Project Report

on

Investigation Of Acrylamide,Maleic Anhydride Hydrogel impregnated with Poly(vinyl) Alcohol

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in

Polymer Technology

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CERTIFICATE

This is to certify that the dissertation entitled "**Investigation Of Acrylamide, Maleic Anhydride Hydrogel impregnated with Poly(vinyl) Alcohol**" is being submitted in partial fulfillment for the award of the degree of Master of Technology, Delhi Technological University (Formerly Delhi College of Engineering, University of Delhi), is a record of an authentic work done by Kratika Jain(2K15/PTE/06) under my supervision and guidance.

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DECLARATION

I hereby declare that this M.tech thesis entitled “Investigation Of Acrylamide ,Maleic Anhydride Hydrogel impregnated with Poly(vinyl) Alcohol” was carried out by me for the degree of master of technology under the joint guidance and supervision of Prof. Archna Rani, Department Of Applied Chemistry, Delhi Technological University,(DTU), Delhi, India

This thesis is a presentation of my original research work. Wherever contributions of others are involved, every effort has been made to indicate this clearly.

For the present thesis, which I am submitting to the University, no degree or diploma has been conferred on me before, either in this or in any other university.

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ABBREVIATIONS:

1. AAm – Acrylamide
2. MAh – Maleic Anhydride
3. PVA – PolyVinyl Alcohol
4. KPS – Potassium PerSulphate
5. N,N'MBA – N,N' Methylene Bisacrylamide
6. IC – concentration of crosslinker
7. P(AAm-MAh) – Hydrogel of Acrylamide and Maleic Anhydride
8. G – Garlic juice
9. FTIR- Fourier transform infrared spectroscopy
10. TGA- Thermo gravimetric analysis
11. DMA- Dynamic mechanical analyser
12. P1G1%- PVA 1% and garlic juice 1% with predetermined amount of other monomers
13. P1G2%- PVA 1% and garlic juice 2% with predetermined amount of other monomers
14. P1G3%- PVA 1% and garlic juice 3% with predetermined amount of other monomers
15. P2G1%- PVA 2% and garlic juice 1% with predetermined amount of other monomers
16. P2G2%- PVA 2% and garlic juice 2% with predetermined amount of other monomers
17. P2G3%- PVA 2% and garlic juice 3% with predetermined amount of other monomers
18. P3G1%- PVA 3% and garlic juice 1% with predetermined amount of other monomers
19. P3G2%- PVA 3% and garlic juice 2% with predetermined amount of other monomers
20. P3G3%- PVA 3% and garlic juice 3% with predetermined amount of other monomers
21. PVA1% - PVA 1% with predetermined amount of other monomers
22. PVA 2% - PVA 2% with predetermined amount of other monomers
23. PVA3%- PVA 3% with predetermined amount of other monomers

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ABSTRACT:

Current investigation is focused on the synthesis of Acrylamide, Maleic Anhydride hydrogel matrix impregnated with Poly (vinyl alcohol), PVA, to obtain a formulation of hydrogel matrix with maximum water swelling property. Thus, series of products, varying the concentration of cross linker and PVA, were synthesized using redox initiator potassium persulphate at 70 ^{o}C. Spectroscopic, Thermal, Mechanical analysis and swelling behaviour of formed hydrogels were studied.

Tremendous swelling behaviour (with swelling percentage 1409%) was by hydrogel with composition of 3% of Poly(vinyl) alcohol, 0.5% of crosslinker, 3.55 gm of acrylamide, 0.908gm of Maleic anhydride

Present study also revealed that the addition of prepared hydrogels in small quantities to sandy soil increased its ability to retain water.

The study was further extended with incorporation of antimicrobial activity in the hydrogel matrix by using different concentration of the product of natural origin ,*Allium sativum*.The results obtained were excellent as the use of *Allium sativum* juice (also known as garlic juice) in hydrogel matrix incorporated antimicrobial activity against plant pathogen (*Agrobacterium tumefaciens*) and human pathogen (*Escherichia coli*) without affecting swelling behaviour of matrix. The hydrogel with 3% PVA 3% *Allium sativum* juice 0.5% crosslinker, 3.55gm acrylamide, 0.908gm maleic anhydride shows best results amongs all the formed hydrogel as zone of inhibition in this hydrogel against *Agrobacterium tumefaciens* is 3.1 cm while against *E.coli* is 1.9 cm and and also shows highest water retention measurement.The maximum difference in percent of water evaporation loss with hydrogel PVA3%, *Allium sativum* juice3%, and one without hydrogel is approximately 41%.

