SUPERABSORBENT POLYMER SPONGES FOR THE DESIGN OF SALIVA ABSORPTION PAD

A Thesis

Submitted By

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Dedicated to my dear Parents.

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CERTIFICATE

This is to certify that the thesis titled **'Superabsorbent polymer sponges for the design of saliva absorption pad'** being submitted by Mr. Paila Ravi Sankar to SCTIMST Trivandrum, for the award of the degree of **Master of Technology in Clinical Engineering** jointly offered by IIT Madras, CMC Vellore and SCTIMST Trivandrum, is a bonafide record of research work done by him under my supervision. The contents of this thesis in full or in parts have not been submitted to any other Institute or University for the award of any degree or diploma.

The research had been carried out at Sree Chitra Institute for Medical Sciences and Technology, Trivandrum.

Dr. Manju. S

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ABSTRACT

Saliva is a major hindrance to most of the dental procedure (e.g. root canal treatment) as the flow of saliva increases in patients undergoing dental treatment due to anxiety. Saliva absorption pads based on SAPs can provide dry oral environment to ease the dental treatment procedure and can reduce the swallowing reflexes that is common during cotton use. In the present study we have designed (preliminary stage) an indigenous saliva absorption pad more suitable for absorbing saliva produced in parotid gland. The design is based on the feedback we received from three dentists. In addition, different superabsorbent sponges (SAP Sponges) using carboxymethyl cellulose were synthesized and characterized using different techniques including Fourier transform infra red spectroscopy (FTIR), residual monomer content using high pressure liquid chromatography (HPLC), thermogravimetric analysis (TGA) and free swell capacity in water and 0.9% saline. Different cross-linking mechanisms are used for the preparation of SAP sponges such as ionic cross-linking using aluminium ammonium sulfate (AlAS) at different weight ratio (say, 2 wt%, 5 wt%, 10 wt% etc) and chemical cross-linking using acrylic acid and methylene bisacrylamide. The possibilities of SAP sponge production via polyelectrolyte complex formation using low molecular weight chitosan and carboxymethyl cellulose were also attempted. Among different SAPs characterized, SAP-2 synthesized using 10 wt% AlAS showed highest free swell capacity both in water and saline (83.21 ± 3.8 g/g and 40.7 ± 3.4 g/g respectively). However, the moisture content of the particular SAP sponge is higher (~13%) compared to the standard limit (ISO 17190-4:2001(E)). Hydrophobic surface modification is recommended to reduce the moisture content to improve the storage stability of SAPs.

1. INTRODUCTION

1.1. Introduction

Saliva is a major hindrance to most of the dental procedure (e.g. root canal treatment) as the flow of saliva increases in patients undergoing dental treatment due to anxiety. Usually cottons placed in a patient's mouth are used to absorb saliva during dental treatment. However, use of cotton for the particular applications does not provide complete isolation, and can stick to the oral mucosa. Also there is a need for frequent replacement of cotton rolls because of saturation. In order to overcome the limitations, superabsorbent polymer sponge is highly effective. Saliva absorption pads based on superabsorbent polymer sponge can provide dry oral environment to ease the dental treatment procedure and can reduce the swallowing reflexes that is common during cotton use.

Superabsorbent polymers are three-dimensional cross-linked polymer networks that can absorb and retain large amount of aqueous fluid (up to 300 times) compared to its dry weight [1]. SAPs having high swelling capacity along with good water retention ability and biodegradability enable them to possess potential applications in various field such as hygiene products (e.g. baby diapers, adult diapers and sanitary napkins), biomedical health care products (e.g. drug delivery systems, wound dressing), agriculture (in holding soil moisture), horticulture, waste water treatment, and self-healing concrete [2]. Superabsorbent polymers are mainly divided into natural SAPs and synthetic SAPs. Commercially available SAPs are synthetic resins that are mainly polymerized using acrylic/vinyl monomers such as acrylic acid, acrylamide, vinyl alcohol and acrylonitrile. Even though, synthetic SAPs currently available in the markets are biocompatible and have no direct threat to human life, disposal of such non-degradable material waste is a source of various environmental problems [3]. Therefore natural polymers based SAPs have received great attentions they are degradable via multiple mechanisms of actions

including enzymatic reactions, microbial attack, and hydrolysis. SAPs based on natural polymers (e.g. cellulose, chitosan, starch and alginate) are renewable, biodegradable and non-toxic in nature [4]. However, the main challenge in the area of biodegradable SAPs is to synthesize fully degradable SAPs that would rapidly and reversibly absorb water and having good mechanical strength. Major limitations of biodegradable SAPs are its poor mechanical properties and high-speed degradation.

1.2. Swelling mechanisms in superabsorbent polymers

The polymer backbone in SAPs contain hydrophilic groups such as hydroxyl (-OH), carboxyl (-COOH) that can form hydrogen bonds with water molecules and promote hydration and rapid absorption of water. Diagrammatic representation of mechanisms of swelling in SAP is shown in the Figure 1. As depicted in the Figure 1, cross-links between polymer chains form a three-dimensional polymer network that can avoid infinite swelling or dissolution. This is attributed to the elastic retraction forces of the polymer network along with decrease in entropy of the polymer chains as it become more rigid in the swollen state [5].

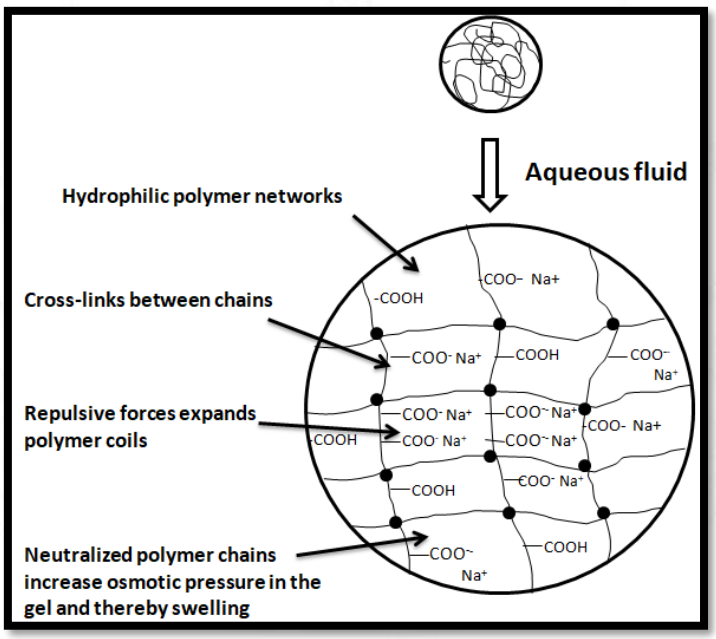

Figure 1: Mechanism of swelling in superabsorbent polymers

Beyond the effect of cross-linking, ionic concentrations in SAPs play a key role in its swelling. In partially neutralized SAPs, some percentages of its negative charges are balanced by cations (e.g. Na^+). During swelling, cations are hydrated which reduces their interactions with carboxylate ions. Hydrated cations are able to move freely within the polymer network and increase osmotic pressure within the gel. The increased osmotic pressure acts as driving force for further swelling of SAPs. Therefore, using ion rich swelling media such as saline or stimulated body fluid outside of the gel will lower the osmotic pressure and thereby reduce the swelling capacity of the hydrogel network.

