An-Najah National University

Faculty of Graduate Studies

New Routes for Synthesis of Environmentally Friendly Superabsorbent Polymers

By
Firas Jaber Abd Alateef Abu Jaber

Supervisor
Dr. Othman Hamed

This Thesis is Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemistry, Faculty of Graduate Studies, An-Najah National University, Nablus, Palestine.

2012

New Routes For Synthesis Of Environmentally Friendly Superabsorbent Polymers

By

Firas Jaber Abd Alateef Abu Jaber

This Thesis was defended successfully on 7/6/2012 and approved by:

Defense Committee Members **Signature**

- Dr. Othman Hamed (Adviser) ---------------

-Dr. Orwa Houshia (External Examiner) Orwa Jaber Houshia ---------------

- Dr. Shehdi Joudi (Internal Examine) Shehdeh Jodeh ---------------

DEDICATION

To my father, my mother, my brothers, my sisters,

and to all my friends

ACKNOWLEDGMENT

Praise and thanks to Allah, the most merciful for assisting and directing me to the right path. Special thanks to my research supervisor Dr. Othman Hamed for the chance given me to work with his research group. I am deeply grateful to him for his constant presence, and his encouragement throughout this research project.

Great thanks to Dr Kamel Odwan for helping me in studying the bacterial activity. My thanks to the thesis committee members for their willingness to read the thesis and provide useful suggestions.

Many thanks to Mr. Omair Nabulsi, the chemistry labs supervisor at An- Najah National University. Special thanks to Dr.Haytham Saadi of the Jordan University for his cooperation and support.

I am indebted to many of my colleagues who supported me: Marwan , Ammar and all my friends. Also I will never forget the support of my students.

الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحت عنوان:

New Routes for Synthesis of Environmentally Friendly Superabsorbent Polymers

طرق جديدة لتحضير بوليمرات فائقة الامتصاص صديقة للبيئة

اقر بأن ما اشتملت عليه الرسالة إنما هي من إنتاجي الشخصي باستثناء ما تمت الإشارة إليه حيثما ورد، وان الرسالة ككل، أو أي جزء منها لم يقدم من قبل لنيل أية درجة علمية أوبحث علمي أو بحثي لدى أية مؤسسة تعليمية أو بحثية أخرى.

Declaration

This work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

Students name :	**اسم الطالب**
Signature :	**التوقيع :**
Date:	**التاريخ:**

List of Contents

List of Tables

List of Figures

List of Graphs

List of Appendices

List of abbreviations

SAPs	Superabsorbent polymers
AS	Allyl Sucrose
EAS	Epoxy Allyl Sucrose
1,4-BDGE	1,4-butanediol diglycidyl ether
EGDA	Ethylene Glycol Diacrylate
M-CPBA	meta Chloroperoxybenzoic acid
PAA	Poly Acrylic Acid
AA	Acrylic Acid
SPAN	Starch – graft polyacrylonitrile
PVA	Polyvinyl alcohol
PEO	Poly ethylene oxide
AM	Acryl amide
PAN	Polyacrylamide
MHQ	Methoxyhydroquinone
DAA	Acrylic Acid Dimer
HPA	Hydroxypropionic acid
MAM	Methacrylamide
MAA	Methacrylic acid
AN	Acrylonitrile
HEMA	2- Hydroxyethylmethacrylate
APMS	2-acrylamido – 2- methyl propane
NVP	N- vinyl pyrrolidone
VSA	vinyl sulphonic acid
VAC	vinyl acetate
DVS	Divinyl sulphone
CMC	Carbomethoxy cellulose
HEC	Hydroxyethyl cellulose
MCAA	Monochloroacetic acid
EDTAD	Ethylene diamine tetraacetic dianhydride
AUL	Absorbency Under Load
NA	Nutrient Agar
SDA	Sabouraud Dextrose
TMPTA	Trimethylolpropane triacrylate
TA	Thermal Analyzers

New Routes for Synthesis of Environmentally Friendly Superabsorbent Polymers

By

Firas Jaber Abu Jaber

supervisor

Dr. Othman Hamed

Abstract

New Sucrose – based monomers were prepared. The prepared monomers are Allyl Sucrose (AS) and Epoxy Ally Sucrose (EAS). Allyl sucrose was prepared by reacting sugar with allyl chloride in an alkaline medium. Allyl sucrose was then converted into epoxy allyl sucrose by epoxidation with m-chloroperoxybenzoic acid (m-CPBA). The prepared sucrose-based monomers were characterized by ^{1}H and ^{13}C NMR spectroscopy. Both sucrose-based monomers were then used as cross-linking agents to prepare an entirely new class of special biodegradable superabsorbent polymers. In addition, other cross-linking agent were also used including 1,4-butanediol diglycidyl ether (1,4-BDGE), and ethylene glycol diacrylate (EGDA). Ethylene glycol diacrylate was chosen because it is a well known cross-linking agent that is reported in the literature as a cross-linking agent for superabsorbent polymers. 1,4-Butanediol diglycidyl ether was used for the first time as cross-linking agent for superabsorbent polymer. The absorbency for the prepared SAP's were evaluated. Free swell for the prepared polymers was measured using the tea bag test, and the absorbency under load was measured using the hanging cell test method. Results showed that the free swells and absorbency under load decrease by increasing percentage of cross-linking agent, lowest absorbency observed at cross-linking about 4%. SAP cross-linked with EAS has the highest absorbent capacity and absorbency under load. This could be because it has the highest polarity and highest number of hydroxyl groups.

The advantages of the prepared polymers over the commercial one are that: first; they are biodegradable as shown by the biodegradability test; second, they are prepared in one step process. Since the commercial SAP is prepared in a two-step process, in the first step the acrylic acid is polymerized with the cross-linking agent then the produced SAP is surface cross-linked to enhance it absorbency under load.

Chapter One

Introduction

1.1 Background

Superabsorbent polymers (SAPs) are hydrophilic networks which have the ability to absorb and retain large amounts of fluid without dissolving and the absorbed fluid is hardly removable even under some pressure [1]. In water SAPs swells to a rubbery gel to their mass can absorb and retain extraordinary large amounts of water or aqueous solution [2]. These ultrahigh absorbing materials can imbibe deionized water as high as 1000-100000% (10-1000g/g) whereas the absorption capacity of common hydrogels is not more than 100% (1g/g). Visual and schematic illustrations of an acrylic – based anionic superabsorbent hydrogel in the dry and water-swollen states are given in Fig.1.1 [3].

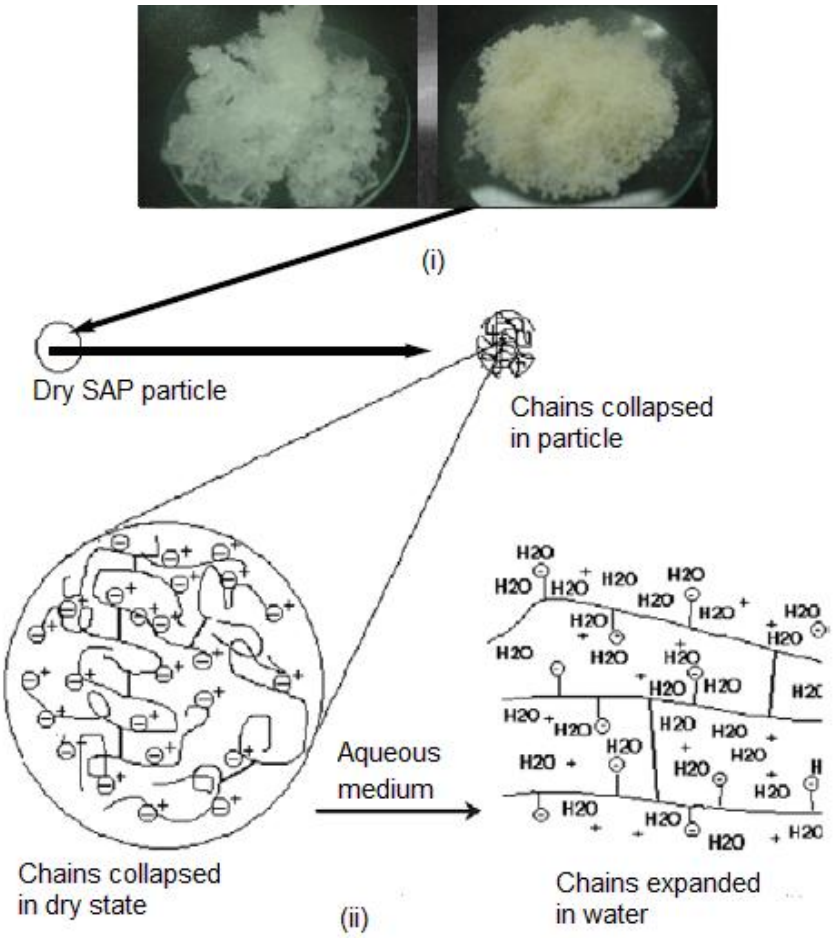


Fig. 1.1: (i) A visual comparison of the SAP single particle in dry (right) and swollen state (left). (ii) A schematic presentation of the SAP swelling [3,4].

Traditional absorbent materials such as tissue paper and polyurethane foams unlike SAPs, will lose most of their absorbed water when they are squeezed.

Table 1.1 : Comparison between the absorbing capacity of common materials with SAP [2-5].

Absorbent Materials	Water Absorbency (wt%)
Filter paper	180
Tissue paper	400
Soft polyurethane sponge	1050
Wood pulp fluff	1200
Cotton ball	1890
Agricultural SAP	20200

1.2 Superabsorbent Polymers Physical Shapes

SAPs are produced in various forms like for instance powder, fiber, foam and film. The SAP particle shape (granula, fiber, film,….etc) has to be basically preserved after water absorption and swelling, i.e ., the swollen gel strength should be high enough to prevent a loosening, mushy, or slimy state [6]. This is a major practical feature that distinguishes SAPs from other hydrogels. Usually this is done by lightly cross-linking of SAPs to produce a net work that can swell in water and hold large amount of fluid while maintaining its shape. Example on crosslinked polymer is shown in Fig.1.2.1 [7].

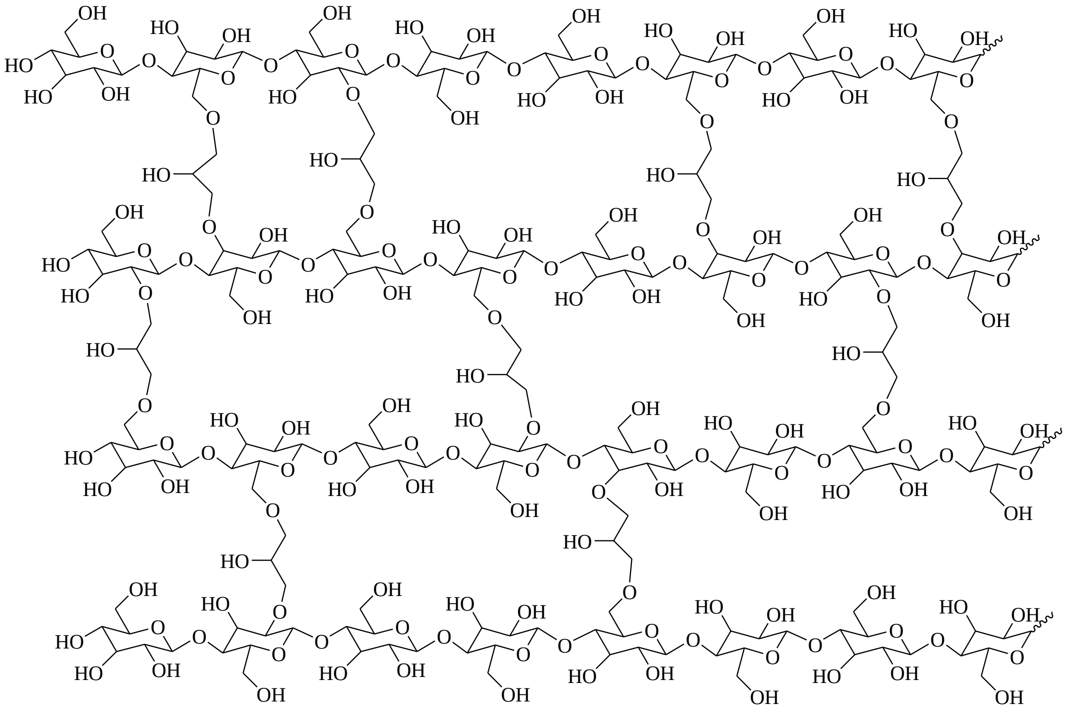
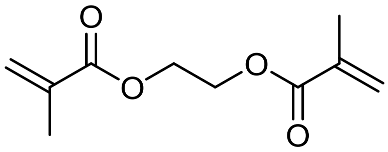
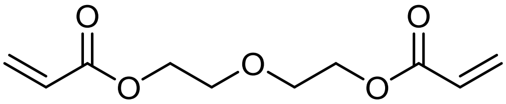


Fig.1.2.1: Cellulose polymer cross-linked with epichlorohydrin.

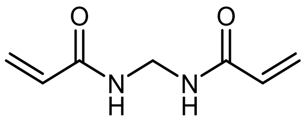
Examples on some of the cross-linking agent used SAP cross linking are summarized in Fig. 1.2.2 that include ethylene glycol dimethacrylate, TMPTA, and diethyleneglycol diacrylate are examples of cross-linkers made by esterification of multifunctional alcohols, N,N'-methylenebisacrylamide (MBA) and 1,4-butanediol diacrylate (BDDA), and epichlorohydrin. These are used as the water and the oil soluble crosslinkers, respectively [8, 9].



Ethylene glycol dimethacrylate

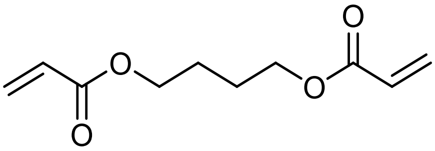


diethyleneglycol diacrylate



N,N'-methylenebisacrylamide

MBA; water-soluble crosslinker



1,4-butanedioldiacrylate

BDDA; water-insoluble crosslinker

Fig. 1.2.2: Structures of some of the cross-linking agents.

1.3 Water Absorbents

Water Absorbent materials are usually categorized into two major classes based on the mechanism of water absorption, i.e., chemical and physical absorptions. Chemical absorbers (e.g., metal hydrides) hold water via chemical reaction converting their entire nature. Physical absorbers hold water via four main mechanisms; (1) reversible changes of their crystal structure (e.g., silica gel and anhydrous inorganic salts); (2) physical trap of water via capillary forces in their macro –porous structure (e.g., soft polyurethane sponge); (3) a combination of the mechanism of physical trap **2** and hydration of functional groups (e.g., cellulose); (4) mechanism that involves combination of mechanisms of **2** and **3** and essentially dissolution and thermodynamically favored expansion of the macromolecular chains limited by cross-linkages [6] .

1.4 Applications

Due to their excellent water absorbing properties, SAPs have an unlimited number of applications. They are used as scaffolds in tissue engineering where they may have human cells in order to repair tissue. Superabsorbent polymers have the ability to sense environmental changes, like as changes of pH, temperature. Hydrophilic networks that are responsive to some molecules, such as glucose or antigens can be used as biosensors as well as in drug systems, disposable sanitary products (for example, diapers, incontinence articles, feminine hygiene products, airlaids and absorbent dressings), and in controlled release drugs [10]. Superabsorbent polymers were also employed in various applications, such as household articles, sealing materials, humectants for agricultural products for soil conditioning, oil-drilling, anti-condensation coatings, water-storing materials in agriculture, absorbent paper products, bandages and surgical pads, pet litter, wound dressings, and as chemical absorbents. Furthermore, they are used in food packaging applications [11].

1.5 History and Market

The synthesis of the first water-absorbent polymer prepared from acrylic acid (AA) and the crosslinking agnet divinylbenzene (Fig.1.5.1), were both thermally polymerized in an aqueous medium, and then the first generation of hydrogels was appeared [12]. These hydrogels were mainly based on hydroxyalkyl methacrylate and related monomers with swelling capacity up to 40-50%.

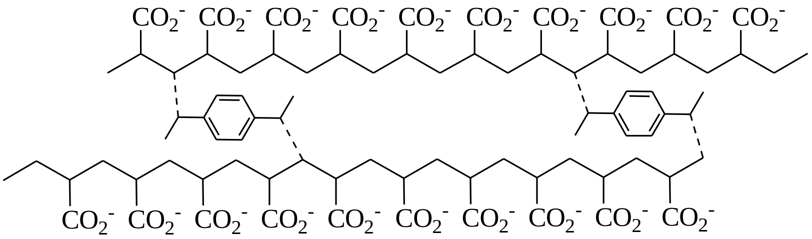


Fig. 1.5.1: Superabsrobent polymer made from acrylic acid and divinylbenzene.

They were used in developing contact lences which have make a revolution in ophthalmology, and the first commercial SAP was produced through alkaline hydrolysis of starch–graft-polyacrylonitrile (SPAN) is shown in Fig.1.5.2.

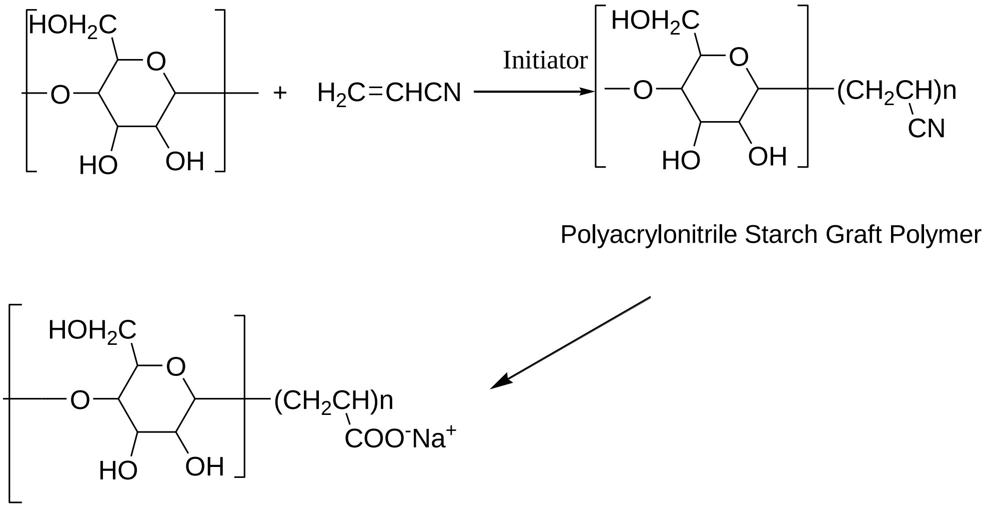


Fig.1.5.2: Superabsrobent polymer made from Starch grafted polyacrylonitrile.

1.6 Types of superabsorbent polymers and methods of preparation

Superabsorbent polymers can be classified based on the basis of presence or absence of electrical charge in the SAPs cross-linked chains as ionic or nonionic polymers. The ionic polymers may be an anionic or a cationic based on the charge present on the polymer chains positive or negative [13].

1.6.1 Nonionic Polymer

Nonionic polymers absorb water and aqueous fluids by means of the energetic and entropic interactions made possible by mixing the aqueous fluids with the hydrophilic groups that are present along the polymer chain. Example on this type of polymer is methylcellulose and ethylcellulose is shown in Fig. 1.6.1.1.

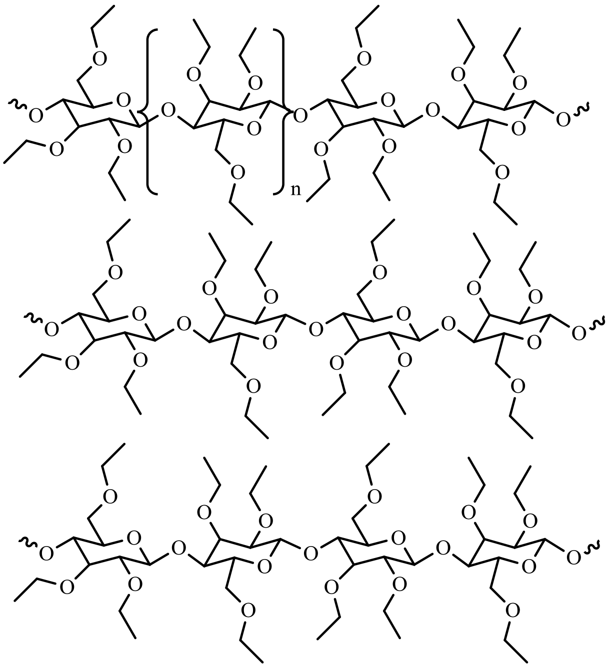


Fig.1.6.1.1: Example on nonionic water soluble SAP.

In this class of absorbents water molecules are solvated through hydrogen bonds. In addition, the entropy of the system may be increased during mixing by a decrease in the partially ordered structure of pure liquid water. These are the same phenomena that lead to the dissolution of water – soluble polymers [14]. The principle distinction of absorbent polymers over water-soluble polymers is the presence of crosslinks within the molecular structure of the absorbent polymers. The crosslinks connect the various polymer chains into a huge insoluble molecule that nevertheless can change its shape and volume as it becomes solvated by water is shown in Fig.1.6.1.2. The result of the absorption of solvent is a swollen, soft gel.

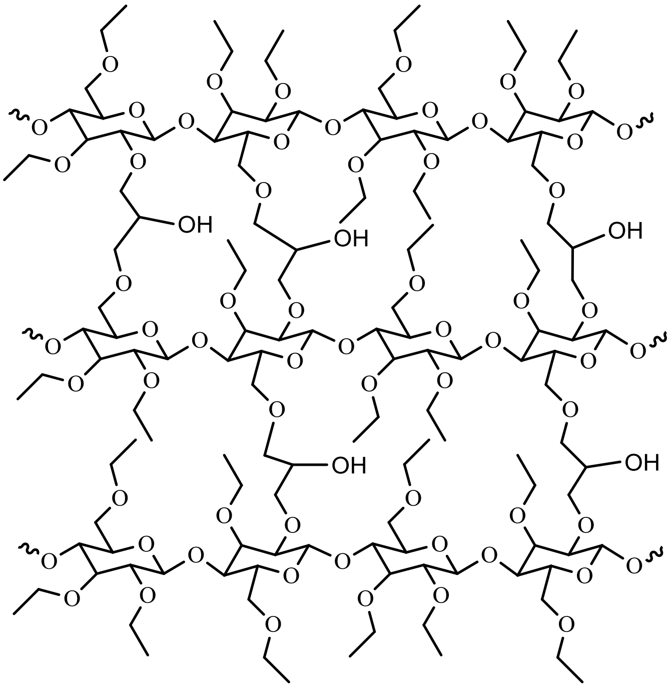


Fig.1.6.1.2: Example on nonionic water insoluble cross-linked SAP, ethylcellulose crosslinked with epichlorohydrin.

The nature of the crosslinks plays a significant role in the properties of superabsorbent polymers. There are three principal bonding types that are used to bind the polymer chains together: covalent, ionic, and hydrogen bonds. Two basic methods are used to introduce covalent crosslinks. First, covalent crosslinks are formed when the major monomers (e.g., acrylic acid) is copolymerized with a di-,tri-, or tetra – vinyl monomer such as N,N-methylenebis(acrylamide), 1,1,1-trimethylolpropanetriacrylate, or tetraallyloxyethane, in a free radical initiated addition polymerization [15].

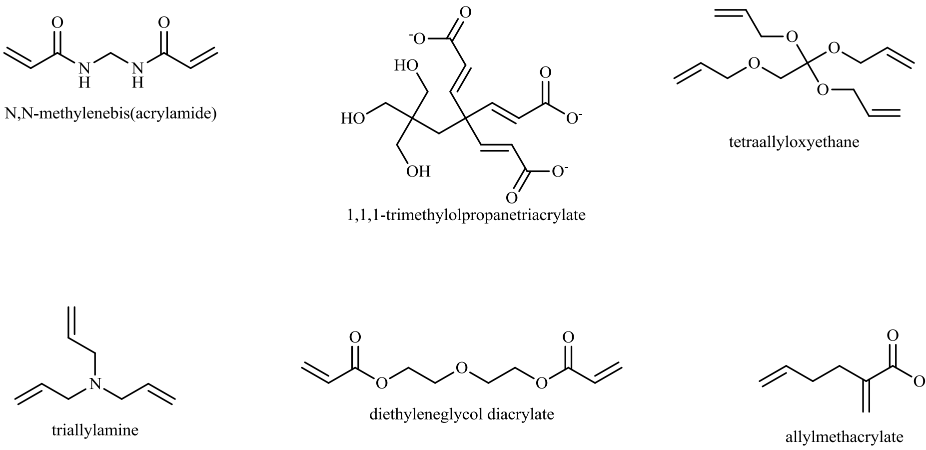


Fig.1.6.1.3: Examples on SAP cross-linking agents.

Covalent cross-links are also introduced by reacting the polymer chains with a di- or tri - functional reagents that reacts with the carboxylic acid groups by means of a condensation or addition reaction.

Second, ionic cross-links are formed by reacting a polyvalent ion of opposite charge with the charged polymer chains. The crosslink forms as a result of charge association of the unlike charges as shown in Fig.1.6.1.4. Because the bond is formed by ion association (charge neutralization) the chemical structure of the cross-linker is less important in determining the placement of the cross-links compared with covalent cross-links. If ionic components are present in the liquid to be absorbed, ion exchange may occur with the ionic cross-links, which may alter the nature of the cross-links and the behavior of the polymer in ways that may be unforeseen. Also because the interionic reaction is very fast.

The incorporation of the crosslink and the resulting structure of the crosslinked polymer can be difficult to control.

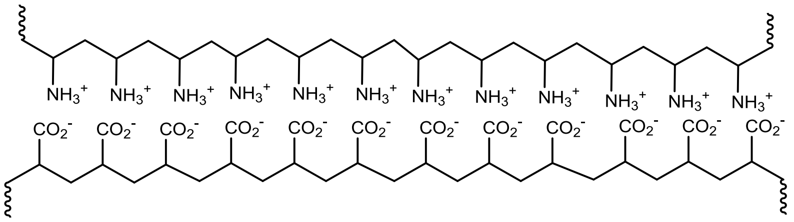


Fig.1.6.1.4: Polyacryl amide cross-linked with polyacrylic acid via attraction between opposite charges**.**

The third type of crosslink is the physical crosslink, which is usually formed by means of hydrogen bonding of segments of one chain with the segments of another chain is shown in Fig.1.6.1.5.

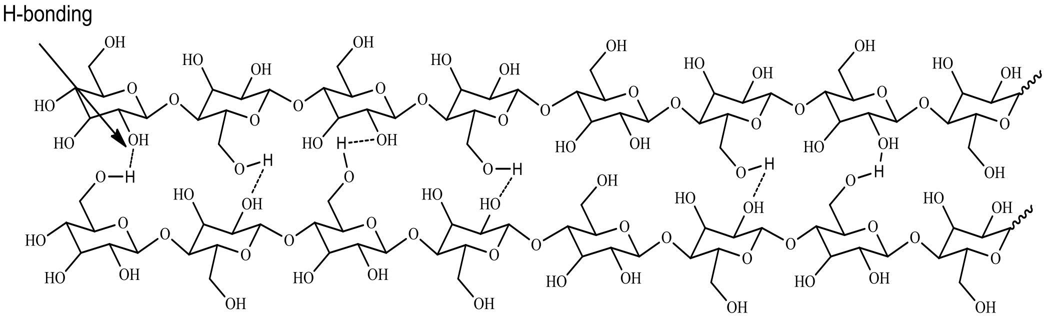


Fig.1.6.1.5: Example on physical crosslink.

A number of nonionic water-soluble polymer types are known, and these may be used as absorbent polymers when cross-linked. Outside of the large contribution of ions to swelling, some of the important characteristics that should be available in polymer to be absorbent polymers are for example, the molecular weight of the polymer chains should be large for optimum absorbency, and the absorbency depends on the mass of the monomer unit and its solvating character. A high-molecular weight, hydrophobic monomer will not yield an absorbent polymer optimized for water absorption on a weight basis [16].