From thermal analysis it is found that the hydrogel remained unaffected from environmental stresses during the period of study of 2 months. Current study can lead to develop a new class of hydrogels that can be used in the agriculture field to provide continous cycle of irrigation and also provide protection to crops from pathogens.

CHAPTER 1

INTRODUCTION

A **hydrogel** is a network of polymer chains that are hydrophilic, sometimes found as a colloidal gel in which water is the dispersion medium. Hydrogels are highly absorbent (they can contain over 90% water) natural or synthetic polymeric networks. Hydrogels is fundamentally a water retaining polymer, which is cross linked, engrossing watery arrangements through hydrogen bonding with water particles. Hydrogels also possess a degree of flexibility very similar to natural tissue, due to their significant watercontent.

Hydrogels are used in various fields, such as- agricultural, diaper industry, tissue engineering, drug release etc. Due to the property to absorb the water much more times its weight it gain popularity in its applications. Emphasizing on the use of agriculture, the need for more arable land in perspective of expanding horticultural creation has restored enthusiasm for the improvement of novel soil conditioner materials with new strategies and lower rates application.

Indian Economy is largely depend on agriculture, still for one of the most important agriculture input country depends upon rainfall which is uncertain, unreliable and erratic in India. In addition sandy soil is unsuitable for agricultural purpose as the water retention property of sandy soil is very poor.

To eradicate this problem, Agriculture hydrogel (are also called water maintenance granules) can be used since they swell to ordinarily their unique size when they interact with water[1].

Also, Pathogenic microorganisms pose a big threat towards food production. Meanwhile, negative impacts on humans and environment are seen by the use of Chemical pesticides .

Till now the work has been conducted on using hydrogel granules as a water retention reservoir but less attention is drawn to its antimicrobial properties which can reduce the harmful chemicals used for antimicrobial property. Moreover, using product of natural origin is ecofriendly and also reduce water pollution and soil pollution.[2]

This thesis emphasize on resolving both the above mentioned problem by providing antimicrobial activity against plant and human pathogens using product from natural origin and enhancing the water retaining property of hydrogels which is useful for agriculture purpose. In hydrogels, the swelling behavior in addition with antimicrobial property opens the wide range of application for hydrogels. Hydrogels can be made of any compound which is water soluble as by further processing they are able to absorb water depending upon the compound properties of how much amount of water they can accumulate within their hydrogel structure. [2]

Fig 1 (a): Dry Hydrogel Granules [1]

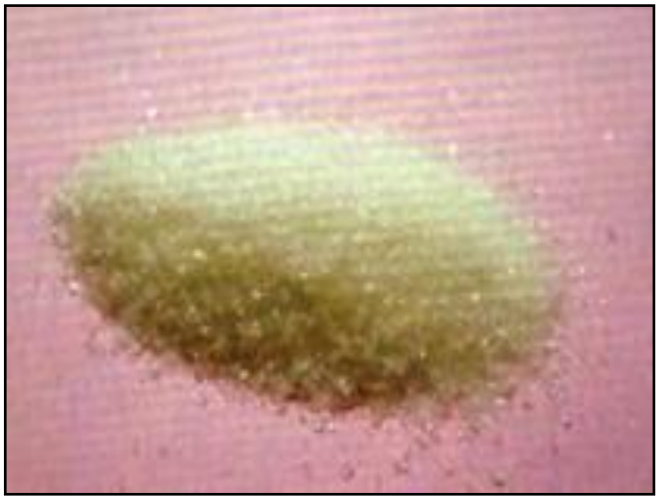


fig 1 (b): Water Swollen Hydrogel [1]

