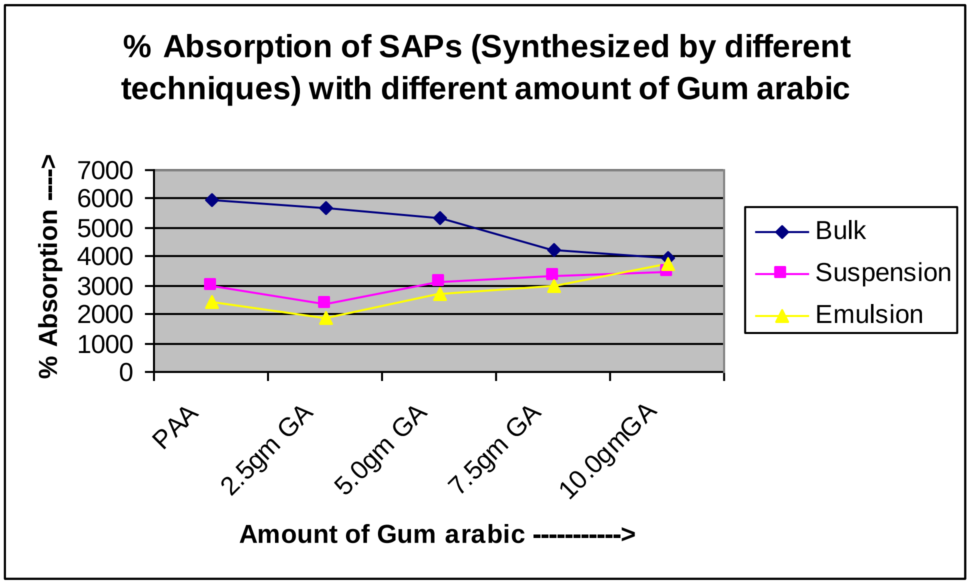


*Figure no – 7b : Variation in % Absorption data of SAPs in pH= 9.2 Solutions, prepared by Thermal Polymerisations with different amount of Gum Arabic :*



## Interpretation of Results:

If we compare the results of % absorbency in different pH solutions with % absorbency in distilled water, we find that much lower value in pH solutions as compared to distilled, actually what happens in different pH solutions can be explained with reference to ionic strength of prepared solution. The pH solutions are generally prepared by dissolving pH buffer tablets (in distilled water) which are nothing but sodium salts of different compounds i.e. pH-9.2 buffer tables are mainly di-sodium tetraborates, pH-7.0 buffer tablets are combination of different salts - Sodium phosphate, dibasic; potassium phosphate, monobasic; sodium chloride and so on. Distilled water is lacking in ionic strength as compare to pH-solutions. Ionic strength can be measured from conductivity meter. Higher the conductivity, higher the ionic strength and vice-versa.

Conductivity of distilled water, at 25 °C = $3.4 \times 10^{-3}$ mv/cm$^3$
Conductivity of pH - 4.0 solution, at 25 °C = 3.4 mv/cm$^3$
Conductivity of pH - 7.0 solution, at 25 °C = 7.2 mv/cm$^3$
Conductivity of pH - 9.2 solution, at 25 °C = 3.2 mv/cm$^3$

This shows that conductivity of pH solutions is1000 times or much higher than distilled water. Thus it can be concluded that pH solutions are having too much ionic strength as in saline solutions leading to higher conductivity as compared to distilled water (lacking in ions).

This explains the high % absorbency in distilled water as compared to different pH solutions, having comparable % absorbency.

## 6.2. Retention Data of SAPs (Prepared by Thermal Polymerisation) in different absorbing solutions :

### i. Retention % in Distilled Water:

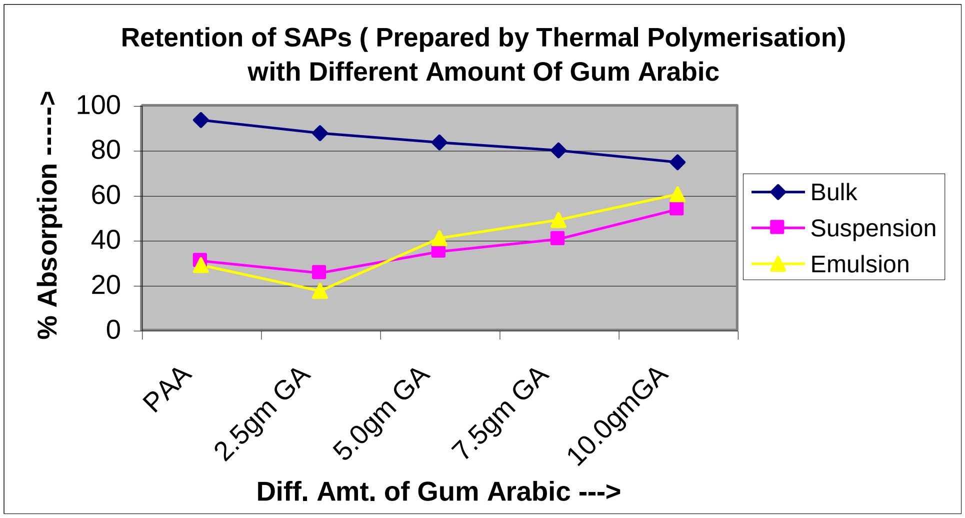
The % water retention decreases with the increasing concentration of Gum arabic in case of bulk polymerisation techniques.

In case of emulsion and suspension polymerisation techniques, synthetic SAPs has around 30 % water retention but firstly when we add 2.5 % gum arabic, then water retention decreases but further increase in gum arabic quantity results in increase of water retention.

Table no - 6 : *Variation in Retention data of SAPs in distilled water prepared by Thermal Polymerisation with different amount of Gum Arabic*

| SNo | Techniques / Systems | Retention | | |
|---|---|---|---|---|
| | | Bulk | Suspension | Emulsion |
| 1 | PAA | 93.39 | 30.70 | 28.87 |
| 2 | PAA + 2.5gm GA | 87.57 | 25.34 | 17.41 |
| 3 | PAA + 5.0gm GA | 83.48 | 34.95 | 40.86 |
| 4 | PAA + 7.5gm GA | 79.89 | 40.44 | 48.98 |
| 5 | PAA + 10.0gmGA | 74.62 | 53.69 | 60.40 |

*Fig 8 : Variation in Retention of SAPs in distilled water prepared by Thermal Polymerisation with different amount of Gum Arabic*



## ii. Retention % in Saline Water:

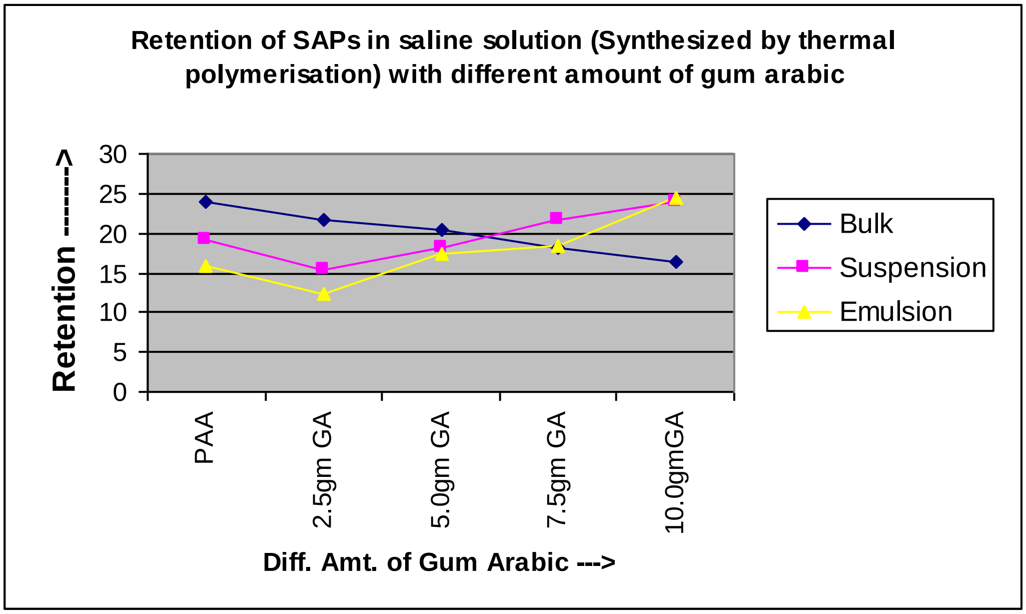
Trend 1:- In case of synthetic SAP which is prepared by Bulk polymerisation has the highest % water retention. In case of semisynthetic SAPs with gum arabic, the results have shown that retention decreases when we increase gum arabic %, in case of polymer obtained by bulk technique.

Trend 2:- The water retention increases with increase in concentration of gum arabic in case of SAP prepared by suspension and emulsion technique.

Table No 7 : *Variation in Retention data of SAPs in Saline prepared by Thermal polymerisation with different amount of Gum Arabic*

| SNo | Techniques / Systems | Retention | | |
|---|---|---|---|---|
| | | Bulk | Suspension | Emulsion |
| 1 | PAA | 23.88 | 19.23 | 15.81 |
| 2 | PAA + 2.5gm GA | 21.80 | 15.27 | 12.38 |
| 3 | PAA + 5.0gm GA | 20.49 | 18.10 | 17.39 |
| 4 | PAA + 7.5gm GA | 18.05 | 21.78 | 18.50 |
| 5 | PAA + 10.0gmGA | 16.37 | 24.00 | 24.42 |

*Fig no - 9: Variation in Retention of SAPs in Saline prepared by Thermal polymerisation with Different Amount of Gum Arabic*



## iii. Retention % in Different pH Solutions :

Better water retention is achieved in synthetic SAPs which are synthesized by bulk polymerization, particularly in pH = 9.2 solution. % water retention increases with increasing pH values in case of the bulk polymerisation techniques but there is no specific trend in case of suspension and emulsion polymerisation.

The % water retention decreases in semisynthetic SAPs with increase in Gum arabic concentration in case of bulk polymerisation in all different pH solutions but it increases with increase in Gum arabic % in semisynthetic SAPs prepared by either suspension and emulsion polymerisation.

Table no -. 8 *: Variation in Retention data of SAPs in different pH solutions prepared by Thermal Polymerisation with different amount of Gum Arabic*

| SNo | Techniques with pH / Systems | Retention | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Bulk | | | Suspension | | | Emulsion | | |
| | | pH=4 | pH=7 | pH=9.2 | pH=4 | pH=7 | pH=9.2 | pH=4 | pH=7 | pH=9.2 |
| 1 | PAA | 32.48 | 36.41 | 47.37 | 20.08 | 20.67 | 22.83 | 16.82 | 17.14 | 16.88 |
| 2 | PAA + 2.5gm GA | 30.55 | 35.49 | 46.41 | 15.69 | 16.04 | 17.34 | 13.12 | 14.56 | 13.04 |
| 3 | PAA + 5.0gm GA | 29.76 | 34.83 | 43.66 | 19.11 | 18.60 | 20.77 | 19.69 | 21.53 | 19.63 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 4 | PAA + 7.5gm GA | 28.33 | 33.32 | 42.20 | 20.55 | 21.69 | 24.39 | 20.28 | 22.09 | 20.45 |
| 5 | PAA + 10.0gmGA | 27.69 | 31.87 | 39.05 | 23.38 | 24.51 | 28.43 | 25.84 | 28.76 | 26.97 |

| SNo | Techniques with pH / Systems | Retention | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | pH=4 | | | pH=7 | | | pH=9.2 | | |
| | | Bulk | Suspension | Emulsion | Bulk | Suspension | Emulsion | Bulk | Suspension | Emulsion |
| 1 | PAA | 32.48 | 20.08 | 16.82 | 36.41 | 20.67 | 17.14 | 47.37 | 22.83 | 16.88 |
| 2 | PAA + 2.5gm GA | 30.55 | 15.69 | 13.12 | 35.49 | 16.04 | 14.56 | 46.41 | 17.34 | 13.04 |
| 3 | PAA + 5.0gm GA | 29.76 | 19.11 | 19.69 | 34.83 | 18.60 | 21.53 | 43.66 | 20.77 | 19.63 |
| 4 | PAA + 7.5gm GA | 28.33 | 20.55 | 20.28 | 33.32 | 21.69 | 22.09 | 42.20 | 24.39 | 20.45 |
| 5 | PAA + 10.0gmGA | 27.69 | 23.38 | 25.84 | 31.87 | 24.51 | 28.76 | 39.05 | 28.43 | 26.97 |