1.3. Cross-linking in superabsorbent polymers

There are two main types of cross-linking in superabsorbent polymers, bulk cross-linking and surface cross-linking. In bulk cross-linking, two or more macromolecules are joined together via inter/intra molecular interactions (e.g. covalent bonding) and is usually taking place during the polymerization stage of SAP synthesis. Among several factors, the nature and amount of cross-linker used in the polymerization process plays a major role in determine the structure of the superabsorbent polymer network. For example, cross-liner having high reactivity ratio in the reaction mixture will be fully consumed in the early stages of the polymerization and any polymer chains made during the latter stages will be less likely to cross-link and end up as extractable. Some common types of cross-linkers used in the synthesis of SAPs are shown below (Figure 2)

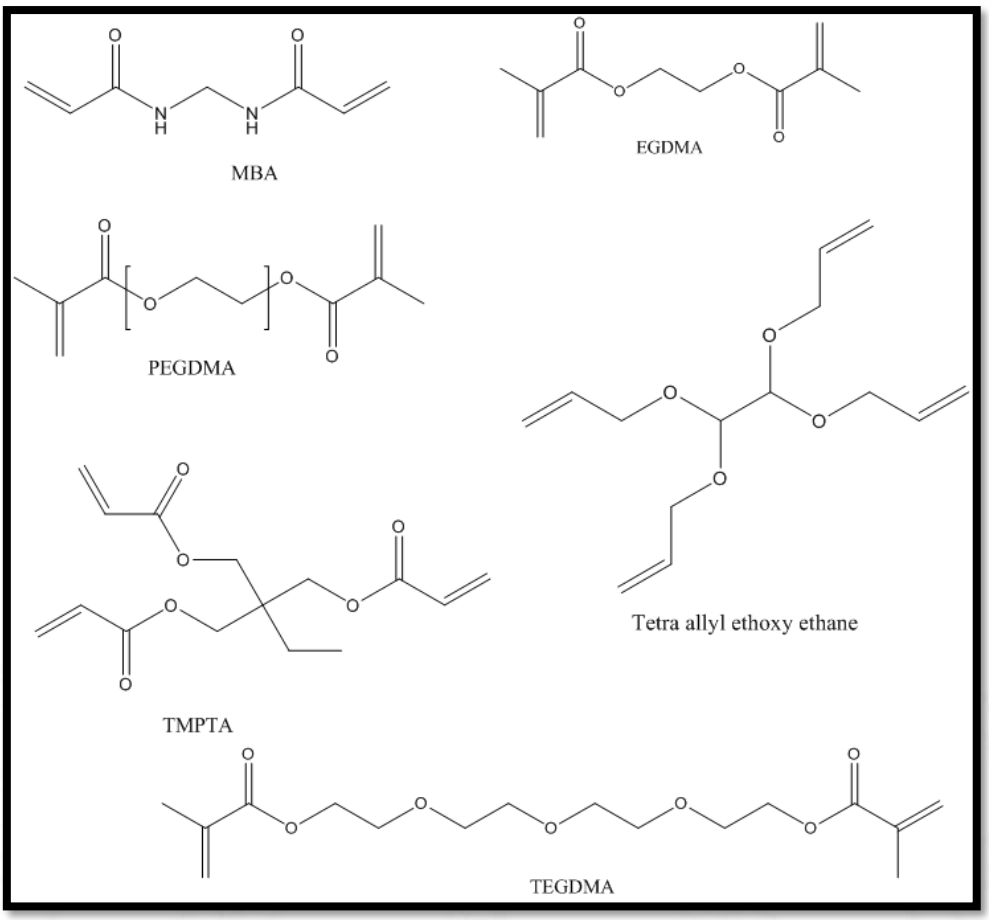

Figure 2: Chemical structure of common cross-linkers used in the synthesis of SAPs

Surface cross-linking improves the absorption against pressure and swelling rate of SAPs by overcoming a phenomenon called gel blocking. The surface cross-linking is the final stage of the synthesis process and is normally performed on the dried, milled and sized SAP particles. The surface cross-linked SAP particles maintain their shape during the swelling process and generate a less densely packed gel bed and thereby the fluid can flow in a less restricted fashion [3]. Core-shell structure of surface cross-linked SAP particles are attributed to the higher cross-linking density of its surface compared to lightly cross-liked bulk polymer network (Figure 3).

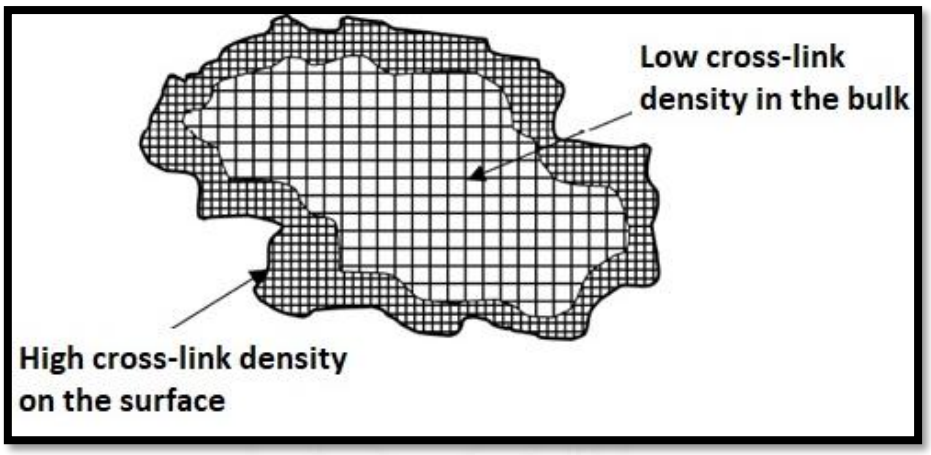

Figure 3: Schematic representation of a surface cross-linked SAP particle

1.3. 1. Cross-linking Vs swelling capacity of superabsorbent polymers

In general, the cross-linking density determines the swelling capacity and the dissolution of the SAPs in aqueous fluid. The absorption capacity increases with increase in cross-link density in SAPs until an optimum point and then decreases [6].

1.4. Classification of superabsorbent polymers

SAPs are classified based on different aspects including its origin (natural or synthetic SAPs), presence or absence of ionic groups located in the cross-liked chains (e.g. ionic, nonionic, ampholytic, and zwitterionic SAPs) etc. The majorities of commercially available SAPs are synthetic and anionic in nature based on partially neutralized acrylic acid (AA) or acrylamide (AM) [7].

1.4.1. Synthetic Superabsorbent polymers

Synthetic superabsorbent polymers are produced from the acrylic/vinyl monomers, most frequently acrylic acid (AA), and acrylamide (AM)[8]. Synthetic Saps are used for multiple applications including hygiene product, biomedical product such as wound dressing material, soil conditioners in agriculture to conserve water in dry zone. In addition, SAPs can also be used for water purification, waste management and self-healing Concrete [9],[10],[11].

Chemical Structures of monomers used in the synthesis of SAPs are shown in the figure 4. Free-radical polymerization of the acrylic/vinyl monomers in the presence of a cross-linking agents are the most common synthetic method used for the preparations of SAPs. Different polymerization techniques such as gel polymerization, suspension polymerization and solution polymerization techniques are established in the pilot production of synthetic SAPs. The major limitations of synthetic SAPs are non-sustainability and non-biodegradability [2].

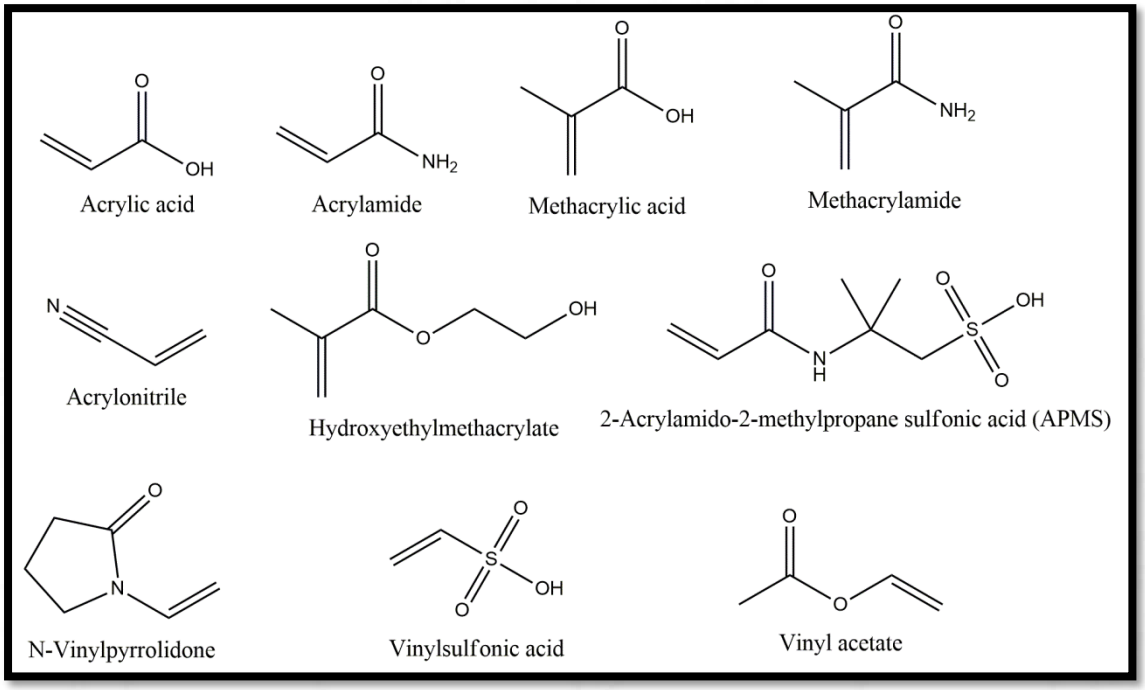

Figure 4: Chemical Structures of monomers used in the synthesis of synthetic SAPs