This Thesis is divided into three parts-

1. Optimization of cross linker - In this part of work optimization of amount of cross linker is done and the result produced by this experiment is further processed with other experiment. This part shows different amount of cross linker starting from 0.1%, 0.5%, 1%, 2%, 3%. The best among these all is decided by the results of swelling studies and FTIR. The monomer used for preparing the hydrogel is acrylamide and malice anhydride.
2. Hydrogel Impregnated with PVA- To enhance the water retention property, polyvinyl alcohol is also added. Polyvinyl alcohol has been perceived as a hydrophilic polymer with amazing physical and mechanical properties. As a water dissolvable polymer, polyvinyl alcohol has poor water resistance.[2] The creep resistance of PVA hydrogels can be expanded by high temperature strengthening; however this procedure likewise falls the pores, diminishing the water content and thus decreasing the lubricity of the hydrogel surface[3].
3. Providing the antimicrobial activity to the hydrogel discs- This hydrogel is enhanced by providing antimicrobial activity against E.coli and Agrobacterium tumefaciens by using garlic juice. Garlic juice contains some amount of organosulphur compounds. Garlic (Allium sativum Linn.) has a vital dietary and therapeutic part for quite a long time. It's helpful uses incorporate useful impacts on the cardiovascular framework, anti-infection, anticancer, mitigating, hypoglycemic, and hormone-like effects. Its pungent smell and antibacterial action rely upon allicin, which is created by enzymatic (alliin lyase) hydrolysis of alliin in the wake of crushing and cutting of the cloves.[4]

fig 1 (c): Hydrogel incorporated farming [1]

CHAPTER 2

2. LITERATURE REVIEW-

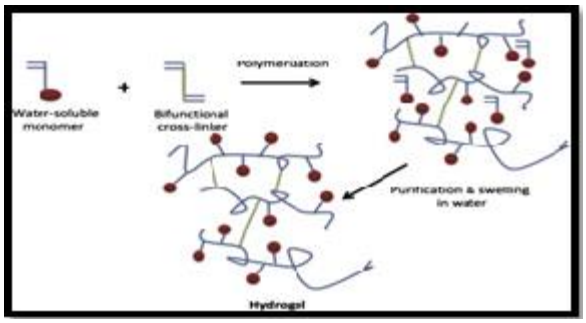
The utilization of polymer in farming is picking up prominence in science, especially in the field of polymer science. This has given answers for the issues of the present day agriculture which is to expand land and water profitability without undermining the earth and the regular assets. Superabsorbent polymer hydrogels possibly impact, infiltration and evaporation rates of water through the soil, surface texture, structure and permeability of soil.

Functionalized polymers were utilized to build the lower use of pesticides and herbicides, permitting lower measurements to be utilized and less amount of these toxins be released in environment causing less harm to environment and to ecosystem.[2]

2.1 HYDROGELS

Hydrogels are 3-dimensional, hydrophilic, polymeric systems equipped for retaining a lot of water or organic liquids. Because of their high water substance, porosity and delicate consistency, they nearly mimic characteristic living tissue, more so than some other class of manufactured biomaterials. Hydrogels might be artificially steady or they may corrupt and in the long run deteriorate and break down.

Hydrogels are called "reversible" or "physical" gels if sub-atomic traps or potentially optional powers, for example, ionic, H-holding or hydrophobic powers assume the fundamental part in shaping the system. Physical gels are regularly reversible and it is conceivable to break down them by changing ecological conditions, for example, pH, and the ionic quality of arrangement or temperature. In chemical or permanent gels, the system of covalent bonds joining distinctive macromolecular chains can be accomplished by cross-connecting polymers in the dry state or in arrangement. These gels might be charged or non-charged relying upon the functional groups exhibit in their structure. The charged hydrogels more often than not show changes in swelling upon varieties in pH, and it is realized that they can experience changes in structure when presented to an electric field.[5]