*Fig 10a: Variation in Retention of SAPs in different pH=4 solutions prepared by Thermal Poymerisation with different amount of Gum Arabic*

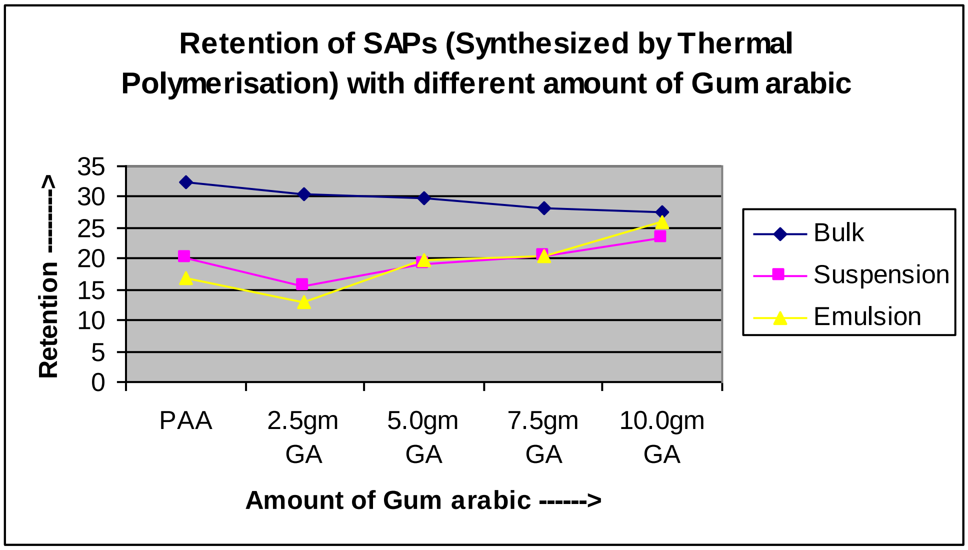
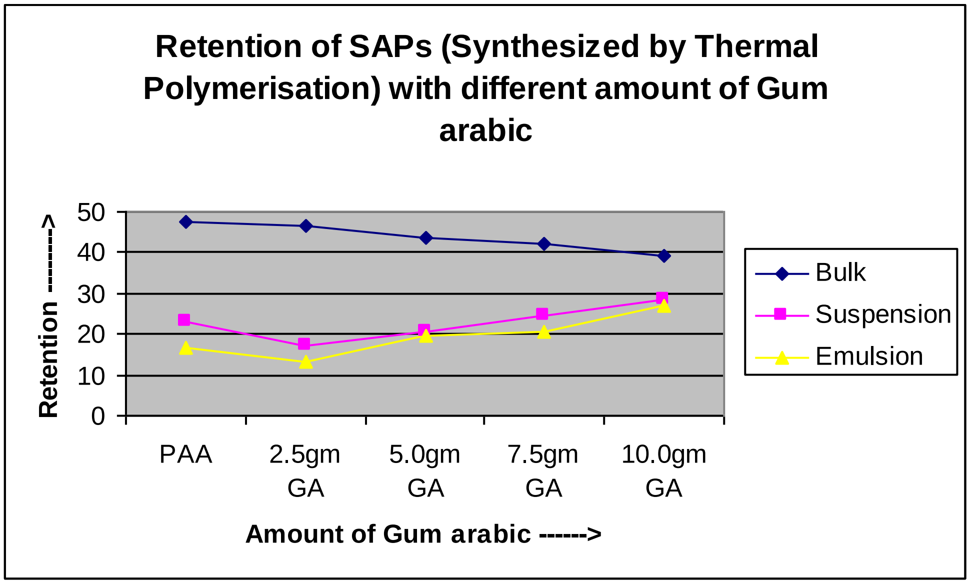


*Fig 10b: Variation in Retention of SAPs in different pH=9.2 solutions prepared by Thermal Poymerisation with different amount of Gum Arabic*



## 6.3 Gel Content Data of SAPs (Prepared by Different Techniques) with different amount of Gum Arabic :

The variations in Gel Content % in SAPs are shown in table no. 9.

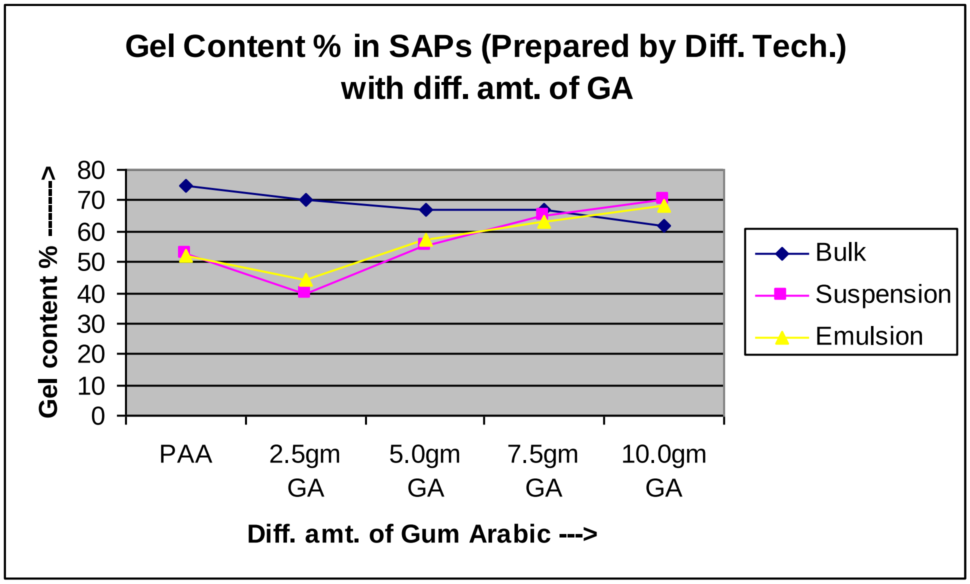
Trend :- The Gel content % in semisynthetic SAPs decreases with the increasing concentration of gum arabic in case of bulk polymerisation. but it first decreases ( 0-2.5 gm) and then increases with increase in amount of Gum Arabic (from 5.0 gm to 10.0gm) in SAPs prepared by emulsion and suspension polymerization techniques.

*Table No. 9 : Variation in Gel content % data of SAPs prepared by Thermal Polymerisation with different amount of Gum Arabic :*

| **SNo** | **Techniques** / **Systems** | **Gel Content %** | | |
|---|---|---|---|---|
| | | **Bulk** | **Emulsion** | **Suspension** |
| **1** | Without Gum Arabic | **75** | **53** | **52** |
| **2** | 2.5gm Gum Arabic | **70** | **40** | **44** |
| **3** | 5.0gm Gum Arabic | **67** | **55** | **57** |

| | | | | |
|---|---|---|---|---|
| **4** | 7.5gm Gum Arabic | **67** | **65** | **63** |
| **5** | 10.0gm Gum Arabic | **62** | **70** | **68** |

Figure 11 : Variation in Gel content % of SAPs prepared by Thermal Polymerisation techniques with different amount of Gum Arabic :



Better Gel content % is achieved in synthetic SAPs which are polymerized by bulk polymerization techniques (Figure no. -11). In case of emulsion and suspension polymerisation, better Gel contents % is achieved in semisynthetic SAPs with 10 gm of Gum arabic.

Gel is nothing but high molar mass polymer absorbing large percentage of water i.e. Gel is somewhat losely-bound crosslinking among chains but not too highly crosslinked, otherwise it leads to less % water absorbence. This trend of Gel content % data can be interrelated with the trend shown by % water absorbency data as in table no. 1, 2, and 3 i.e Higher the Gel content, higher the % absorbency & also higher water retention and vice-versa.

Such superabsorbents polymers (SAPs) which have high Gel content % are used to improve water retention for baby diapers and soil additives.

## 6.4 Fourier transform infrared spectroscopy (FTIR) Studies :

The samples were characterized by Fourier Transform Infrared Spectroscopy (FTIR) was done on a Perkin Elmer Instruments Spectrum One model, using the KBr disc technique. FTIR spectra of gum arabic (a), gum-free acrylic-based polymer (b), and the AG-acrylic acid Hybrid (c ), is shown below :

In graph (a), characteristic band of the polysodium acrylate are presented in the SAP. The strong, broad peak at 3427 $cm^{-1}$ is related to the OH stretching of the carboxylic and hydroxyl groups of either acrylic or carbohydrate parts. The strong peaks at 1567 $cm^{-1}$ (1560-1630 $cm^{-1}$) are related to the carboxylate C==O stretching, originating mainly from the acrylate part of the hydrogel hybrid.

In graph (b), both characteristic bands of the gum arabic and of the polysodium acrylate are presented in the SAP hybrid. The strong, broad peak at 3427 $cm^{-1}$ is related to the OH stretching of the carboxylic and hydroxyl groups of either acrylic or carbohydrate parts. The medium peaks at 1042 $cm^{-1}$ (1030-1070 $cm^{-1}$), due to stretching vibration of C-O-C and C-O-H bonds, confirms that saccharide structure of the SAPs hybrid. The strong peaks at 1567 $cm^{-1}$ (1560-1630 $cm^{-1}$) are related to the carboxylate C==O stretching, originating mainly from the acrylate part of the hydrogel hybrid. Since the hybrid had already been extracted to remove the soluble contents, its FTIR analysis proved that the gel network was not a physical mixture and but chemical linkages have been formed during the free radical polymerization reaction. Threrefore, the hybrid is composed most likely of a grafted, crosslinked copolymeric structure.

Fig 12 - FTIR GRAPH of NaPAC (Bulk Polymerisation )
‘a’