1.4.2. Natural superabsorbent polymers

Although majority of the superabsorbent polymers are manufactured from synthetic polymers due to their superior water absorption capacity and mechanical properties, environmental protection or plastic waste management potentially support the development of greener alternatives. Polysaccharides are major sources of natural SAPs [12]. Vast numbers of SAPs have been reported in the literature using starch, carboxymethyl cellulose (CMC), alginate, and chitosan etc. The advantages of these polysaccharide-based SAPs compared to synthetic SAPs are their sustainability, biodegradability and non-toxicity. The mechanical properties of 100 %

natural SAPs are stumpy and that limit its applications. So, in most of the reported work semi synthetic SAPs are synthesized via direct cross-linking of polysaccharides or graft copolymerization of acrylic/vinyl monomers on polysaccharides in the presence of cross-linker. In graft co-polymerization, a polysaccharide is reacted with vinyl monomers in presence of an initiator. For example, initiator such as persulphate (e.g. ammonium persulfate) can introduce free radicals on the backbone of polysaccharide via taking out hydrogen free radicals from hydroxyl groups. These free radicals initiate the graft polymerization of monomers on polysaccharides [13],[14]. In most of the cases vinylic compounds such as divinyl sulphone and polyfunctional compounds such as glycerol, epichlorohydrin and glyoxal are used as cross-linker. In the case of direct cross-linking reaction, semisynthetic polysaccharides (e.g. carboxymethyl cellulose (CMC)) are cross-linked with polyacids to form cross-linked polymer network via ester linkages. For example, CMC-and hydroxyethyl cellulose (HEC) based SAPs was prepared via cross-linking with citric acid in the presence of diethylsulfone.

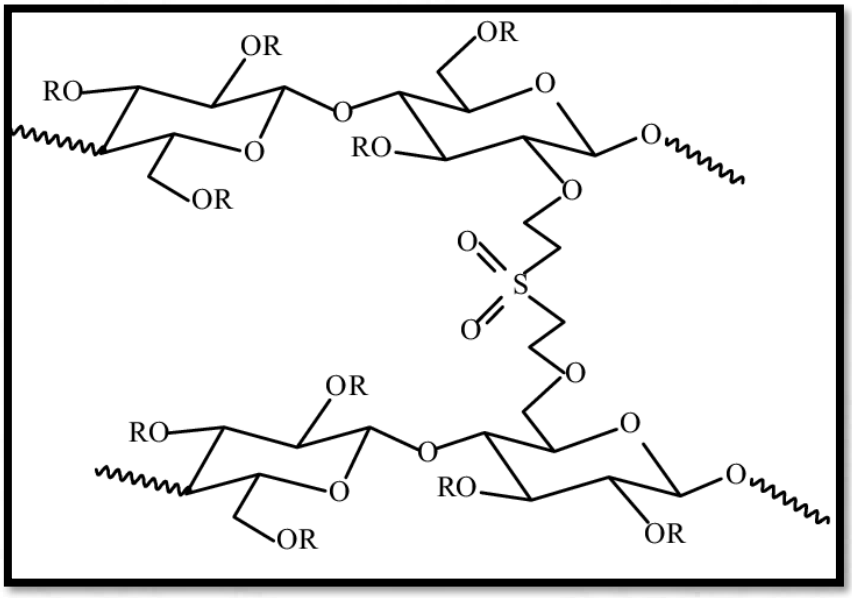

Figure 5: Typical cellulose-based SAP prepared via direct cross-linking of sodium carboxymethyl cellulose and hydroxyethyl cellulose [7].

1.5. OBJECTIVES OF THE WORK

The present objective of the thesis is to synthesize and optimize carboxymethyl cellulose based superabsorbent polymer sponges for the development of saliva absorption pad. In addition, the study aims for an indigenous saliva absorption pad design optimization based on the feedback from dentists.

2. LITERATURE REVIEWS

2.1. INTRODUCTION

A series of articles have been published in the area of superabsorbent polymers and its applications. In general, researchers are mainly focused on the synthesis and applications of SAPs. Both synthetic SAPs and natural SAPs are modified for different application to impart biodegradability and mechanical properties respectively [15]. The preparation of the first superabsorbent polymer was performed in 1961 by Russell et al., in which acrylonitrile was grafted to starch [7]. In another study, Fanta et al. demonstrated that the superabsorbent polymer based on starch derivatives possessed excellent water absorbing capacity and could retain them under a certain pressure [16]. In 1978, Japan began the commercial production of SAP for female napkins. After further developments, in 1980s, Germany and France employed SAP materials in baby diapers [17].

2.2. Poly acrylic acid based super absorbent polymers

Yan Liu *et al.* studied a multi-functional superabsorbent polymer of carboxymethyl cellulose using solid waste of Semi coke via the free-radical polymerization. It was shown that 10 wt% semicoke based SAP had a high swelling capacity of 64.8 g/g in saline with a wide pH application range [18]. Quang Bui *et al.* demonstrated the water absorption capacity of poly (acrylic acid),poly (acrylic acid-co-vinylsulfonic acid)and poly (4-styrenessulfonic acid-co-maleic acid) interpenetrated in a poly(acrylic acid) network hydrogels [19].An efficient and eco-friendly SAP was prepared by Seyed Mostafa Hosseini *et al.* for removing methylene blue as cationic dye from water using synthetic acrylic-urethane cross-linker the acrylic acid was cross-linked in xanthan/graphene oxide solution [20]. *Reyhaneh Aminyan et al.* demonstrated

gas-assisted electrospinning of poly(acrylic acid) in the presence of 1,4-butanediol diglycidyl ether as cross-linking agent to produce nanofibrous SAP. AT 30% neutralization nanofibrous superabsorbent had the highest swelling ratio of 10,000% in Saline [21]. Heidy Cruz *et al.* studied the effective absorbents for ammonium removal from domestic waste water using tailored poly(acrylic acid)-based (NaPAA) hydrogels. The study showed that in 10 min, 25-51% ammonium was removed using NaPAA hydrogel from synthetic stream range of 200-400% which is more than common sewage [22]. Mingyue Zhang *et al.* fabricated a novel composite hydrogel using acrylic acid and maize bran and N,N′-methylenebis acrylamide via UV irradiation copolymerization. It was reported maize bran−poly(acrylic acid) based SAP showed a free swelling capacity of 658 g g−1 in Saline. Swelling was extremely sensitive to the ionic strength, type of cation and anion [23].Tang *et al. fabricated a* poly(acrylic acid)/graphite oxide superabsorbent composite by solution intercalation polymerization of acrylic acid and graphite oxide using N,N-methylene-bis-acrylamide as a cross-linker and potassium persulfate as an initiator. The absorption capacity of the SAP showed to be 508 g/g[24]. Francis *et al.* synthesized superabsorbent polymers using carrageenan and partially neutralized acrylic acid via gamma polymerization method. The equilibrium degree of swelling of hydrogels with 3% and 5% carrageenan were observed to be 797 and 842 g/g in water [25].