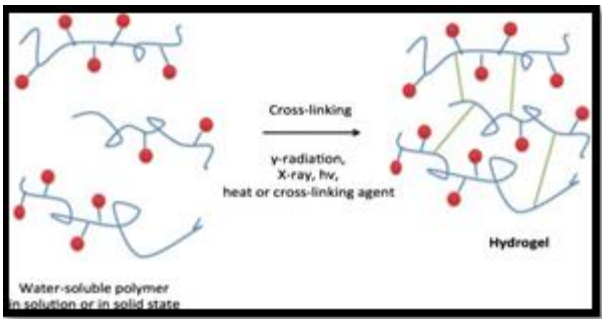


Fig 2.1 (a): Synthesis of hydrogel by 3-D polymer[5]

Fig 2.1 (b): Synthesis of hydrogel by cross –linking of readymade water soluble polymers[5]

2.1.1 Hydrogel Classification

The hydrogel items can be arranged on various basis as point by point underneath:

1. Based on source
    a) natural origin
    b) synthetic origin

2. Based on composition

(a) Homopolymeric -Hydrogels are formed from one kind of monomer which is a fundamental basic unit involving any polymer arrange. Homopolymers may have cross-connected skeletal structure contingent upon the idea of the monomer and polymerization method.

(b) Copolymeric- Copolymeric hydrogels are involved at least two distinctive monomer species with no less than one hydrophilic part, organized in an arbitrary, piece or rotating design along the chain of the polymer arrange.

(c) Multipolymer- Interpenetrating polymeric hydrogel (IPN), an imperative class of hydrogels, is made of two autonomous cross-connected manufactured or potentially common polymer segment, contained in a system frame. In semi-IPN hydrogel, one part is a cross-connected polymer and other segment is a non-cross-connected polymer.

3. Based on Configuration

(a) Crystalline
(b) Semi- Crystalline
(c) Amorphous

4. Based on type of cross-linking

(a) Chemical Crosslinking - They formed permanent bonds
(b) Physical Crosslinking - They formed transient bonds because of chain entanglement or due to ionic interaction or hydrophobic interaction

5. Based on physical appearance

(a) Film

(b) microsphere

(c) matrix

6. Based on Electrical charge network

(a) Non-ionic

(b) ionic

(c) Amphoteric electrolyte

(d) Zwitter ionic [5]