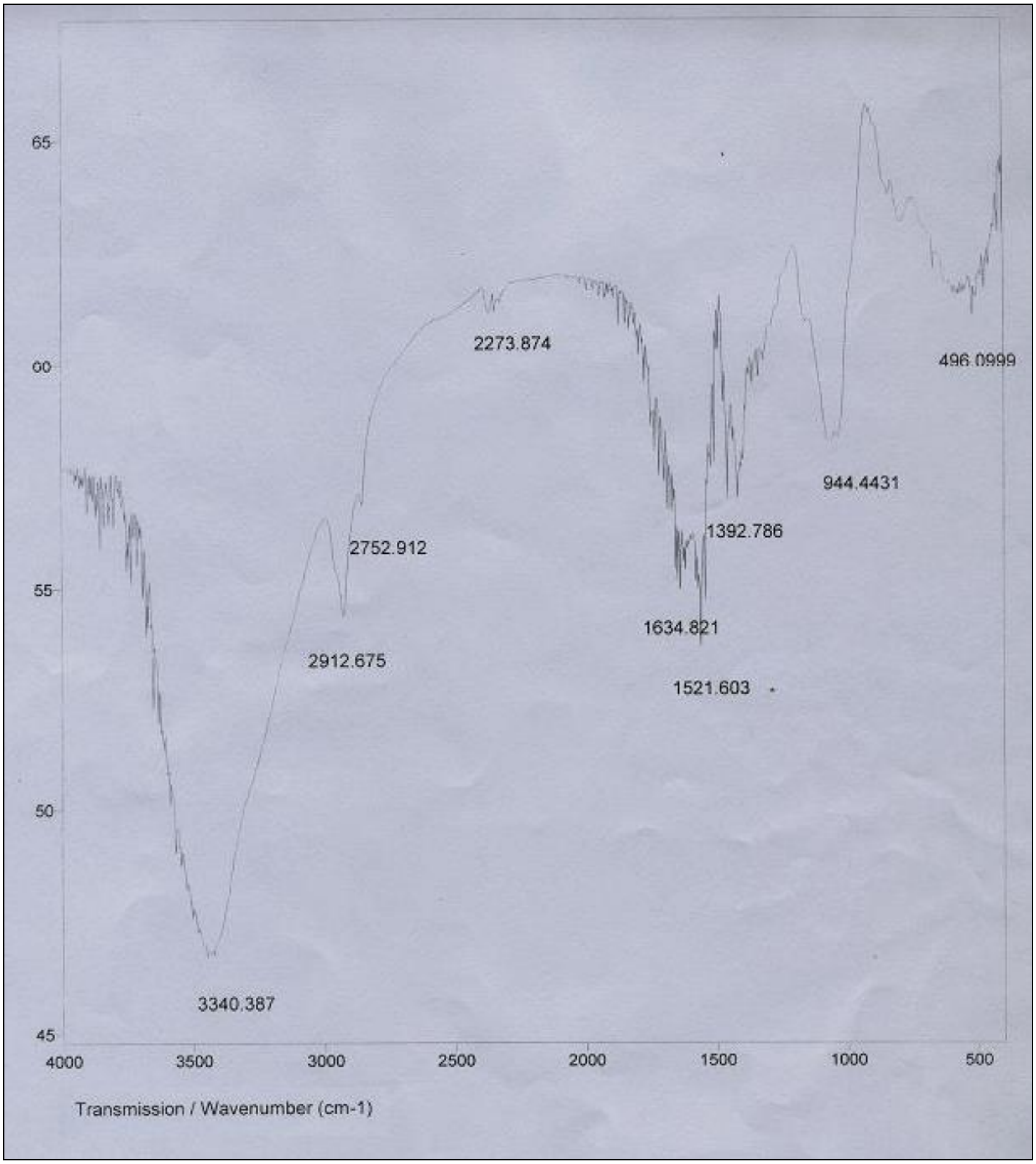
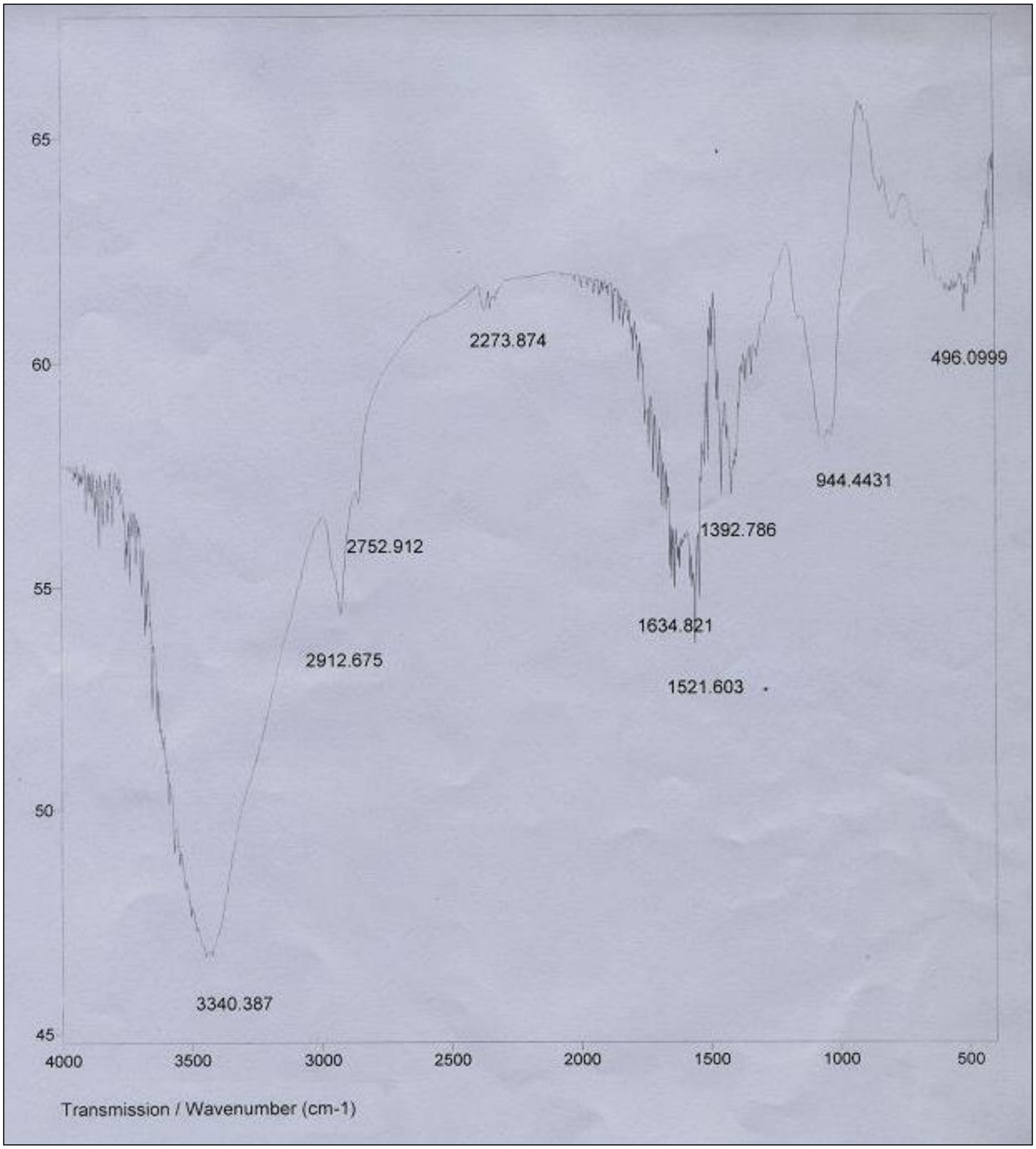


Fig 13 - FTIR GRAPH of NaPAC with 7.5 gm of Gum arabic
( Suspension Polymerisation), ‘b’



## 6.4 TGA Studies

**T**hermogravimetic Analysis (TGA) is a thermal analysis technique used to measure changes in the weight (mass) of a sample as function of temperature and /or time.TGA is a commonly used to determine polymer degradation temperatures.

**TGA thermograms of the intact gum, the gum free acrylic based SAPs and hybrid SAPs are shown below as :**

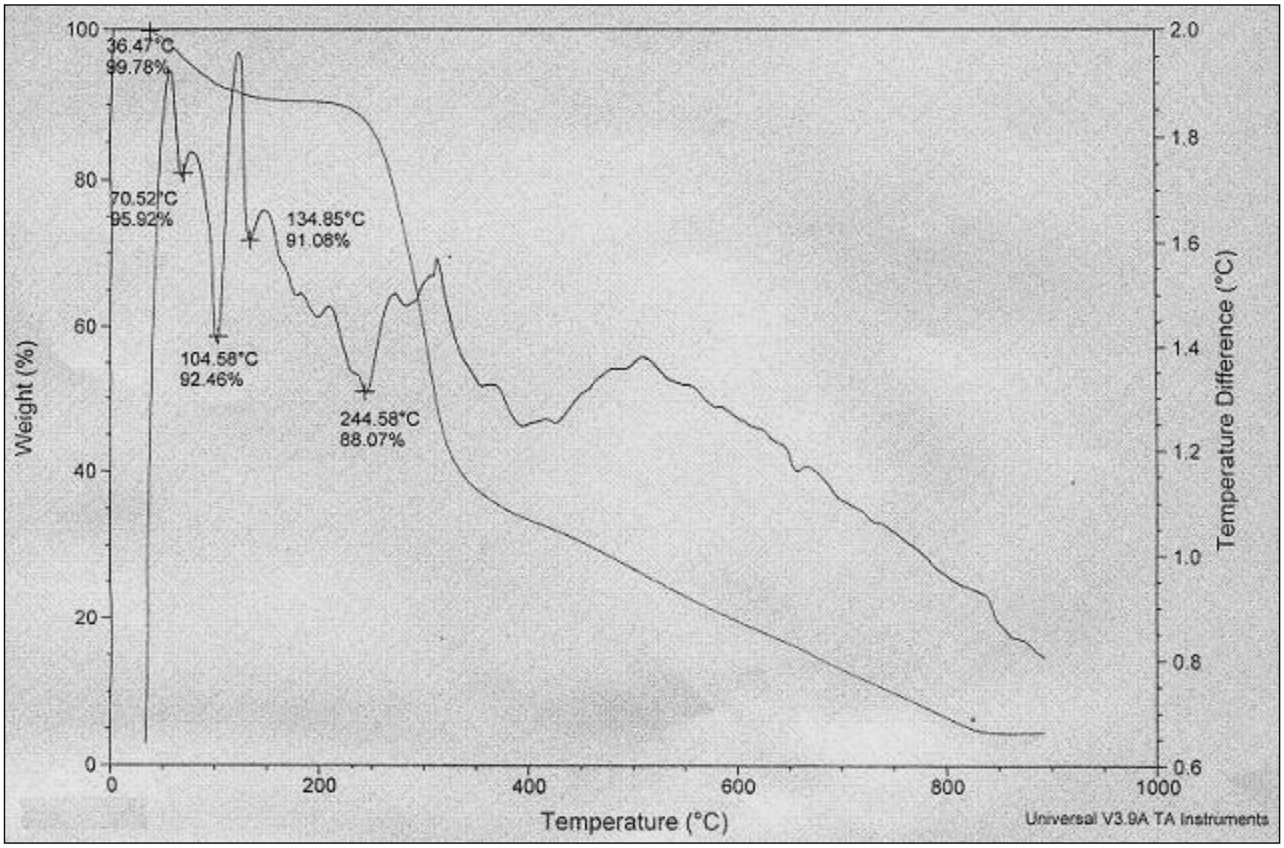


Fig 14 - TGA thermogram of Gum Arabic

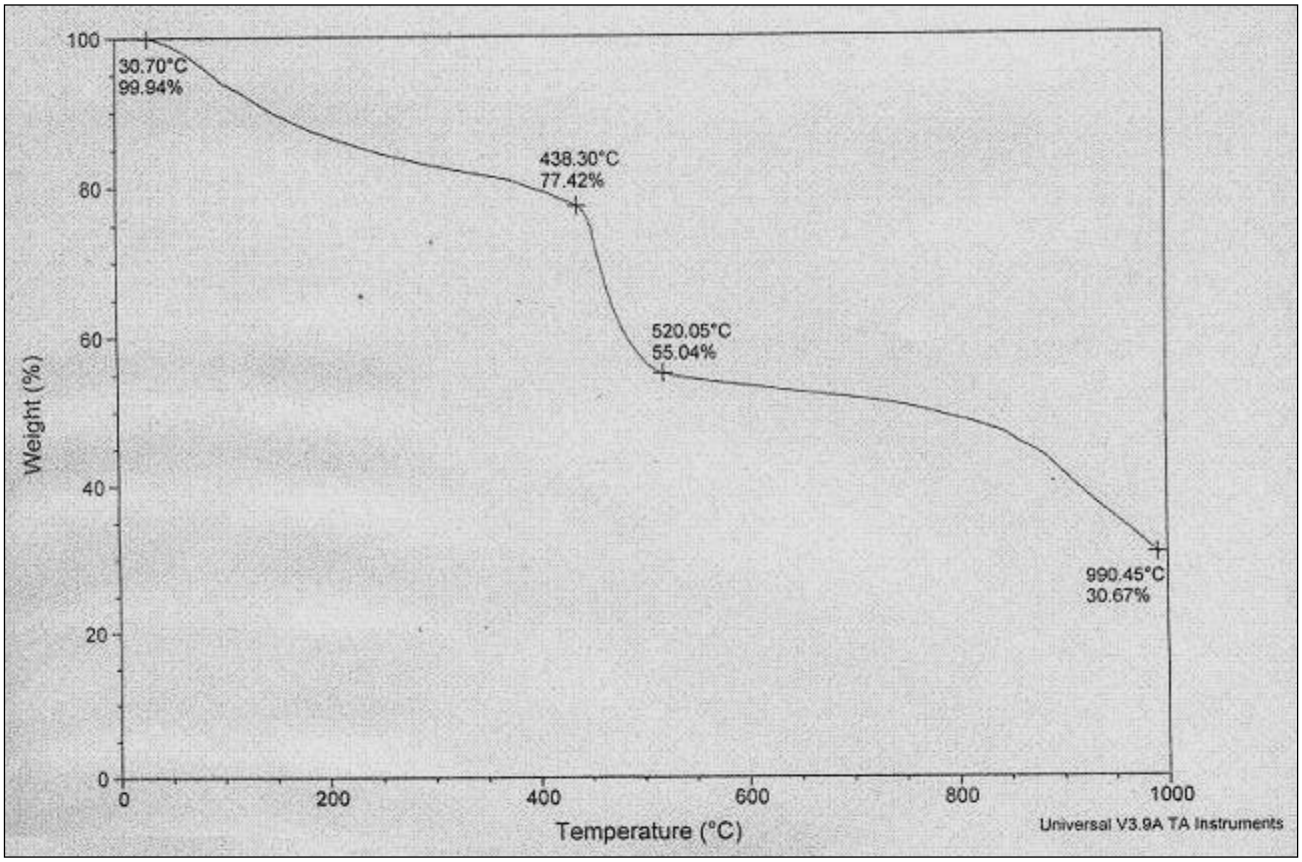


Fig 15 - TGA therogram of NaPAC (Synthesisd by Bulk Polymerisation)