2.3. Cellulose-based superabsorbent polymers

In one of the study Cheng *et al*. demonstrate superabsorbent resin, hydroxymethyl cellulose sodium-g-poly (acrylic acid-co-2- acrylamido-2-methyl-1-propanesulfonic acid)/laterite (NaHMC-g-P (AA-co-AMPS)/ laterite to prevent water evaporation in soil. At a particular composition of hydroxymethyl cellulose sodium, AMPS, APS, MBA and laterite (12wt%, 30wt%,0.8 wt% and 2 wt% of AA respectively), the superabsorbent resin showed an absorption capacity of 140g/g in saline [26]. Alam *et al*. explained a biodegradable aqueous-based process of cellulose-based superabsorbent polymer which was superior swelling capacity in saline. In

the study carboxymethyl cellulose was cross-linked with epichlorohydrin. It was reported that swelling capacity of the gel in saline was 118 g /g SAP [27]. Tian *et al.* prepared a superabsorbent polymer using cellulose and sodium acrylate and aluminum hydroxide cross-linker. The study demonstrated a swelling capacity of 118 g/g in saline at a particular composition of cellulose to AA, APS to AA, Al(OH) to AA, and the neutralization degree of 39 wt%, 0.67 wt%, 0.89 %, and 76 %, respectively. Under the same condition, the hydrogel synthesized by traditional cross-linker N, N-methylenebisacrylamide was only 84 g/g in saline [28]. Kim *et al.* designed an eco-friendly biodegradable SAP comprising poly (IA-co-cellulose-co-VSA-co-AA; ICVA). The core-SAP was synthesized through radical polymerization using monomers like itaconic acid (IA), acrylic acid (AA), cellulose, and vinyl sulfonic acid. Surface-cross-linking technology was applied to the core-SAP synthesized with the optimal composition ratio to increase its absorption performance and gel strength. Its biodegradability was found to be 54% compared to the 100% biodegradable cellulose hydrogel in the control group [29]. In another study, Kumar *et al,* covalently cross-linked polyvinyl alcohol and carboxymethyl cellulose (PVA/CMC) without using any cross-linker in the presence of catalyst. PVA/CMC-1/1 show dense porous morphology than the other polymeric materials. PVA/CMC-1/1 depicts the water absorption capacity to be 237 g/g as compared to each of the constituent polymers. The ester linkage significantly enhanced the physical properties of PVA/CMC materials [30]. Jeong *et al.* used a sequential dual cross-linking strategy to produce new CMC-based interpenetrating polymer network (IPN) with high mechanical strength and superabsorbent properties. The newly synthesized CMC-based IPN hydrogels were first cross-linked with CMC using ethylene glycol diglycidyl ether (EGDE) under basic conditions and were then subjected to secondary radical polymerization by adding acrylamide, *N*,*N*′-methylene bis-acrylamide (MBA), and ammonium peroxodisulfate. The synthesized CMC/PAM IPN hydrogels exhibited highly enhanced mechanical strength with high density

internal structure due to the double cross-linking of CMC and PAM. The tensile length and compressive strengths of CMC/PAM-1 IPN hydrogels were up to 2.6 and 4.5 times higher than that of the CMC gel, respectively. Moreover, CMC/PAM-1 IPN hydrogels presented higher superabsorbent properties than any other CMC-based IPN hydrogels reported so far. These hydrogels do not show biotoxicity against *in vitro* animal cell and has the potential to be used as a biomaterial [31].Tang *et al.* investigated the swelling properties of a series of model polyelectrolyte gels, namely tetra-polyacrylic acid-polyethylene glycol gels (Tetra-PAA-PEG gels), and determined the applicability of the FRGDM model. The swelling ratio (V_s/V_0) was well reproduced by the FRGDM model in the moderate swelling regime ($V_s/V_0 < 10$). However, in the high swelling regime ($V_s/V_0 > 10$), the FRGDM model is approx. 1.6 times larger than the experimental results. These results reveal that finite extensibility is one of the factors determining the swelling equilibrium of highly charged polyelectrolyte gels. The modified FRGDM model reproduces well the swelling behavior of a wide range of polyelectrolyte gels [32].In one of the study Shen *et al.* synthesized an antibacterial superabsorbent polymer (SAP) by grafting acrylic acid (AA) onto carboxymethyl cellulose (CMC) and mixing with silver particles, and *N*,*N*′-methylenebisacrylamide as cross-linker and potassium persulfate as an initiator. Silver nanoparticles were produced through the reaction between glucose and silver nitrate. The effects of silver nitrate on the swelling ratio of SAPs were investigated and the maximum swelling capacity observed to be 71 g/g SAP while using 50 mg of silver nitrate in the system [33]. Nanocelluloses (NC) are an excellent option to improve hydrogel physicochemical characteristics. In one of the study, Lima et al., demonstrated CMC-hydrogels using citric acid, and NC as a filler. Incorporation of 3% of NC resulted in a material with a degree of swelling of, approximately 100 g.g−1. The NCs act as an excellent filler and improved the storage modulus significantly, i.e., the mechanical resistance of the material. [34].

2.4. Alginate based superabsorbent polymers

Mignon *et al.* study the effect of varying the degree of methacrylation and use of a combination of acrylic acid and acrylamide on alginate based SAP. The materials showed high gel fractions and a strong swelling capacity up to 630 g/g SAP at a low degree of substitution. The SAPs also showed only a limited hydrolysis in aqueous and cement filtrate solutions [35]. Olad *et al.* demonstrated a semi-interpenetrating polymer network based on montmorillonite (MMT) and (NaAlg)-g-poly(acrylic acid(AA))/polyvinylpyrrolidone. Here semi-IPN superabsorbent nanocomposite showed an equilibrium swelling capacity of 618.92 g/g. It was shown that good reswelling capability of semi –IPN can make it efficient water reservoir that is more suitable for agricultural applications [36]. Thakur *et al.* studied the use of SAPs for the removal of methylene blue using titania incorporated sodium alginate cross-linked polyacrylic acid (SA-cl-poly(AA)-TiO_2). The hydrogel was prepared by graft copolymerization of acrylic acid (AA) onto sodium alginate (SA) biopolymer in the presence of a cross-linking agent, a free radical initiator and TiO_2 nanoparticles. The hydrogel exhibited a swelling capacity of 412.98 g/g [37]. Subhan *et al.* fabricated of novel sodium alginate-grafted-poly (*N*-vinyl formamide-*co*-acrylic acid)-bentonite clay hydrogel. In distilled water, the superabsorbent attained swelling equilibrium in 23 h and the extent of percent swelling increased with rise in pH of water. Due to remarkable swelling of 8049 %, the hydrogel composite may be used as superabsorbent in oil and gas industries for elimination of trace water from fuels and as sorbent for eradication of hazardous cationic dyes from industrial effluents [38]. Pan *et al.* fabricated the alginate/chitosan composite aerogels based on electrostatic interactions and noncovalent cross-linking using sol-gel method followed by freeze-drying process. After cross-linking, the aerogels presented the improved thermal stability and higher mechanical properties, as well as stronger antibacterial activities against *Staphylococcus aureus* and *Escherichia coli*. Therefore, the enhanced physical and antimicrobial properties of the alginate/chitosan aerogels

may be achieved by modulation of electrostatic interactions and noncovalent cross-linking, suggesting the promising applications of these composite aerogels as active food packaging materials [39].

Knijnenburg et al. investigated the use of alginate/PVA/nano-ZnO beads for fertilizer applications and demonstrate that pure CaAlg and ZnAlg beads, either with or without incorporation of nano-ZnO, formed small beads with tunable water absorption and retention capacity. Due to their tunable Zn release and water absorption and retention, the prepared nano-ZnO-containing alginate/PVA beads may be attractive for Zn fertilizer applications under water-limited conditions. [40]. Nita *et al.* describes a part of a larger study regarding the preparation of new hydrogels based on sodium alginate and phytic acid obtained through physical cross-links. The properties of hydrogels depend on the ratio between alginate and phytic acid cross-linker. The gel showed a swelling sensitivity in buffer solutions of pH = 5.4 and had a degree of swelling over 1700% [41]. Mokhtari Herein, porous ionically cross-linked biofoams were prepared by freeze-drying of chitosan (CS)/sodium alginate (SA) complex (CSA). Accordingly, CSA and its nanocomposite containing 15 wt% cellulose nanofibers ($CSAC_{15}$) exhibited a fast and efficient adsorption of 2297 mg/g for Eriochrome black-T (EBT) [42]. Sharma *et al. studied* a novel self-healing, stretchable and transparent superabsorbent film based on dextrin-polyacrylamide and boric Acid (D_{EX}-cl-polyAAm). The film showed an absorption capacity of 3156% in distilled water. The film showed structural integrity in urea solution, phosphate buffer and solutions of different pH. [43].