1.6.1.1 Polyacrylamide

Polyacrylamide is a well-known water soluble polymer and has been cross-linked by numerous methods to form an absorbent polymer [17]. Unless some of the amide functions are hydrolyzed to anionic carboxylates, the polymer is nonionic. Acrylamide is one of the very few monomers that can be easily polymerized to extremely high molecular weight (~10 million g/mol), which is an advantage for making absorbent polymers. Example on acrylamide is shown in Fig.1.6.1.1.1. A major disadvantage is the practical difficulty of removing the quantity of unpolymerized acrylamide in the final product. This is a well documented toxicology of acrylamide monomer [18].

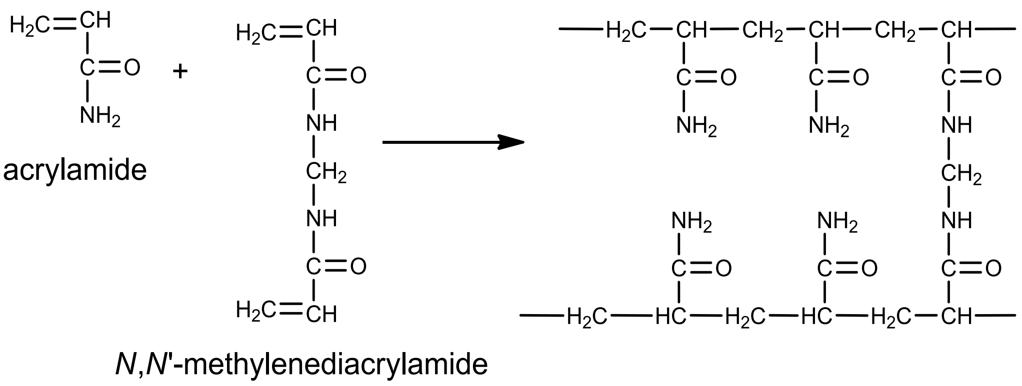


Fig.1.6.1.1.1: Preparation of polyacrylamide polymer [19].

1.6.1.2 Polyvinyl Alcohol (PVA)

Polyvinyl alcohol gels have been used as absorbent polymer. They are prepared by reacting vinyl acetate to form poly (vinyl acetate) followed by hydrolyzing the poly (vinyl acetate) to poly (vinyl alcohol) as shown in Fig.1.6.1.2.1, and finally reacting with a crosslinker such as a polycarboxylic acid (forming ester crosslinks). Poly (vinyl alcohol) is limited to practical molecular weight of about 700,000 g/mol as a result significant chain transfer reactions to the monomer and can be highly crystalline; both features limit the swelling properties of PVA. The monomer is moderately expensive when compared to acrylamide [20].

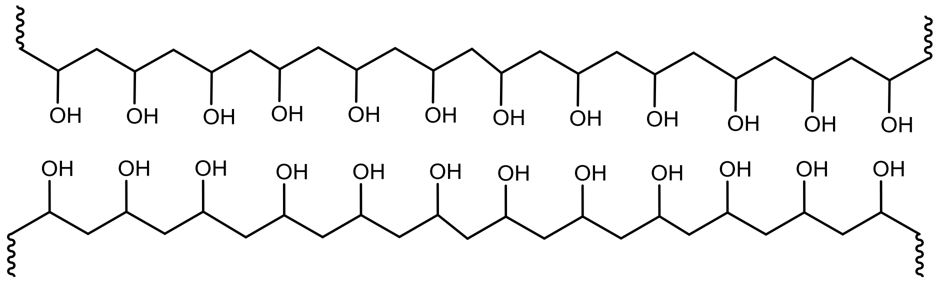


Fig.1.6.1.2.1: A representative structure of PVA.

1.6.1.3 Polyethylene Oxide (PEO).

Polyethylene oxide has rarely been used as an absorbent polymer, even though the monomer has relatively lower price. The polymer is usually prepared from polymerizing of ethylene oxide shown in Fig.1.6.1.3.1. The molecular weight of the polyoxide is limited to about 600,000 g/mol. Cross-linking may occur either by end linking the hydroxyl end groups with an appropriate reagents such as for example polyisocyanates or by means of radiation treatment. Efficient end linking is quite difficult for very high molecular weight polymers as a consequence of the low concentration of end groups. Poly (ethylene oxide) is known to be highly crystalline, which makes its water absorbency decrease [21,22].

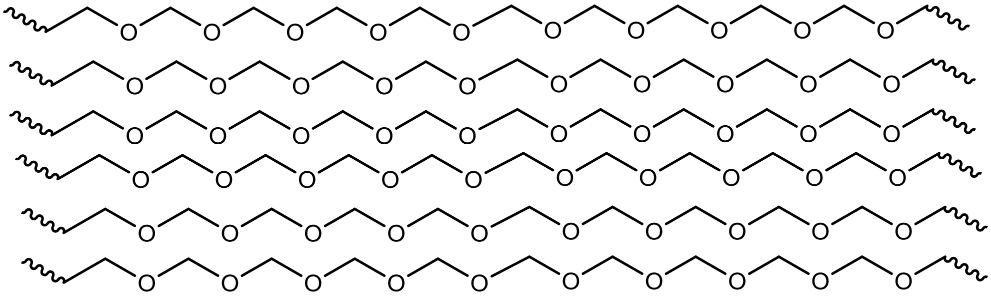
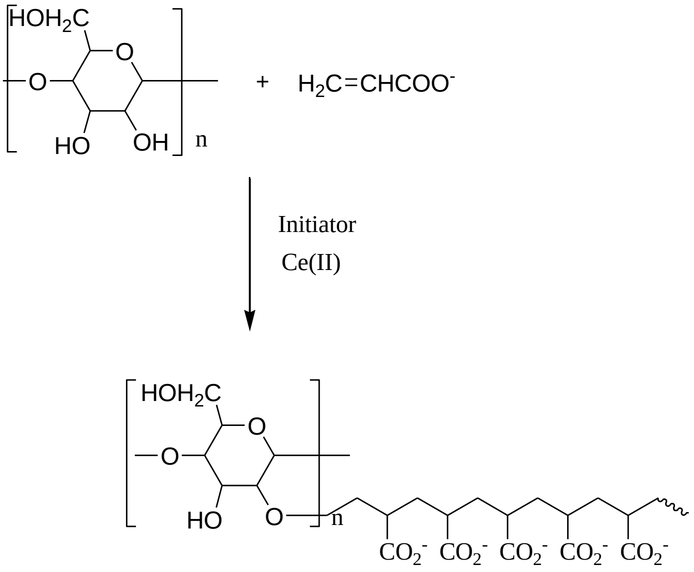


Fig.1.6.1.3.1: A representative structure of PEO

1.6.2 Natural Polymer

Natural polymer are divided into two main groups: polysaccharides and polypeptides (proteins). SAPs are prepared from natural polymer through addition of some synthetic parts onto the natural substrates, e.g., graft copolymerization of vinyl monomers on polysaccharides. Example on this type of polymer is shown in Fig.1.6.2. In this figure a structure of starch grafted with polyacrylic acid is shown.



Polyacrylic acid Starch Graft Polymer

Fig.1.6.2: A representative structure of starch grafted with PAA.

SAPs are also classified based on the type of monomeric unit in their chemical structure, thus the most traditional SAPs fall in one of the following categories: [23]

1. Cross-linked polyacrylates and polyacrylamides.
2. Hydrolyzed cellulose-polyacrylonitrile (PAN) or starch –PAN graft copolymers.
3. Cross- linked copolymers of maleic anhydride.

1.6.2.1 Anionic Superabsorbent Polymers

The most conventional type of anionic SAPs is the acrylic polymer that comprises a copolymeric net-work based on the partially neutralized acrylic acid (AA) or Acrylamide (AM); As shown in Fig.1.6.2.1. Polyacrylic polymer has partial neutralization products of polymerized acrylic acid monomer, its salts, and acrylamide via solution or inverse-suspension polymerization techniques such as starch-acrylonitrile and starch –acrylic acid graft copolymers and polyacrylic acids.

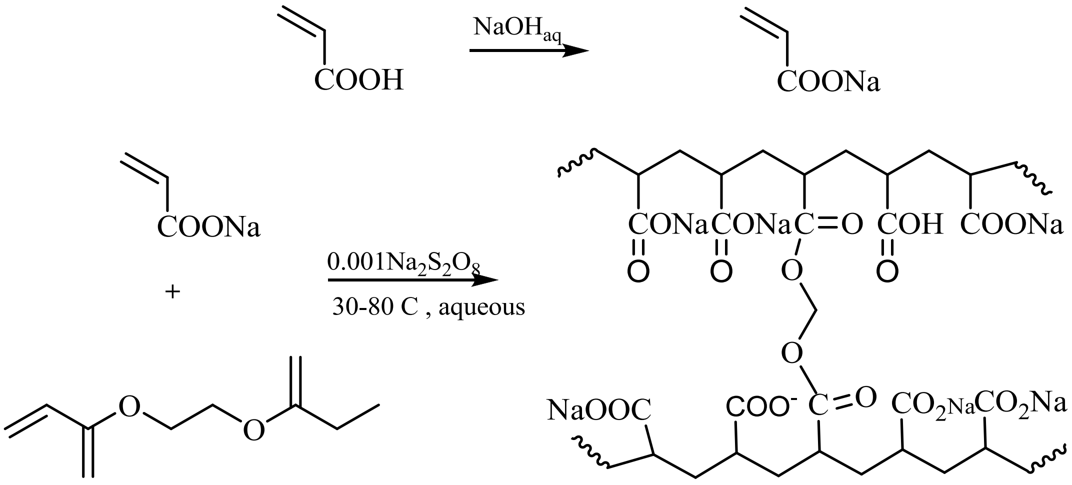


Fig.1.6.2.1: Polymerization of Superabsorbent Polyacrylates.

The materials biodegradability is a main focus in this research because of the rebuilt concern towards environmental protection issues. The half life is in general in the range 5-7 years, and they decompose into carbon dioxide, ammonium, and water [24].

1.6.2.2 Monomers for Acrylic Anionic Polymers

Acrylic acid (AA) and its sodium or potassium salts, and acrylamide (AM) are most often used in the industrial production of SAPs.

The AA monomer is unstable dimerize or trimerizes at room temperature in presence of air to form dimer as shown in Fig.1.6.2.2.1. This process is usually inhibited by free radical scavenger methoxyhydroquinone (MHQ). In industrial production, the inhibitor is not usually removed due to some technical reasons [25]. Meanwhile, AA is converted to an undesired dimer that must be removed or minimized.

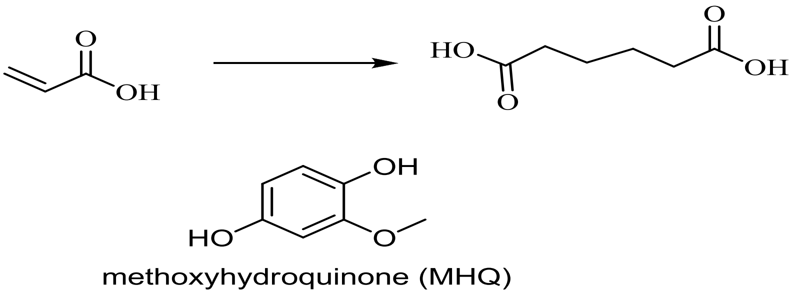


Fig.1.6.2.2.1: Dimerization of acrylic acid**.**

The minimization of acrylic acid dimer (DAA) in the monomer is important due to its indirect adverse effects on the final product. As soon as AA is produced, diacrylic acid (β-acryloxypropionic acid) is formed spontaneously in the bulk of AA via a sluggish Michael-addition reaction as shown in Fig.1.6.2.2.2 [26].

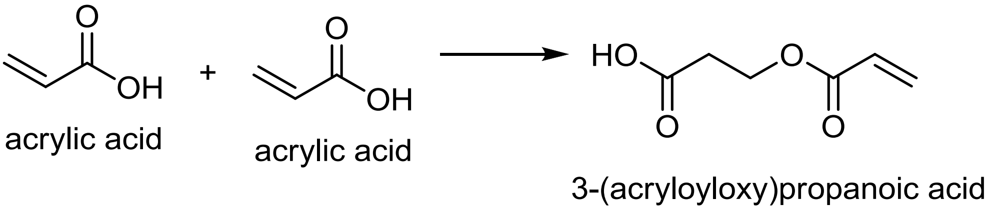


Fig 1.6.2.2.2: Michael addition of acrylic acid**.**

Since temperature, water content, and pH have impact on the rate of DAA formation, the rate can be minimized by controlling the temperature of stored monomer and excluding the moisture. Increasing water concentration has a relatively small impact on the DAA formation rate. The rate of dimerization roughly doubles for every 5 C° increase in temperature.

For example, in an AA sample having 0.5% water, the dimerization rate is 76 and 1672 ppm/day at 20 C° and 40 C°, respectively. DAA, however, can be hydrolyzed in alkaline media as shown in Fig.1.6.2.2.3 to produce AA and β-hydroxypropionic acid (HPA). Since the latter is unable to be polymerized, it remains as part of the SAP soluble fraction. Fortunately, alkaline media used conventionally for AA neutralization with NaOH favors this hydrolytic reaction. For instance, in an 80% neutralized AA, the dimerization rate at 23 C° and 40 C° has been determined to be 125 and 770 ppm/day, respectively [27].

DAA can also be polymerized to go into the SAP network by using strong base or by heating in the drying step of the final product. As a result, free AA will be released and causes the enhancement of the level of residual monomer as shown in Fig1.6.2.2.3 [2,28].

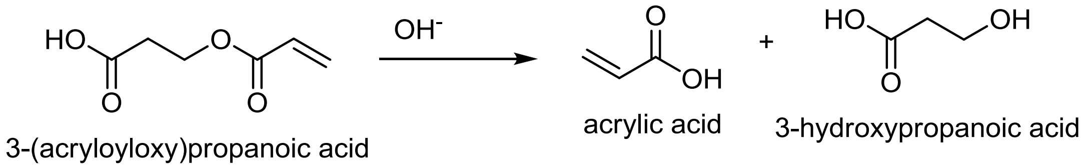


Fig.1.6.2.2.3: Hydrolysis of the Michael addition product of acrylic acid.

1.7 Preparation of Superabsorbent Polyacrylates

Superabsorbent polyacrylates are prepared by free-radical initiated polymerization of acrylic acid and its salts with a cross-linker in aqueous solution or as a suspension of drops of aqueous solution in a hydrocarbon. The polymerization is shown in Fig1.6.2.1. The two principle processes, bulk solution polymerization and suspension polymerization share many features. The monomer and crosslinker concentration, the initiator type and concentration, polymerization modifiers, the relative reactivities of the monomer, the basic polymerization kinetics, and the reaction temperature are all significant factors in both processes [29].

In either process, the monomer is dissolved in water at concentration of 20-40 wt%, and the polymerization is initiated by free radicals in the aqueous phase. Several types of free-radical sources may be used, including thermally decomposable initiator, redox systems, photochemical initiator, and combinations of them

The monomers are polymerized either in the acid form (pH 2- 5) or as the partially neutralized salt (pH 5-7). Inexpensive bases, such as sodium hydroxide and sodium carbonate are used as neutralizing agents. A choice would be made based on consideration of the pH of the base solution and the resulting potential for hydrolyzing the cross-linker, the solubility limits of the base in water and on the solubility of the monomer salt in water. In suspension polymerization, the acrylic acid must be neutralized prior to polymerization because of a substantial partition coefficient of acrylic acid in the liquid hydrocarbons used as continuous phase [30].

The polymers made from acrylic acid (and neutralized later) or from the partially neutralized monomer are somewhat different because of the presence or absence of charged monomers and polymers during the formation of the polymer network.

Small amounts of cross-linker play a major role in modifying the properties of superabsorbent polymers. The co-polymerizable cross-linkers used in superabsorbent polymers range from di-functional compounds mentioned earlier in this chapter [31].

In addition to modifying the swelling and mechanical properties, the cross-linker affects the amount of soluble polymer formed during the polymerization as a result of its relative reactivity with acrylic acid or sodium acrylate. Efficiency of cross-linking will also depend on steric hindrance and reduced mobility at the site of pendant double bonds, the tendency of a given cross-linker to undergo intermolecular addition reactions (cyclopolymerization), and the solubility of the cross-linker in the monomer mixture [32].

Other monomers that are used to make anionic SAP include monomers such as methacrylic acid (MAA), methacrylamide (MAM), acrylonitrile (AN), 2-hydroxyethylmethacrylate (HEMA), 2-acrylamido-2-

methylpropane sulphonic acid (APMS), N-vinylpyrrolidone (NVP), vinyl sulphonic acid (VSA) and vinyl acetate (VAC).

Major disadvantage about these synthetic polymers is poor in degradability, and then there remains an environmental problem with superabsorbent polymers [33].

1.8 Superabsorbent Polymers Origins

The greatest volume of SAPs comprises full synthetic or of petrochemical origin. They are produced from the acrylic monomers, mostly made up from acrylic acid (AA), its salts and acrylamide (AM). (Fig.1.8) shows two ways to prepare acrylic SAP networks, i.e., simultaneous polymerization and crosslinking by a polyvinylic cross-linker, and cross-linking of a water–soluble prepolymer by a polyfunctional cross-linker [33].

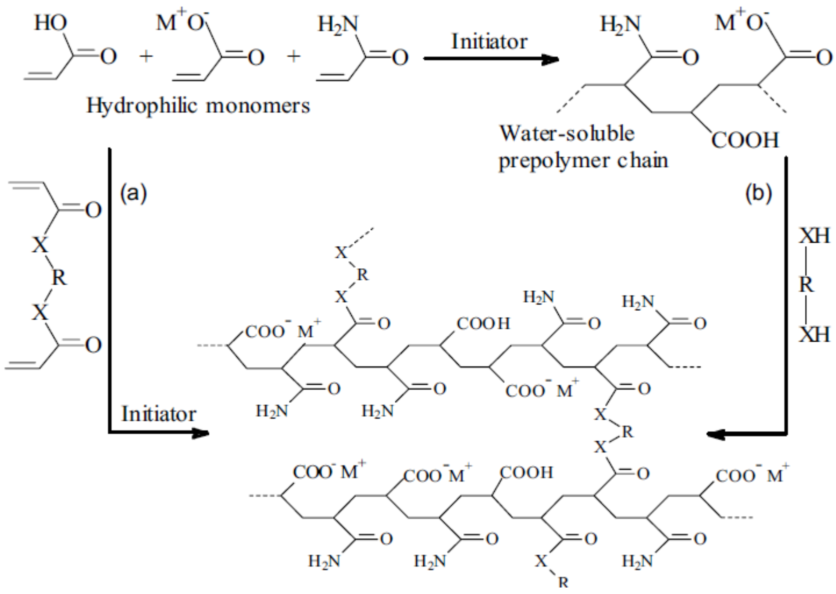


Fig.1.8: Chemical structure of the reactants and general ways to prepare an acrylic SAP network: (a) cross-linking polymerization by a polyvinylic cross-linker, (b) cross-linking of water – soluble prepolymer by a polyfunctional cross-linker. R is aliphatic group. M = sodium or potassium cations. X= O, NH [33].

1.9 Polysaccharide-Based Superabsorbent Polymers

Polysaccharides are polymers of monosaccharides, which are cellulose, starch, and natural gums (such as xanthan, guar, and alginates) are some of the most important polysaccharides.

Preparing polysaccharide-based SAPs fall under two main groups; (a) graft copolymerization of vinyl monomer(s) on polysaccharide in the presence of cross-linker, and (b) direct cross-linking of polysaccharide [34].

1.9.1 Preparation of SAP Based Polysaccharides by Graft Polymerization

In graft co-polymerization, a polysaccharide is reacted with vinyl monomers in presence of an initiator by two separate ways. First, the neighboring OHs on the saccharide units and the initiator interact to form redox pair-based complexes. These complexes are dissociated to form carbon radicals on the polysaccharide substrate via homogeneous cleavage of the saccharide C-C bonds. The free radicals initiate the graft polymerization of the vinyl monomers and cross-linker on the substrate.

The second way for initiation, an initiator such as persulphate ($Na_2S_2O_8$) may abstract hydrogen radicals from the OHs of the polysaccharide to produce the initiating radicals on the polysaccharide backbone [35].

The earliest commercial SAPs were produced from starch and acrylonitrile (AN) monomer by the first mentioned method without employing a cross-linker. The starch g-PAN copolymer (SPAN) was then treated in alkaline medium to produce a hydrolyzed SAP (HSPAN) while an in-situ cross-linking occurred simultaneously. This approach is summarized in Fig.1.9.1.

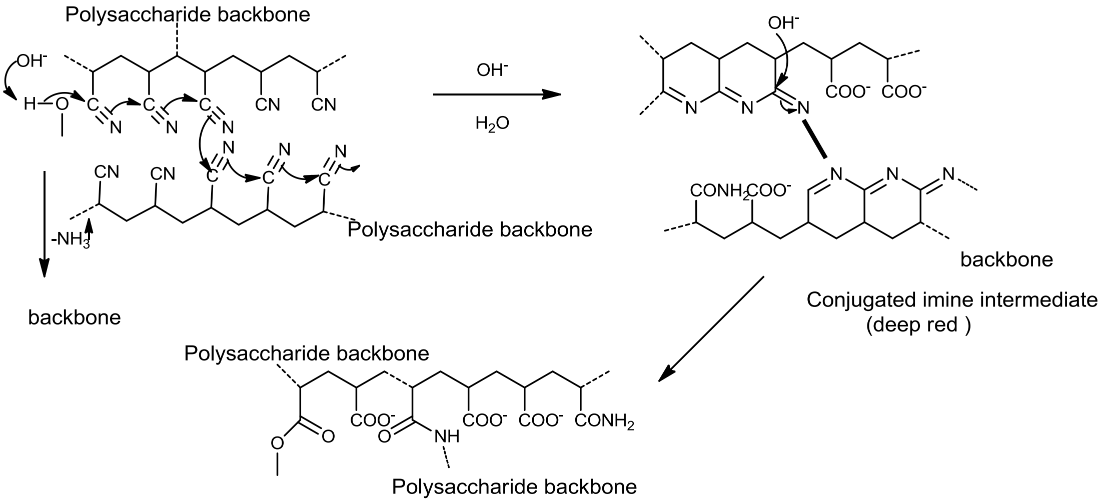


Fig.1.9.1: The mechanism of in-situ cross-linking during the alkaline hydrolysis of polysaccharide-g-PAN copolymer to yield superabsorbing hybrid materials **[33].**

In the method direct cross-linking of polysaccharide, polyvinylic compounds (e.g., divinyl sulphone, DVS) or polyfunctional compounds (e.g., glycerol, epichlorohydrin and glyoxal) are often employed, $POCl_3$ is also used for the cross-linking [18].

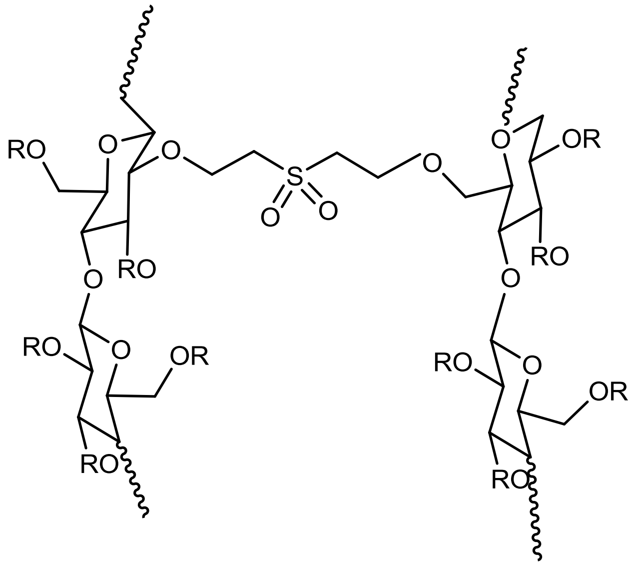
1.9.2 Preparation of SAP Based Polysaccharides by Cross-linking

Polysaccharide based polymer such as carboxymethyl cellulose (CMC) is crosslinked with polyacids to form crosslinked polymer via ester covalent bonds. Sodium carboxymethyl cellulose is a semisynthetic polymer made by reacting chloroacetic acid with sodium cellulose in slurry with isopropanol and water. Sodium cellulose is made by swelling highly crystalline cellulose with an aqueous solution of sodium hydroxide to decrystallize the cellulose and allow homogeneous penetration of the chloroacetic acid. The rigidity of the cyclic cellulose backbone polymer provides for good superabsorbency when the soluble Sodium carboxymethyl cellulose is crosslinked.

Crosslinked Sodium carboxymethyl cellulose has several disadvantages, however. The molecular weight of cellulose that is isolated in a pulping process from tree fiber is low (350,000 g/mol) compared with some of the synthetic polymers, but, at additional cost, cotton linters can provide cellulose with higher molecular weight (1.2 million g/mol) necessary for improved absorbency [17].

Preparing a superabsorbent from Sodium carboxymethyl cellulose also requires crosslinking of a viscous polymer solution, which adds to the cost of this material. In addition, crosslinking Sodium carboxymethyl cellulose is inefficient with typical crosslinkers like divinyl sulfone or glyoxal, because the most reactive hydroxyl groups of cellulose have been substituted with carboxyl groups [36].

As shown in Fig.1.9.2.1 the crosslinked of CMC-and hydroxyethyl cellulose (HEC) – based SAPs with diethylsulfone was prepared by Saninno et al converted into natural SAP hydrogels via cross-linking with citric acid [37].



R= CH_2COO^-

Fig.1.9.2.1: Typical cellulose – based SAP prepared via direct cross-linking of sodium carboxylmethyl cellulose (CMC; R=H, COO^-Na^+) or hydroxyethyl cellulose (HEC; R=H, CH2CH2OH) [36].

Sodium carboxymethyl cellulose belongs to the the class of ionic polymers that are based on naturally occurring polysaccharides. Sodium carboxymethyl cellulose is used in detergents, mining and oil industry, the cosmetics and personal hygiene industries, the paper industry, and food industry. It is prepared as shown in Fig1.9.2.2 by dissolving cellulose in 50% sodium hydroxide solution, slurrying the mixture in isopropanol , and reacting with monochloroacetic acid (MCAA). The product is neutralized with hydrochloric acid and dried [38].

Other ionic polysaccharides include the sodium alginate, carrageenans (from seaweeds), pectins (from plant extracts), and xanthan (from microbial fermentation process). These polymers also become superabsorbent when crosslinked.

Another example on anionic SAP based natural polymer is sodium alginate which is a polysaccharide produced by brown seaweeds such as the giant kelp and isolated by extraction and precipitation of the polysaccharide from the seaweed. The molecular weight of the product is about 250,000 g/mol. The polymer is relatively expensive as a result of the harvesting and extraction processes used in its isolation [39].

A number of cationic polymers are also known and can function as superabsorbent when crosslinked, including poly (diallyldimethylammonium chloride), poly(vinyl pyridine), poly(vinylbenzyltrimethylammonium salts), cationic starches, and hydrolyzed chitin (chitosan), which is derived from the exoskeletons of arthropods such as lobster. A cationic monomer is co-polymerized with a less expensive nonionic monomer such as acrylamide to make the cationic polymer. In general, a combination of complex processing conditions and relatively low molecular weight leads to higher cost and lower effectiveness of the cationic polymers compared with the anionic polymers [40].

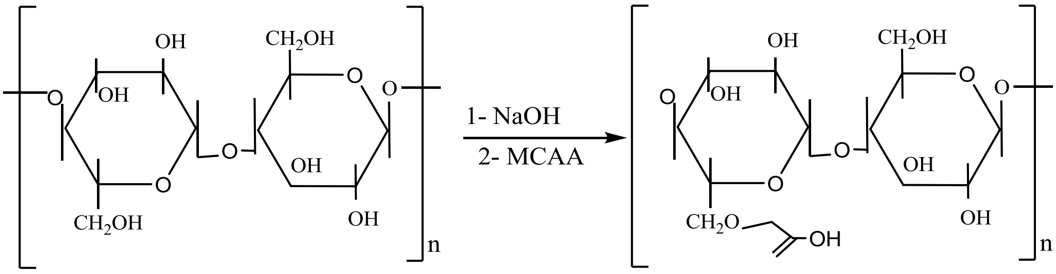


Fig.1.9.2.2: Chemical structure and general ways to prepare Sodium carboxymethyl cellulose.