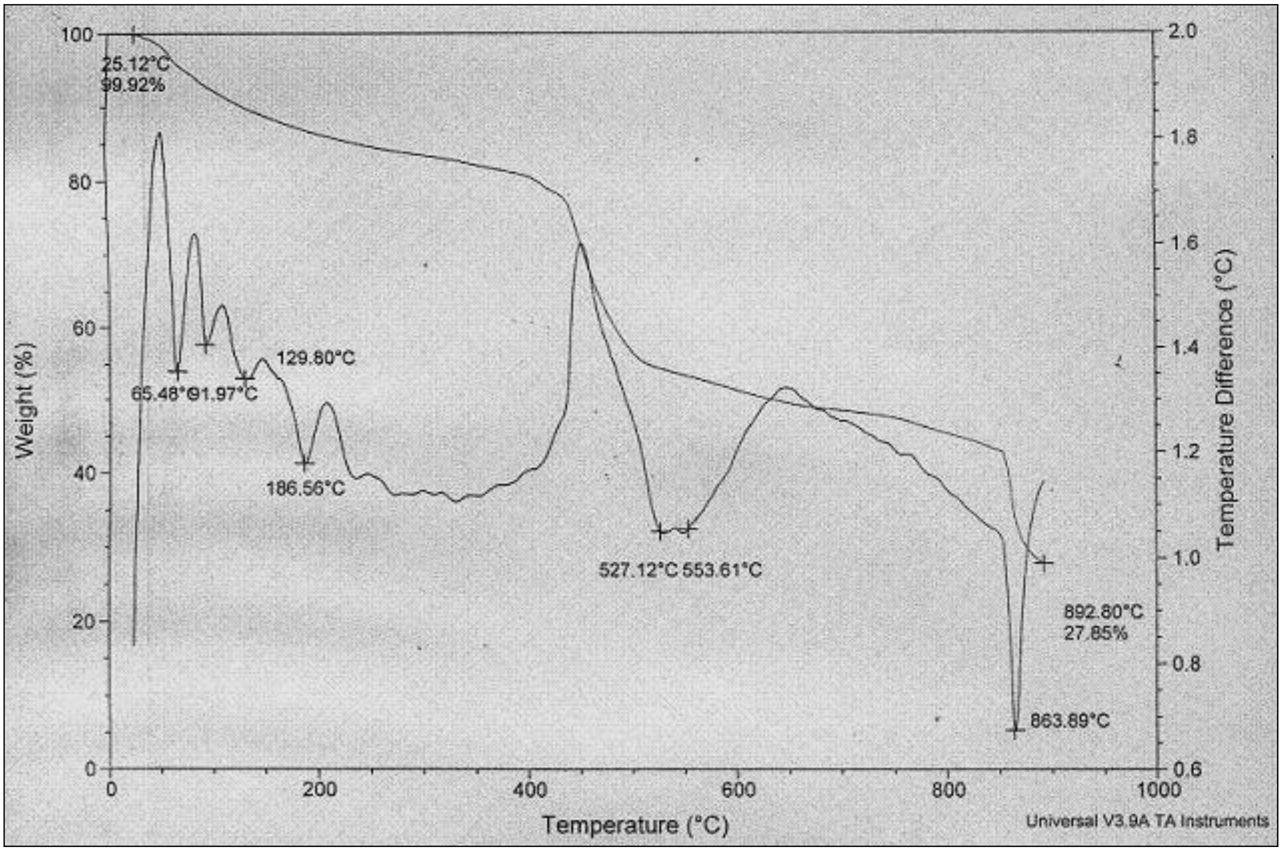


Fig 16 - TGA thermogram of NaPAC (Synthesisd by Suspension Polymerisation)

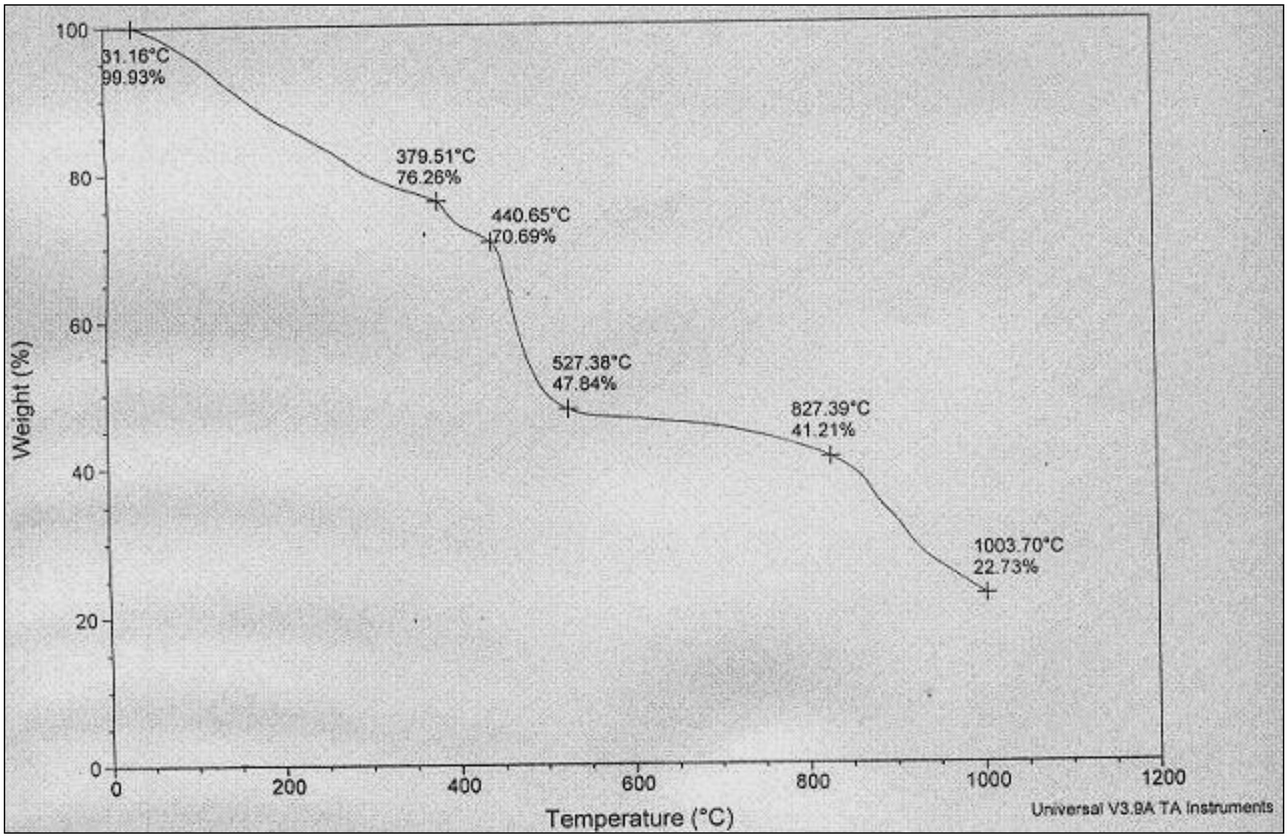


Fig 17 - TGA thermogram of NaPAC (Synthesisd by Emulsion Polymerisation)

## TGA thermogram of hybrid SAP (Synthesisd by Bulk Polymerisation)

TGA method was employed to thermally characterize the hybrid SAPs in comparision with the intact gum and the gum-free acrylic based. In contrast to the untreated AG that showed an initial decomposition temperature (IDT) of 245 °C without a char residue at ~825 °C, the gum-free acrylic based exhibited a pattern with a IDT around of 440 was observed in its thermogram carried by all thermal polymerization techniques. In the hybrid SAPs, an IDT is observed at around 441 in its thermogram.

Therefore, it may be concluded that the synthetic part of the SAPs hybrid maintain its thermal stability

# Chapter - 7 Results and Discussion - Radiation Polymerisation

## 7.1. Absorption % Data of SAPs(Prepared by Radiation technique) with different amount of Gum arabic :

### i. % Absorption in Distilled Water :

The variations in % water absorption of SAPs are shown in table no. 10. The values show the two trends.

Trend 1:- The % absorption is highest in SAPs which are synthesized at 40 KGrey by the Radiation Polymerisation Technique. % water absorption decreases with increasing doses i.e. 60, 80 and 90 KGrey.

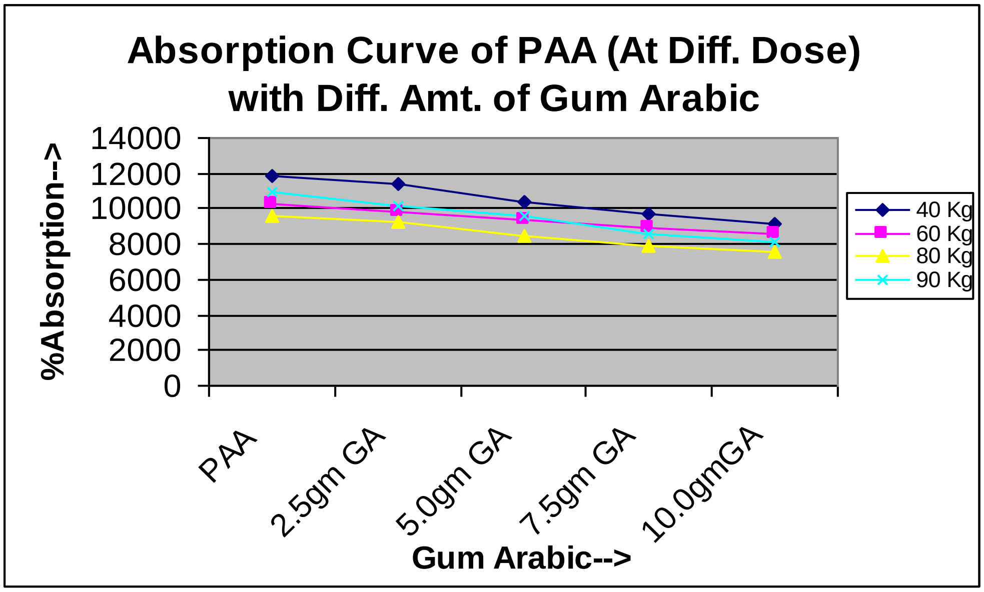
Trend 2:- The % absorption also decreases with increasing Gum Arabic % in SAPs (from 2.5gm to 10.0gm) at different dose rate.

*Table No. 10 :Variation in % Absorption data of SAPs in Distilled Water prepared by Radiation Technique at different doses with Different Amount of Gum Arabic :*

| S.No | Doses / Systems | % ABSORPTIONS | | | |
|---|---|---|---|---|---|
| | | **40 KGrey** | **60 KGrey** | **80 KGrey** | **90 KGrey** |
| 1 | PAA | 11870 | 10243 | 9603 | 10913 |
| 2 | PAA + 2.5gm GA | 11426 | 9783 | 9232 | 10215 |
| 3 | PAA + 5.0gm GA | 10366 | 9417 | 8430 | 9103 |
| 4 | PAA + 7.5gm GA | 9747 | 8900 | 7856 | 8573 |
| 5 | PAA +10.0gmGA | 9168 | 8561 | 7584 | 8185 |

The figure-12 clearly shows the trend as in above table. These trends can be explained by considering the energy used for radiation polymerization. In case of 40 KGrey, less energy is used, thereby crosslinking attained is also less in the polymer chains & when crosslinking decreases among polymer chains, then swelling behaviour increases. When we increases the dose rate (40 KGrey- 80 KGrey), water absorption decreases. Further increase in dose rate, 90 KGrey, increases the water absorption. This is because by increase of dose rate breakage of linkage between polymer chains takes place.

*Figure. 18 :Variation in % Absorption of SAPs in Distilled Water prepared by Radiation Polymerisation at different doses with different amount of Gum Arabic :*



## ii. % Absorption in Saline Water :

The variations in % absorption of SAPs in saline are shown in table no. 11. The trend is same as followed in case of KGrey Distilled water.The values show the trends as :

Trend 1:- The % absorption is highest in SAPs which are prepared at 40 KGrey as compared to SAPs prepared at other doses 60, 80 and 90 KGrey and goes on decreasing with increasing doses.