2.5. Chitosan based super absorbent polymers

In one of the studies, Ioana *et al.* demonstrated superabsorbent hydrogel using chitosan, Citraconic anhydride, acrylic acid (AA), methacrylic acid (AM) and l-arginine. The SAP showed hemostatic properties with a swelling capacity of 12,000%. [44]. Batista aimed to

develop SAPs of Chitosan/Xanthan gum (CG), Chitosan/Alginate (CA) and controlled Chitosan (C), Xanthan gum (G), and Alginate (A) produced using “onion-like” methodology. Swelling analysis showed that chitosan has a strong influence on the maintenance of hydrogels structure after swelling, mainly in the acid environment (pH = 2). The chitosan:xanthan gum (1:1 and 2:1) hydrogels were the best combination regarding swelling performance in an acid environment, reaching 1665% and 2024%, respectively, as well at pH 7.0, presenting 1005% and 667% [45]. Mignon *et al.* demonstrated pH-responsive superabsorbent polymers. Polysaccharides (alginate, chitosan and agarose) were methacrylated and cross-linked with amine-based monomers (dimethylaminoethyl methacrylate and dimethylaminopropyl methacrylamide) to induce varying pH-sensitivity. These materials showed a strong cross-linking efficiency and induced moisture uptake capacities up to 122% at 95% relative humidity with a negligible hysteresis. Additionally, interesting pH-responsive swelling capacities were obtained, especially for SAPs based on chitosan and agarose with values up to 110g /g SAP in water [46]. da Costa *et al.* stated that a new nanocomposite hydrogel can be prepared by forming a cross-linked hybrid polymer network based on chitosan and pectin in the presence of montmorillonite clay. The influence of clay concentration (0.5and 2% wt) as well as polymer ratios (1:1, 1:2 and 2:1) was investigated carefully. Most samples presented swelling degree above 1000%, which permits characterizing them as superabsorbent material. Thermogravimetric analysis results revealed that the incorporation of clay in the samples provided greater thermal stability to the hydrogels. The compression resistance also increased with addition of clay [47]. de Almeida reported the hydrogels (with or without AuNPs) containing the highest pectin content (at 4.12 pectin/chitosan weight ratio). Composites obtained at 3.75 pectin/chitosan weight ratio disintegrate between 25 and 30% after 14 days in phosphate buffer (physiological condition = pH 7.4). The AuNPs reinforce the hydrogel structures, increasing the elastic modulus (from 3.5 to 7.6 Pa) and water absorption capacity of

2976%. 3.75 PT/CS weight ratio and 3.0×10^{-4} M Au (III) content provide a durable, cytocompatible, and superabsorbent hydrogel composite suitable for drug delivery purposes [48]. Elbarbary *et al.* demonstrated an SAP synthesized by radiation cross-linking of polyacrylamide (PAAm) with low MW Na-alginate (Alg) or chitosan (CS) and their effect on growth of maize plants was performed for possible use as a soil conditioner in the agricultural applications. It was found that the water absorbency of PAAm, PAAm/Alg, PAAm/CS and PAAm/Alg/CS was 390, 578, 348 and 378 (g/g), respectively. It was observed that the presence of Alg with PAAm hydrogel improves hydrogel water retention capability and decreases its water loss. The results showed the ability of the SAP to promote quality and quantity of maize plants due to the growth promotion effect of Alg and CS. The productivity of maize plant in presence of PAAm/Alg hydrogels was the highest with 50% increase in grain yield confirming their possible use as soil conditioner [49]. Fang *et al.* produced a new kind of eco-friendly superabsorbent polymer synthesized using 2-pyridyl acetyl chitosan chloride, acrylamide and acrylic acid in aqueous solution by a free radical polymerization. The results showed that the novel superabsorbent polymer exhibits excellent water absorbency, which can absorb 44 g/g saline with an excellent water retention and reusability [50]. In one of the study Yu *et al.*, demonstrated superabsorbent polymer synthesized via graft copolymerization of dimethyldiallylammonium chloride along with acrylic acid onto carboxymethyl chitosan. The water swelling behavior of the prepared polymer has been studied at different conditions. At the optimal conditions SAP showed the highest swelling ratio of 81 g/g in saline. [51]. Fang *et al.* synthesized an SAP by the free radical polymerization reaction of ammonia ethyl chitosan with acrylic acid. The result showed an uptake of 644 g/g in water [52]. Sangeetha *et al.* studied an SAP based on hydrothermal reaction of a mixture of chitosan (CH), itaconic acid (IT) and urea (UR). At a weight ratio of CH:IT:UR at1:3:3, the SAP showed a water uptake capacity of 100 g/g (10,000%) and was observed suitable for hydroponic growth of seeds [53].

Chitosan/gelatin (CG) composite sponges containing oxidized cellulose fibers (OF) cross-linked with tannic acid were fabricated by freeze-drying as hemostatic agents. The cellulose fibers were oxidized by 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO). Addition of increased the swelling ratio of CG sponges. The biocomposite sponge fabricated by addition of 30% OF suspension into CG solution showed the lowest amount of bleeding and the highest bio-absorbability in 21 days. [54]. Narayanan *et al. synthesized SAP* with maximum water absorption capacity of~1250 g/g via hydrothermal synthesis from sustainable and biodegradable resources such as chitosan, citric acid and urea (CHCAUR). Pure and saline water absorption study showed that CHCAUR could be a better adsorbent compared to those SAPs used in commercial diaper material. The mechanism of water absorption is shown to arise out of a combination of electrostatic attraction of water to the ionic cross-links and the presence of macropores surface due to the formation of nanofibrous bundles. When applied to soil CHCAUR was found to decrease water evaporation rate significantly [55].

3. MATERIALS AND MEDTHODS

3.1.MATERIALS

Chitosan (50000-190000 Da), acrylic acid, sodium hydroxide, N,N'methylene bis acrylamide, ammonium persulphate, were purchased from Sigma-Aldrich and used without further purification. Sodium salt of carboxymethyl cellulose (1200-1600cps) and sodium chloride, was purchased from Nice Chemical Private Limited. Aluminium ammonium sulfate dodecahydrate, urea, aluminium sulfate and citric acid were purchased from Merck Life Sciences. All other reagents were of analytical grade and used as such without any further purification.

3.2.Methods

3.2.1. Preparation of superabsorbent polymer Sponges

Different batches of **s**uperabsorbent polymer sponges were prepared. In the first batch SAPs were synthesized using carboxymethyl cellulose, and acrylic acid at different molar ratio (say 80/20, 90/10) via free radical polymerization using ammonium persulfate as the initiator and 0.2 mol% methylene bioacrylamide as crosslinker at a temperature of 70 ^{o}C for 2 h. The reaction product (hydrogel) was transferred to a petri dish and freeze dried for 24 h. The corresponding sponges were denoted as SAP-PAA 1 and SAP-PAA-2. In the second batch, carboxymethyl cellulose (CMC) based SAP sponges were prepared using different weight ratios of aluminium ammonium sulphate (AlAS) (say 2 wt%, 5 wt %, 10 wt % and 15 wt %). 2 % CMC solution is stirred mechanically at 1000 rpm for 30 minutes at room temperature. To the homogenous CMC solution equivalent amount of AlAS solution at a concentration of 50 mg/ mL in distilled water was added at a stretch. Continued the stirring for 2h at 1000 rpm and the reaction product (hydrogel) were transferred to a petri dish and freeze dried for 48 h. The corresponding sponge was denoted as SAP-2, Third batch of SAPs were prepared via

polyelectrolyte complex formation using equal volume of 2 % chitosan in 1.5 % acetic acid and 2 % carboxymethyl cellulose in distilled water. The above CMC solution was mechanically stirred at 1000 rpm for 15 minutes and added 2% chitosan solution slowly while stirring. Continue the stirring for 1 h and transferred the hydrogel solution to a petri dish and freeze dried for 48 h. The corresponding sponge is denoted as SAP-1. In all these three batches there are no purification steps to make the synthesis as simple as possible.

3.2.2. Evaluation of residual monomer content

Residual acrylic acid was extracted from 1 g of SAP using 200 mL of 0.9 % saline. The solution was stirred at 500 rpm for 60 min and allowed to settle for 5 min. Filtered the supernatant through 0.45 µm filter and analyzed using HPLC.20 µL of the above extract was injected into the column and run the sample using 1 % of acetonitrile–phosphoric acid solution (10:90) at a flow rate of 0.8 mL/min. UV detector at 210 nm was used to record the graph. Calibration curves were constructed using standard solutions of acrylic acid (1mg/L, 2 mg/L, 3 mg/L, 4 mg/L) by plotting the peak area against the concentration. Acetonitrile extract of SAP was analyzed in triplicate and concentrations were calculated using the calibration plot.

Residual Monomer $Wa = \rho sam \frac{200}{msap}$

Wa; mass fraction of residual acrylic acid #

ρsam; mass concentration of the extraction solution

m sap; mass of SAP expressed in grams

3.2.3. FTIR studies

Infrared qualitative analysis was carried out to confirm the complete conception of acrylic acid during polymerization using Nicolet 5700 FTIR Spectrometer in ATR mode. Transmission spectra were collected in the range of 4000-400 cm^{-1}.