1.10 Polyamino Acid - Based Superabsorbent Polymers

Proteins from soybean, fish, and collagen – based proteins are the most frequently used hetero-polypeptides for preparation of super – swelling hydrogels.

Soy and fish proteins are converted into SAP by a two period process, in the first stage protein react with Ethylenediaminetetraacetic Dianhydride (EDTAD). EDTAD has low toxicity. In the second stage, the remaining amino groups of the hydrophilized protein are lightly cross-linked by glutaraldehyde to yield a hydrogel network with superabsorbing properties. The SAP was capable of absorbing and retaining 100-350 g of water/g of dry gel after centrifugating it holds about 214 g /g hydrogel, depending on the extent of protein structure, cross-link density, and environmental conditions such as pH, ionic strength, and temperature [41].

On the other hand proteins are modified by polysaccharides or synthetics to produce hydrogels with super-swelling properties, modified proteins with some water-soluble, hydrophilic, biodegradable, and nontoxic polymers, e.g., sodium carboxymethyl cellulose, poly(ethelene glycol), poly(vinyl alcohol), chitosan [42].

Collagen –based proteins including gelatin and hydrolyzed collagen (H-collagen) have been used for preparing SAP materials, e.g., gelatin-g-poly(NaAA-co-AM) hydrogel has been synthesized through simultaneous cross-linking and graft polymerization of AA / AM mixtures onto gelatin H-collagen was also graft copolymerized with AA, binary mixtures of AA and AM, AM and methacrylic acid (MAA) for preparation of SAP hybrid materials.

Homo-poly(amino acid) of poly(aspartic acid), poly(L-lysine) and poly(γ-glutamic acid) have also been employed to prepare SAP materials, super – swelling hydrogels on poly(γ-glutamic acid), PGA, has been prepared by cross-linking reactions via both irradiation and chemical approaches. Similar to PGA, highly swollen hydrogels based on L-lysine homopolymer have been also prepared simply by γ-irradiation of their aqueous solutions [43].

1.11 Importance of Biodegradable Superabsorbent Polymers

Because about 90% of all superabsorbent materials are used in disposal articles, most of which are disposed of in landfills or by incineration, there is a perceived environmental problem with superabsorbant polymers, life cycle analyses of both disposable and cloth diapers manufactured have shown that there is no clearly superior choice in terms of environmental impact [44].

Disposable diapers have been modified to use fewer raw materials, which should result in a reduced solid waste burden, reduced packaging cost, and reduced transportation costs. Despite the technical analysis, consumer clearly perceives disposable absorbent products, specifically diapers, as having a negative impact on the environment. Therefore, superabsorbent polymer producers have been interested in developing biodegradable superabsorbent polymers to serve as a component in a fully biodegradable diaper or other absorbent product [45].

Articles incorporating biodegradable superabsorbents might be disposed of in municipal composting facilities or flushed down to the toilet to degrade in domestic septic tanks or at municipal waste water plant. Several diapers claiming biodegradability have been marketed, but none has enjoyed commercial success. It should be emphasized that the superabsorbent polymer is only one component of a disposable absorbent article. Significant challenges in the developments of biodegradable alternative to other components in the absorbants article, such as water-impermeable back sheet and adhesive tape, remain to be solved [46].

Some of the issues pertinent to biodegradable superabsorbent polymers are also relevant to low molecular weight water soluble polymers, therefor, new developments of biodegradable detergents builders and soil anti - redeposition agents may have implication for biodegradable superabsorbent polymer [47].

1.12 Bio-Degradability Versus Chemical Structure

The world creates billions of pounds of petroleum based waste materials per year.

A substantial portion of the waste is discarded packaging materials and water-absorbent materials such as disposable diapers and hygienic products. Unfortunately, this waste is substantially non-biodegradable; in fact, it takes approximately 450 years to degrade into polyethylene, a major constituent of plastic waste [48].

Accordingly, environmentally unsound and potentially hazardous methods of disposing this waste are utilized, as for example, by landfill or incineration. Furthermore, non-biodegradable plastic is often used in garbage bags, which in addition to creating a waste problem in of themselves, are impermeable to most bacterial agents thereby preventing microbial degradation of the contents within and, thus compounding the problem of waste disposal. These problems have led the health and environmental agencies in the world leader countries to have recently increased interest in products made of "biodegradable" materials. Accordingly, this have initiated research all over the world for making biodegradable materials based on natural products such as starch, cellulose, sugars and others [49].

Biodegradable describe a polymer that can be reduced to carbon dioxide, methane, water, and biomass under biochemical action. Biodegradability may be contrasted with the more generic term degradable.

A degradable polymer undergoes decomposition or degradation under unspecified environmental influences. The final products of a degradable polymer are unspecified; while a biodegradable polymer degrades ultimately to carbon dioxide, methane and water (mineralizes) there are several useful reviews on biodegradable water soluble polymers. Some of the generalization that has been made about biodegradability to chemical structure includes:

1. Naturally produced polymers biodegrade, and Chemical modified natural polymers may biodegrade, depending on the extent of modification.
2. Synthetic addition polymers with carbon- carbon backbone do not biodegrade at molecular weights greater than about 500g/mol.
3. Synthetic addition polymer with heteroatom in their backbone may biodegrade.
4. Synthetic step-growth or condensation polymers are generally biodegradable to a greater or lesser extent, depending on the chemical nature of the chain coupling, molecular weight, morphology and hydrophilicity [50].
5. Water solubility does not guarantee biodegradability.

Based on these generalities three approaches to achieving truly biodegradable bioabsorbents materials are apparent: modification of a superabsorbant to enhance its biodegradability or modification of a biodegradable polymer (e.g natural polymer) to enhance its superabsorbency [51].

The first approach would entail incorporating some biochemical cross-linker that degrades to form smaller chain polymers. The second approach would involve incorporating charged functional group into a hydrophilic biopolymer to enhance its absorbency, then crosslinking the polymer to achieve desired absorbance properties. These modifications may impact the biodegradability of the polymer [52].

The third approach of mixing biodegradable fillers with nonbiodegradable superabsorbance has also been attempted; however these approaches has not led to a fully biodegradable product.

In this research we are concerned with making biodegradable sugar based polymers using approach, and thereafter biodegradable commercial products. The reason behind choosing sugar as the starting material in this proposal is that, sugar is most abundant pure natural organic chemical in the world and available at low cost [53].

The potential value of sucrose as a raw material has been recognized for many years and has been the subject of considerable research. Although relatively few successful derivatives of sucrose have been commercialized, there has been substantial interest in developing sugar-based synthetic technology. Sucrose is a particularly appropriate material for use in the formation of specialty polymers and monomers produced currently from petroleum-based materials since it is:

(a) naturally occurring and relatively inexpensive material;

(b) it is polyfunctional with three reactive primary alcohols that can

readily be derivatized (Fig.1.12) ;

(c) it is a non-reducing sugar and thus does not have the potential for the wide variety of side-reactions that reducing sugars have and

(d) it has a relatively easily hydrolyzed glycosidic linkage that allow

sucrose polymers to be potentially more biodegradable than polymers made with other carbohydrates [52].

Sugar-based polymers are not entirely new. For example, the principal investigator was involved in synthesis, characterization, and applications of sucrose-based epoxy materials developed at USDA laboratories (New Orleans, LA, USA). It has been shown that: a) sucrose can be converted into epoxy in two steps process in over 85% overall yield using commercial available reagents and solvents that could be recycled at low cost; and b) the developed epoxy material is useful in creating new class of superabsorbent polymer [53].

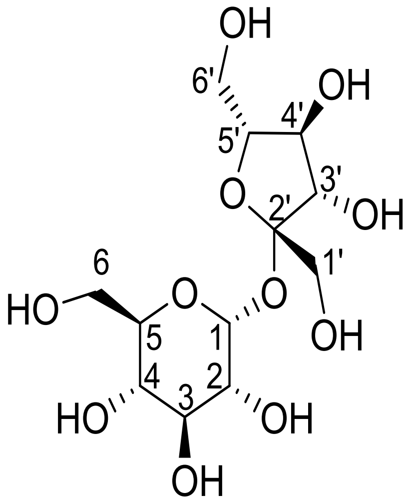


Fig.1.12: Sugar structure**.**

As shown in Fig.1.12, sucrose consists of two monosaccharides, namely glucose (C-1 to C-6) and fructose (C-1' to C-6'), positions 1', 6, and 6' contain primary hydroxyl group, where the rest of hydroxyl groups are secondary.

Chapter Two
Experimental

All chemicals were purchased from Aldrich Chemical Company and used without any further purification unless otherwise stated. All new compounds were characterized by ^{1}H-NMR, ^{13}C-NMR, and IR spectroscopy. Nuclear Magnetic Resonance spectra were recorded on Varian Gemini 2000,300 MHz instrument.

All ^{1}H-NMR experiments are reported in δ units, (ppm) downfield from tetramethylsilane (TMS). All ^{13}C-NMR spectra are reported in ppm relative to the signal of the deuterchloroform (77.0 ppm). Infrared spectra were recorded on Perkin Elmer Model 1310 Infrared spectrometer.

Purification of samples was performed by flash chromatography on silica gel (100-200) mesh.

2.1 Preparation of Allyl Sucrose (AS.)

Method A

In this method a solution of sucrose (10 g, 29.0 mmol in 50 mL solvent) in N,N-dimethylacetamide (DMAc) was first prepared by stirring a mixture of sugar in DMAc at about 60 C^{o} under an inert atmosphere of dry N_2 in a round bottom flask, then the solution was transferred to an additional flask and added dropwise to a funnel that contain a suspension of DMAc and sodium hydride (60% in oil, 20.0 g, 415 mmol, washed four times with 15 mL of dry hexane) at 10 C° over a period of 30 minutes. The procedure was performed under an inert atmosphere of N_2 to the produced sodium sucrate mixture at 10 C°. Allyl chloride (25.0 mL added over 30 minutes) was added. After the addition was complete, the temperature equilibrated to about 50 C°, and the contents stirred for about 90 minutes. Later the contents were cooled to about 10 C°, quenched with 5% aqueous sodium hydroxide (50 mL), diluted with water (500 mL) and extracted with ethyl acetate (3×100 mL). The organic extracts were combined, washed sequentially with water and brine (3×150 mL each), dried over anhydrous sodium sulfate, filtered through charcoal and then concentrated in vacuum to provide the desired products (18.0 mmol, 11.9 g) in 62% yields. The reaction is represented in Fig.2.1.

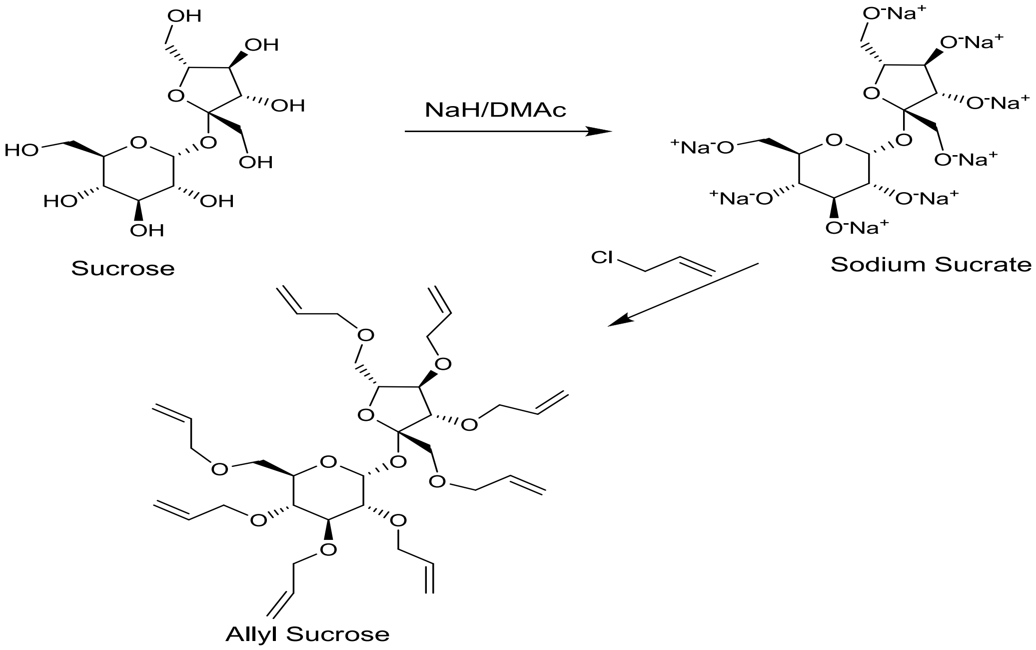


Fig. 2.1: Preparation of Allyl sucrose by method A.

Method B

In this method, sucrose (100 g, 0.29 mol, 2.33 mol hydroxyl groups) and aqueous NaOH (140.2 g in 140 mL water, 3.5 mol, 1.5 eq. /hydroxyl group) were added to a Parr pressure vessel. The vessel was sealed, heated with stirring to about 80 C° over 30 minutes, and maintained at that temperature for about one hour to dissolve the reagents. The contents were then cooled to about 60 C°, the vessel opened, and charged with cold allyl chloride (300 mL, 3.5 mol, 1.5 equiv./hydroxyl group) in one portion. The reactor was then sealed and pressurized with nitrogen gas (50 PSI). The internal temperature was equilibrated to about 100 C° over a period of two hours, and the contents were stirred overnight. Subsequently, the vessel was cooled to room temperature, placed in an ice bath, depressurized, opened, and diluted with ice water (500 mL) to dissolve the salts. The contents were transferred to a separatory funnel and the mixture was extracted with ethyl acetate (3 × 150 mL). The combined organic layers were then washed serially with water (1 × 200 mL) and brine (1 × 200 mL), dried over sodium sulfate, filtered, and concentrated in vacuo (40-50 C°). Allyl sucrose $C_{36}H_{54}O_{19}$, 178.7 g, 0.27 mol) was obtained in 80.3% yield. The average degree of allyl substitution was 6.0 (DS=6.0, by NMR).

^{1}H-NMR for allyl sucrose ($CDCl_3$) δ (ppm): 3.26-4.28 sucrose[s] hydrogens; 5.23 Ha of the glucopyranosyl moieties; 5.24 (geminal terminal olefin hydrogens, Hb), 5.89 internal olefin Hc.). ^{13}C-NMR of allyl sucrose (CDC_3) δ(ppm): 68.23-88.70; 104.13-104.44 (C-3 resonances of the fructofuranosyl moieties of allyl sucrose); 118 (CH_2-1 vinyl), 135.21 (CH_2-2 vinyl).

2.2 Preparation of Epoxy Allyl Sucrose (EAS)

Method A

To a mechanically stirred solution of allyl sucrose (10 g), urea (120 g), sodium bicarbonate (0.6 g), and manganese sulfate (0.02 g) in 20 ml water and 110 ml of dichloromethane at 25 C° was added dropwise over a period of four hours 20 ml of 30% of these an aqueous hydrogen peroxide. After four hours, the reaction mixture was extracted with (4 x 50) ml diethyl ether. The combined organic layer was dried over anhydrous sodium sulfate, and evaporated to provide the desired product in 20% yield.

Method B

A three-neck round bottomed flask, fitted with a high torque overhead mechanical stirrer, pressure-equalized addition funnel, and a condenser connected to a nitrogen gas line, was placed in an ice water bath. The flask was charged with allyl sucrose (average molecular weight 660 g, 15 mmol, 91 mmol double bonds) dissolved in ethyl acetate (50 mL), and sodium acetate (1 g, 10% of the number of moles of m-chlororperoxy benzoic acid) was then added to the solution. The contents were cooled to about 5 C°, and m-chlororperoxy benzoic acid (30% in ethyl acate, 110 mol) was added dropwise into the mixture over about two hours. The temperature was then raised to about 10 C°, and the contents stirred overnight. Subsequently, the mixture was diluted with ethyl acetate (200 mL), transferred to a separatory funnel, and washed serially with cold water (2×50 mL), cold aqueous saturated sodium carbonate (1×50 mL), and brine (2×50 mL). The organic layer was then separated, dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo (at 50 C°) to yield EAS as an oil that is clear and light yellow in appearance in 93% yield (9.24 g, 11.7 mmol.). No further purification was needed. The synthesis of epoxy allyl sucrose is shown schematically in Fig. 2.2.

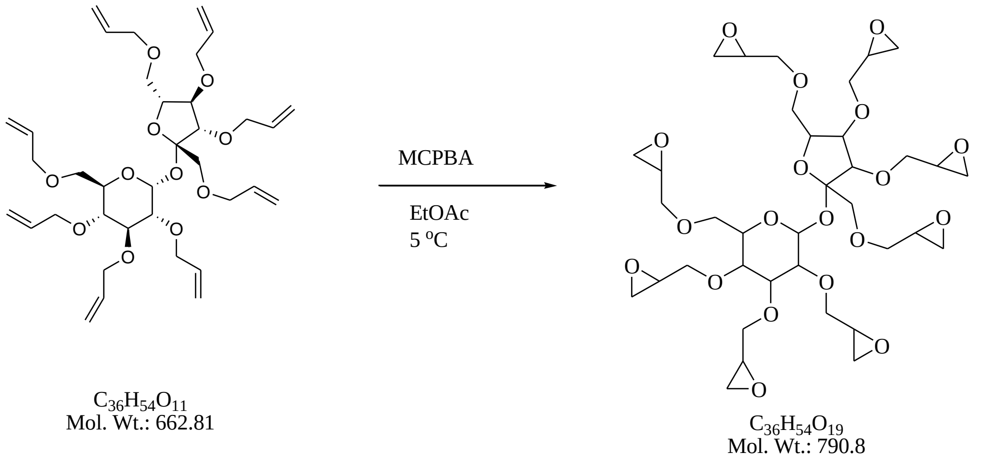


Fig. 2.2: Preparation of Epoxy allyl sucrose by method B.

The ^{1}H-NMR for epoxy allyl sucrose (EAS) ($CDCl_3$): 2.67 (H-c, geminal methylene of the epoxy group) 3.0-4.3 (sucrose protons and methylenes), 4.82-4.98 (residual geminal terminal olefin hydrogens), 5.55 (H-1 signal of the glucopyranosyl moieties of the epoxy methallyl sucrose isomers).

^{13}C-NMR for epoxy allyl sucrose ($CDCl_3$) δ(ppm): 19.24 (residual allylic CH_3-d,), 51.5 (terminal epoxy allyl carbon CH_2-c′), 56.1 (internal epoxy allyl carbon C-b′) 66 to 86 (sucroses carbons and methylenes CH_2), 89.6 (C-1 resonances of the glucopyranosyl moieties of the epoxy allyl sucrose), 104.2 (C-2′ resonances of the fructofuranosyl moieties of epoxy allyl sucrose isomers) and 105 (C-2′ residual resonances of the fructofuranosyl moieties of unepoxidized methallyl sucrose isomers), 111.7 (residual CH_2-c), 141.3 (residual tetrasubstituted olefin carbons C-b).

2.3 Preparation of Superabsorbent Polymer

Method A:

In this method neutralization of prepared SAP was performed after polymerization.

2.3.1 Superabsorbent Polymer cross-linked with Allyl Sucrose (PAA-AS.)

To a two neck round- bottomed flask under an inert atmosphere (N_2) fitted with a condenser equipped with an magnetic stirrer, allyl sucrose (1, 0.5, 0.37, 0.25, 0.06 g) and 25 ml acrylic acid were added and the reaction mixture was stirred for 10 minutes. Then the $K_2S_2O_8$ (1 mL, 10%) was added into the flask to initiate the reaction. First, the reaction was heated at low temperature (about 60 C^{o}) once the exothermic reaction started, the heat was turned off and reaction continued for about two hours. Gelation was observed after about 40 minutes. After two hours, the produced mass was treated with 1M sodium carbonate (40 ml) for partially neutralization. The produced solid gel dried for 24 hours at about 80 C^o. The dried solid was then grinded for further evaluation.

2.3.2 Superabsorbent Polymer cross-linked with Epoxy Allyl Sucrose (PAA-EAS.)

Procedure reported in section 2.3.1 was repeated exactly except that; ally sucrose was replaced with epoxy ally sucrose.

2.3.3 Superabsorbent Polymer cross-linked with 1,4-Butanediol Diglycidyl Ether (PAA-1,4-BDGE.)

Procedure reported in section 2.3.1 was repeated exactly except that; ally sucrose was replaced with 1, 4-butanediol diglycidyl ether.

2.3.4 Superabsorbent Polymer cross-linked with Ethylene Glycol Diacrylate (PAA-EGDA.)

Procedure reported in section 2.3.1 was repeated exactly except that; ally sucrose was replaced with ethylene glycol diacrylate.

2.4 Preparation of Superabsorbent Polymer

Method B:

In this method, acrylic monomer was first neutralized to a pH of about 6.0, then polymerization performed on neutralized acrylic acid.

2.4.1 Superabsorbent Polymer cross-linked with Allyl Sucrose

Acrylic acid (25 ml) was dissolved in 20 ml distilled water and then neutralized with 37.5 ml of sodium hydroxide solution (8.3 M) to pH 6. Then acrylic acid transferred into a two neck round- bottomed flask fitted with a condenser equipped with a magnetic stirrer and placed under an inert atmosphere (N_2). To the previous preparation, the cross-linking agent allyl sucrose was added by (1, 0.5, 0.37, 0.25, 0.06 g) respectively, followed by the addition of $K_2S_2O_8$ (1 mL, 10%). The reaction flask with its contents was placed in a water bath at about 40 C^o and stirred until an exothermic reaction has started. Then the water bath was removed and the reaction continued on its own for about two hours. The produced solid mass was dried for 24 hours at about 80 C^o. The dried solid was then grinded for further evaluation.

2.4.2. Superabsorbent Polymer cross-linked with Epoxy Allyl Sucrose

Procedure reported in section 2.4.1 was repeated exactly except that; ally sucrose was replaced with epoxy ally sucrose.

2.4.3 Superabsorbent Polymer cross-linked with 1,4-Butanediol Diglycidyl ether

Procedure reported in section 2.4.1 was repeated exactly except that; ally sucrose was replaced with 1,4-butanediol diglycidyl ether.

2.4.4 Superabsorbent Polymer cross-linked with Ethylene Glycol Diacrylate

Procedure reported in section 2.4.1 was repeated exactly except that; ally sucrose was replaced with ethylene glycol diacrylate**.**

2.5 Tea- bag Method

SAP (0.1000 g) sample (W_0) was placed into a pre-weighed tea bag and stabled. The bag was dipped in an excess amount of water or saline (0.9 %) solution for one hour to reach the equilibrium swelling. Then excess solution was removed by hanging bag until no liquid was dropped off. The tea bag was weighed (W_1) and the swelling capacity was calculated by equation (1).

$$\text{Free swell} = \frac{W_1 - W_0}{W_0}$$

2.5.1Tea bag test in water

Table 2.5.1.1: Free swell results of SAP cross-linked with Allyl sucrose.

AS. cross-linking agent (%)	Weight of SAP sample (g)	Weight of swelled SAP (g)	Swelling capacity g liquid/g SAP
4.0	0.1000	3.399	32.99
2.0	0.1000	3.481	33.81
1.5	0.1000	3.883	37.83
1.0	0.1000	4.392	42.92
0.5	0.1000	4.464	43.64

Table 2.5.1.2: Free swell results of SAP cross-linked with Epoxy allyl sucrose.

EAS. cross-linking agent (%)	**Weight of SAP sample (g)**	**Weight of swelled SAP (g)**	**Swelling capacity g liquid/g SAP**
4.0	0.1000	3.612	35.12
2.0	0.1000	4.205	41.05
1.5	0.1000	4.467	43.67
1.0	0.1000	4.850	47.50
0.5	0.1000	4.854	47.54

Table 2.5.1.3: Free swell results of SAP cross-linked with 1,4-Butanediol diglycidyl ether.

1,4-BDGE. cross-linking agent (%)	**Weight of SAP sample (g)**	**Weight of swelled SAP (g)**	**Swelling capacity G liquid/g SAP**
4.0	0.1000	3.370	32.70
2.0	0.1000	3.416	33.16
1.5	0.1000	3.642	35.42
1.0	0.1000	3.875	37.75
0.5	0.1000	3.625	35.25

Table 2.5.1.4: Free swell results of SAP cross-linked with Ethylene glycol diacrylate.

EGDA. cross-linking agent (%)	Weight of SAP sample (g)	Weight of swelled SAP (g)	Swelling capacity g liquid/g SAP
4.0	0.1000	3.380	32.80
2.0	0.1000	3.448	33.48
1.5	0.1000	3.663	35.63
1.0	0.1000	4.262	41.62
0.5	0.1000	4.242	41.42

2.5.2 Tea bag test in saline solution (0.9 %)

Table 2.5.2.1: Free swell results of SAP cross-linked with Allyl sucrose.

AS. Cross-linking agent (%)	Weight of SAP sample (g)	Weight of swelled SAP (g)	Swelling capacity g liquid/g SAP
4.0	0.1000	2.606	25.06
2.0	0.1000	2.650	25.50
1.5	0.1000	2.723	26.23
1.0	0.1000	2.739	26.39
0.5	0.1000	2.808	27.08

Table 2.5.2.2: Free swell results of SAP cross-linked with Epoxy allyl sucrose.

EAS. cross-linking agent (%)	**Weight of SAP sample (g)**	**Weight of swelled SAP (g)**	**Swelling capacity g liquid/g SAP**
4.0	0.1000	2.792	26.92
2.0	0.1000	3.047	29.47
1.5	0.1000	3.045	29.45
1.0	0.1000	3.090	29.90
0.5	0.1000	3.080	29.80

Table 2.5.2.3: Free swell results of SAP cross-linked with 1,4-Butanediol diglycidyl ether.

1,4-BDGE cross-linking agent (%)	**Weight of SAP sample (g)**	**Weight of swelled SAP (g)**	**Swelling capacity g liquid/g SAP**
4.0	0.1000	2.517	24.17
2.0	0.1000	2.315	22.15
1.5	0.1000	2.589	24.89
1.0	0.1000	2.605	25.05
0.5	0.1000	2.777	26.77

Table2.5.2.4: Free swell results of SAP cross-linked with Ethylene glycol diacrylate.

EGDA. cross-linking agent (%)	**Weight of SAP sample (g)**	**Weight of swelled SAP (g)**	**Swelling capacity g liquid/g SAP**
4.0	0.1000	2.485	23.85
2.0	0.1000	2.407	23.07
1.5	0.1000	2.640	25.40
1.0	0.1000	2.643	25.43
0.5	0.1000	2.837	27.37

2.6 Absorbency Under Load (AUL)

Dried SAP sample (0.1 g) was placed on the surface of gauze located on the sintered glass (cell). A cylindrical solid load (Teflon, 3 mm height) was put on the dry SAP particles while it could be freely slipped in the cell. Desired load was placed on the SAP sample (Fig. 2.6). The saline solution (0.9% NaCl) was then added until the liquid level was equal the height of the sintered glass filter. The whole set was covered to prevent surface evaporation and probable change in the saline concentration. After one hour, the swollen particles were weighed again, and AUL was calculated using equation (2).

Absorbence under load (AUL)
g solution/g SAP

$$= \frac{W_2 - W_1}{W_1}$$

where W1 and W2 denote the weight of dry swollen SAP, respectively.