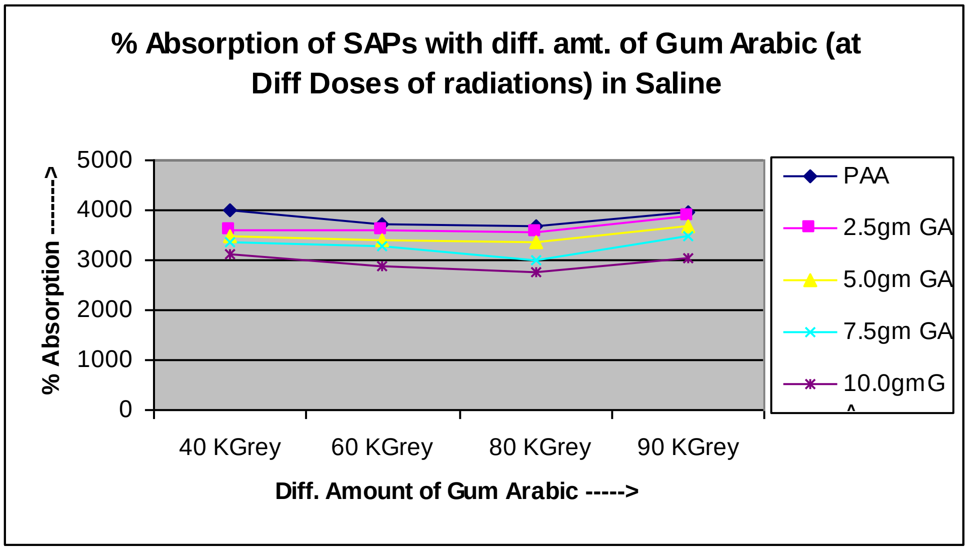
Trend 2:- The % absorption decreases with increasing Gum Arabic % in SAPs (from 2.5gm to 10.0gm) in SAPs at all dose rate.

*Table No. 11 :Variation in % Absorption data of SAPs in Saline prepared by Radiation Technique at different doses with Different Amount of Gum Arabic :*

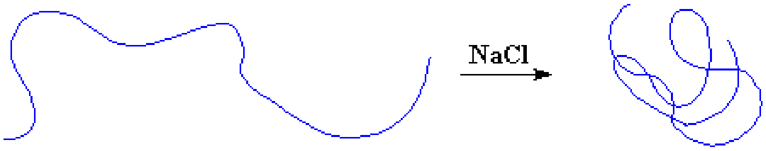
| S.No | Doses / Systems | % ABSORPTIONS | | | |
|---|---|---|---|---|---|
| | | 40 KGrey | 60KGrey | 80 KGrey | 90 KGrey |
| 1 | PAA | 3865 | 3732 | 3663 | 3964 |
| 2 | PAA + 2.5gm GA | 3610 | 3589 | 3555 | 3900 |
| 3 | PAA + 5.0gm GA | 3475 | 3398 | 3363 | 3664 |
| 4 | PAA + 7.5gm GA | 3358 | 3288 | 3013 | 3487 |
| 5 | PAA +10.0gmGA | 3121 | 2873 | 2759 | 3029 |

These trends can be explained by the energy used for radiation polymerization.

*Fig 19 : Variation in % Absorption data of SAPs in Saline prepared by Radiation Technique at different doses with Diferent Amount of Gum Arabic*



But the % absorbency is lower in saline compared with % absorbency in distilled water.When salt is added, each ion of sodium ($Na^+$) and each ion of chlorine($Cl^-$) is quickly surrounded by six molecules of water which is drawn out from the polymer-water complex. The presence of sodium chloride in the solution greatly decreases the ability of polyacrylate to absorb and retain water. In the case of a negatively charged polyelectrolyte, the positively charged $Na^+$ ions will get in between the negative charges on the polymer, and cancel their effect. When this occures, the polymer chain collapses into random coil again.



Salt makes polyelectrolytes in solution collapse into random coils.

### iii. % Absorption in different pH Solutions :

The variations in % absorption of SAPs in different pH solutions are shown in table no. 12.

In case of semisynthetic SAPs % absorption decreases with the increase of Gum Arabic % (from 2.5gm to 10.0gm) in SAPs in all pH solutions. % Absorbency is more in pH = 7 solution at all dose rates. When radiation dose rate increases, % Absorbency decreases in all pH solutions. Better % absorbency are achieved at 40 KGrey dose rate.

*Table No 12 : Variation in % Absorption data of SAPs in Saline prepared by Radiation Technique at different doses with different amount of Gum Arabic*

| S.No | Doses with pH<br>Systems | % Absorption | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 40 KGrey | | | 60 KGrey | | | 80 KGrey | | |
| | | pH=4 | pH=7 | pH=9.2 | pH=4 | pH=7 | pH=9.2 | pH=4 | pH=7 | pH=9.2 |
| 1 | PAA | 3992 | 4253 | 3902 | 3883 | 3920 | 3848 | 3754 | 3839 | 3701 |
| 2 | PAA + 2.5gm GA | 3837 | 4057 | 3732 | 3711 | 3826 | 3640 | 3679 | 3797 | 3575 |
| 3 | PAA + 5.0gm GA | 3632 | 3744 | 3484 | 3520 | 3771 | 3499 | 3588 | 3699 | 3337 |
| 4 | PAA + 7.5gm GA | 3488 | 3573 | 3413 | 3388 | 3435 | 3315 | 3258 | 3313 | 3198 |
| 5 | PAA +10.0gmGA | 3392 | 3441 | 3355 | 3031 | 3207 | 2956 | 2937 | 3146 | 2864 |

| S.No | Doses with pH<br>Systems | % Absorption | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | pH=4 | | | pH=7 | | | pH=9.2 | | |
| | | 40KG | 60KG | 80 KG | 40KG | 60 KG | 80KG | 40 KG | 60 KG | 80 KG |
| 1 | PAA | 3992 | 3883 | 3754 | 4253 | 3920 | 3839 | 3992 | 3848 | 3701 |
| 2 | PAA + 2.5gm GA | 3837 | 3711 | 3679 | 4057 | 3826 | 3797 | 3732 | 3640 | 3575 |
| 3 | PAA + 5.0gm GA | 3632 | 3520 | 3588 | 3744 | 3771 | 3699 | 3484 | 3499 | 3337 |
| 4 | PAA + 7.5gm GA | 3488 | 3388 | 3258 | 3573 | 3435 | 3313 | 3413 | 3315 | 3198 |
| 5 | PAA +10.0gmGA | 3292 | 3031 | 2937 | 3441 | 3207 | 3146 | 3355 | 2956 | 2864 |

*Figure 20a : Variation in % Absorption of SAPs at different doses with different amount of Gum Arabic*

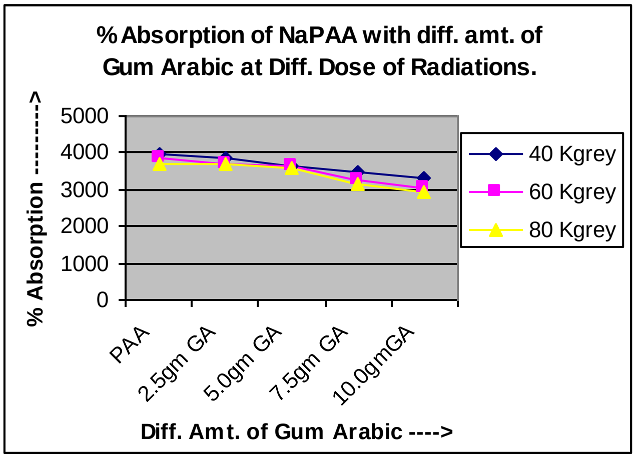
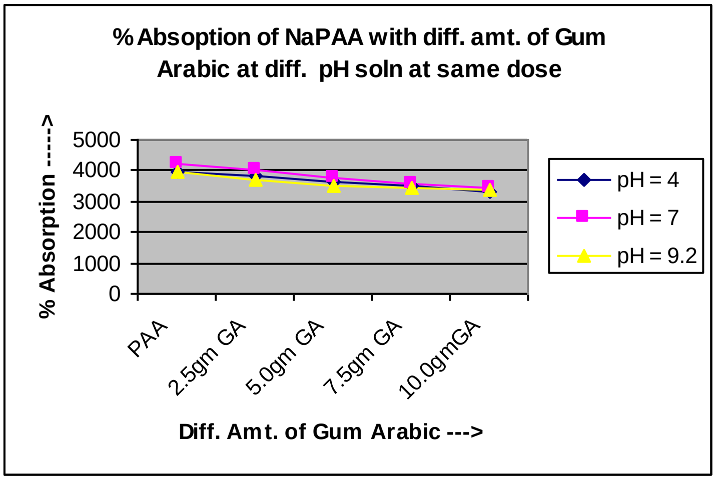


*Figure 20b : Variation in % Absorption of SAPs in different pH solutions at same dose with different amount of Gum Arabic*



% absorbency in different pH solutions is much less then % absorbency in distilled water, this is because there is more ion concentration in pH solutions (like as in saline solutions) as compared to distilled water. Actually pH solutions have been prepared by dissolving pH buffer tablets (in distilled water) which are nothing but sodium salts of different compounds for example pH-9.2 buffer tables are mainly di-sodium tetraborates, pH-7.0 buffer tablets are combination of different salts - Sodium phosphate, dibasic; potassium phosphate, monobasic; sodium chloride while pH = 4 solution are prepared by buffer tablets which are nothing but is o-toludiene. Distilled water does not have such so much ionic concentration. Ion concentration can be judged by measuring conductivity of pH solution using conductivity meter. Higher the conductivity, higher the ionic concentration and vice-versa.

Conductivity of distilled water, at 25 °C = $3.4 \times 10^{-3}$ mv/cm$^3$
Conductivity of pH - 4.0 solution, at 25 °C = 3.4 mv/cm$^3$
Conductivity of pH - 7.0 solution, at 25 °C = 7.2 mv/cm$^3$
Conductivity of pH - 9.2 solution, at 25 °C = 3.2 mv/cm$^3$

This shows that conductivity of pH solutions are1000 times or much higher than distilled water. Conductivity is directly related to ion concentration. Thus pH solution has high concentration of ions which results in less absorbency. it can be concluded that pH solutions are having too much ionic strength leading to higher conductivity as compared to distilled water (lacking in ions). Ionic strength of pH=9.2 soln is high which results in little bit less absorbency as compared to pH=7 solution.

This explains the high % absorbency in distilled water as compared to different pH solutions.

## 7.2 Retention Data of SAPs(Prepared by Radiation technique) with different amount of GUM ARABIC :

### i. Retention in Distilled Water :

The variations in retention of SAPs are shown in table no. 13. The values show the two trends.

Trend 1:- The retention is highest in SAPs which are synthesized at 40 KGrey by the Radiation Polymerisation Technique. Retention decreases with increasing doses i.e. 60, 80 and 90 KGrey.

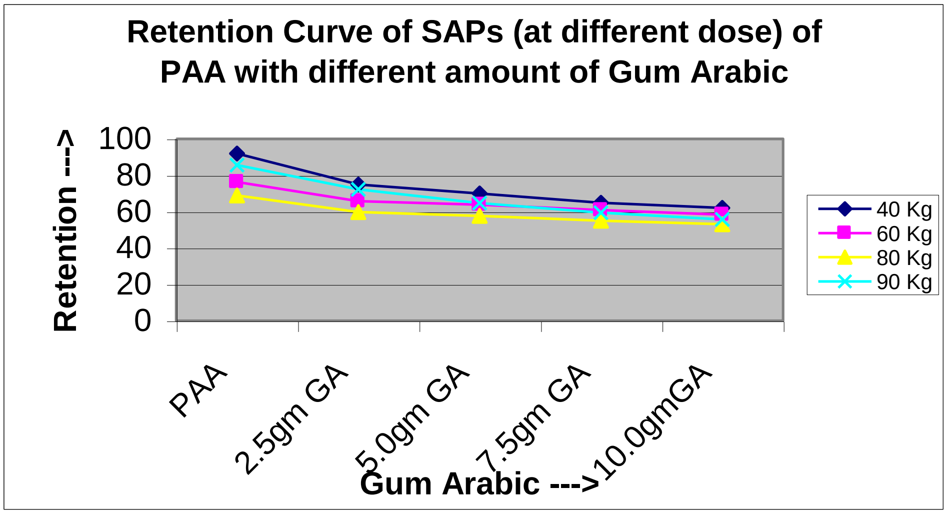
Trend 2:- The retention also decreases with increasing Gum Arabic % (from 2.5gm to 10.0gm) in semi-synthetic SAPs at particular dose rate.