3.2.4. Thermogravimetric Analysis

The thermogravimetric analysis (TGA) of the dried SAP sponge were carried out on an SDT Q600 (simultaneous TGA-DTA, TA Instruments) in the temperature range of RT to 800^{o}C at a scan rate of 10^{o}C/min under nitrogen atmosphere.

3.2.5. Free Swelling Capacity

200 mg of SAP sponges were weighed and transferred to heat sealable bag. The sponge is positioned horizontally in the bag and laid them on the surface of the saline solution or distilled water along with two blank bags. Allowed each bag to wet for 1 min and pushed it under the liquid surface. Removed bags from saline solution after 30 min and hanged them diagonally on a line from one of the double-sealed corners for (10 ± 1) min. Weighed each bag and recorded the mass (mw). Experiments were repeated quadruple.

Free swell capacity expressed in (g/g) mass fraction

$$w = \frac{mw - mb - ms}{ms}$$

ms- mass of dry SAP sponge

mb - Average mass of the wet blank bag

mw - Mass of the wet bag containing SAP sponge

3.2.6. Determination of moisture content by mass loss upon heating of SAP sponge

Before starting the experiment placed four petri dishes and lids into the oven at 105 °C for 3 h according to the standard. After cooling for 30 min, weighed the empty lidded petri dishes in grams (m_1). Removed the lid and added approximately 0.2 g of SAP sponge in each petri dish. Replaced the lid and weighed the lidded dish containing the sample immediately (m_2). Placed open dishes with SAP sponge and lids together in the oven at 105 °C. After 3 h, immediately lidded the dish and placed in desiccators and allowed to cool for 30 min. Removed and weighed immediately (m_3). Experiments were done in quadruplicate.

$$Moisture\ content\ Wm = \frac{(m2 - m3)}{m2 - m1} * 100$$

4. RESULTS AND DISCUSSION

Carboxymethyl cellulose based superabsorbent polymers were prepared by different cross-linking mechanisms such as ionic cross-linking using aluminum ammonium sulfate and chemical cross-linking using N,N'methylene bis acrylamide in the presence of partially neutralized polyacrylic acid via free radical solution polymerization. The superabsorbent polymer obtained was analyzed for its swelling capacities both in water and saline. SAP having optimum swelling capacity and ease of production will be used for the development of saliva absorption pad. The mass fraction of residual acrylic acid present in the sponge measured to be 2.3 ± 0.05 g/Kg and 3.05 ± 0.03 g/Kg respectively for SAP synthesized using 10 mol% and 20 mol % acrylic acid (SAP-PAA-2 and SAP-PAA-1 respectively). The complete consumption of acrylic acid during the SAP-PAA-1 and SAP-PAA-2 were confirmed using FTIR (Figure 6). The FTIR studies showed >99% polymerization. The wide absorption bands at 3200–3600 cm^{-1} are attributed to vast amount of carboxyl groups present in SAPs. The absorption peaks at 1721 cm^{-1} were assigned to the C=O stretching vibration due to the carboxylate groups of AA. There is an intense peak of =CH bending in acrylic acid at 815.6 cm^{-1}. Whereas no significant peak of =CH bending present for both SAP-PAA-1 and SAP-PAA-2 indicating almost complete consumption of acrylic acid during reaction.

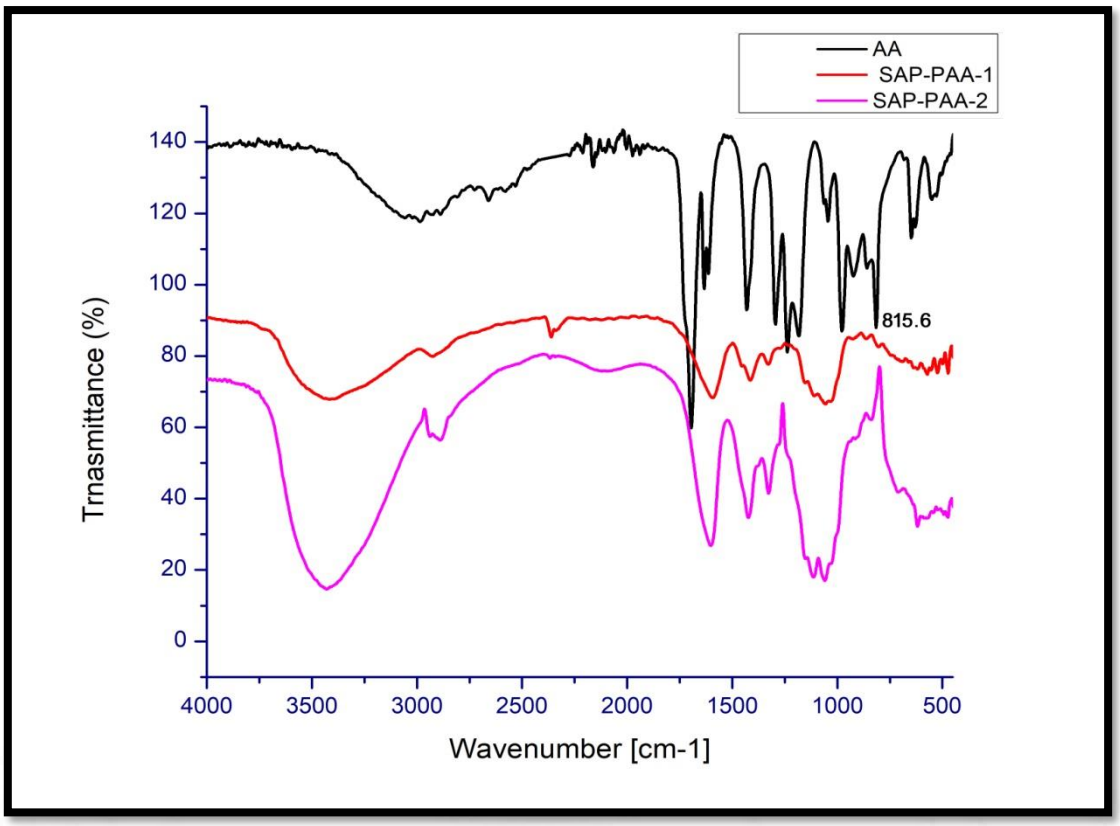

Figure 6: FTIR spectra of Acrylic acid (black line), SAP-PAA-1 (red line) and SAP-PAA-2 (Pink line). There is an intense peak of =CH bending at 815.6 cm^{-1} in Acrylic acid spectrum. Whereas no significant peak of =CH bending present both in SAP-PAA-1 and SAP-PAA-2 for indicating almost complete consumption of acrylic acid during reaction.

Thermal decomposition studies were carried out to confirm the thermal stability of carboxymethyl cellulose based SAPs having optimum swelling characteristics. Thermogravimetric analysis of SAP-1, SAP-PAA-2, and SAP-2 showed a percentage weight loss of ~ 82 % at 800^{o}C. Whereas, in SAP-PAA-1, only 60 % weight loss is observed at 800^{o}C. This is mainly attributed to the presence of higher percentage of synthetic counterpart, where 20 mol% of acrylic acid is copolymerized with carboxymethyl cellulose. It can also be observed that in all these SAP sponges ~ 20% weight loss is observed around 100 ^{o}C. The weight loss at 100 ^{o}C can be mainly due to the presence of absorbed moisture. In all these sponges a drastic weight loss is seen after 300 °C due to the pyrolysis following chain scission.