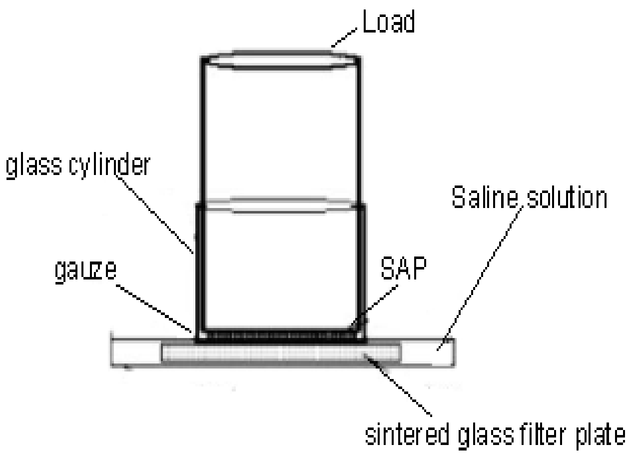


Fig. 2.6 : A typical AUL tester picture and various parts [33].

Absorbency Under Load Test (AUL)

Table 2.6.1: AUL results of PAA-AS.

AS. cross-linking agent (%)	Weight of SAP sample (g)	Weight of swelled SAP (g)	AUL g Liquid/g SAP
4.0	0.1000	1.734	17.34
2.0	0.1000	1.992	19.93
1.5	0.1000	2.190	21.93
1.0	0.1000	2.474	24.73
0.5	0.1000	2.663	26.63

Table 2.6.2: AUL results of PAA-EAS.

EAS. Cross-linking agent (%)	Weight of SAP sample (g)	Weight of swelled SAP (g)	AUL g liquid/g SAP
4.0	0.1000	5.921	59.21
2.0	0.1000	5.888	58.88
1.5	0.1000	6.291	62.91
1.0	0.1000	6.492	64.92
0.5	0.1000	5.888	58.88

Table 2.6.3: AUL results of PAA-1,4-BDGE.

1,4-BDGE. cross-linking agent (%)	Weight of SAP sample (g)	Weight of swelled SAP (g)	AUL g liquid/g SAP
4.0	0.1000	2.603	26.03
2.0	0.1000	2.612	26.12
1.5	0.1000	2.623	26.23
1.0	0.1000	2.648	26.48
0.5	0.1000	2.721	27.21

Table 2.6.4: AUL results of PAA-EGDA.

EGDA. Cross-linking agent (%)	Weight of SAP sample (g)	Weight of swelled SAP (g)	AUL g liquid/g SAP
4.0	0.1000	1.688	16.88
2.0	0.1000	3.163	31.63
1.5	0.1000	3.072	30.72
1.0	0.1000	3.436	34.36
0.5	0.1000	3.467	34.67

2.7 pH Neutrality after swelling in water

Powder of each SAP (1 g) with 4% cross-linking percentage was suspended into 100 ml de-ionized water. The mixture was stirred for about 10 minutes, and then the pH values were measured using a pH-meter. Results are shown in the following table:

Table 2.7: pH of superabsorbent polymers.

Superabsorbent polymer	pH
PAA-AS	6.2
PAA-EAS	5.92
PAA-EGDA	5.45
PAA-1,4-BDGE	5.28

2.8 Rewetting of SAP in water.

SAP (0.1 g) sample (W_0) was placed in a tea bag, then tea bag was dipped in an excess amount of water solution for one hour to reach the equilibrium swelling. Then excess solution was removed by hanging bag until no liquid was dropped off. The tea bag was weighed (W_1) and the swelling capacity was calculated. Then bag was dried for three days and SAP was heated until returned to initial weight and bag test applied again and the results showed that no loss in absorbency of the polymer.

2.9 Rewetting of SAP in saline.

SAP (0.1 g) sample (W_0) was placed in a tea bag, then tea bag was dipped in an excess amount of 0.95% saline solution for one hour to reach the equilibrium swelling. Then excess solution was removed by hanging bag until no liquid was dropped off. The tea bag was weighed (W_1) and the swelling capacity was calculated. Then bag was dried for three days and

SAP was heated until returned to initial weight and bag test applied again and the results showed that no loss in absorbency of the polymer.

2.10 Polymer Extracts

To 250 ml Erlenmeyer flask containing 20 ml ethanol and 1g (W_1) of each SAP (4%) was poured with stirring for one hour, then SAP was collected by filtration, dried and weight (W_2), then % extract was calculated.

Table 2.10: Percentage of SAP extracts.

SAP with 4% cross-linker	Weight of SAP before extraction (g)	Weight of SAP after extraction (g)	% extraction
AS.	1.05	1.05	0 %
EAS.	0.9775	0.9782	0.07 %
1,4-BDGE.	0.9904	0.9907	0.03 %
EGDA.	0.9641	0.9643	0.02 %

2.11 Biodegradability

2.11.1Test Microorganisms

The organisms used for the degradation experiments were Pseudomonas aeruginosa and Trichophyton rubrum.

Pseudomonas aeruginosa isolate was maintained on Nutrient Agar (NA) (Oxoid) plates and incubated for 48 hours at $37C^{\circ}$ prior to use. Trichophyton rubrum was isolated from superficial skin of human dermatomycoses patients. The isolated fungal isolate was maintained on Sabouraud Dextrose Agar (SDA).

2.11.2 Biodegradation Experiments

Biodegradation experiment was performed using the plate assay, which detects polymer -degrading activity based on the formation of a clear zone surrounding the fungal colonies or growth of bacterial isolates as clear colonies on media with the polymer as a sole carbon source [54].

The assay medium used in the study was Mineral salt media (MSM). The MSM per 1000 mL distilled water was prepared as follows: K_2HPO_4, 1 g; KH_2PO_4, 0.2 g; NaCl, 1 g; $CaCl_2.2H_2O$, 0.002 g; boric acid, 0.005 g; $(NH_4)_2SO_4$, 1 g; $MgSO_4.7H_2O$, 0.5 g; $CuSO_4.5H_2O$, 0.001 g; $ZnSO_4.7H_2O$, 0.001 g; $MnSO_4.H_2O$, 0.001 g and $FeSO_4.7H_2O$.

Fungal biodegradation experiment was screened using MSM containing 0.5% (w/v) of the polymer either allyl sucrose or epoxy sucrose as a sole carbon source, which was solidified with 1% agar at pH 6.0.

For bacterial biodegradation, the MSM containing about 0.5% (w/v) of dry polymer (either Allyl sucrose or Epoxy sucrose) as a sole carbon source and solidified with 2% agar at pH 7.0 was used.

After autoclaving, the media were poured into plates and allowing the agar to set, a loopful of the bacterium or fungal strain were then inoculated on the agar and the inoculated plates were sealed with parafilm. The plates inoculated with bacteria were incubated at 37 C^o for seven days under aerobic conditions. Plates inoculated with fungi were incubated at room temperature for 1-3 weeks [54].

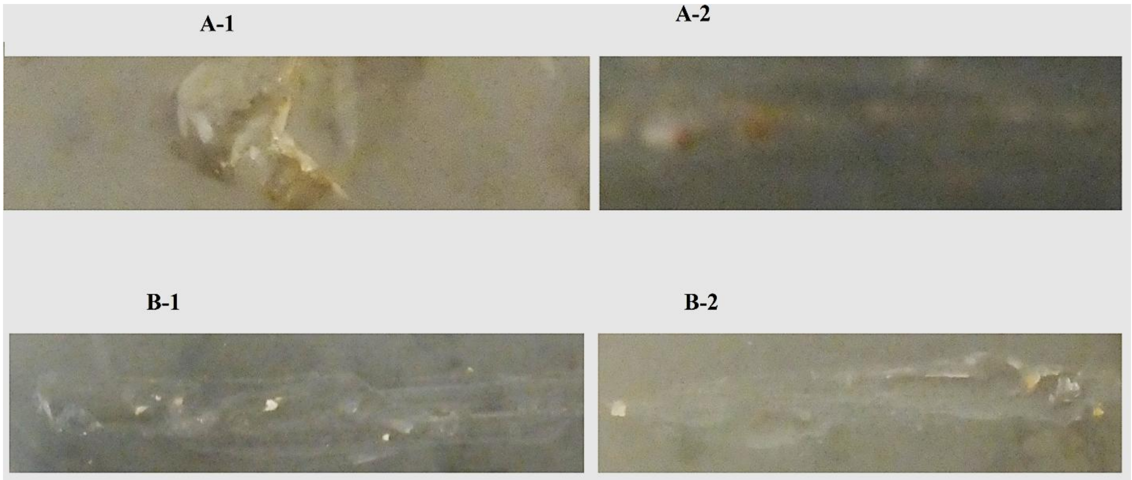
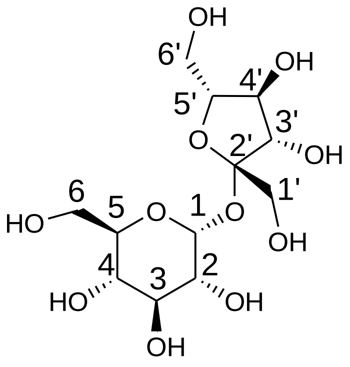


Fig. 2.11.2. Plate assay to visualize biodegradation of Allyl sucrose and Epoxy allyl sucrose by Pseudomonas aeruginosa and Trichophyton rubrum. A-1, biodegradation of Allyl sucrose by Pseudomonas aeruginosa; A-2, biodegradation of Epoxy allyl sucrose by Pseudomonas aeruginosa; B-1, biodegradation of Allyl sucrose by Trichophyton rubrum; B-2 biodegradation of Epoxy allyl sucrose by Trichophyton rubrum**.**

Chapter Three
Results and Discussion

The most abundant pure organic chemical in the world is sucrose. As shown in Fig. 3 (structure and ^{1}H-NMR of sucrose), sucrose consists of two monosaccharides, namely glucose (C-1 to C-6) and fructose (C-1' and C-6'), positions 1', 6, and 6' contain primary hydroxyl group, whereas the rest of hydroxyl groups are secondary [55].

The structure and conformation of sucrose was determined by X-ray crystallography, and ^{1}H and ^{13}C-NMR. The primary hydroxyl group in sucrose are sterically nonequivalent, and afford the opportunity to selectively manipulate them. It is known that the 6 and 6' ends are more reactive than the neopentyl 1' end. The reactivity trend among primary hydroxyl groups in sucrose is different when sucrose is subjected to acetylation with enzyme. The overall reactivity patterns of hydroxyl groups in sucrose may be roughly put in the following order OH-6 = OH-6'>OH-1'>OH at 2,3,3',4' >OH-4 [56].



Sucrose

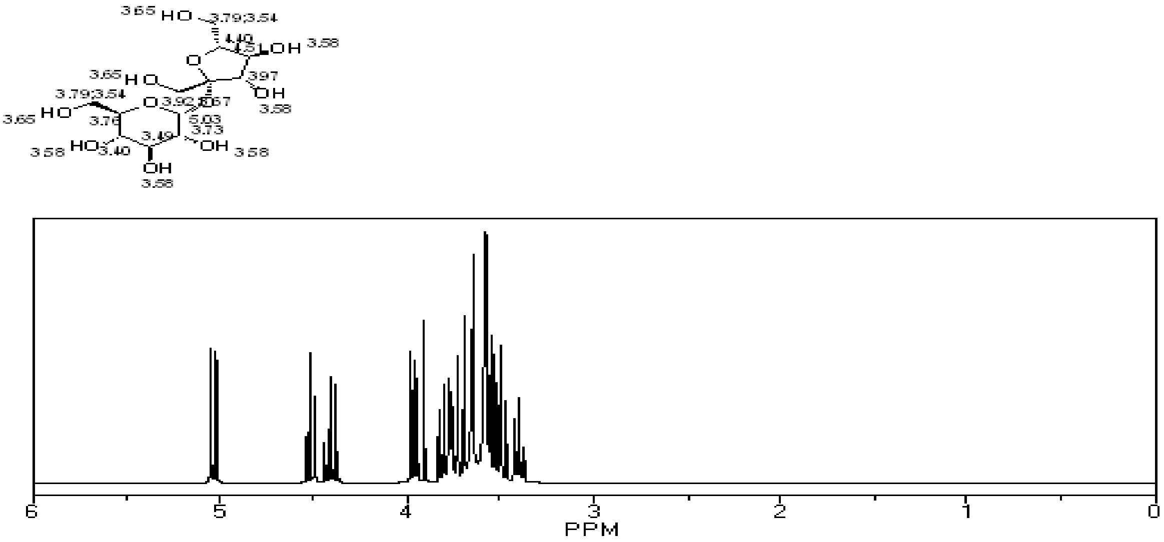


Fig 3: The chemical structure and ^{1}H-NMR of sucrose**.**

The potential value of sucrose as a raw material has been recognized for many years and has been the subject of considerable research. Although relatively few successful derivatives of sucrose have been commercialized, there has been substantial interest in developing sugar-based polymers with commercial values. Sucrose is a particularly appropriate material for use in the formation of speciality polymers and monomers produced currently from petroleum-based materials since it is:

(a) Naturally occurring and relatively inexpensive material;

(b) It is polyfunctional with three reactive primary alcohols that can readily be derivatized (Fig.3) ;

(c) It is a non-reducing sugar and thus does not have the potential for the wide variety of side-reactions that reducing sugars have; and

(d) It has a relatively easily hydrolyzed glycosidic linkage that allows sucrose polymers to be potentially more biodegradable than polymers made with other carbohydrates.

Sugar-based polymers are not entirely new. For example, a major investigator was carried out on synthesis, characterization, and applications of sucrose-based epoxy materials developed at USDA laboratories (New Orleans, LA). It has been shown that: a) Sucrose can be converted into epoxy in two steps process in over 85% overall yield using commercial available reagents and solvents that could be recycled at low cost; and b) the developed epoxy material is useful in creating new class of super-adhesives [57].

Sucrose is a particularly appropriate material for use in the formation of etherified products produced currently made from petroleum-based materials [58]. The usual technique for the synthesis of carbohydrate ethers involves a reaction of the carbohydrate with alkyl halides in a basic organic solvent or aqueous solvent (O-alkylation reactions). Partial O-alkylation of sucrose occurs in aqueous alkali upon treatment with alkylating agent at about 100 C^o. However, octa-o-alkylation results when the pressure is raised to about 500 psi. Selective methylation of sucrose could be obtained using diazomethane in the presence of Lewis acids in methylene chloride [59]. Treatment of sucrose with ethylene oxide or propylene oxide in the presence of aqueous sodium hydroxide results in formation of octa-O-hydroxyethyl and octa-O-hydroxypropyl sucrose respectively [60]. The reaction of sucrose with epichlorohydrin results in the formation of polyether polyols and glycidyl sucrose monomers. Penta-O-alkyl derivatives of sucrose can be synthesized in high yields by use of protecting group strategies such as 1', 6, 6'-tri Otritylation. Followed by penta-O-alkylation and detritylation. Octa-O-alkylation could be conducted by use of hydride bases in polar aprotic solvents, followed by addition of alkyl halides [61].

In this research we were concerned about preparing polymerizable monomers from sugar, sugar with unsaturated functional group that undergoes polymerization in the presence of free radical initiator [62]. Then use the monomers for making biodegradable sugar based superabsorbent polymers. The reason behind choosing sugar is mentioned earlier in this section, it is the most abundant pure natural organic chemical, available at low cost, hydrophilic, and biodegradable. Two polymerizable sugar monomers were synthesized, they are allyl sucrose and epoxy allyl sucrose [63].

3.1 Monomer Characterization

The allyl sucrose monomers produced in accordance with previous methods are characterized by chromatography, and one-dimensional NMR techniques proton and carbon-13, and IR.

3.1.1 ^{1}H- NMR Spectroscopy of Allyl Sucrose (AS)

^{1}H-NMR for Allyl sucrose is shown in Fig. 3.1.1 ($CDCl_3$) δ (ppm): 3.26-4.28 sucrose[s] hydrogens; 5.23 Ha of the glucopyranosyl moieties; 5.24 (geminal terminal olefin hydrogens, Hb), 5.89 internal olefin Hc).

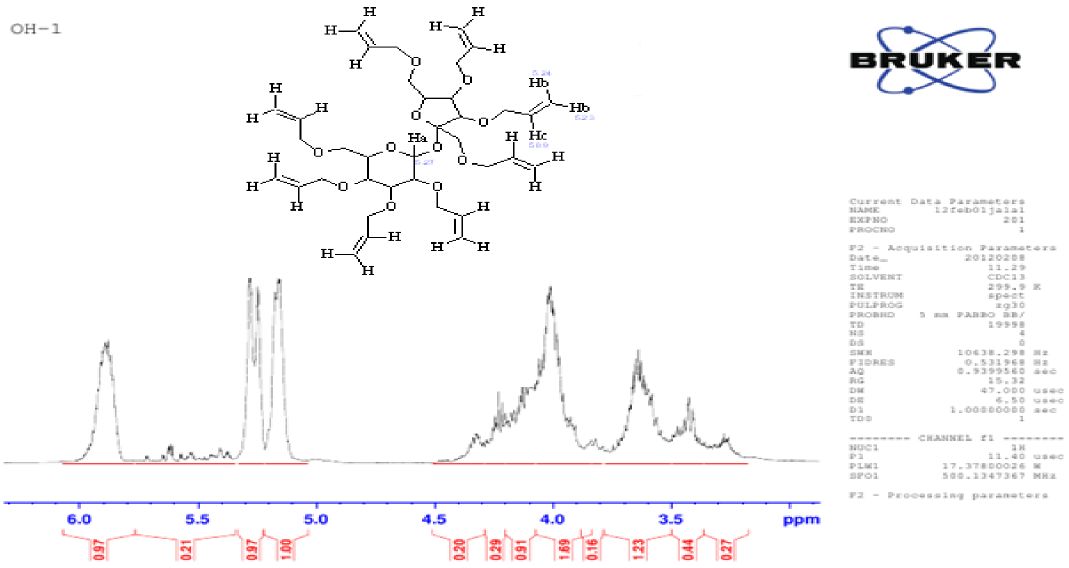
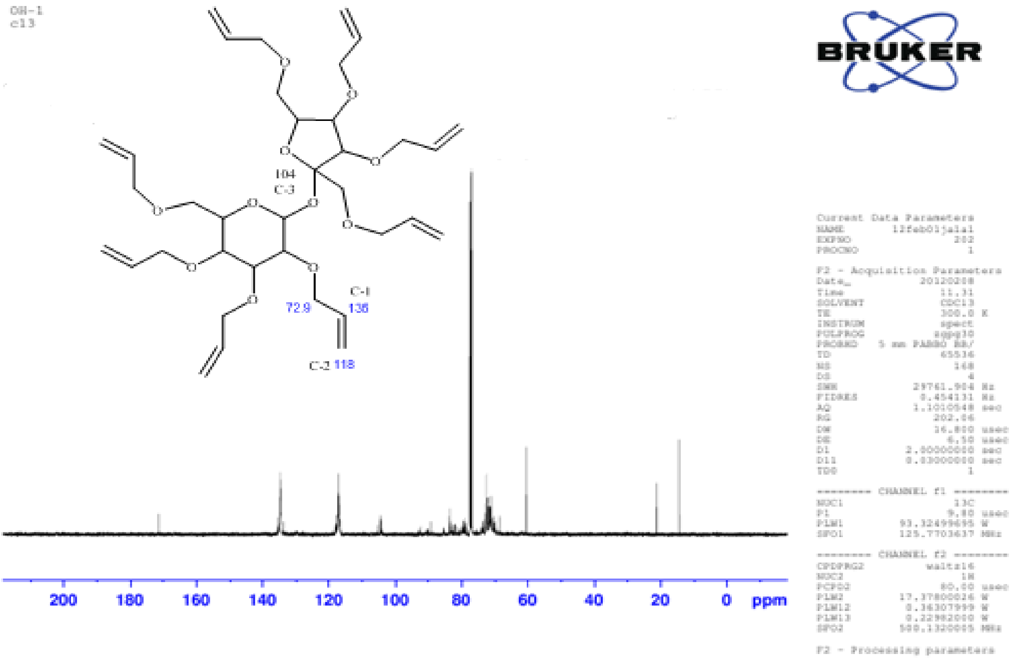


Fig. 3.1.1: 1H-NMR of Allyl Sucrose.

3.1.2 ^{13}C-NMR Spectroscopy of Allyl Sucrose:

^{13}C-NMR of allyl sucrose is shown in Fig. 3.1.2, δ(ppm): 68.23-88.70; 104.13-104.44 (C-3 resonances of the fructofuranosyl moieties of allyl sucrose); 118 (CH_2-1 vinyl), 135.21 (CH_2-2 vinyl).

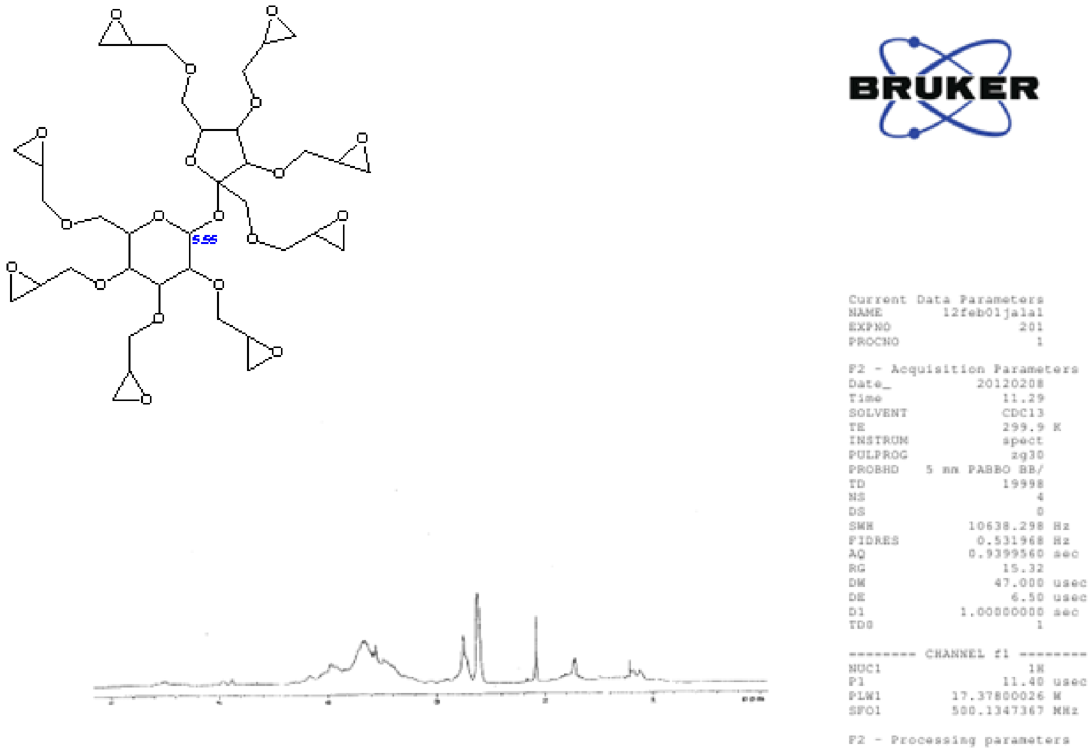


```
Current Data Parameters
NAME        12feb01jalal
EXPNO                202
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120208
Time               11.31
SOLVENT            CDCl3
TE                 300.0 K
INSTRUM            spect
PULPROG          zgpg30
PROBHD   5 mm PABBO BB/
TD                 65536
NS                   168
DS                     4
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ             1.1010548 sec
RG                202.06
DW                16.800 usec
DE                  6.50 usec
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.80 usec
PLW1         93.32499695 W
SFO1         125.7703637 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PLW2         17.37800026 W
PLW12         0.36307999 W
PLW13         0.22982000 W
SFO2         500.1320005 MHz

F2 - Processing parameters
```

Fig. 3.1.2: ^{13}C-NMR of Allyl Sucrose**.**

3.1.3 ^{1}H- NMR Spectroscopy of Epoxy Allyl Sucrose (EAS)

The ^{1}H-NMR for epoxy allyl sucrose (EAS) ($CDCl_3$) is shown in Fig.3.1.3, 2.67 (H-c, geminal methylene of the epoxy group) 3.0-4.3 (sucrose protons and methylenes), 4.82-4.98 (residual geminal terminal olefin hydrogens), 5.55 (H-1 signal of the glucopyranosyl moieties of the epoxy methallyl sucrose isomers).

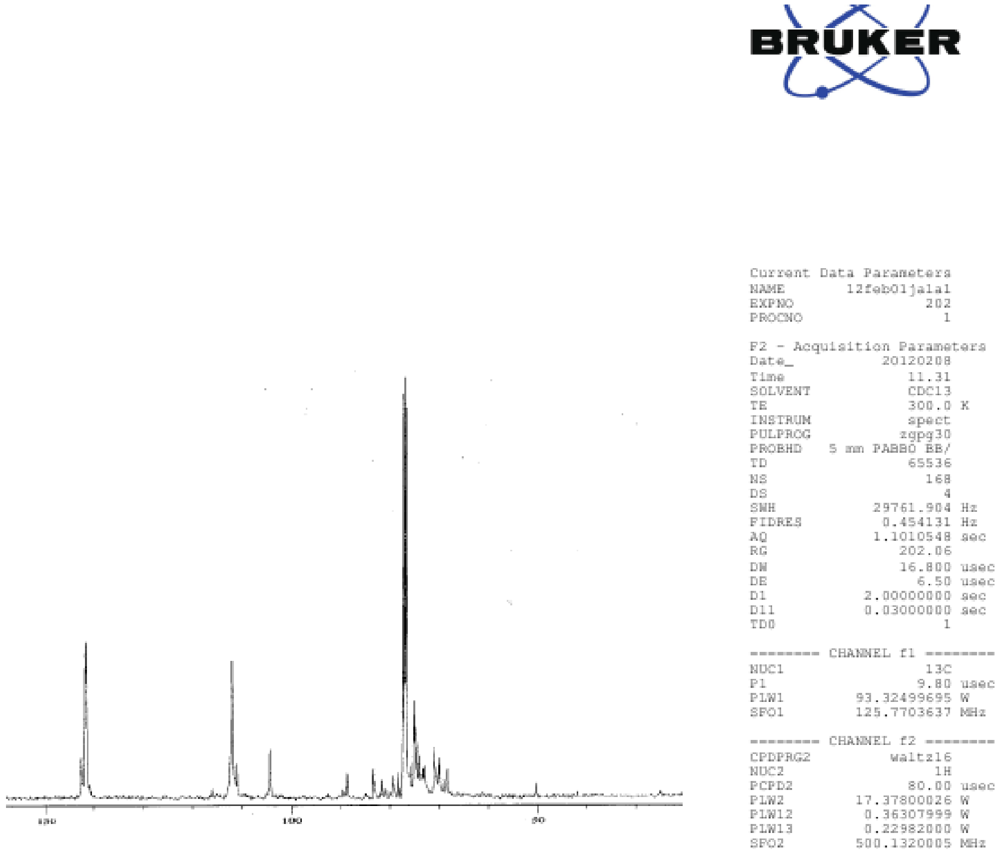


```
Current Data Parameters
NAME        12feb01jala1
EXPNO                201
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120208
Time               11.29
SOLVENT            CDCl3
TE                 299.9 K
INSTRUM            spect
PULPROG             zg30
PROBHD   5 mm PABBO BB/
TD                 19998
NS                     4
DS                     0
SWH           10638.298 Hz
FIDRES         0.531968 Hz
AQ            0.9399560 sec
RG                 15.32
DW                47.000 usec
DE                  6.50 usec
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.40 usec
PLW1         17.37800026 W
SFO1         500.1347367 MHz

F2 - Processing parameters
```

Fig. 3.1.3: ^{1}H- NMR of Epoxy Allyl Sucrose

3.1.4 ^{13}C-NMR Spectroscopy of Epoxy Allyl Sucrose

^{13}C-NMR for epoxy sucrose ($CDCl_3$) is shown in Fig. 3.1.4, δ(ppm): 19.24 (residual allylic CH_3-d,), 51.5 (terminal epoxy allyl carbon CH_2-c′), 56.1 (internal epoxy allyl carbon C-b′) 66 to 86 (sucroses carbons and methylenes CH_2), 89.6 (C-1 resonances of the glucopyranosyl moieties of the epoxy allyl sucrose), 104.2 (C-2′ resonances of the fructofuranosyl moieties of epoxy allyl sucrose isomers) and 105 (C-2′ residual resonances of the fructofuranosyl moieties of unepoxidized methallyl sucrose isomers), 111.7 (residual CH_2-c), 141.3 (residual tetrasubstituted olefin carbons C-b).



```
Current Data Parameters
NAME       12feb01jalal
EXPNO               202
PROCNO                1

F2 - Acquisition Parameters
Date_          20120208
Time              11.31
SOLVENT           CDCl3
TE                300.0 K
INSTRUM           spect
PULPROG         zgpg30
PROBHD   5 mm PABBO BB/
TD                65536
NS                  168
DS                    4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010548 sec
RG               202.06
DW               16.800 usec
DE                 6.50 usec
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.80 usec
PLW1        93.32499695 W
SFO1        125.7703637 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PLW2        17.37800026 W
PLW12        0.36307999 W
PLW13        0.22982000 W
SFO2        500.1320005 MHz
```

Fig. 3.1.4: ^{13}C-NMR of Epoxy Allyl Sucrose.