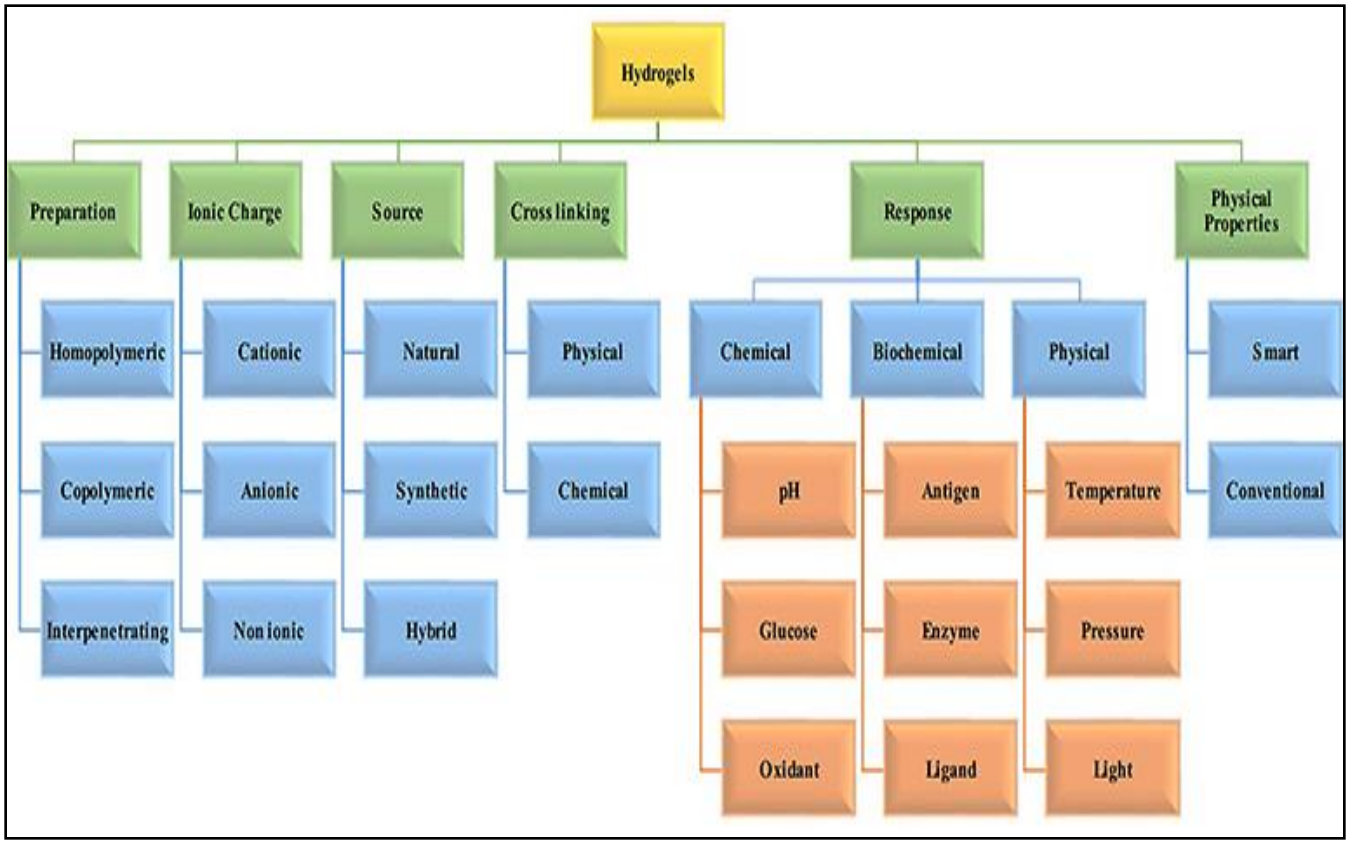


Fig 2.1.1 (a): Classification of Hydrogel [6]

2.1.2 Types Of Hydrogels

(a) pH Sensitive

(b) temperature sensitive

(c) Electro sensitive

(d) Light responsive [1]

2.1.3 Current application of hydrogels

Hydrogels are used in many fields. This is due to their specific structures and compatibility with different conditions of use. Flexibility of hydrogels, which is because of their water content, makes it possible to use them in different conditions ranging from industrial to biological, and the biocompatibility of the materials used to produce them and also their chemical behavior in biological environments, which can be nontoxic, extends their applications to the medical sciences. Major applications and some examples of hydrogel usages are listed below. Note that it is not a complete listing but considers the most practical applications of hydrogels in medicine and industry [1]

(a) **Drug Delivery System** - Controlled medication conveyance frameworks, which are utilized to convey drugs at specific rates for predefined timeframes, have been utilized to beat the confinements of normal medication plans. The glorious properties of hydrogels settle on them an awesome decision in medicate conveyance applications. The hydrogel structures with high porosity can be gotten by controlling two elements: the level of cross-connecting in the framework and the fondness of hydrogel to the fluid condition in which swelling happens. Because of the permeable structures, hydrogels are exceptionally penetrable to various types of medications and in this way medications can be stacked and, in appropriate conditions, discharged. The likelihood of discharging pharmaceuticals for drawn out stretches of time (maintained discharge) is the fundamental favorable position acquired from hydrogels in tranquilize conveyance examinations, which brings about providing a high centralization of a dynamic pharmaceutical substance to a particular area over a drawn out stretch of time. Both physical (electrostatic co-operations) and synthetic (covalent holding) techniques can be utilized to upgrade the authoritative between a stacked medication and the hydrogel network

to expand the span of medication discharge. Hydrogels can store and shield different medications from threatening conditions, and discharge them at a coveted energy of the discharge. Medication discharge can be enacted on request by neighborhood changes in pH, temperature, the nearness of particular catalysts, or by remote physical jolts.[7]