*Table No 13 : Variation in Retention data of SAPs distilled water prepared by Radiation Technique at different doses with different amount of Gum Arabic*

| S.No | Doses ---- > Systems | RETENTION | | | |
|---|---|---|---|---|---|
| | | **40 KGrey** | **60 KGrey** | **80 KGrey** | **90 KGrey** |
| 1 | PAA | 91.84 | 76.23 | 68.81 | 85.55 |
| 2 | PAA + 2.5gm GA | 74.84 | 65.69 | 59.67 | 72.15 |
| 3 | PAA + 5.0gm GA | 69.94 | 63.78 | 57.63 | 64.64 |
| 4 | PAA + 7.5gm GA | 6486 | 60.83 | 54.96 | 59.38 |
| 5 | PAA +10.0gmGA | 62.02 | 58.41 | 53.08 | 55.79 |

In case of 40 KGrey, less energy is used, thereby crosslinking attained is also less in the polymer chains & when crosslinking decreases among polymer chains, then retention increases. When we increases the dose rate (40 KGrey- 80 KGrey), retention decreases. Further increase in dose rate i.e. 90 KGrey, increases the retention, (Figure no – 15) This is because by increase of dose rate crosslinking break among polymer chains takes place.

Fig 21 : Variation in Retention data of SAPs distilled water prepared by Radiation Technique at different doses with different amount of Gum Arabic



## ii. Retention in Saline Water :

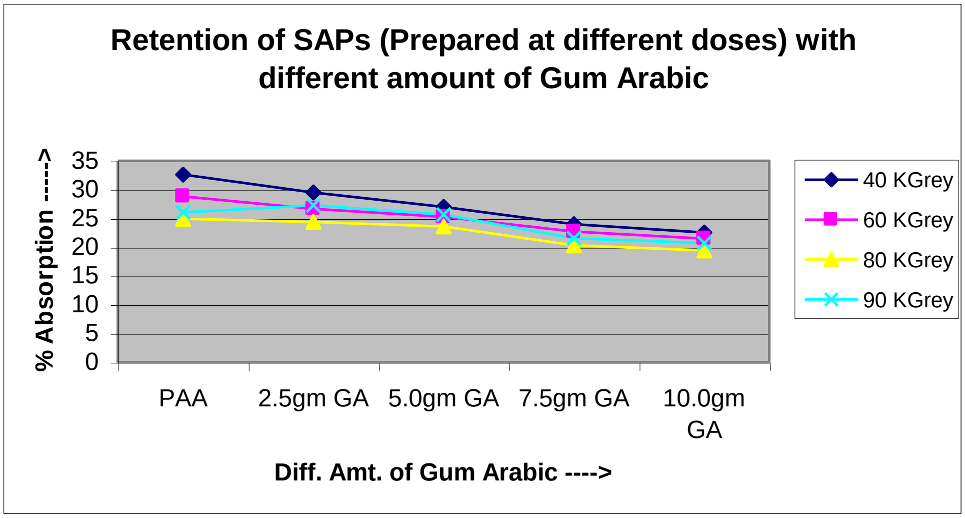
Trend 1:- In case of synthetic SAP which is prepared by at 40 KGrey dose rate has maximum retention. In case of semisynthetic SAPs with gum arabic, retention decreases when we increase gum arabic %.

*Table No 14 : Variation in Retention data of SAPs in Saline prepared by Radiation Technique at different doses with different amount of Gum Arabic*

| S.No | Doses ---- ><br>Systems | RETENTION | | | |
|---|---|---|---|---|---|
| | | **40 KGrey** | **60 KGrey** | **80 KGrey** | **90 KGrey** |
| 1 | PAA | 32.61 | 28.80 | 24.95 | 26.06 |
| 2 | PAA + 2.5gm GA | 29.48 | 26.67 | 24.38 | 27.27 |
| 3 | PAA + 5.0gm GA | 26.97 | 25.29 | 23.57 | 25.67 |
| 4 | PAA + 7.5gm GA | 24.01 | 22.68 | 20.33 | 21.56 |
| 5 | PAA +10.0gmGA | 22.51 | 21.49 | 19.42 | 20.68 |

Retention is an important property, which is required in baby diapers where it face more pressure. The % absorbency is lower in saline compared with % absorbency in distilled water.When salt is added, each ion of sodium ($Na^+$) and each ion of chlorine($Cl^-$) is quickly surrounded by six molecules of water which is drawn out from the polymer-water complex. The presence of sodium chloride in the solution greatly decreases the ability of polyacrylate to retain water.

Fig *22 : Variation in Retention data of SAPs in Saline prepared by Radiation Technique at different doses with different amount of Gum Arabic*

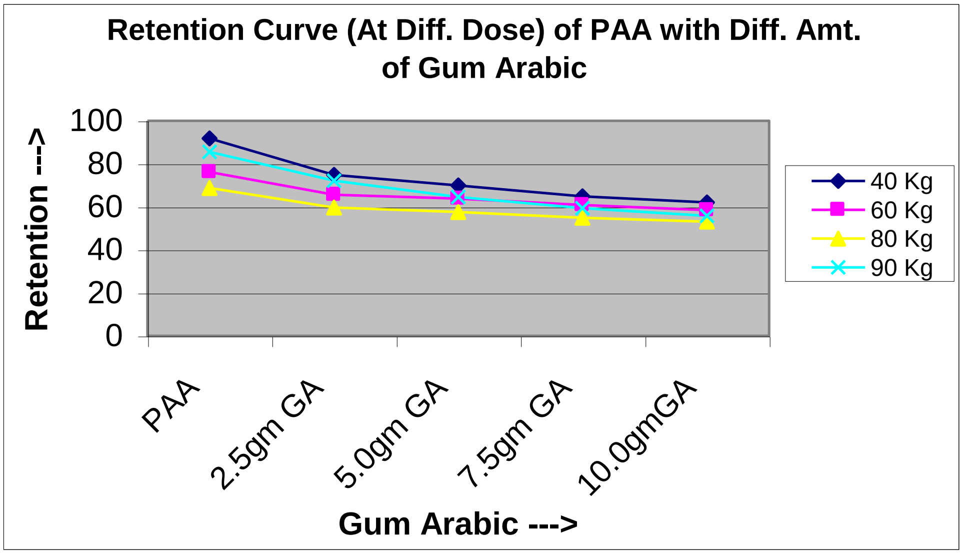


## iii. Retention in different pH Solutions :

*Table No 15 : Variation in Retention data of SAPs distilled water prepared by Radiation Technique at different doses with Diff. Amount of Gum Arabic*

| S.No | Doses with pH | RETENTION | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 40 KGrey | | | 60 KGrey | | | 80 KGrey | | |
| | Systems | pH=4 | pH=7 | pH=9.2 | pH=4 | pH=7 | pH=9.2 | pH=4 | pH=7 | pH=9.2 |
| 1 | PAA | 33.41 | 35.24 | 33.41 | 30.31 | 32.22 | 29.66 | 26.66 | 29.02 | 25.00 |
| 2 | PAA + 2.5gm GA | 31.32 | 32.58 | 28.35 | 28.54 | 30.39 | 26.28 | 27.94 | 29.49 | 25.29 |
| 3 | PAA + 5.0gm GA | 29.43 | 30.88 | 27.65 | 27.99 | 29.11 | 26.11 | 25.05 | 27.64 | 24.30 |
| 4 | PAA + 7.5gm GA | 25.94 | 28.11 | 24.12 | 24.17 | 26.05 | 23.25 | 21.92 | 24.04 | 22.08 |
| 5 | PAA +10.0gmGA | 24.54 | 26.30 | 22.87 | 22.55 | 24.57 | 22.03 | 21.70 | 23.11 | 20.85 |

*Fig 23 : Variation in Retention data of SAPs distilled water prepared by Radiation Technique at different doses with Diff. Amount of Gum Arabic*



## 7.3 Gel Content % Data of SAPs (Prepared by Different Techniques) with different amount of Gum Arabic :

The variations in Gel Content % in SAPs are shown in table no. 16 & 17.

**Trend 1.** Gel content % decreases with increase in amount of Gum Arabic (from 2.5 gm to 10.0gm) in SAPs at same dose given

**Trend 2.** Gel content % increases with increase in radiation doses.(from 60 KGrey to 80 KGrey). Further increase in dose rate i.e. 90 KGrey results in decreases in Gel content %

*Table No.16:Variation in Gel % data of SAPs at same dose with diff. Amount of Gum Arabic*

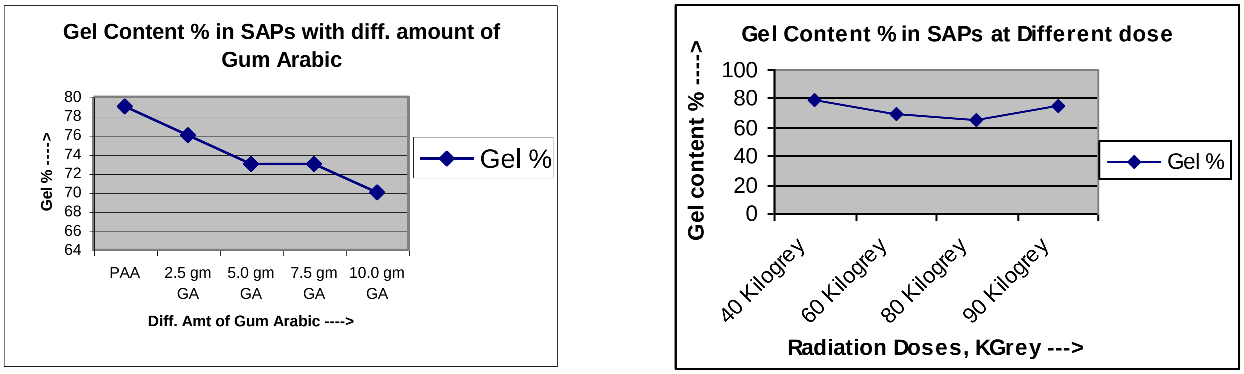
| SNo | Doses<br>Systems | Fixed Radiation Dose, 40 KGrey |
|---|---|---|
| **1** | Without Gum Arabic | **71** |
| **2** | 2.5gm Gum Arabic | **65** |
| **3** | 5.0gm Gum Arabic | **58** |
| **4** | 7.5gm Gum Arabic | **58** |
| **5** | 10.0gm Gum Arabic | **55** |

*Table No.17: Variation in Gel % data SAPs at Diff. doses with same Amount of Gum Arab*

| S.No | Radiation Doses KGrey | Gel Content % |
|---|---|---|
| **1** | 40 Kilogrey | **71** |
| **2** | 60 Kilogrey | **75** |
| **3** | 80 Kilogrey | **81** |
| **4** | 90 Kilogrey | **75** |

The variations in Gel % are clearly visible from the Figures 18 (a, b) shown downside. There may not be the proper crosslinking between Gum Arabic and Acrylic Acid as monomers with increase in Gum Arabic amount in SAPs for gelation. But with increase in dose amount crosslinking among chains increases thereby favourable Gel % decreases ( but overall increases) causes  % absorbency to decrease.