3.2 Discussion of prepared polymers

The prepared monomers in addition to other commercial monomer were used as cross-linking agents for polymer prepared from polyacrylic acid. Some of the chosen commercial monomers we never used as cross-linking agents for polyacrylic acid.

3.2.1 Polyacrylic Acid cross-linked with Allyl Sucrose (PAA-AS).

Polyacrylic acid was polymerized in presence of various amounts of AS. The polymerization was performed in presence of free radical initiator sodium persulfate ($Na_2S_2O_8$) under an inert atmosphere (N_2). First, the reaction was heated at low temperature (about 60 C^o) once the exothermic reaction started, the heat was turned off, and the reaction continued for about two hours. The produced solid mass was dried and grinded into powder for evaluation. The general reaction for polymerizing acrylic acid in presence of cross-linking agent allyl sucrose is shown in Fig. 3.2.1. The procedure was performed on partially neutralized acrylic acid and on another reaction neutralization was performed after polymerization.

The neutralization was performed by treating the polymer or the monomer (AA) with a solution of sodium hydroxide to a pH of about 6.0. In this reaction a radical is expected to be developed on both AS and AA and that causes chain growth polymerization to occur and where the sugar molecule forms like a bridge connecting the polyacrylic acid chains which resulted in formation of a net work polymer as shown in Fig. 3.2.1.

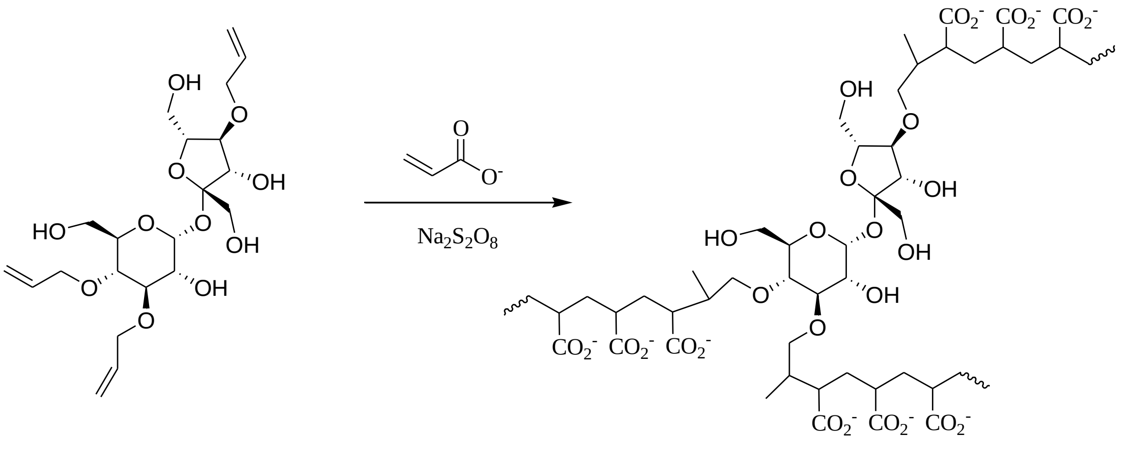


Fig. 3.2.1: Polymerization of acrylic acid in presence of crosslinker AS.

3.2.2 Polyacrylic Acid cross-linked with Epoxy Allyl Sucrose (PAA-EAS).

Polyacrylic acid was polymerized in presence of various amounts of EAS. The polymerization was performed in presence of free radical initiator sodium persulfate ($Na_2S_2O_8$) under an inert atmosphere (N_2). First, the reaction was heated at low temperature (about 60 C^o) once the exothermic reaction started, the heat was turned off, and the reaction continued for about two hours. The produced solid mass was dried and grinded into powder for evaluation. The general reaction for polymerizing acrylic acid in presence of cross-linking agent epoxy allyl sucrose is shown in Fig. 3.2.2. The procedure was performed on partially neutralized acrylic acid and on another reaction neutralization was performed after polymerization. The neutralization was performed by treating the polymer or the monomer (AA) with a solution of sodium hydroxide to a pH of about 6.0.

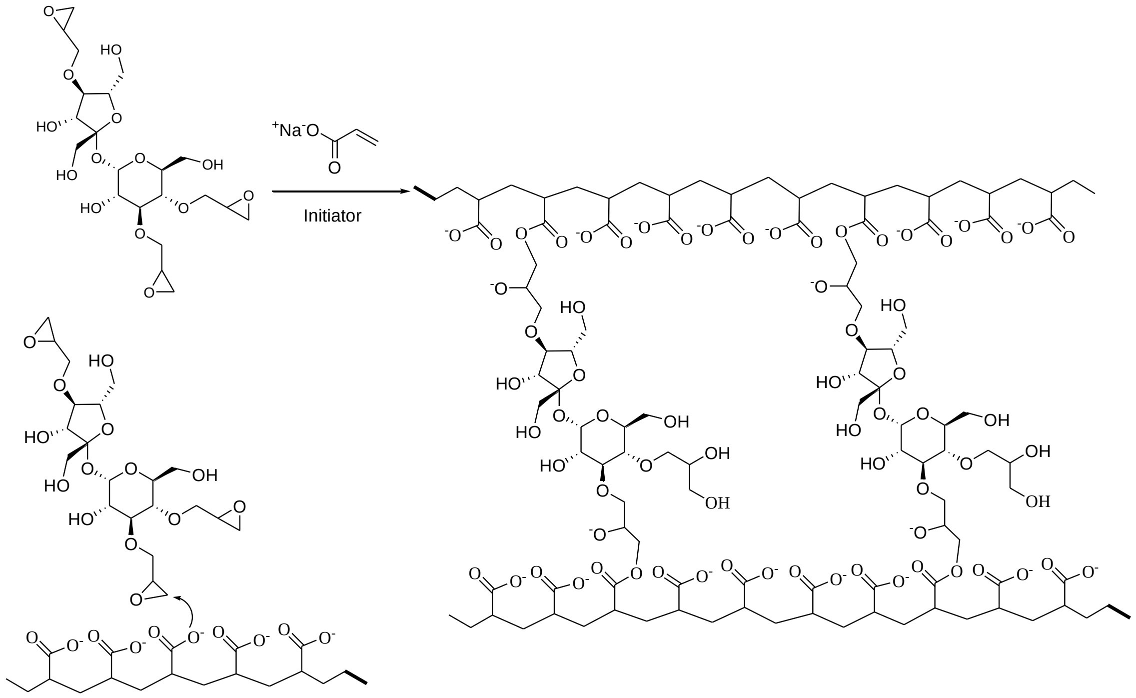


Fig.3.2.2: Polymerization of acrylic acid with cross-linking agent EAS.

3.2.3 Polyacrylic Acid cross-linked with 1,4-Butanediol Diglycidyl Ether (PAA-1, 4-BDGE).

Polyacrylic acid was polymerized in presence of various amounts of 1,4-BDGE. The polymerization was performed in presence of free radical initiator sodium persulfate ($Na_2S_2O_8$) under an inert atmosphere (N_2). First , the reaction was heated at low temperature (about 60 C^o) once the exothermic reaction started, the heat was turned off, and the reaction continued for about two hours. The produced solid mass was dried and grinded into powder for evaluation. The general reaction for polymerizing acrylic acid in presence of cross-linking agent 1,4-BDGE is shown in Fig.3.2.3. The procedure was performed on partially neutralized acrylic acid and on other reactions neutralization was performed after polymerization. The neutralization was performed by treating the polymer or the monomer (AA) with a solution of sodium hydroxide to a pH of about 6.0.

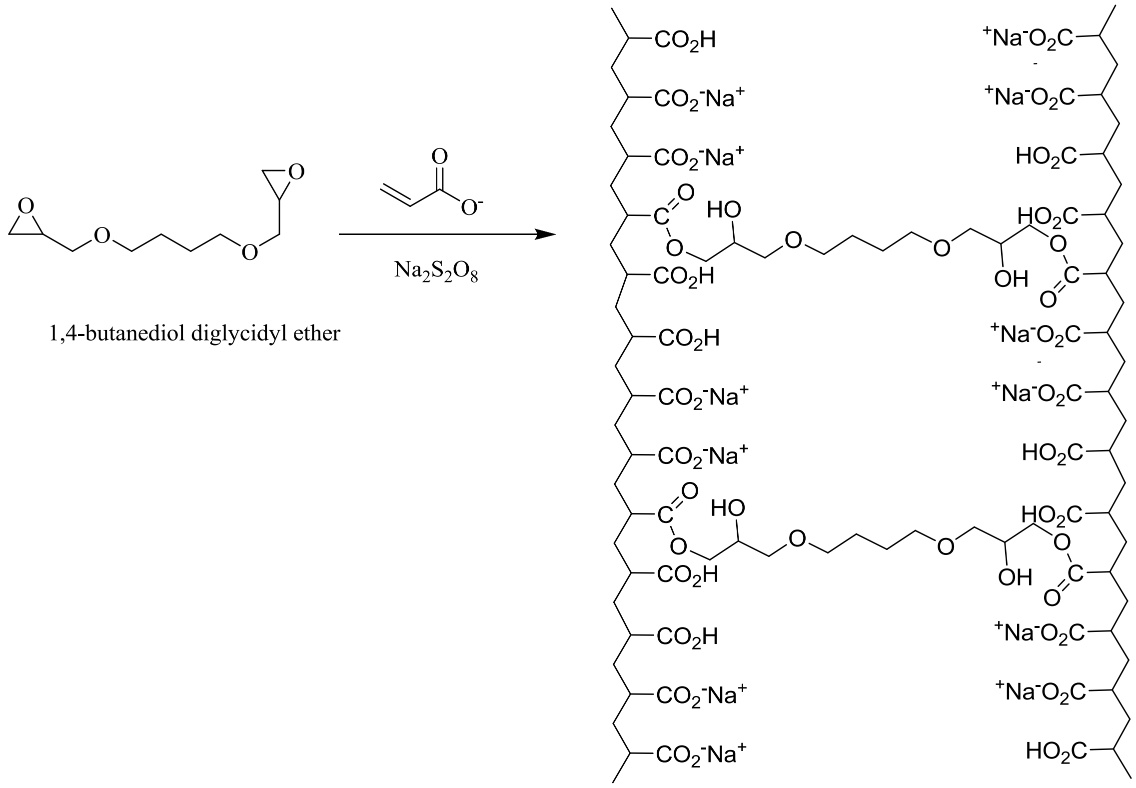


Fig. 3.2.3: Polyacrylic acid cross-linked with 1,4-BDGE.

3.2.4 Polyacrylic Acid cross-linked with Ethylene Glycol Diacrylate (PAA-EGDA).

Polyacrylic acid was also polymerized in presence of various amounts of EGDA. The polymerization was performed in presence of free radical initiator sodium persulfate ($Na_2S_2O_8$) under an inert atmosphere (N_2). First, the reaction was heated at low temperature (about 60 ^oC) once the exothermic reaction started the heat was turned off, and the reaction continued for about two hours. The produced solid mass was dried and grinded into powder for evaluation. The general reaction for polymerizing acrylic acid in presence of cross-linking agent EGDA is shown in Fig.3.2.4. The procedure was performed on partially neutralized acrylic acid and in other reactions neutralization was performed after polymerization. The neutralization was performed by treating the polymer or the monomer (AA) with a solution of sodium hydroxide to a pH of about 6.0. SAP polymer produced with this was used as reference since it is known and well documented.

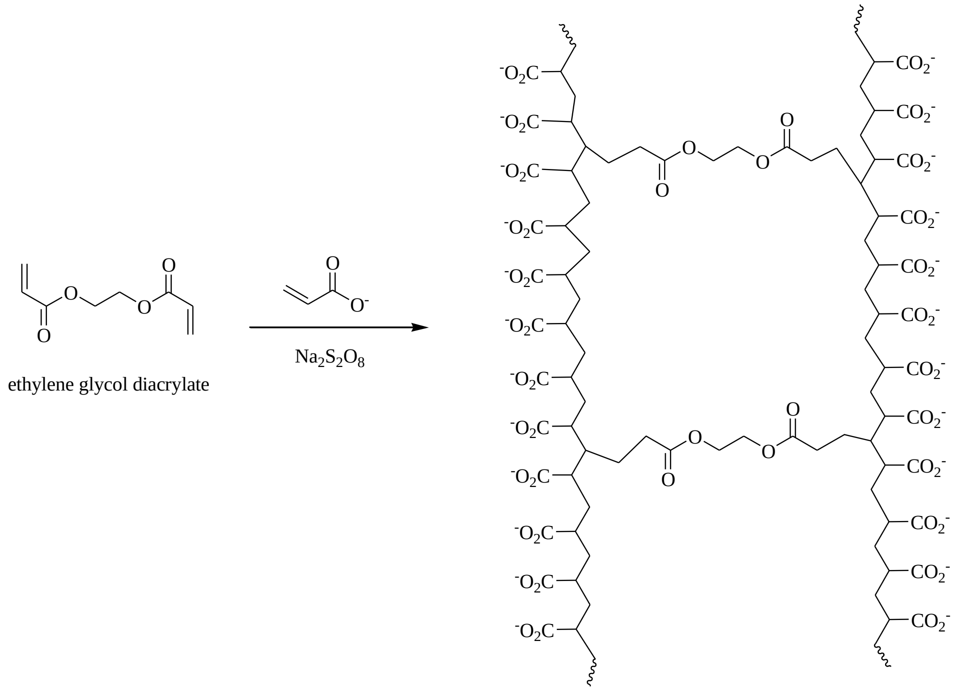


Fig.3.2.4: Polyacrylic acid cross-linked with EGDA**.**

3.3 Polymer Analysis

Analysis of synthesized polymers were performed various techniques such as IR, scanning electronic microscope (SEM), and differential scanning calorimeter (DSC).

3.3.1 Infrared Spectra (IR) Results:

IR spectra of samples as KBr pellets were taken using a Nicolet 560 spectrometer (Nicolet Co., USA).

The IR of the three polymers made from acrylic acid and cross-linking agents are shown in Fig. 3.3.1. Individual IR spectra are shown in the appendix (figures a1, a2 and a3). As can be seen from Fig. 3.3.1, the three spectra show that the main characteristic peaks at 3350 cm^{-1}(O-H stretch), and 2906 cm^{-1}(C-H stretch). The small peaks at 1639 cm^{-1} result from –C=O stretching. The absorption bands at 1372 cm^{-1} and 898 cm^{-1} are ascribed to C-H bending vibration. The peak at 1318 cm^{-1} is attributed to O-H bending vibration. Furthermore, the bands at 1556 and 1407 correspond to the carbonyl band.

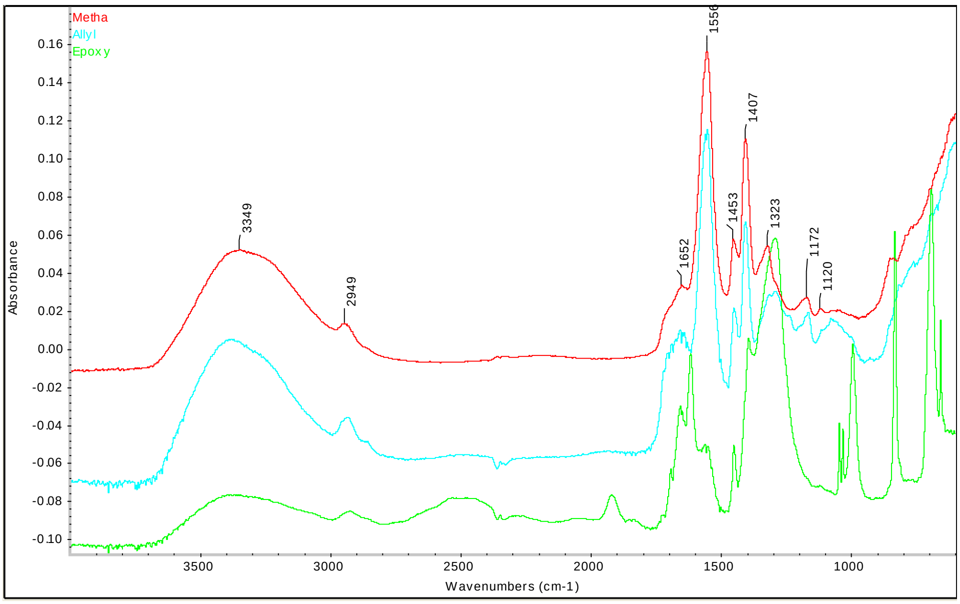


Fig. 3.3.1: IR for three of the prepared SAPs**.**

3.3.2 DSC Results:

The cross-linking was also supported by DSC analysis, as shown in Fig. 3.3.7. DSC of SAP cross-linked with AS shows a weight loss in two stages. The first stage ranged between 40 and 70 C^{o} and showed about 2.5% loss in weight, this may be due to the loss of absorbed and bound water. The second stage of weight loss started at 130 C^{o} and continued to 210 C^{o}, during which 78% weight loss may correspond to the degradation of cross-linker.

3.3.3 Morphological Analysis

SEM micrographs of prepared superabsorbent polymers are shown in Fig.3.3.3. The differences are obvious. The conventional superabsorbent polymer made from acrylic acid and EGDA cross-linking agent (Fig. 3.3.3.C) has a solid smooth non porous surface. While the other two superabsorbent polymers made from acrylic acids and sugar monomers AS and EAS show some porosity, highest porosity could be seen clearly from the monograph of superabsorbent polymer cross-linked with EAS, the pores are connected with each other. The porosity can clearly be seen in the enlarged view (Fig. 3.3.3. B).

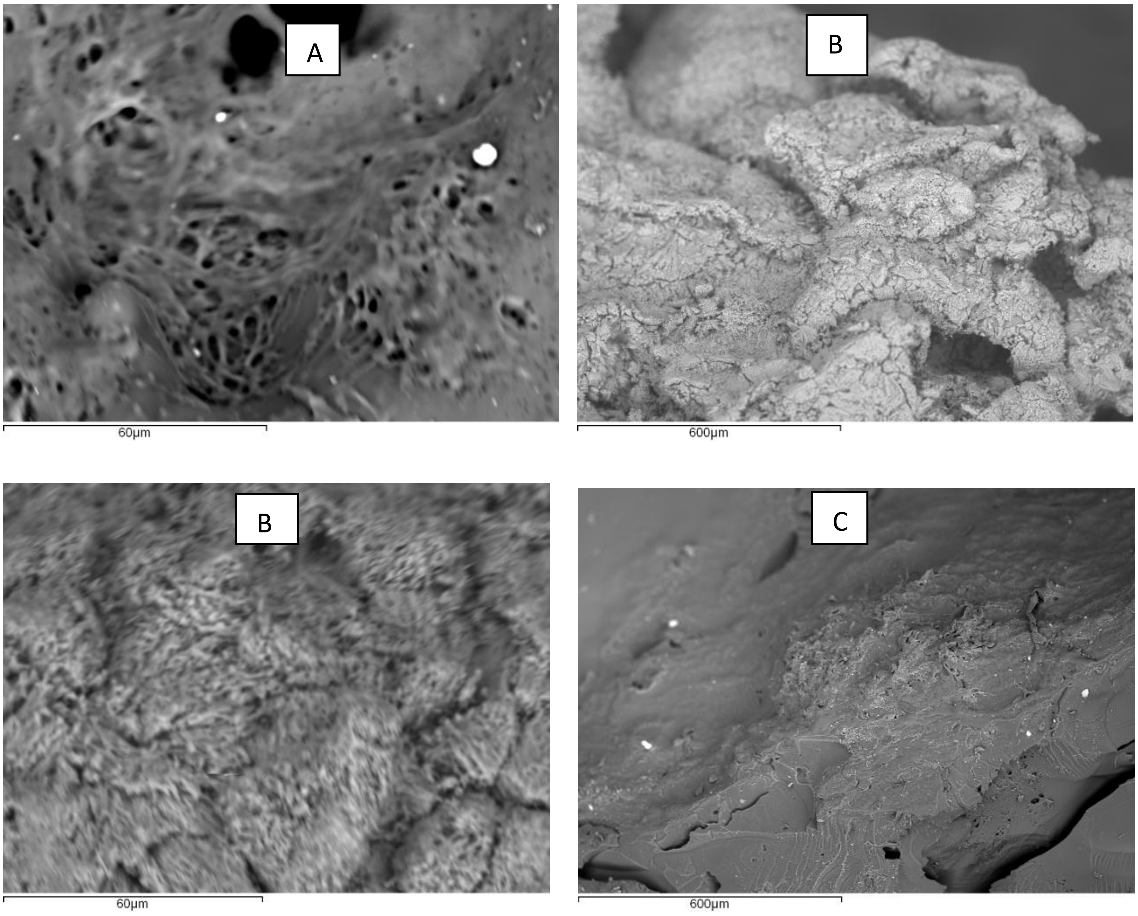


Fig. 3.3.3: SEM micrographs of prepared SAP's: A is for superabsorbent polymer cross-linked with 5% AS (PAA-AS) x1000; B is for superabsorbent polymer cross-linked with 5% EAS (PAA-EAS) x500; B is for superabsorbent polymer cross-linked with 5% EAS (PAA-EAS) x1000. C is for superabsorbent polymer cross-linked with 5% EGDA (PAA-EGDA) x1000.

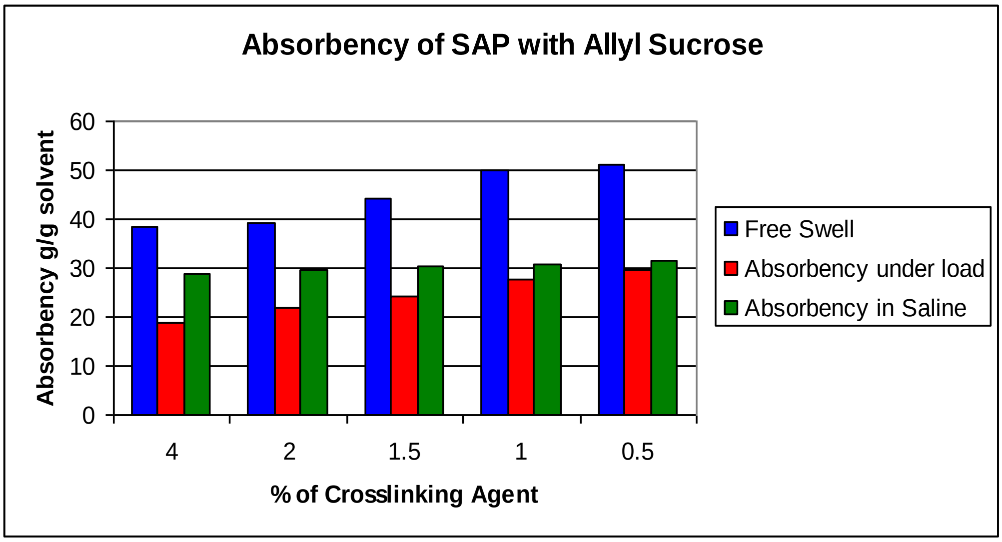
3.3.4: Superabsorbent Polymer Absorbency

Desired features of superabsorbent polymers are high swelling capacity, high swelling rate and high strength of the swollen gel. These properties make SAP's ideal for use as mentioned in the introduction in water absorbing applications such as disposable diapers, feminine napkins, and agriculture, cosmetic and absorbent pads. The absorbency of the prepared polymer for water and saline solution was evaluated. Results are summarized in tables 3.3.4.1, 3.3.4.2, 3.3.4.3 and 3.3.4.4, and in graphs 3.3.4.1, 2, 3, and 4. The absorbency of prepared SAP's in water was measured using tea bag test. In this test about 0.1g of polymer is placed in a pre-weighed tea bag and immersed in water for one hour. Then hanged for one minute to remove unabsorbed water and its mass is determined. The absorbency of polymers evaluated using this test is listed in the tables as free swell g water/g SAP. As shown in the tables and graphs the free swell increases by decreasing the percentage the cross-linker in all cases. Polymer cross-linked with EAS showed the highest absorbency at percentage of 0.5% was about 57 g water/ g SAP. The high absorbency of PAA-EAS could be attributed to the high polarity of the polymer. PAA-1,4-BDGE showed the lowest absorbency since it has the longest hydrophobic chain, which makes them least polar than other polymers. The absorbency of the prepared polymers was also evaluated in saline solution. The absorbency for all polymers were lower than that in water due to presence of salt which is known to lower the absorbency. This has been previous prepared. The presence of charges in the SAP structure causes an osmotic pressure difference between the gel and the solvent phase. This pressure difference produces a strong driving force to diffuse solvent to the gel phase. The diffusion process continues until the osmotic pressure difference becomes zero. The osmotic pressure difference is reduced in salts solutions, which leads to less swelling in comparison with distilled water [64].

The absorbency was also evaluated under load (0.3 PSI). This is an important test since it gives an indication about the ability of the SAP to absorb and retain liquid under load, which is important for most commercial applications of SAP. Also gives an indication about the gel strength (Swollen SAP) [65].

Table 3.3.4.1: Absorbency of PAA-AS.

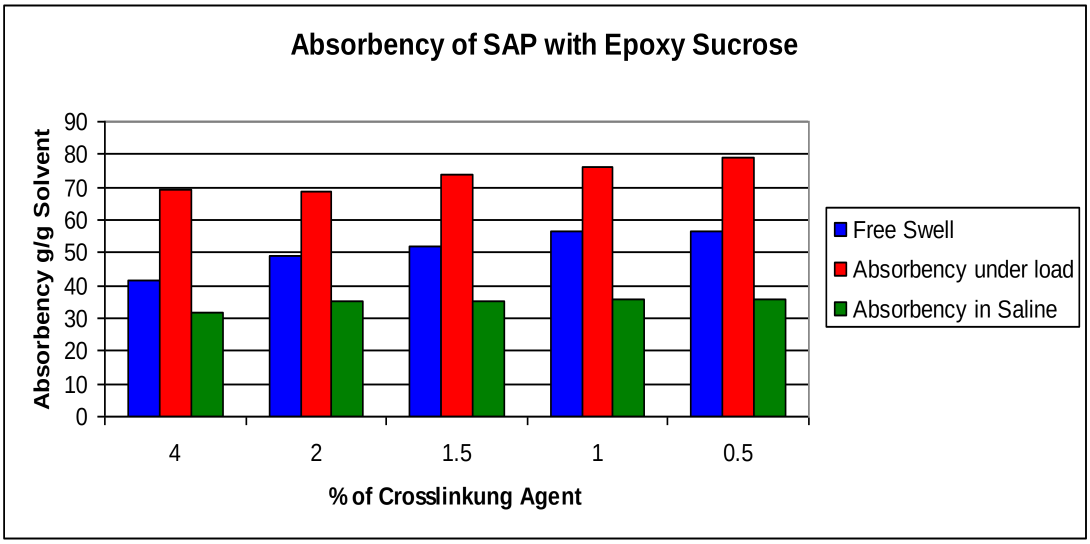
% of Cross-linker	Free Swell	Absorbency under load	Absorbency in Saline
4.00	38.50	19.00	29
2.00	39.30	22.00	29.7
1.50	44.20	24.30	30.5
1.00	50.00	27.60	30.7
0.50	51.00	29.80	31.5



Graph 3.3.4.1: Absorbency of PAA-AS.