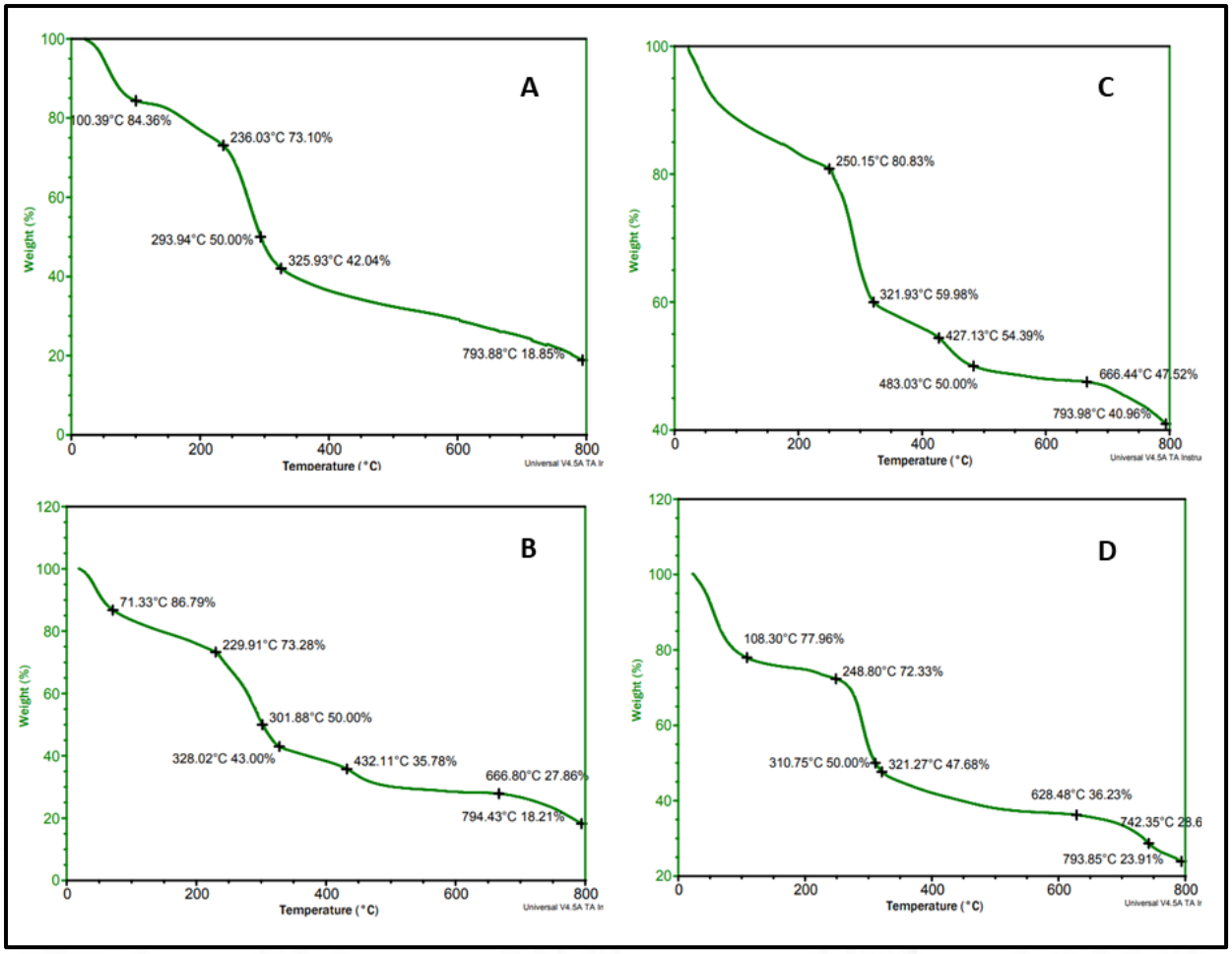

Figure 7. Thermogravimetric analysiscurves of (A) SAP-1 (B) SAP-PAA-2 (C) SAP-PAA-1 (D) SAP-2 indicating the percentage weight loss at different temperature upto 800^{o}C

Absorption capacities of SAP sponges were studied at different conditions, free swell capacity and centrifugal retention capacity in distilled water, and 0.9% saline. The free swell capacity of SAP sponges in distilled water is higher than that measured in saline. This is because of the high ionic concentration of saline reduces osmotic pressure inside the gel and there by less water intake compared to that in distilled water.

Table 1: Free swelling capacity in distilled water and 0.9% saline expressed in mass fraction g/g

Sample ID	Free swell capacity expressed in mass fraction (g/g)	
	Water	0.9% Saline
SAP-1	23.5 ± 1.89	19.48 ± 2.3
SAP-PAA-1	18.15 ± 0.35	13.48 ± 0.43
SAP-PAA-2	42.4 ± 3.9	33.78 ± 2.42
SAP-2	83.21 ± 3.8	40.7 ± 3.44

SAP-2 showed high free swell capacity in the group. In SAP-2 sodium salt of carboxymethyl cellulose is ionically cross-linked using 10 weight % aluminium ammonium sulfate. Free swell capacity of SAP-2 is reduced > 50 % in saline compared to that in distilled water. Each gram of SAP-2 absorbed 40.7 g of saline. SAP synthesized by cross-linking with polyacrylic acid and methylene bisacrylamide, SAP-PAA-2 and SAP-PAA-1 showed a free swell capacity of 13.48 g/g and 33.78 g/g respectively. When compared to SAP-2, free swell capacity reduction saline is only 17 %, 25.7 %, 20.3 % respectively for SAP-1, SAP-PAA-1, and SAP-PAA-2 respectively. The high free swell capacity reduction in SAP-2 is mainly because of the high ionic content compared to that of other groups. The synthesis of SAP-2 is simple as it involves proper mixing of CMC and cross-linker solution at a particular concentration at room temperature followed by freeze drying for 48 h. Considering the high swelling and simple preparation procedure, SAP-2 is studied further to optimize the cross-linker content and saturation swelling time (Figure 8 & Figure 9). As shown in the figure 8, free swell capacity of SAP-2 increases with increase in the weight % of AlAS up to10 wt %. After that there is no significant increase in swelling. The SAP-2 at 10 wt % cross-linker content is further characterized for its saturation swelling time in water. As shown in the figure 9, 15 % and 29 % increase in free swell capacity at 1 h and 2 h respectively compared swelling capacity at 30 min. Considering the application of these SAP sponge, further studies need to be carried out

using SAP-2 at 10 wt % AlAS to confirm the same trend of free swell capacity in saline and artificial saliva.

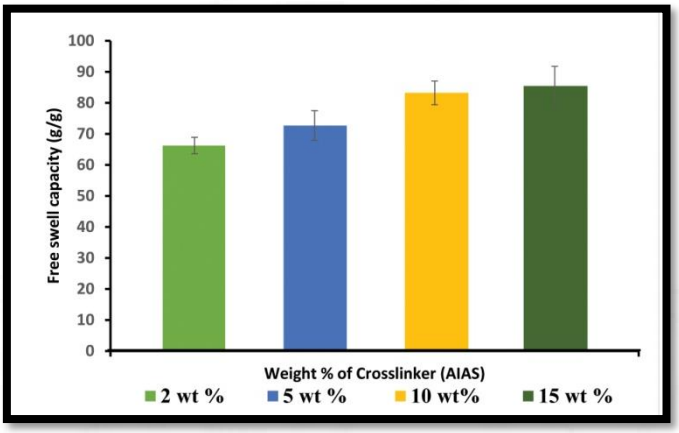

Figure 8. Free swell capacity of carboxymethyl cellulose based SAP cross-linked using aluminium ammonium sulfate (SAP-2) at different weight ratio expressed in mass fraction (g/g)

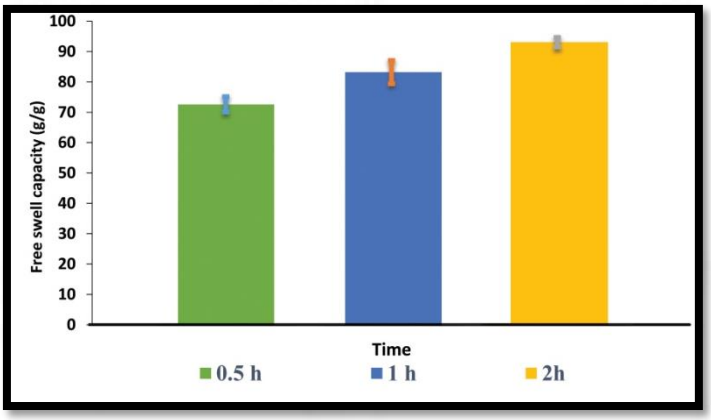

Figure 9. Free swell capacity of carboxymethyl cellulose based SAP cross-linked using 10 wt % aluminium ammonium sulfate (SAP-2) at different swelling time expressed in mass fraction (g/g)

To determine the mass loss upon dehydration of SAP sponges was kept in an electric oven at 105 ± 2 °C for a period of 3 h. average moisture content Wm, calculated to be 13.33 ± 2.35 %.