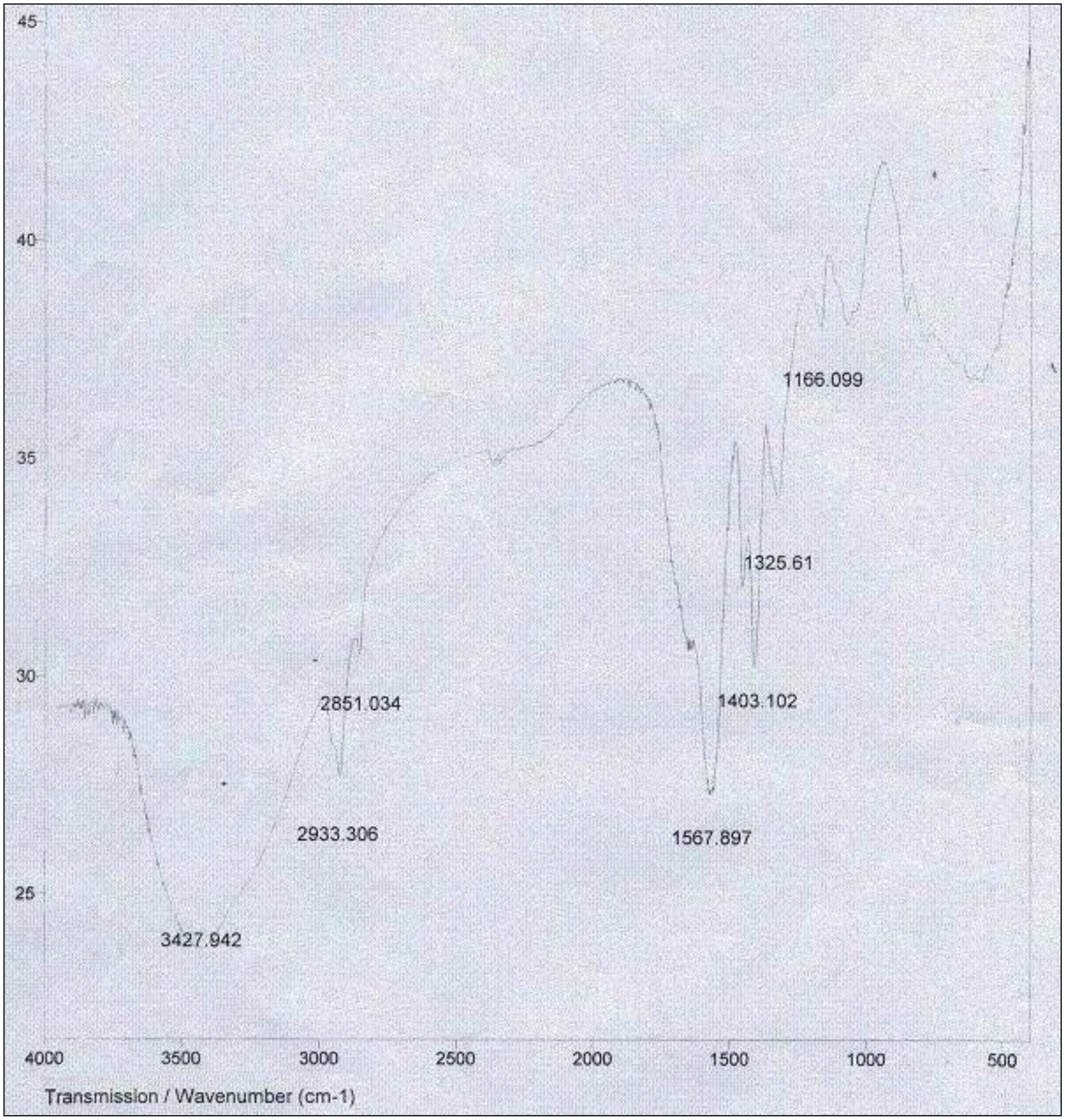
Fig. 24 (a, b) : Variation in  Gel content %  data of SAPs synthesized at different radiation doses with different amount of Gum Arabic :



## 7.4 Fourier transform infrared spectroscopy (FTIR) :

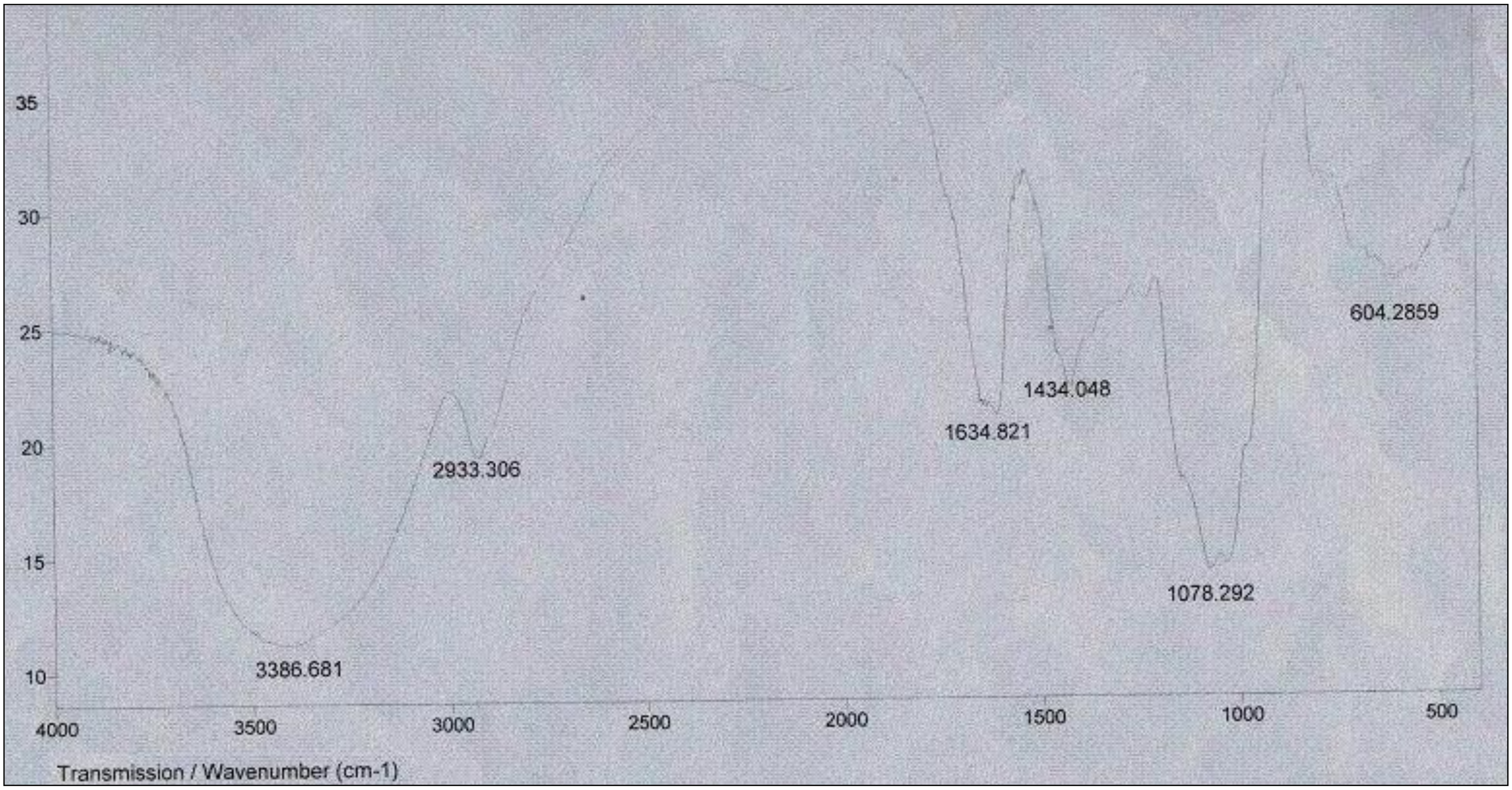
The samples were characterized by Fourier Transform Infrared Spectroscopy (FTIR) was done on a Perkin Elmer Instruments Spectrum One model, using the KBr disc technique. FTIR spectra of gum arabic (a), gum-free acrylic-based polymer (b), and the AG-acrylic acid Hybrid (c ), is shown below :

Fig 25 - **FTIR spectra of the AG-acrylic acid Hybrid SAP**



In graph, both characteristic bands of the gum arabic and of the polysodium acrylate are presented in the SAP hybrid. The strong, broad peak at 3427 cm$^{-1}$ is related to the OH stretching of the carboxylic and hydroxyl groups of either acrylic or carbohydrate parts. The medium peaks at 1042 cm$^{-1}$ (1030-1080 cm$^{-1}$), due to stretching vibration of C-O-C and C-O-H bonds, confirms that saccharide structure of the SAPs hybrid. The strong peaks at 1567 cm$^{-1}$ (1560-1630 cm$^{-1}$) are related to the carboxylate C==O stretching, originating mainly from the acrylate part of the SAP hybrid. Since the hybrid had already been extracted to remove the soluble contents, its FTIR analysis proved that the gel network was not a physical mixture and but chemical linkages have been formed during the free radical polymerization reaction. Threrefore, the hybrid is composed most likely of a grafted, crosslinked copolymeric structure. In addition, the semi-interpenetrating polymer network (semi-IPN) structure is probable. The exact chemical structure of the hybrid remains a subject of debate at this stage of our study.

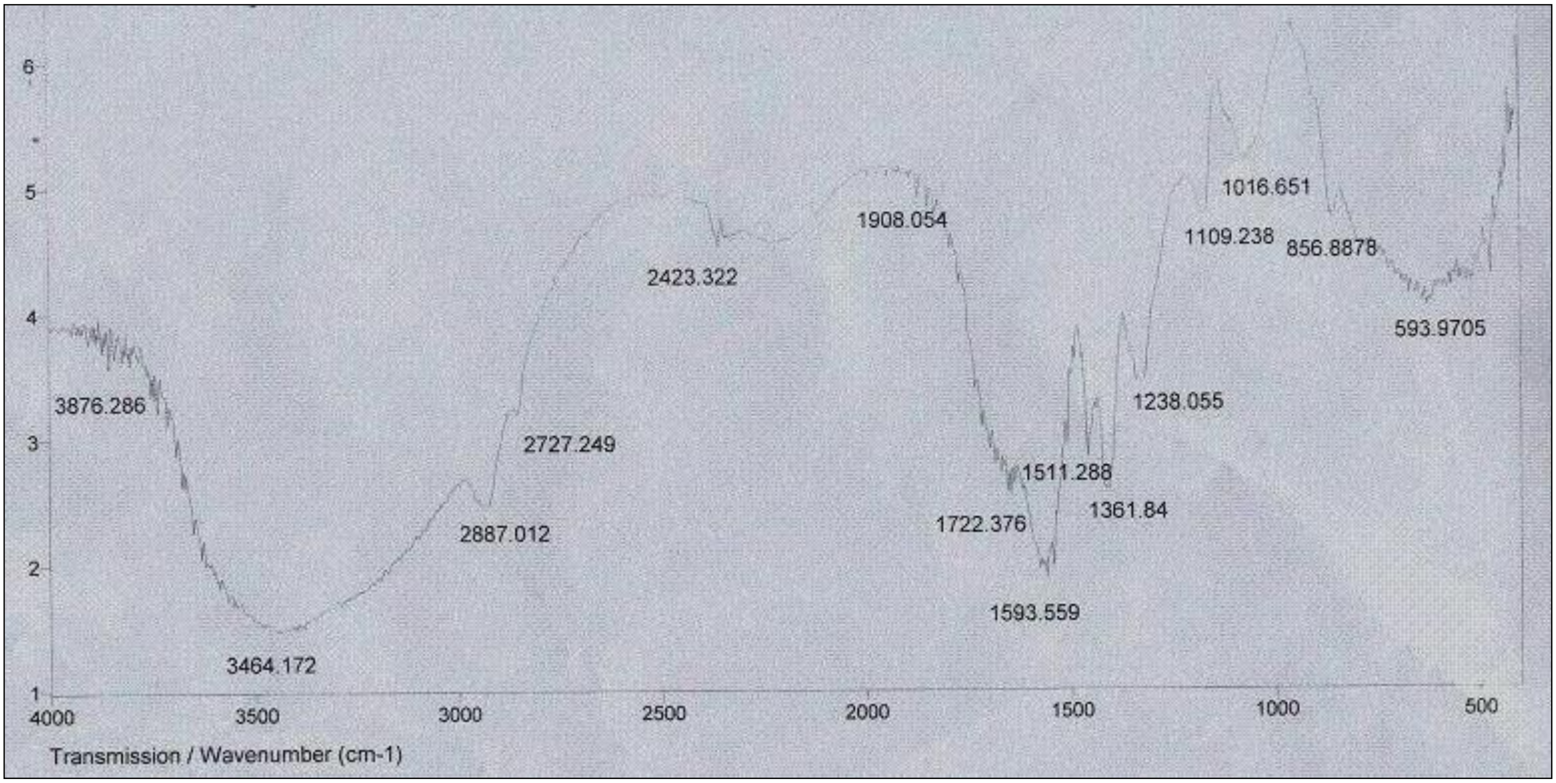
**FTIR Spectra of Gum Arabic**: In graph, characteristic band of the gum arabic in FTIR Spectra. The strong, broad peak at 3427 cm$^{-1}$ is related to the OH stretching of the carboxylic and hydroxyl groups of either acrylic or carbohydrate parts. The medium peaks at 1078 cm$^{-1}$ (1030-1080 cm$^{-1}$), due to stretching vibration of C-O-C and C-O-H bonds, confirms that saccharide structure of gum Arabic (Fig 26)



**FTIR Spectra of Sodium Polyacrylate SAP**

In graph, characteristic band of the polysodium acrylate is presented in the SAP hybrid. The strong, broad peak at 3427 $cm^{-1}$ is related to the OH stretching of the carboxylic and hydroxyl groups of either acrylic or carbohydrate parts. The strong peaks at 1567 $cm^{-1}$ (1560-1630 $cm^{-1}$) are related to the carboxylate C==O stretching, originating mainly from the acrylate part of the SAP.