Table 3.3.4.2: Absorbency of PAA-EAS.

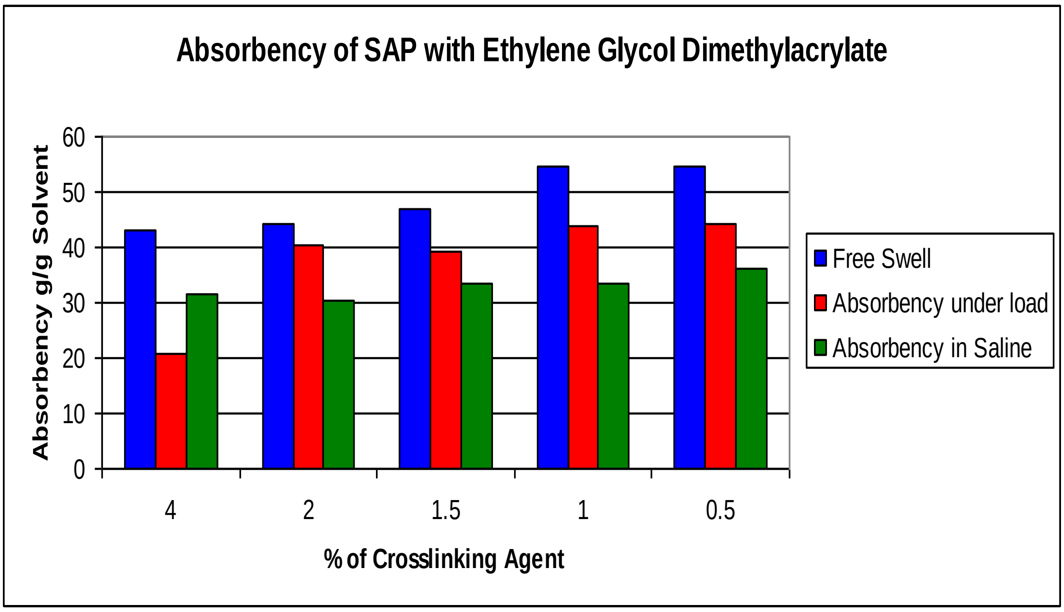
% of Cross-linker	**Free Swell**	**Absorbency under load**	**Absorbency in Saline**
4.00	41.8	69.3	32.0
2.00	48.9	68.9	35.1
1.50	52	73.7	35.1
1.00	56.6	76.1	35.6
0.50	56.6	78.9	35.5



Graph 3.3.4.2: Absorbency of PAA-EAS.

Table3.3.4.3: Absorbency of PAA-EGDA.

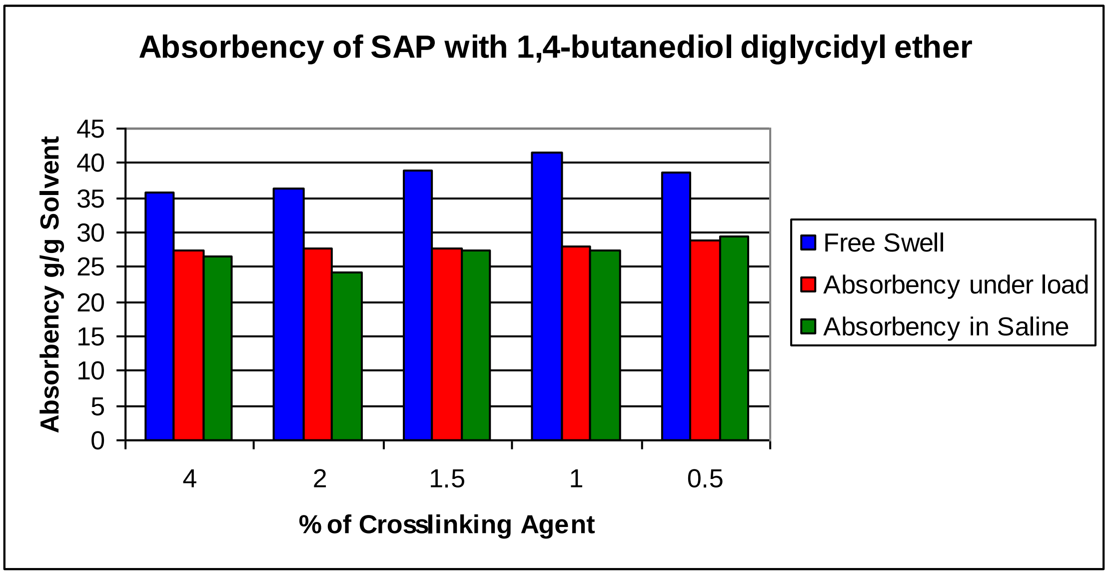
% of Cross-linker	**Free Swell**	**Absorbency under load**	**Absorbency in Saline**
4.00	43.2	20.9	31.4
2.00	44.1	40.3	30.4
1.50	46.9	39.1	33.4
1.00	54.8	43.9	33.5
0.50	54.5	44.3	36



Graph 3.3.4.3: Absorbency of PAA-EGDA.

Table 3.3.4.4: Absorbency of PAA-1,4-BDGE.

% of Cross-linker	Free Swell	Absorbency under load	Absorbency in Saline
4.00	35.9	27.5	26.6
2.00	36.4	27.6	24.3
1.50	38.9	27.8	27.4
1.00	41.5	28	27.5
0.50	38.7	28.8	29.4



Graph 3.3.4.4: Absorbency of PAA-1,4-BDGE.

3.3.5 Rewetting of Superabsorbent Polymers

Rewetting is a test used to evaluate the ability of superabsorbent polymer to re-absorb after is being saturated with liquid and dried. The rewetting property of the prepared SAP's were evaluated, results showed that no loss in absorbency of the polymer upon wetting, drying and then rewetting.

3.3.6 pH Neutrality of SAP's after swelling in water 4% cross-linking

In this test, SAP is suspended in certain volume of distilled water (see experimental part), mixed for few minutes, then pH is measured. Results of this test are summarized in Table 3.3.6. As shown in table, pH of all SAP are close to neutral. Which is important for certain application especially those where SAP gets in contact with human skin.

Table 3.3.6: pH of prepared superabsorbent polymers.

No.	**SAP**	**pH**
1	PAA-AS	6.2
2	PAA-EAS	5.92
3	PAA-EGDA	5.45
4	PAA-1,4-BDGE.	5.28

3.3.7 Thermal stability of prepared Superabsorbent Polymers

TA Instruments (Newcastle, DE, 2920). DSC was used in these experiments. A standard heating ramp of 28 C^o/min. was chosen and a modulation period of 60 s and modulation temperature amplitude of 0.328 C^o was chosen based upon the recommended specifications. N_2 purge was used for all experiments. Baseline calibration was performed regularly with empty pans at 2 and 108 C^o/min., and a four point temperature calibration was performed with different metal standards.

Combustion took place under oxidative conditions within a temperature range from 30 to 300 C^o, using a gas flow of 120 ml $min.^{-1}$ (20% O_2 / 80% He). The sample (16 mg) was combusted in an Al_2O_3 pan. Self-controlled calibration was carried out. DSC curves were corrected by subtracting the DSC curve of the empty pan from the recorded sample curve. Thermograms produced by DSC analysis of prepared polymers are shown in Fig.3.3.7: PAA-EAS showed the highest stability. PAA-EAS

Polymer degradation started at about 195 C^{o}. The lowest stability was shown by PAA-EGDA polymer which starts degrading at 170 C^{o}. All samples showed two peaks at about 50-55 C^{o} and 150-155 C^{o}, which could be related to decomposition or melting side products produced during polymerization such formation of dimmers or evaporation of solvent.

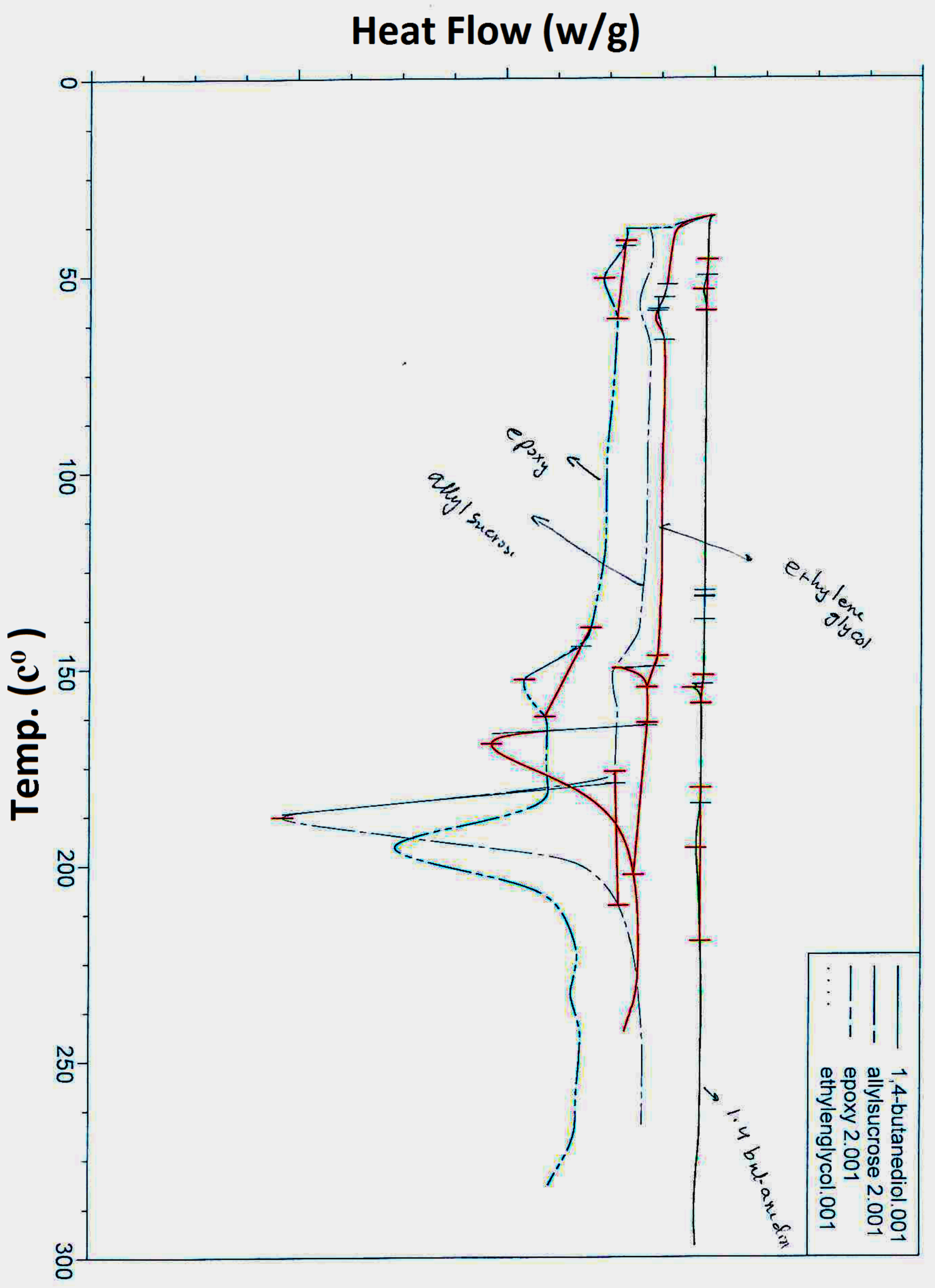


Fig.3.3.7: DSC for prepared SAPs. (AS., EAS., 1,4-BDGE., EGDA.)

3.3.8 Polymer Extracts

Polymer extract is defined as the residual un-reacted monomers or small chain polymer that present in superabsorbent polymer and soluble in water or polar solvent such as ethanol. In this test a known weight of SAP (W_1) is suspended in 20 ml of ethanol and stirred for one hour as shown in the experimental part. Then SAP is collected by filtration dried and weight (W_2). The % extract is calculated as shown in equation (3).

% extracts = $[W_2 - W_1 / W_1] \times 100\%$

Table 3.3.8: SAP extract in prepared polymers.

SAP with 4% cross-linker	Weight of SAP before extraction (g)	Weight of SAP after extraction (g)	% extraction
AS	1.05	1.05	0 %
EAS	0.9775	0.9782	0.07 %
1,4-BDGE	0.9904	0.9907	0.03 %
EGDA	0.9641	0.9643	0.02 %

As shown in table 3.3.8, the percent extract is close to zero in all prepared polymers. Which indicate that no residual monomer is present, a property that is crucial to several industrial application of SAP, especially those where the SAP gets in contact with human skin.

3.4 Biodegradability

Prepared superabsorbent polymers specially those cross-linked with sugar based monomers were subjected to biodegradability test using the organism Pseudomonas aeruginosa and Trichophyton rubrum, which is known to consume sugar molecules. The test was carried out as shown in detail in the experimental part. Result showed that there is some bacteria growth as can be seen in Fig.3.4. This is an indication that the cross-links between the polymer chains that are made up from sugar monomers are degrading and the polymers chains are breaking a part.

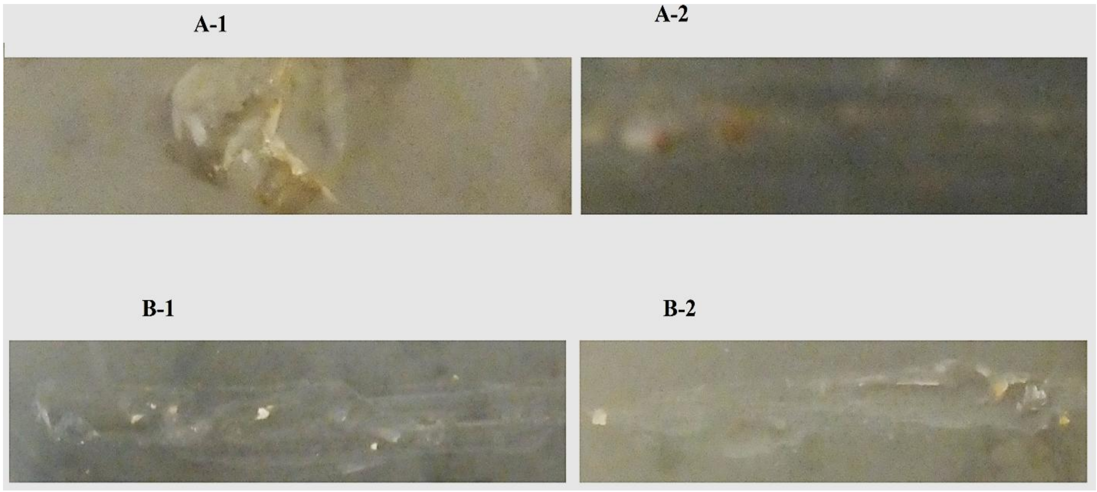


Fig. 3.4: Plate assay to visualize biodegradation of Allyl sucrose and Epoxy allyl sucrose by Pseudomonas aeruginosa and Trichophyton rubrum. A-1, biodegradation of Allyl sucrose by Pseudomonas aeruginosa; A-2, biodegradation of Epoxy allyl sucrose by Pseudomonas aeruginosa; B-1, biodegradation of Allyl sucrose by Trichophyton rubrum; B-2 biodegradation of Epoxy allyl sucrose by Trichophyton rubrum **[33].**

The organisms used for the degradation experiments were Pseudomonas aeruginosa and Trichophyton rubrum.

Pseudomonas aeruginosa isolate was maintained on Nutrient Agar (NA) (Oxoid) plates and incubated for 48 hours at 37 C° prior to use Trichophyton rubrum was isolated from superficial skin of human dermatomycosis patients. The isolated fungal was maintained on Sabouraud Dextrose Agar (SDA).

CONCLUSION

1. Allyl Sucrose and Epoxy Allyl Sucrose were synthesized and characterized by various spectroscopic techniques.

2. The prepared sucrose-based monomers were used as cross-linking agents for superabsorbent polymers.

3. Four different superabsorbent polymers were synthesized and characterized by IR, DSC, and SEM.

4. Two of the prepared superabsorbent polymers were cross-linked with sucrose-based monomers AS and EAS, and the other two were cross linked with 1,4-BDGE and EGDA.

5. The absorbent properties of the prepared superabsorbent polymers were evaluated in water and in saline solution, results indicate that the SAP cross-linked with EAS has the highest absorbent capacity and absorbency under load. This could be because it has the highest polarity, highest number of hydroxyl groups.

6. Superabsorbent polymers cross-linked with AS and EAS are biodegradable as shown by the biodegradability test.

7. Superabsorbent polymers cross-linked with AS and EAS have an economic advantages over conventional, petrochemical-derived SAP in that they are biodegradable and prepared in one step process.

References

1. Allison JH et al., Effect of N,N,N,N- **tetramethylethelenediamine on the migration of proteins in SDS polyacrylamide gels**, Anal Biochem. 58,592-601, 1974.

2. Andrade MM, Barros MT. **Facile conversion of O-sylil protected sugars into their corresponding formates using POCl3**.**DMF complex**. Tetrahedron;60:9235–43, 2004.

3. Bandyopadhyay, Abhijit; Chandra Basak, G. "***Studies on photocatalytic degradation of polystyrene"***. Materials Science and Technology 23 (3): 307–317. 2007.

4. Bandyopadhyay, Abhijit; Chandra Basak, G.. "***Studies on photocatalytic degradation of polystyrene"***. Materials Science and Technology **23** (3): 307–317, (2007)

5. Bandyopadhyay, Abhijit; Chandra Basak, G.. "***Studies on photocatalytic degradation of polystyrene"***. Materials Science and Technology **23** (3): 307–317,2007.

6. Barros MT, Petrova K, Ramos AM. **Regioselective copolymerization of acryl sucrose monomers**. J Org Chem.; 69: 72–75,2004.

7. Barros MT, Petrova K, Ramos AM. **Regioselective copolymerization of acryl sucrose monomers**. J Org Chem;69:7772–5, 2004.

8. Barros MT, Petrova KT, Ramos AM. **Biodegradable polymers based on a- or b-pinene and sugar derivatives or styrene, obtained under normal conditions and microwave irradiation**. Eur J Org Chem:1357–63, 2007.

9. Berger, J., Reist, M., Chenite, A., Felt-Baeyens, O., Mayer, J. M., & Gurny, R. ***Pseudo-thermosetting chitosan hydrogels for biomedical application.*** **International Journal of Pharmaceutics, 288, 17–25.2005.**

10. Buchholz F., and Graham A. T., **Modern Superabsorbent polymer Technology**. WILLEY- VCH. 1998.

11. Buchholz FL, Graham AT, **Modern Superabsorbent Polymer Technology**, Wiley-VCH, New York, Ch 1-7, 1998.

12. Buchholz FL, Graham AT, **Modern Superabsorbent Polymer Technology**, Wiley-VCH, New York, Ch 1-7, 1998.

13. C.H. Hamann, S. Fischer, H. Polligkeit, P.Wolf, Carbohydr. Chem. 12 173, 1993.

14. Damodaran S, Hwang D-C, **Carboxyl-modified superabsorbent protein hydrogel**, US Patents 5,847,089, 1998.

15. Demitri C, Delsole R, Scalera F, Sannino A,Vasapollo G, Maffezzoli A, Nicolais L, **Novel superabsorbent cellulose-based hydrogels crosslinked with citric acid**, *J Appl Polym Sci*, 2008.

16. F.L. Buchholz, T. Graham, **Modern Superabsorbent Polymer Technology**, Wiley-VCH, New York, pp. 1–152, 1998

17. Fanta GF, Doane WM, In: **Agricultural and Synthetic Polymers: Biodegradability and Utilization**, **Glass JE**, Swift G (Eds.), American Chemical Society, Washington DC,288-303,1990.

18. Fanton E, Fayet C, Gelas J, Deffieux A, Fontanille M, Jhurry D. **Synthesis of 4-O- and 6-O-monoacryloyl derivatives of sucrose by selective hydrolysis of 4, 6-O-(1-ethoxy-2-propenylidene)sucrose.**

19. H. Karl, C.K. Lee, R. Khan, Carbohydr. Res. 101, (1982).

20. Hayashi T. et al., Biosci. Biotech. Biochem., 58, 444-446, 1994.

21. Hwang D-C, Damodaran S. **Equilibrium swelling properties of a novel ethylenediamine tetraacetic dianhydride (EDTAD)-modified soy protein hydrogel**. J Appl Polym Sci, 62, 1285-1293, 1996.

22. Ichikawa T, Nakajima T, Superabsorptive Polymers (from natural polysaceharides and polypeptides), In: **Polymeric Materials**

Encyclopedia, Salamone (Ed), CRC, Boca Raton(Florida), 8051-8059, 1996.

23. Jarosz S, Mach M. **Regio- and stereoselective transformations of sucrose at the terminal position**s. Eur J Org Chem:769–80,2002.

24. Jihuai Wu, Yueling Wei, Jianming Lin, Songbai Lin. **Study on starch-graft-acrylamide/mineralpowdersuperabsorbent composite**.Science Direct. Polymer 44, 6513–6520, 2003.

25. Kabiri . K., and Zohuriaan-Mehr, M. J. **Superabsorbent Hydrogels from Concentrated solution Terpolymerization.Iranian Polymer Journa**l. 13 (5), 423-430, 2004.

26. Kathleen L. Opper, Kenneth B. **WagenerJournal of Polymer Science Part A: Polymer Chemistry** , *49* (4), 821-831,2011

27. Kirk-Othmer, **Encyclopedia of Chemical Technology**, 3rd Edition, Volume 21, John Wiley & Sons, New York, pages 921-948, 1983.

28. Kuang.Jia, Young Yuk Kun, Moo Huh Kang. Polysaccharide-based superporous hydrogels with fast swelling and superabsorbent properties. Carbohydrate Polymers 83, 284-290,2011

29. Kulicke W-M, Nottelmann H, **Structure andswelling of some synthetic, semisynthetic, andbiopolymer hydrogels**, Adv Chem Ser, 223, 15-44,1989.

30. Lee, W. F., & Yang, L. G. Superabsorbent polymeric materials. XII. **Effect of montmorillonite on water absorbency for poly(sodium acrylate) and montmorillonite nanocomposite superabsorbents**. Journal of Applied Polymer Science, 92, 3422–3429.2004.

31. Lichtenthaler FW, Peters S. **Carbohydrates as green raw materials for the chemical industry**. C R Chim;7:65–90, 2004.

32. Lichtenthaler FW, Peters S. **Carbohydrates as green raw materials for the chemical industry**. C R Chim;7:65–90 ,2004

33. Liu M, Liang R, Zhan F, Liu Z, Niu A, **Synthesis of a slow-release and superabsorbent nitrogen fertilizer and its properties**, Polym Adv Technol,**17**, 430-438, 2006

34. Mathur AM, Moorjani SK, **Scranton AB,Methods for synthesis of hydrogel networks: Areview**, J Macromol Sci-Rev Macromol ChemPhys, C36, 405-430, 1996.

35. Miller,M.l.,**In Encyclopedia of polymer Science and Technology**, Wiley I|nter science,New York,pp. 197-226,1997.

36. Mohamadnia Z, Zohuriaan-Mehr MJ, Kabiri K,Razavi-Nouri M, **Tragacanthgum-graft-polyacrylonitrile:Synthesis, characterization and hydrolysis**,*J Polym Res*, **15**, 173-180, 2008.

37. Mohammad J. Zohuriaan-Mehr. and Kourosh Kabiri. ***Superabsorbent Polymer Materials***. **Iranian Polymer Journal 17, 451-477, 2008.**

38. Obenski B.J., Nonwovens Industry (Nov 1994).

39. Omidian H, Zohuriaan-Mehr MJ, Kabiri K, ShahK**, Polymer chemistry attractiveness: Synthesisand swelling studies of gluttonous hydrogels in the advanced academic laboratory**, Polym Mater, 21,281-292, 2004.

40. Perez, in: M. Mathlouthi, P.P. Reiser (Eds.), **Sucrose: Properties and Applications**, Chapman & Hall, , pp. 11, 1995.

41. Po R, **Water-absorbent polymers**: A patent survey,JMacromol. Sci-Rev MacromolChemPhys, C34,607-662, 1994.

42. **Polymerisation and copolymerisation with styrene**. Carbohydr Res;240:143–52,1993.

43. Potier P, Bouchou A, Descotes G, Queneau Y. **Proteinase N-catalysed transesterifications in DMSO-water and DMF-water: preparation of sucrose monomethacrylate**. Tetrahedron;41:3597–600, 2000.

44. Potier P, Bouchou A, Descotes G, Queneau Y. **Proteinase N-catalysed transesterifications in DMSO-water and DMF-water:**

preparation of sucrose monomethacrylate. Tetrahedron;41:3597–600,2000.

45. Potier P,Bouchou A,DescotesG, ***New generation of super absorber nano-fibroses hybrid fabric by electro-spinning*, Journal of Materials Processing Technology**, Volume 199, Issues 1–3, , Pages 193–198, 2008.

46. Pourjavadi A, Salimi H, **A new protein-based hydrogel with superabsorbing properties: Effect of monomer ratio on swelling behavior and kinetics**, Ind Eng Chem Res, 2008.

47. Raju, K. M., Raju, M. P., & Mohan, Y. M. **Synthesis of superabsorbent copolymers as water manageable materials**. Polym International, 52,768–772, 2003.

48. Sachinvala, N.D.; Hamed, O.A.; Winsor, D.L. "***A New Liquid Epoxy from Sugar Cane"* Science Blog June 10, 1999**.

49. Sannino A., Esposito A., De Rosa A., Cozzolino A., Ambrosio L., Nicolais L., **Biomedical application of a superabsorbent hydrogel for body water elimination in the treatment of edemas**, J BiomedMater Res, 67A, 1016-1024, 2003.

50. Shakhashiri, B. Z. **In Chemical Demonstrations**: A Handbook for Teachers of Chemistry; The University of Wisconsin Press: Vol. 3, p 368-371,1989.

51. SUO, A. L., Qian, J. M., and Yao, Y. , et al. ***Synthesis and properties of carboxymethyl cellulose-graft-cellulose-based superabsorbent***, **Journal of Applied polymer science 103(3), 1382-1388, 2007.**

52. **Superabsorbent hydrogels**, Website of the leading Iranian manufacturer of superabsorbent polymers;Rahab Resin Co., Ltd.; www.rahabresin.com,available in 10 September 2007.

53. Superabsorbents, Website of the European Disposables and Nonwovens Association(EDANA); www.edana.org, available in 28 May,2008.

54. Takeda H. and Taniguchi Y., **Production process for highly water absorbable polymer**, USPatent 4,525, 527. 1985.

55. Wampler.F.M, **Formation of Diacrylic Acid During Acrylic Acid Storage** ,AIChE presentation, Houston, 7, 183-189, 1988.

56. Weisz, P.B, Ind. Eng. Chem. Res., 34, 2692-2699(1995).

57. William Rathje and Cullen Murphy. Rubbish! The Archeology of Garbage. 1989.

58. Yin Y. L., Prudhomme R. K., Stanley F.W.,and Jr. , **In Polylectrolyte Gets, ACS Symp**. Ser. Vol. 480, American Chemical Society, Washington,D.C. 1992.

59. Yu C, and Hui-min T,. **Crosslinkedcarboxymethylchitosan-g poly(acrylic acid) copolymeras a novel superabsorbent polymer**.Carbohydrate Research 341,887–896, 2006.

60. Yu. C., Yun-fei. L, Hui-min.T, and Jian-xin. J. **Synthesis and characterization of a novel superabsorbent polymer of N,Ocarboxymethyl chitosan graft copolymerized with vinyl monomers**. Carbohydrate Polymers 75, 287–292, (2009).