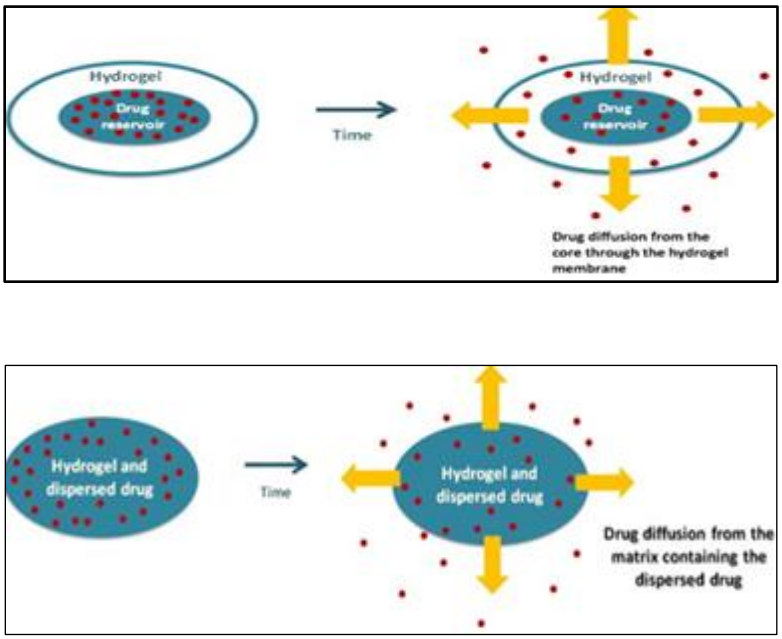


Fig 2.1.3 (a): Diagrammatic representation of Drug delivery system [7]

(b) **Tissue Scaffold engineering** -Tissue designing is a later use of hydrogels, in which they can be connected as space filling specialists, as conveyance vehicles for bioactive substances or as three-dimensional structures that arrange cells and present boosts to guarantee the improvement of a required tissue. Space filling specialists are the most normally utilized gathering of platforms and they are utilized for building, to avert bond, and as a natural 'paste'.

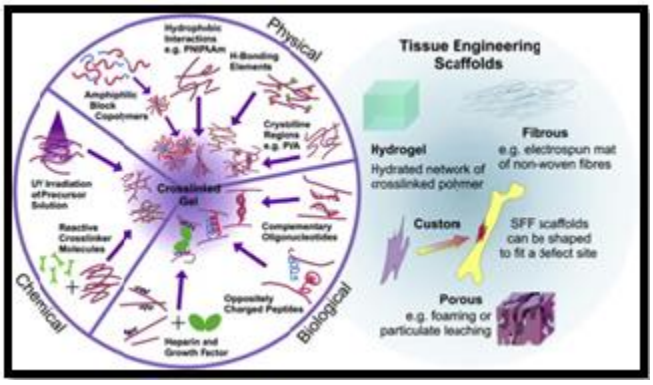


Fig 2.1.3 (b): Tissue Engineering Scaffold [5]

Medications can be conveyed from hydrogel frameworks in various applications including advancement of angiogenesis and exemplification of secretory cells. Furthermore, hydrogel platforms have additionally been connected to transplant cells and to build many tissues in the body, including ligament, bone, and smooth muscle.

A vital property is the biocompatibility of hydrogels, which could be characterized as the capacity of a material to be in contact with the body organs with no harms for the encompassing tissues and without setting off any undesirable reaction. Manufactured materials fit for framing hydrogels appropriate for tissue building incorporate poly(ethylene oxide), poly(vinyl liquor), poly(acrylic corrosive), poly(propylene fumarate-co-ethylene glycol), and polypeptides. Agarose, alginate, chitosan, collagen, fibrin, gelatin, and hyaluronic corrosive are actually determined polymers that could likewise be utilized for this reason.