As the moisture content of the SAP-2 is high compared to the standard limit (≤ 5 %), further modification of the SAP-2 sponge is necessary to improve the storage stability.

Dental Absorption Pad

The broad objective of the work is to develop an indigenous saliva absorption pad. Towards this goal we have designed a prototype (preliminary stage). The outer and inner lining of the saliva absorption pad need to be optimized. Right now, we have non-woven polypropylene fabric both as inner and outer liner. The schematic representation of saliva absorption pad in which superabsorbent sponge is sandwiched between hydrophobic outer saliva blocking layer and porous inner layer through which saliva can diffuses into the sandwiched SAP sponge is shown in the figure (Figure 10).

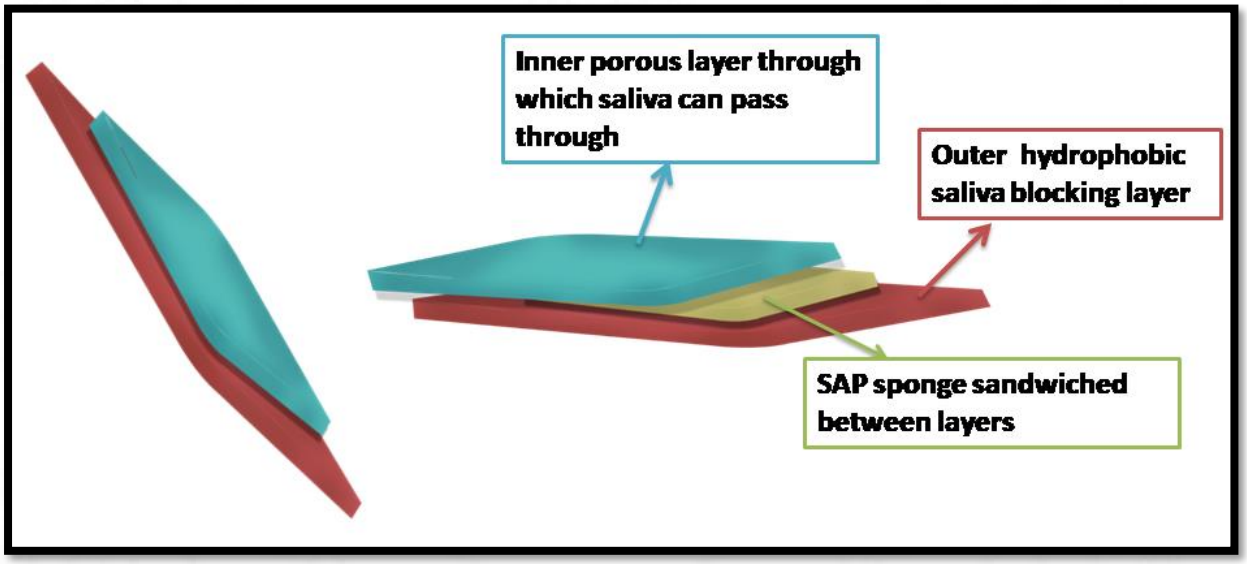

Figure 10: Schematic representation of 3 D view of saliva absorption pad.

Depending on the absorption capacity of SAP sponge, saliva absorption pads can provide dry oral environment to ease the dental treatment procedure. In addition to this, saliva absorption pad can also reduce the swallowing reflexes that are common while using cotton pieces for saliva absorption during dental procedure. Figure 11 showed inner and outer layer dimension of saliva absorption pad designed in the lab. The dimensions were designed based on the

feedback from dentists we have consulted. Further optimization of the design is needed to finalize the dimensions (and that is one of the future scopes of this study). The designed saliva absorption pad of above dimension is suitable for controlling the saliva produced by the parotid gland. The designed absorption pad can be directly placing in between cheek and gum. Saliva produced in the parotid gland can be absorbed immediately using these pads and make the area dry to facilitate dental restoration, root canal treatment or any surgical procedure.

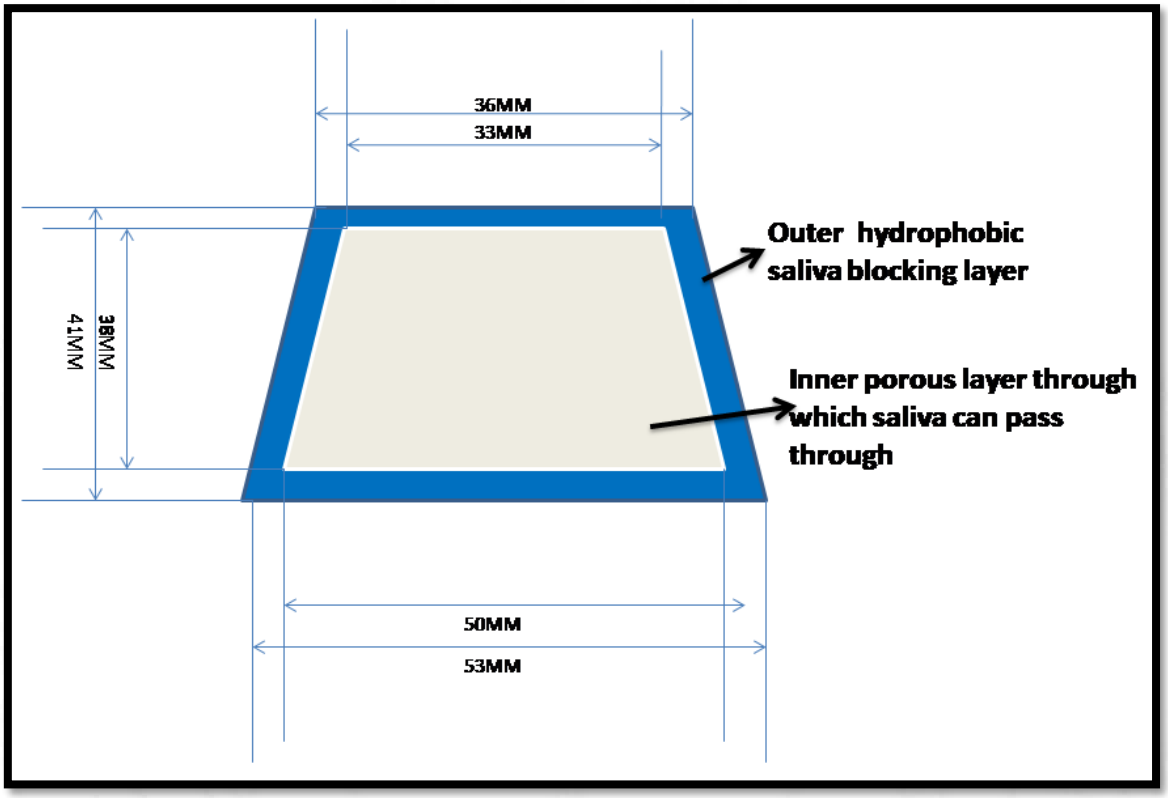

Figure 11: Schematic representation of detailed dimensions of inner and outer layer of saliva absorption pad designed in the lab.

5. CONCLUSIONS

Towards the aim of developing indigenous saliva absorption pad, superabsorbent polymer sponges (SAP sponges) were prepared using carboxymethyl cellulose as the main polymer matrix. As a first step for the development of saliva absorption pad, superabsorbent polymers were prepared and characterized using different cross-linking mechanisms. Towards the effort different cross-linking agents at different weight ratios were studied. Different SAP sponges were characterized for its complete polymerization using FTIR and HPLC method. Both SAP-PAA-1 and SAP-PAA-2 showed no C=H bending peak at ~815 cm^{-1}that is prominent in free acrylic acid. Evaluation of free swell capacity of different SAP sponges both in distilled water and saline were completed. The results showed a higher absorption capacity for the SAP-2 sponges (83.21 ± 3.8 in distilled water & 40.7 ± 3.4 in saline) in which carboxymethyl cellulose is ionically cross-linked using aluminium ammonium sulfate via simple one step process. SAP-2 sponge is further characterized to optimize the cross-linking density using different weight ratios of AlAS. It was observed an optimum swelling pf SAP-2 at 10 wt % of AlAS. Moisture content of the particular SAP sponge is higher (~13%) compared to the standard limit. The end use of the SAP sponge is projected to develop saliva absorption pad. However, due to the time restriction and further need of optimization of SAP-2 sponge towards its moisture content and mechanical properties, the study is limited to the design of saliva absorption pad. Based on the feedback from dentists and related products available in the market, our design is more flexible for the intended application.

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