61. Zhang J., Li A., and Wang A., **Synthesis and characterization of multifunctionalpoly(acrylicacid-co-acrylamide)/sodium humatesuperabsorbent composite**. Reactive & Functional Polymers 66 , 747–756,2006.

62. Zhang Ji, Yuan Kun, Wang Yun-Pu. **Preparation and properties of polyacrylate/bentonite superabsorbent hybrid via intercalated polymerization**. Materials Letters 61, 316-320, 2007

63. Zhang, H., Kallimanis, A., Koukkou, A. I. and Drainas, C. **Isolation and characterization of novel bacteria degrading polycyclic aromatic hydrocarbons from polluted Greek soils.** Applied Microbiology Biotechnology 65, 124-131,2004.

64. Zohuriaan-Mehr MJ, Super-Absorbents (inPersian), **Iran Polymer Society**, Tehran, 2-4, 2006.

65. Zohuriaan-Mehr,M. J., and KabiriK.**Superabsorbent Polymer Materials:A Review**, Iranian Polymer Journal17 (6), 451-477,2008.

66. Zoua W,YuaL,Liua X, Chena L, Zhangb X, QiaoaD,andZhanga R,. **Effects of amylose/amylopectin ratio on starch-based superabsorbent polymers.** Carbohydrate Polymers 87 1583– 1588, 2012.

Appendix

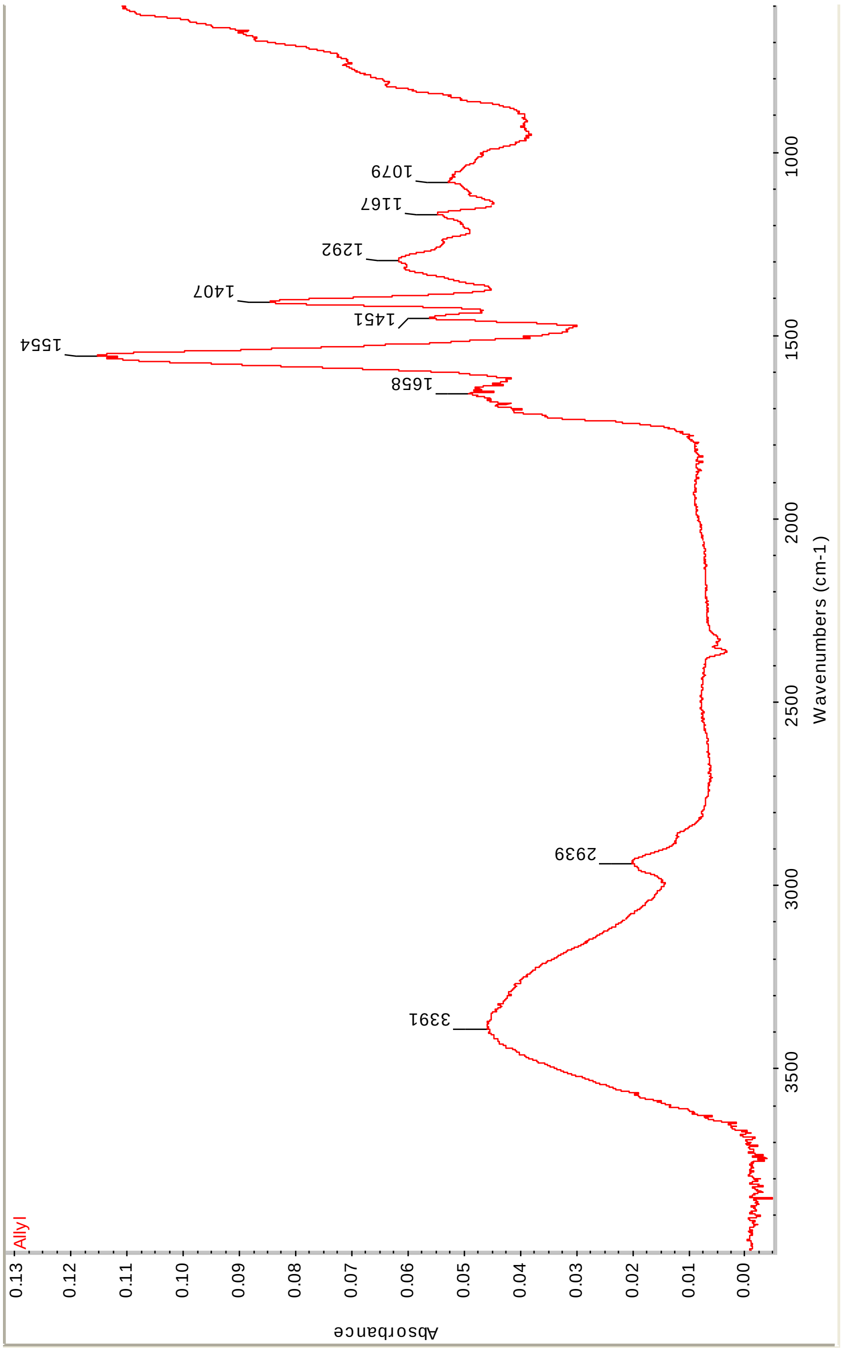


Fig. a1: IR for prepared SAP (PAA- AS).

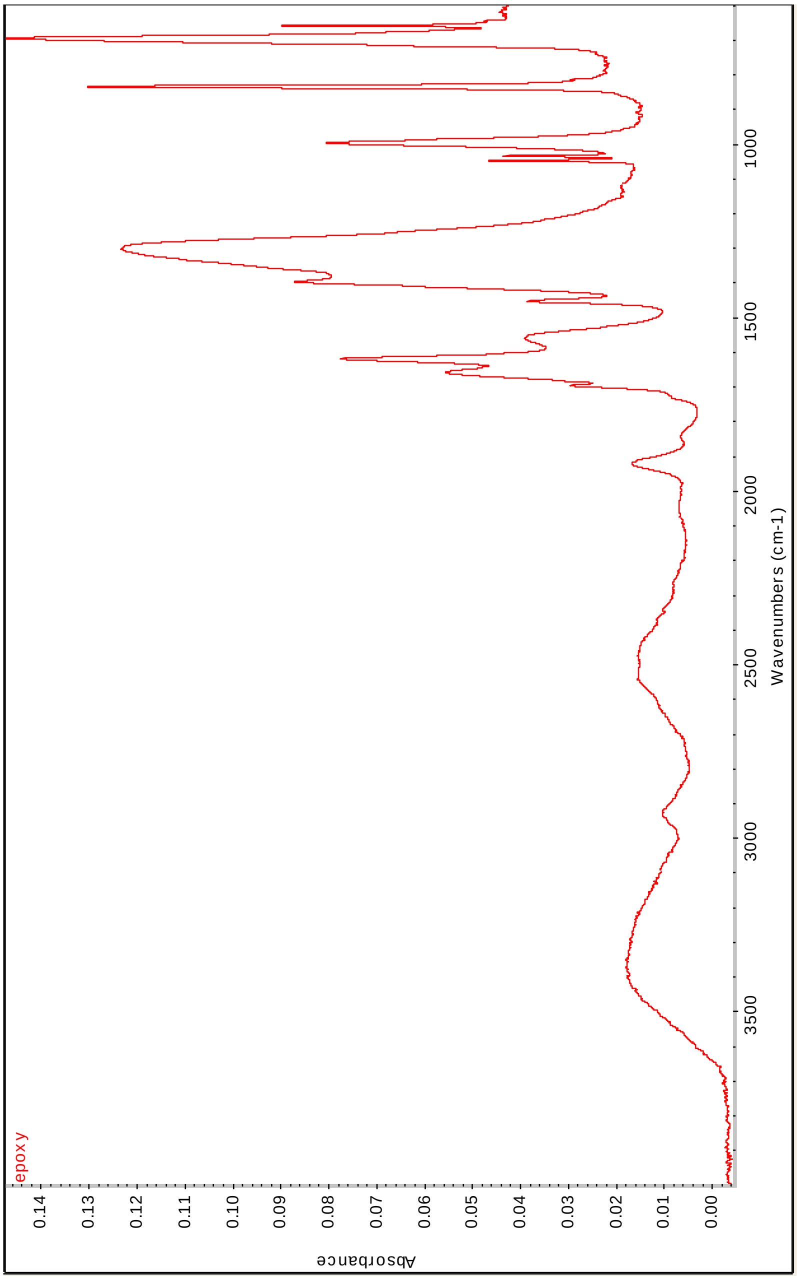


Fig. a2: IR for prepared SAP (PAA-EAS).

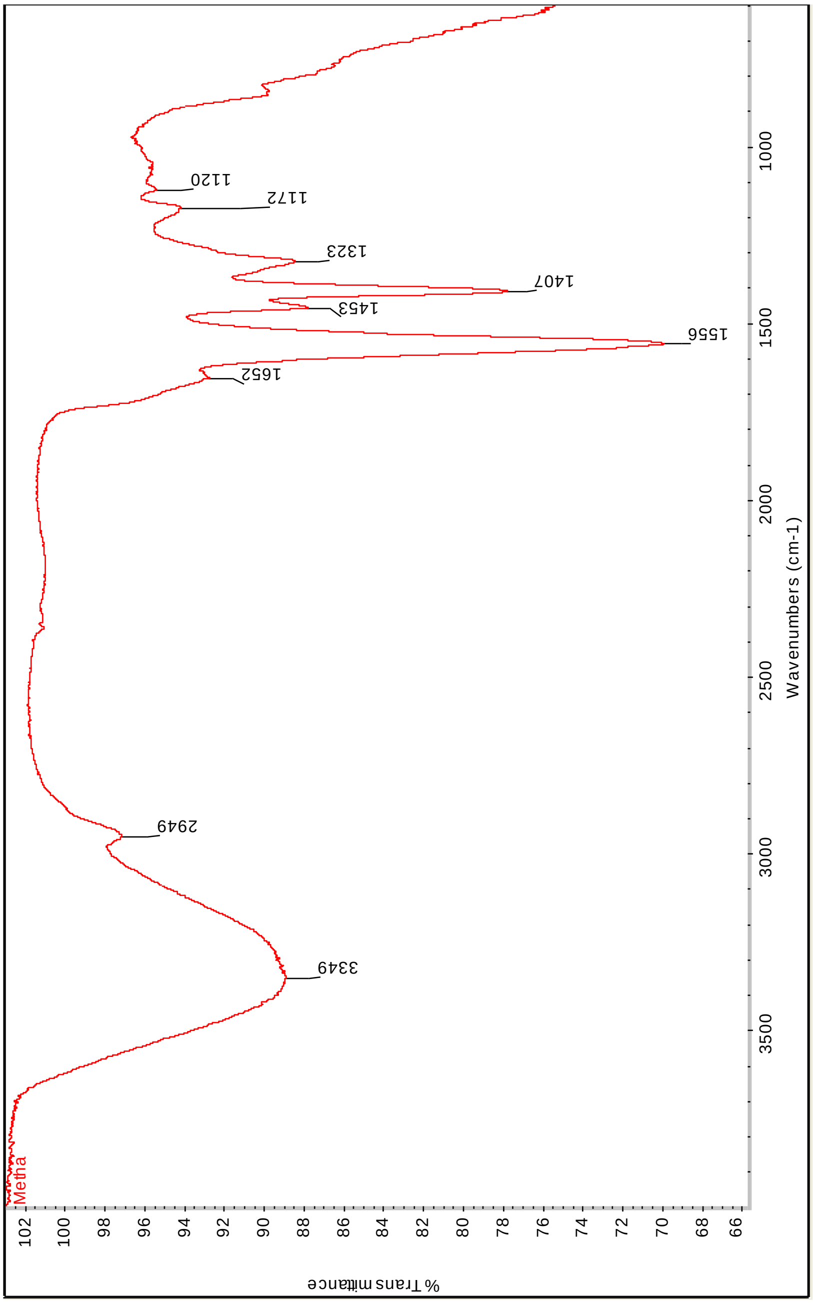


Fig. a3: IR for prepared SAP (PAA-EGDA).

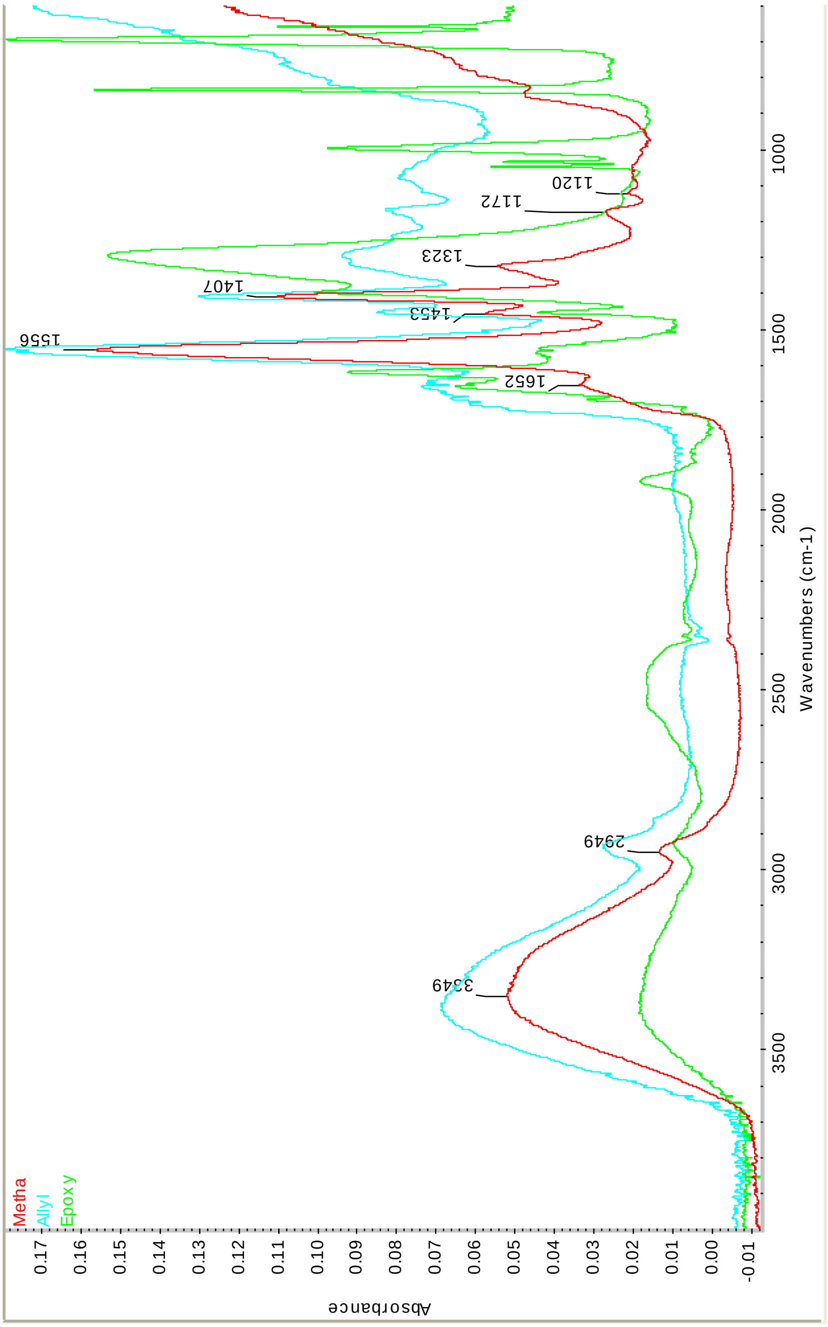


Fig. a4: IR for prepared SAPs (PAA- AS , EAS, EGDA).

Fig. a5: Electronic Image for prepared SAP (PAA-AS), Input Source: Secondary electron detector, Image Width: 1.263 mm

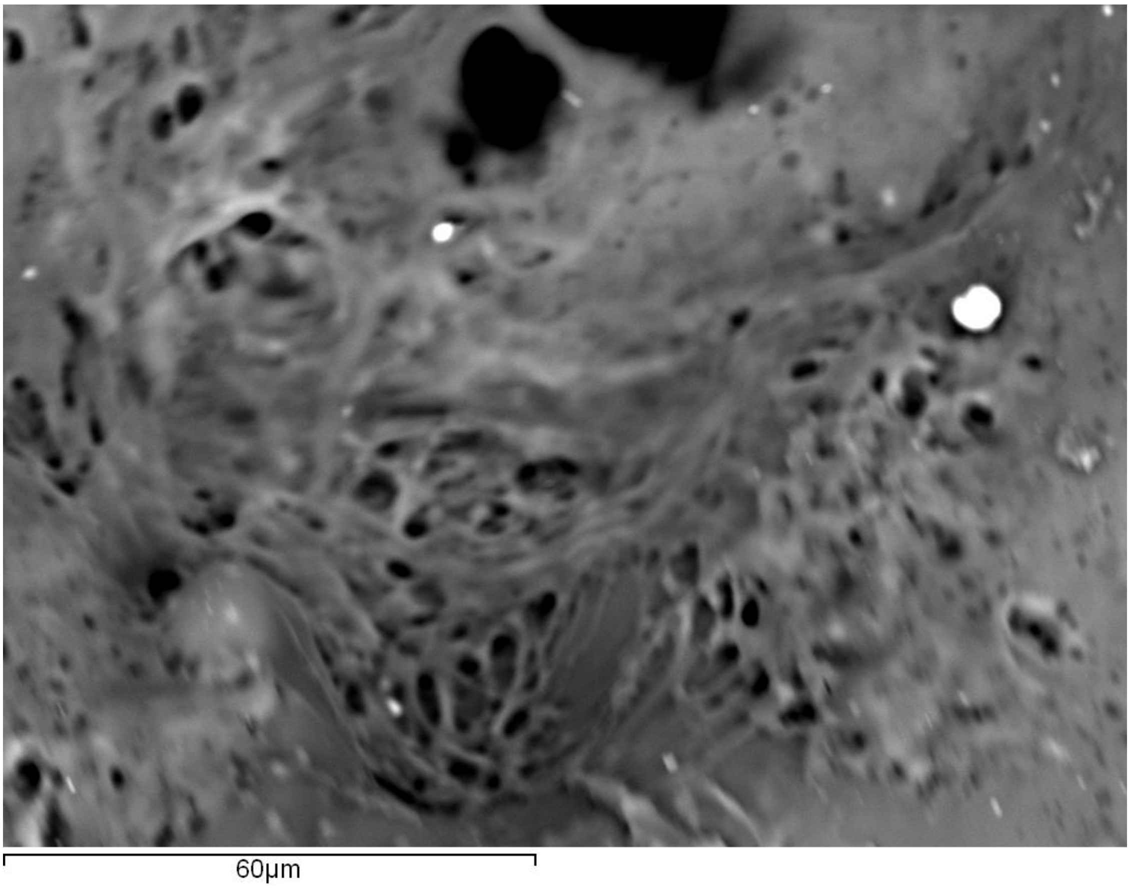


Fig. a6: Electronic Image for prepared SAP (PAA-AS), Input Source: Secondary electron detector, Image Width: 126.3 mm

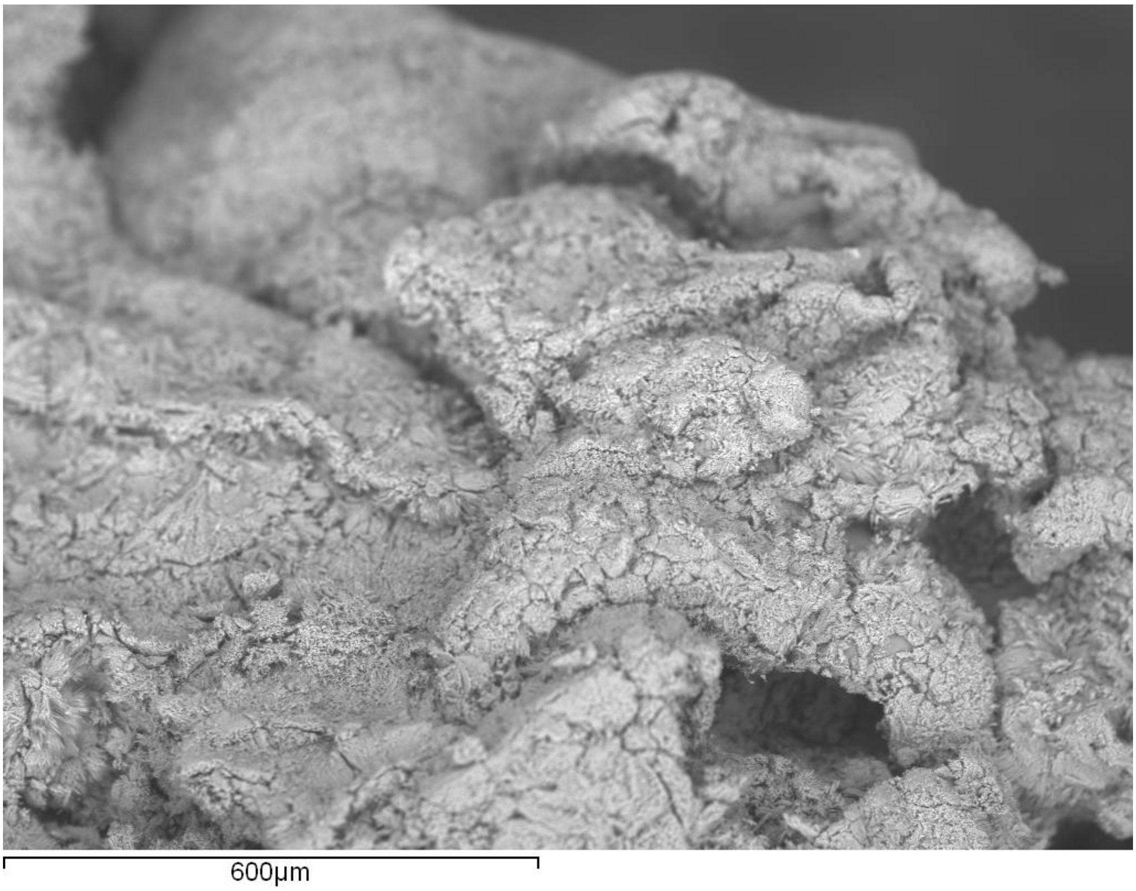


Fig. a7: Electronic Image for prepared SAP (PAA-EAS), Input Source: Secondary electron detector, Image Width: 1.263 mm

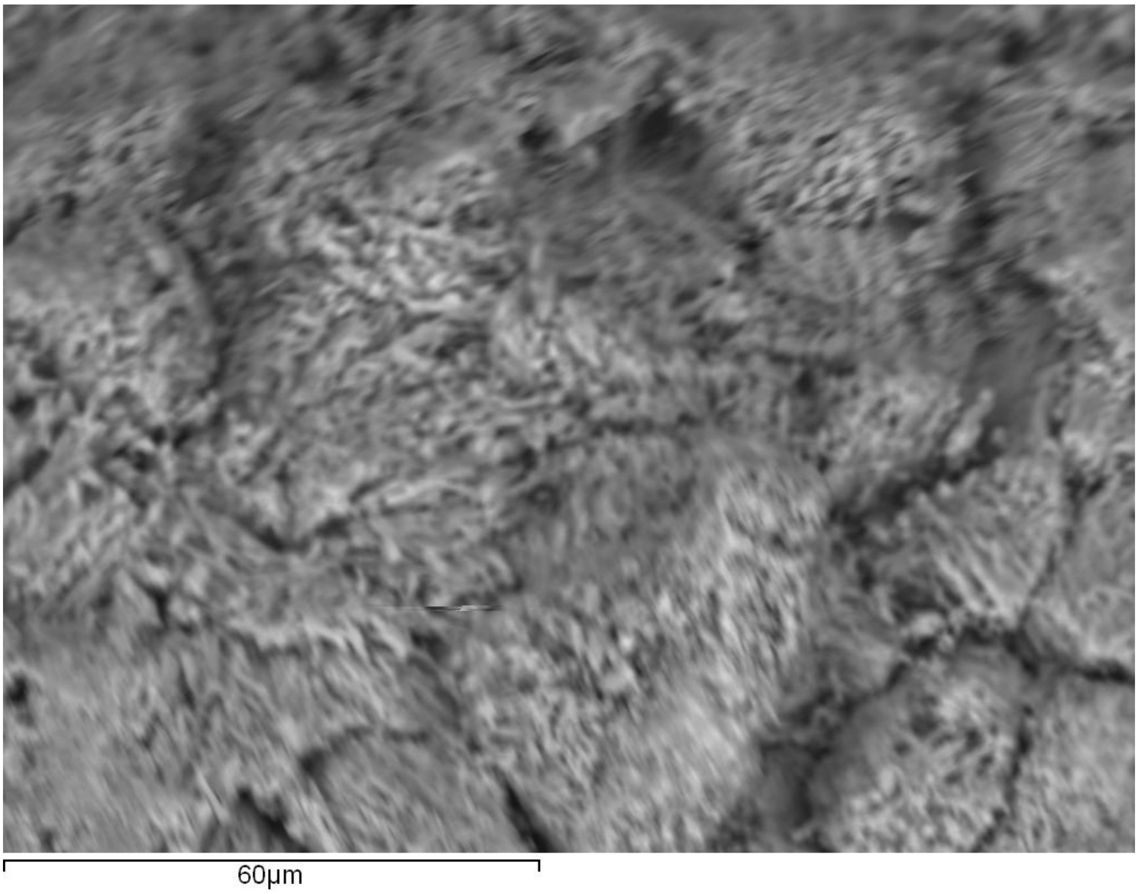


Fig. a8: Electronic Image for prepared SAP (PAA-EAS), Input Source: Secondary electron detector, Image Width: 126.3 mm

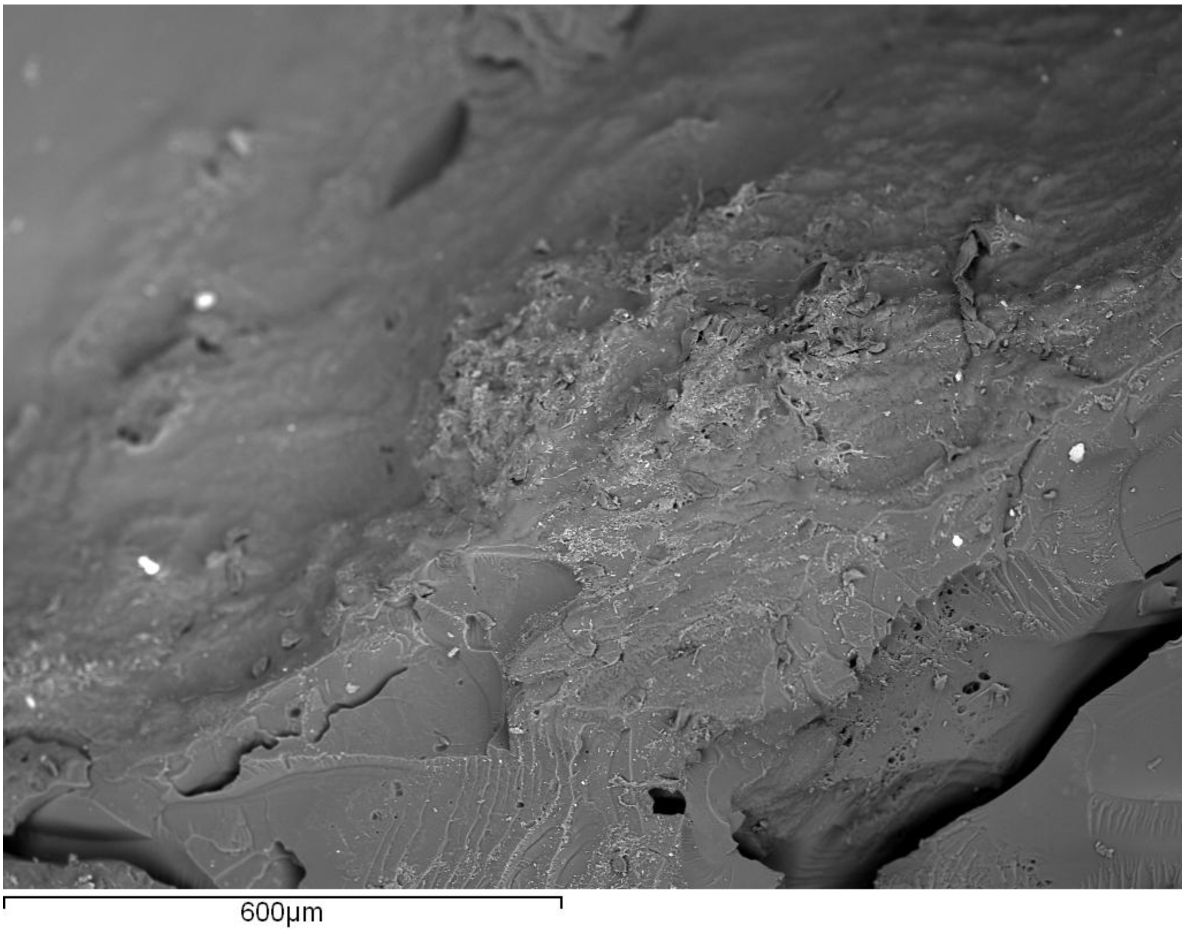


Fig. a9: Electronic Image for prepared SAP (PAA-EGDA), Input Source: Secondary electron detector, Image Width: 1.263 mm