Some other field where it has applications is diaper industry, cosmetics, perfume delivery, Plastic Surgery, immunotherapy and vaccine, bacterial culture etc.[5]

(c) **Watering globules for plants**: The use of hydrogels comprises in unpleasant powders of polyacrylamide or potassium polyacrylate matrix sold with a colossal scope of names (Plant-Gel, Super Crystals and Water Gel Crystals) and utilized as long haul repository of water for plant development in cultivating, local and here and there mechanical agriculture. On the inverse side as the one of diaper's hydrogel, these materials are upgraded for their capacity of discharging water, rather than the capacity of holding it. The managed arrival of numerous assorted species is, surely, one of the principle qualities of hydrogels available, from planting to

hereditary building. Be that as it may, regardless of the possibility that organizations delivering such gems are advancing their common sense and flexibility, in the most recent years mainstream researchers is addressing about their genuine utility. As Chalker-Scott from Washington State University called attention to in her productions on the subject, since the usually utilized watering precious stones are made out of non-inexhaustible materials, whose monomers can be lethal (e.g. acrylamide), the potential dangers of their utilization are path higher than the advantages of water stockpiling and controlled discharge that can, furthermore, be acquired in numerous different courses with bring down natural effect.[6]

2.2 *Allium sativum* (**also known as garlic**)

Garlic is one of the edible plants which has generated a lot of interest throughout human history as a medicinal panacea. A wide range of microorganisms including bacteria, fungi, protozoa and viruses have been shown to be sensitive to crushed garlic preparations. Moreover, garlic has been reported to reduce blood lipids and to have anticancer effects. Chemical analyses of garlic cloves have revealed an unusual concentration of sulfur-containing compounds (1–3%).

Analysis of steam distillations of crushed garlic cloves performed over a century ago showed a variety of allyl sulfides. However, it was not until 1944 that Cavallito and his colleagues isolated and identified the component responsible for the remarkable antibacterial activity of crushed garlic cloves. The compound turned out to be an oxygenated sulfur compound which they termed allicin, from the Latin name of the garlic plant, Allium sativum. Pure allicin is a volatile molecule that is poorly miscible in aqueous solutions and which has the typical odor of freshly crushed garlic. Final proof of the chemical structure of allicin (figure 2.2(a)) came in 1947, when it was shown that allicin could be synthesized by mild oxidation of diallyl disulfide. The debate on the presence of allicin in crushed cloves versus its absence in odorless intact cloves was resolved after Stoll and Seebeck isolated, identified, and synthesized an oxygenated sulfur amino acid that is present in large quantities in garlic cloves and which they named alliin (figure 2.2(a)). Alliin was found to be the stable precursor that is converted to allicin by the action of an enzyme termed alliinase which is also present in the cloves. Only one isomer of alliin ((+)-S-allyl-L-cysteine-sulfoxide) was found to be present, which in itself had no antimicrobial activity. The amounts of alliin and allicin present in different strains of garlic were studied by numerous investigators. Considerable variations have been reported, ranging from 2.8 to 7.7 mg/gram found in Romanian red.

The transformation of alliin into the biologically active allicin molecule upon crushing of a garlic clove is extremely rapid, being complete in seconds. The enzyme responsible for the lysis is alliinase, or alliin-lyase (E.C.4.4.1.4), a pyridoxal 5-phosphate-dependent glyco- protein consisting of two subunits. Alliinase is present in unusually high amounts in garlic cloves: at least 10% of the total protein content (10 mg/g fresh weight).Garlic cloves are odor-free until

crushed. Cross-section studies have indicated that the substrate alliin and the enzyme alliinase are located in different compartments. This unique organization suggests that it is designed as a potential defense mechanism against microbial pathogens of the soil. Invasion of the cloves by fungi and other soil pathogens begins by destroying the membrane which encloses the compartments that contain the enzyme and the substrate. This causes the interaction between alliin and alliinase that rapidly produces allicin and which in turn inactivates the invader. The reactive allicin molecules produced have a very short half-life, as they react with many of the surrounding proteins, including the alliinase enzyme, making it into a quasi-suicidal enzyme. This very efficient organization ensures that the clove defense mechanism is only activated in a very small location and for a short period of time, whereas the rest of the alliin and allinase remain preserved in their respective compartments and are available for interaction in case of subsequent microbial attacks. Moreover, since massive generation of allicin could also be toxic for the plant tissues and enzymes, its very limited production and short-lived reactivity, which is confined to the area where the microbial attack takes place, minimizes any potential self-damage to the plant.