**Fig 27 - FTIR of Sodium Polyacrylate sythesized by radiation polymerisation**



## 7.5 Thermogravimety Analysis (TGA) :

**T**hermogravimetic Analysis (TGA) is a thermal analysis technique used to measure changes in the weight (mass) of a sample as function of temperature and /or time.TGA is a commonly used to determine polymer degradation temperatures.

**TGA thermograms of the intact gum, the gum free acrylic based SAPs and hybrid SAPs are shown below as :**

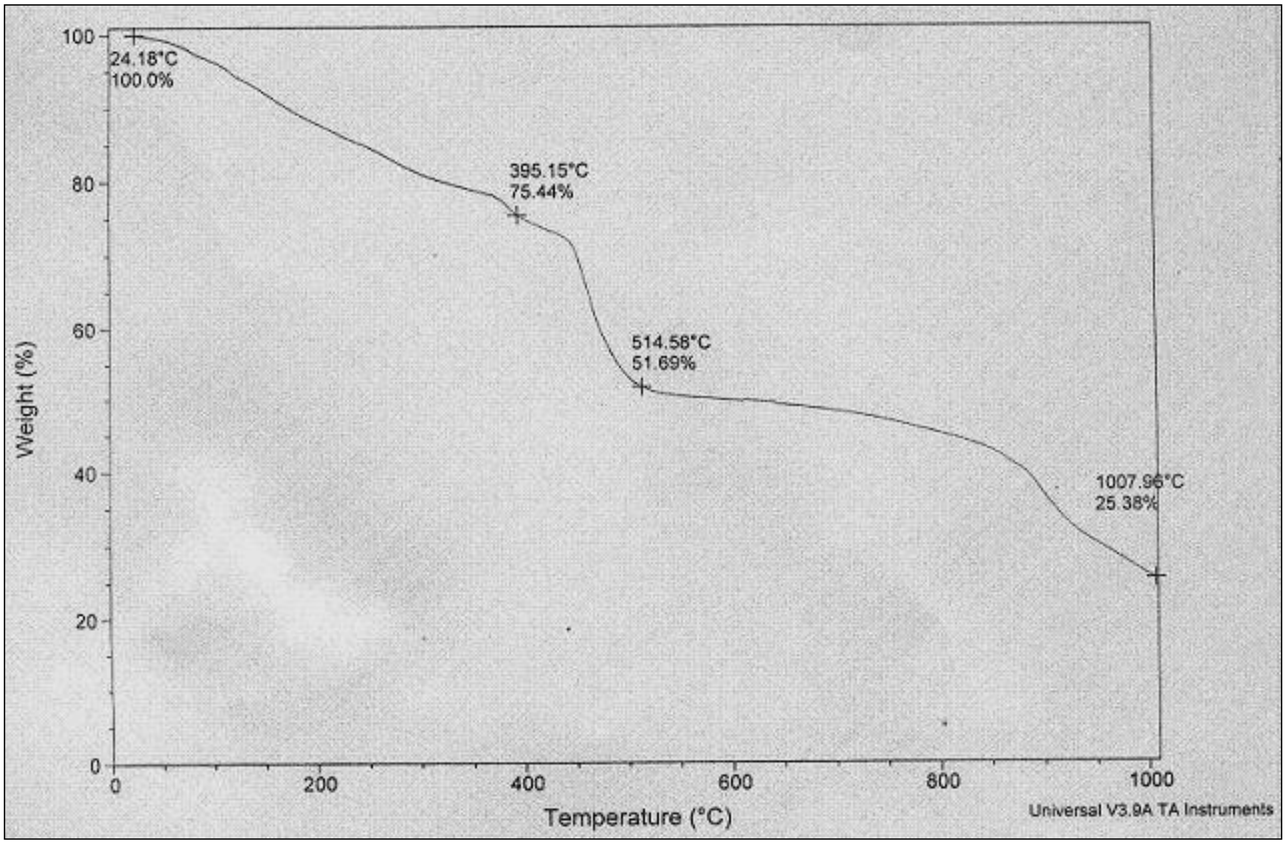


**Fig 28-**TGA thermogram of NaPAC (Synthesisd by Radiation Polymerisation)

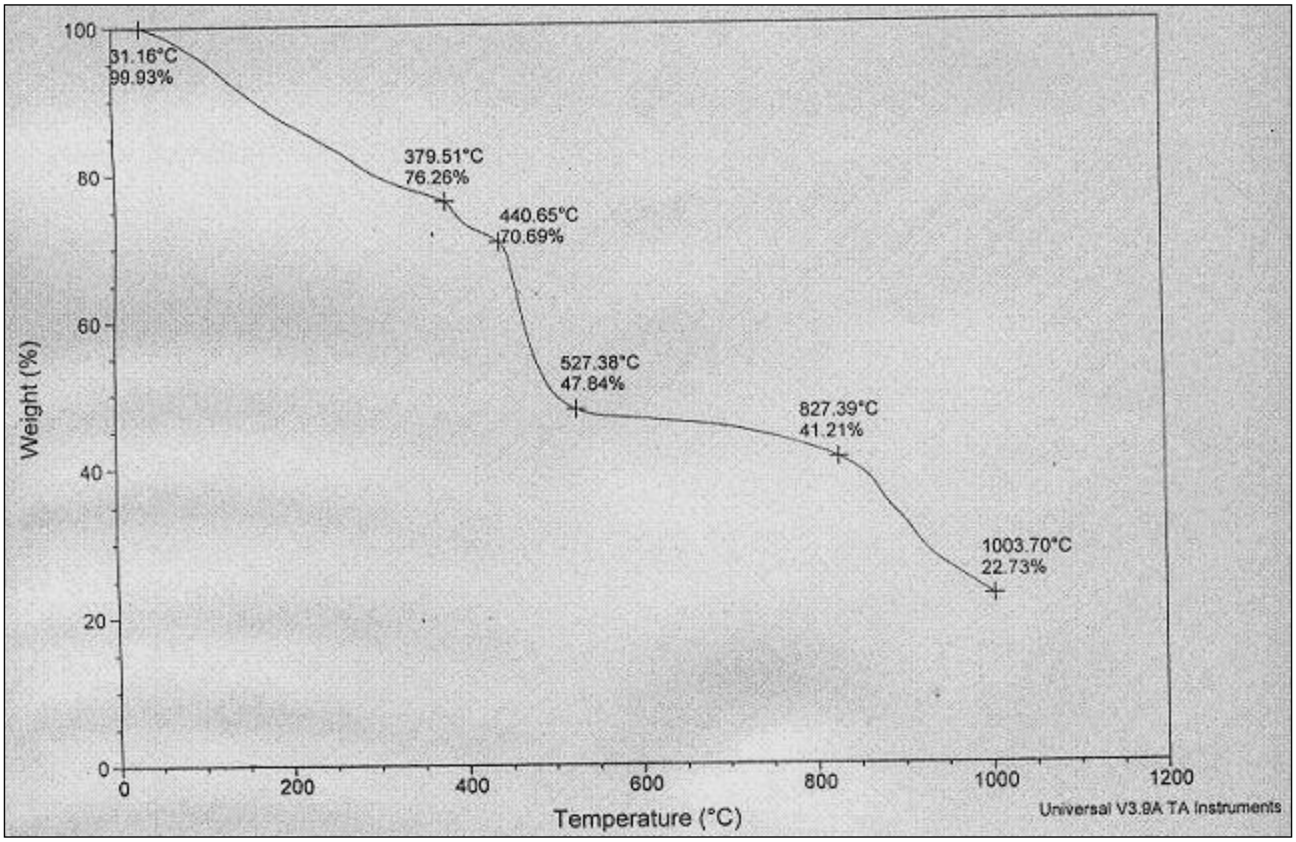


**Fig 29 -** TGA thermogram of NaPAC with 5.0gm Gum arabic (Synthesisd by Radiation Polymerisation)

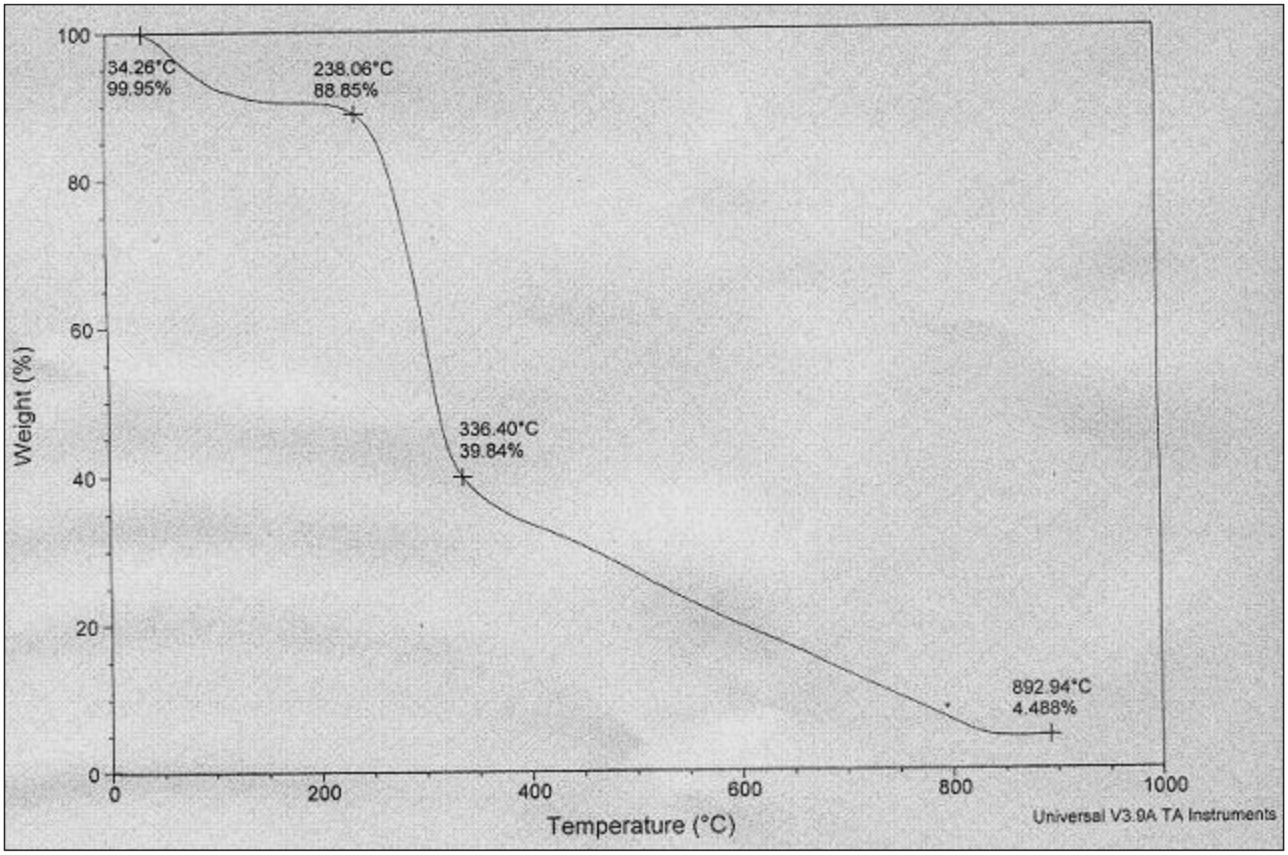


**Fig 29 -** TGA thermogram of Gum Arabic

TGA method was employed to thermally characterize the hybrid SAPs in comparision with the intact gum and the gum-free acrylic based. In contrast to the untreated AG that showed an initial decomposition temperature (IDT) of 245 °C without a char residue at ~825 °C, the gum-free acrylic based exhibited a pattern with a IDT around of 440 was observed in its thermogram. In the hybrid SAPs, an IDT is observed at around 441 in its thermogram.

Therefore, it may be concluded that the synthetic part of the SAPs hybrid maintain its thermal stability.

# Conclusion

# References

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