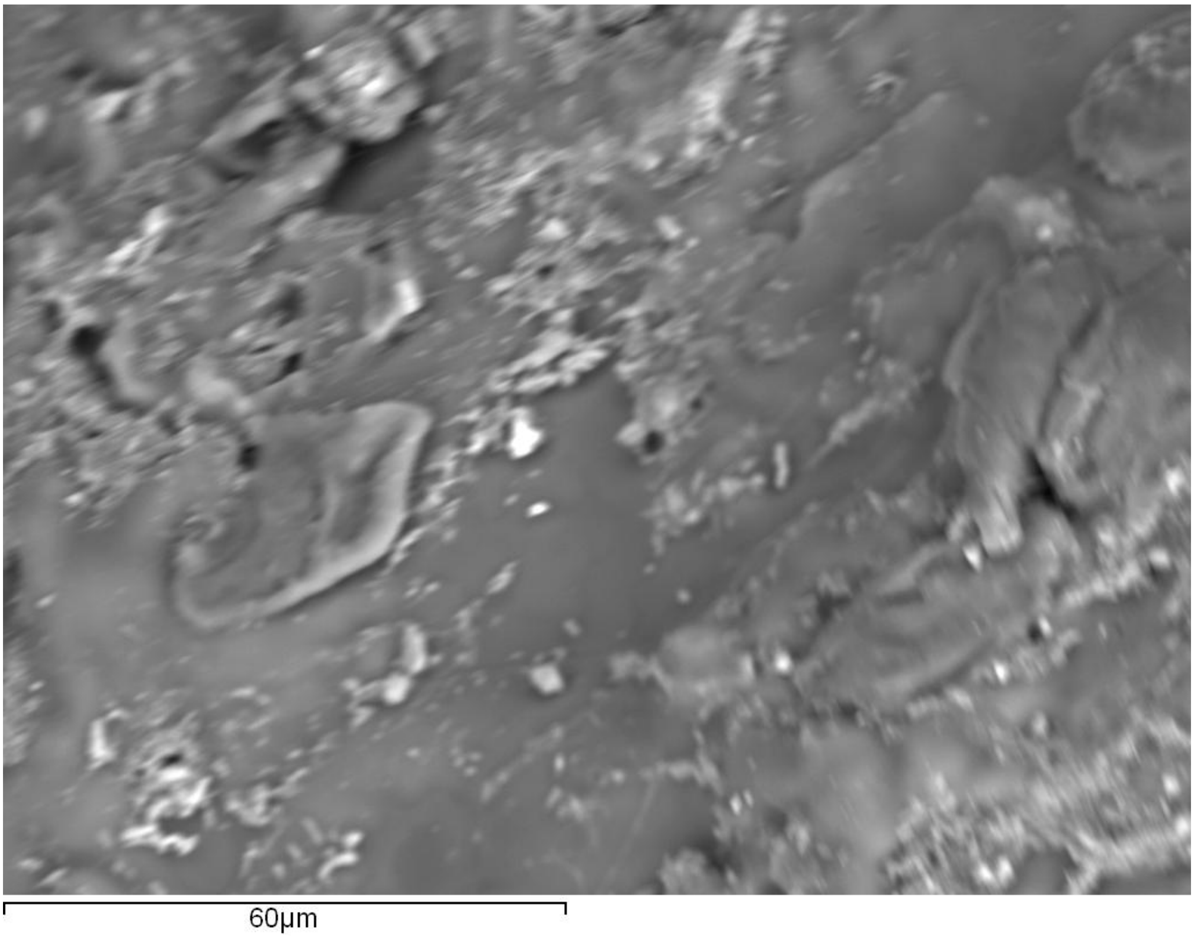


Fig. a10 : Electronic Image for prepared SAP (PAA-EGDA), Input Source: Secondary electron detector, Image Width: 126.3 mm

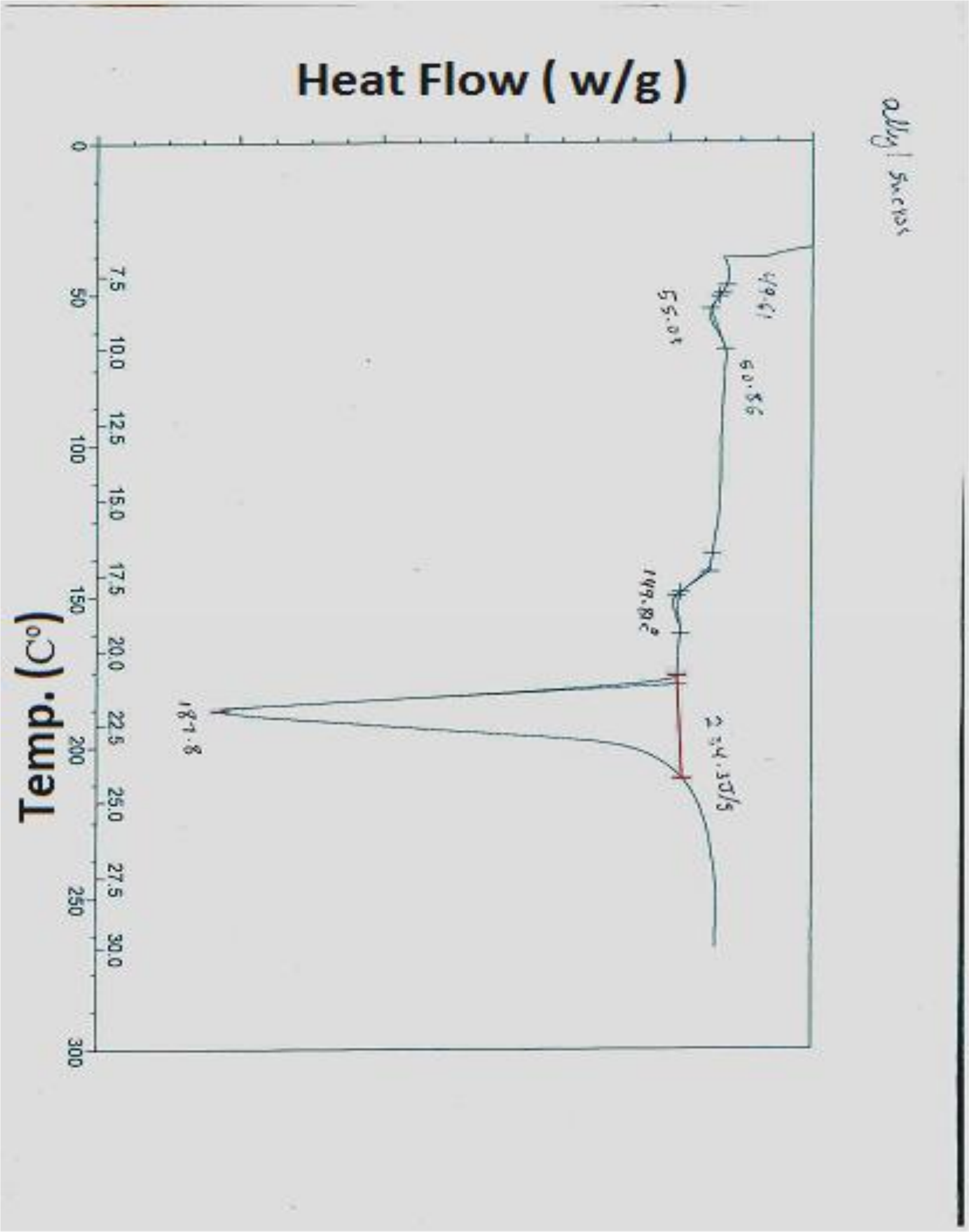


Fig. a11: DSC for prepared SAP (PAA-AS).

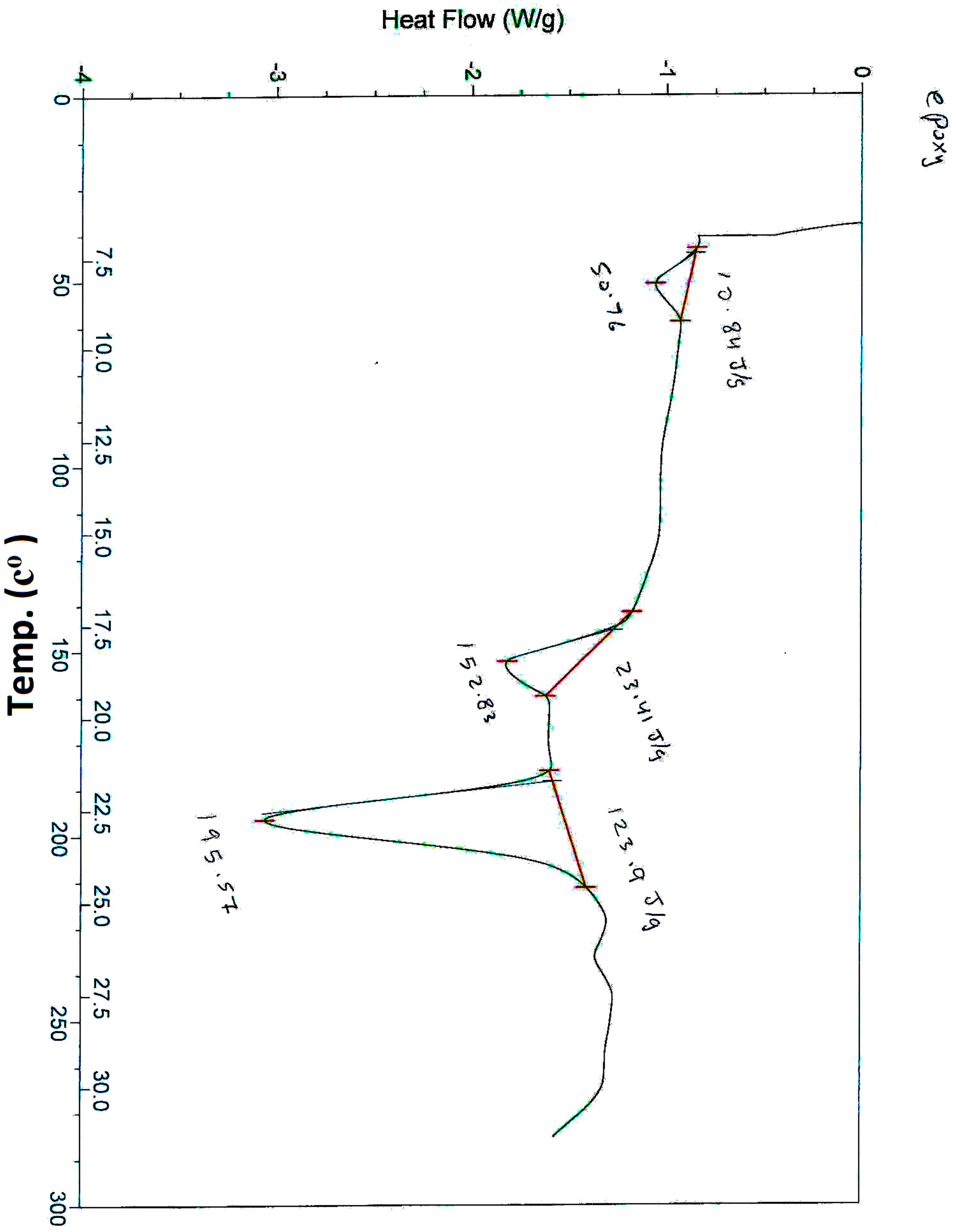


Fig. a12: DSC for prepared SAP (PAA-EAS).

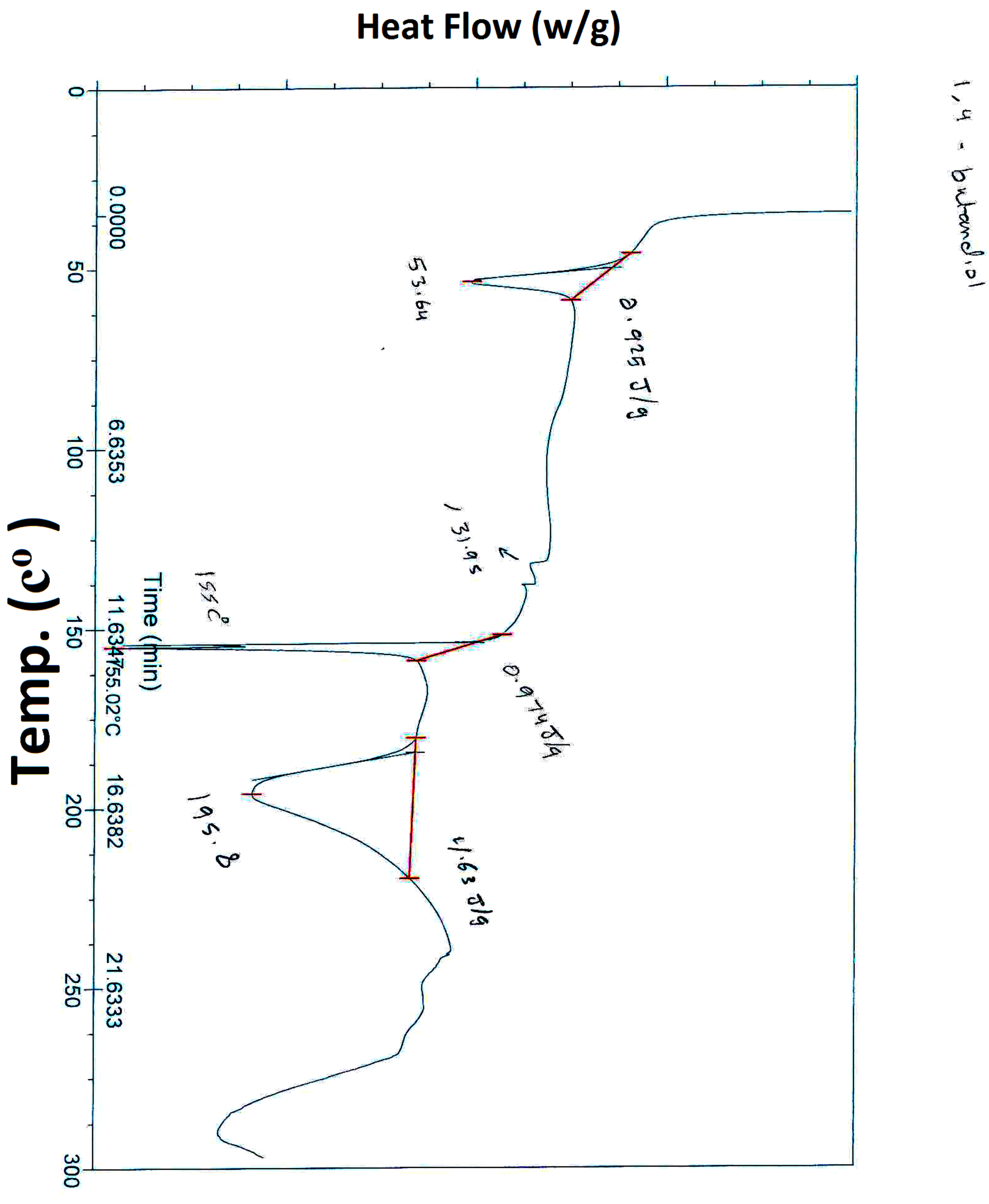


Fig. a13: DSC for prepared SAP (PAA-1,4-BDGE).

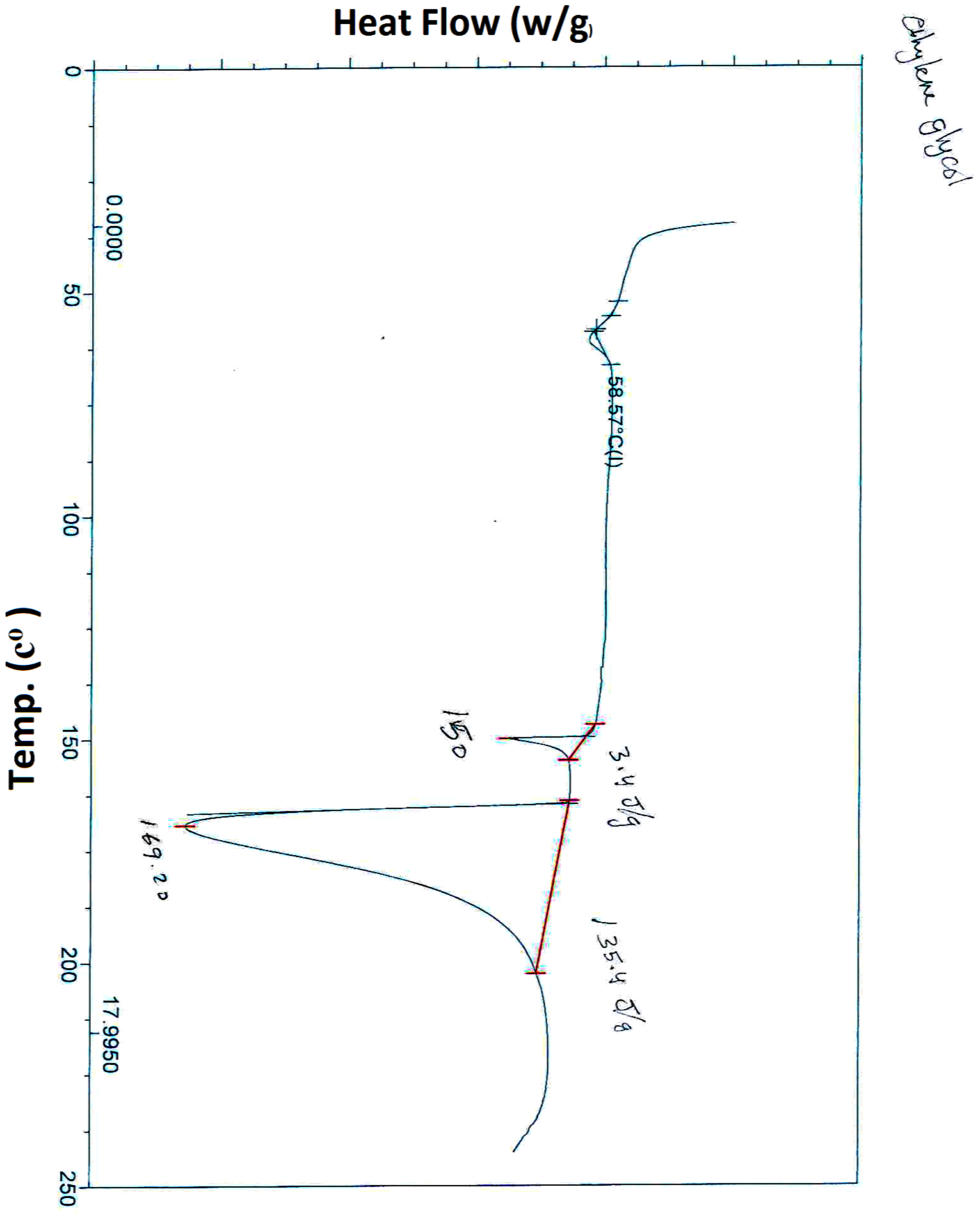


Fig. a14: DSC for prepared SAP (PAA-EGDA).

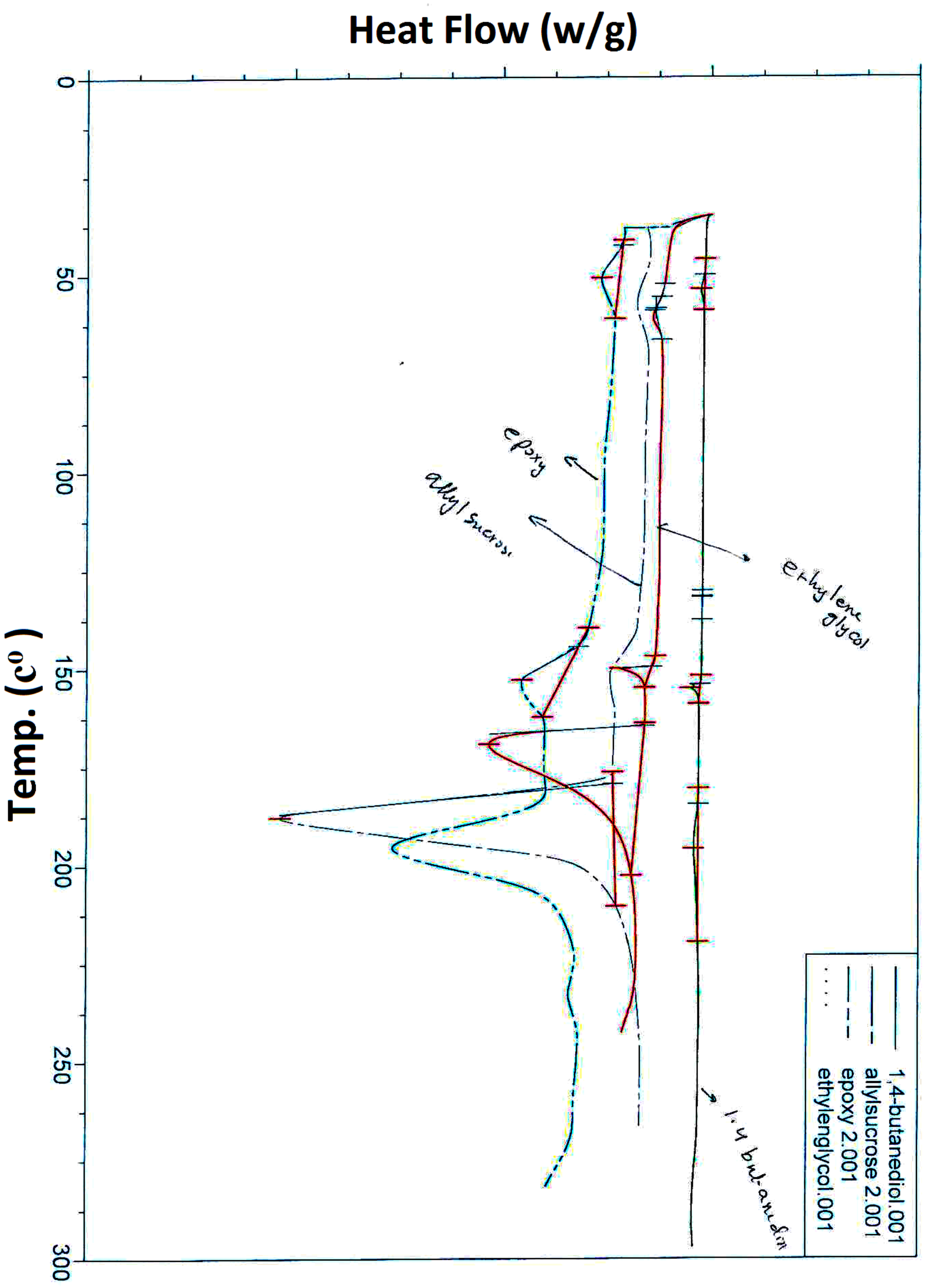


Fig. a15: DSC for prepared SAPs. (PAA-AS, EAS, 1,4-BDGE, EGDA).

جامعة النجاح الوطنية

كلية الدراسات العليا

طرق جديدة لتحضير بوليمرات فائقة الامتصاص صديقة للبيئة

اعداد
فراس جابر عبد اللطيف أبو جابر

اشراف
د. عثمان حامد

قدمت هذه الرسالة استكمالا لمتطلبات الحصول على درجة الماجستير في الكيمياء بكلية الدراسات العليا في جامعة النجاح الوطنية، نابلس-فلسطين.

2012 م

طرق جديدة لتحضير بوليمرات فائقة الامتصاص صديقة للبيئة

اعداد

فراس جابر عبد اللطيف أبو جابر

اشراف

د. عثمان حامد

الملخص

تعد البوليمرات العضوية ذات اهمية بالغة في حياة الانسان اذ تدخل في الوقت الحاضر في مكونات غذائه وكسائه ومسكنه ، وقد لوحظ في الاونة الاخيرة الاعتماد الكبير على البوليمرات في الكثير من الصناعات، وهذا ناتج عن التطور الهائل الذي حصل في الصناعات الكيماوية والقائمة على النفط ومشتقاته وهذه تتميز بصفات ميكانيكية جيدة كما تتميز برخص الثمن وتوفرها بشكل كبير ، كما تم استخدامها في صناعة الادوات المنزلية والصناعات الحربية والمدنية.

ان التقدم الكبير في مجال الصناعات البتروكيميائية فتح الباب على مصراعيه في مجال صناعة البوليمرات واحدث نقلة نوعية في انتاجها واستخدامها، على ان المأخذ الرئيسي على استخدامها هو قدرة تلك المركبات على البقاء مما تشكل تهديدا كبيرا للبيئة، ولذلك في ظل التطور الهائل في صناعة البوليمرات يجب ان تكون مقرونة بابحاث مكثفة عن كيفية التخلص من النفايات المترتبة على استخدامها، وعن امكانية تدويرها .

تم في هذه الدراسة تحضير مونمرات من مصدر طبيعي لحل مشكلة تراكم النفايات وتقليل ضررها على البيئة، والمصدر الطبيعي الذي وقع عليه الاختيار هو السكروز لتحضير مونمرات تستخدم في تكوين بوليمرات فائقة الامتصاص صديقة للبيئة وقابلة للتحلل في نفس الوقت.

فتم تحضير نوعين من المونمرات هما اليل سكروز (AS) وابوكسي اليل سكروز (EAS) باكثر من طريقة. حيث تم تحضير النوع الاول من مفاعلة السكر مع الاليل كلوريد في وسط قاعدي، ثم أكسدة المركب الناتج بواسطة m-CPBA ليتحول الى ابوكسي اليل سكروز. ثم قمنا باستخدام نوعين أخرين من المونمرات الجاهزة هما (1,4-BDGE) و (EGDA)، حيث استخدمت هذه المونمرات كعامل ربط مع الاكريلك أسيد (AA) لتحضير بوليمرات فائقة الامتصاص صديقة للبيئة، مع العلم ان المونمرات الجاهزة تستخدم لاول مرة في تحضير البوليمرات .

ومن خلال استخدام تراكيز مختلفة من هذه المونمرات تم الحصول على عدة بوليمرات تم المقارنة بينها من حيث القدرة على الامتصاص تحت ظروف متغيرة كما هو موضح في الجانب العملي، وأثبتت النتائج ان نسبة الامتصاص تزداد كلما قلت نسبة عامل الربط المستخدم، واقل نسبة امتصاص عند 4% كما هو موضح في جانب النتائج والمناقشة .

واثبتت النتائج ان نسبة امتصاص (EAS) اعلى من غيرها من البوليمرات وهذا يعود الى القطبية العالية والى عدد مجموعات الهيدروكسيل الموجودة. كما تمتاز البوليمرات التي تم تحضيرها عن البوليمرات التجارية في :

أولاً : انها قابلة للتحلل كما هو مبين في فحص تأثير البكتيريا عليها .

ثانياً : انها تحضر من خطوة واحدة بالمقارنة مع البوليمرات التجارية التي تحضر بخطوتين .