Allicin, one of the active principles of freshly crushed garlic homogenates, has a variety of antimicrobial activities. Allicin in its pure form was found to exhibit i) antibacterial activity against a wide range of Gram-negative and Gram-positive bacteria, including multidrug-resistant enterotoxicogenic strains of Escherichia coli; ii) antifungal activity, particularly against Candida albicans; iii) antiparasitic activity, including some major human intestinal protozoan parasites such as Entamoeba histolytica and Giardia lamblia; and iv) antiviral activity. The main antimicrobial effect of allicin is due to its chemical reaction with thiol groups of various enzymes, e.g. alcohol dehydrogenase, thioredoxin reductase, and RNA polymerase, which can affect essential metabolism of cysteine proteinase activity involved in the virulence of E. histolytical[4]

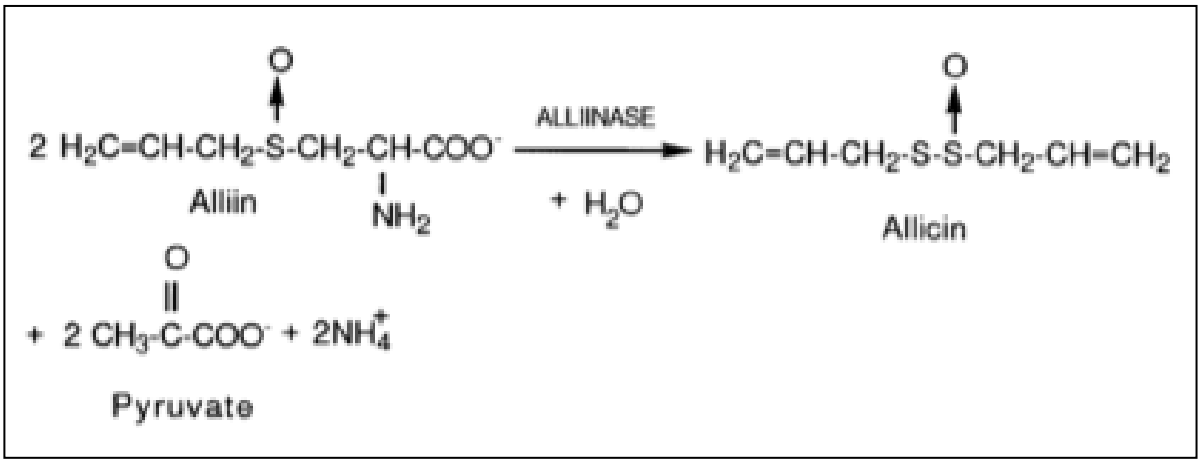


Fig 2.2 (a): Generation of allicin in a garlic clove[4]

2.3 POLYVINYL ALCOHOL-

PVA hydrogels have physical properties such as rubbery or elastic nature and high degrees of swelling in water.

Amounts of PVA not incorporated in PVA networks (degree of cross-linking of PVA) result from the increased matrix swelling after a certain critical percent of PVA chains become incorporated in developing matrices. This critical degree of matrix conversion results in networks of specific density and physical entanglement that maintain the observed degree of water association, viscoelasticity and swelling character.[8]

Polyvinyl alcohol (PVA) hydrogels have been specically proposed as promising prosthetic biomaterials to replace articular cartilage. Articular cartilage is, in fact, a natural "ber-reinforced hydrogel composed of proteoglycans, type II collagen, and approximately 75% water by weight. PVA hydrogels may be synthesized to mimic the water content of articular cartilage and possess a low coefficient of friction, which is an important characteristic for lubrication of articular joints. The biocompatibility of PVA hydrogels has been studied. Oka et al.[8] reported no inflammatory or degenerative changes in the articular cartilage or synovial membrane surrounding PVA hydrogel implants after 52 weeks.

While PVA hydrogels possess similar water content to articular cartilage, a critical barrier to their use is the lack of sufficient mechanical properties to withstand the severe loading

conditions imposed on articular joint surfaces. Articular joints are subjected to rapidly apply compressive and shear forces up to several times body weight in magnitude for millions of cycles over a lifetime. The properties of hydrogels are determined by the monomer composition, cross-linking density, and polymerization conditions. [8]

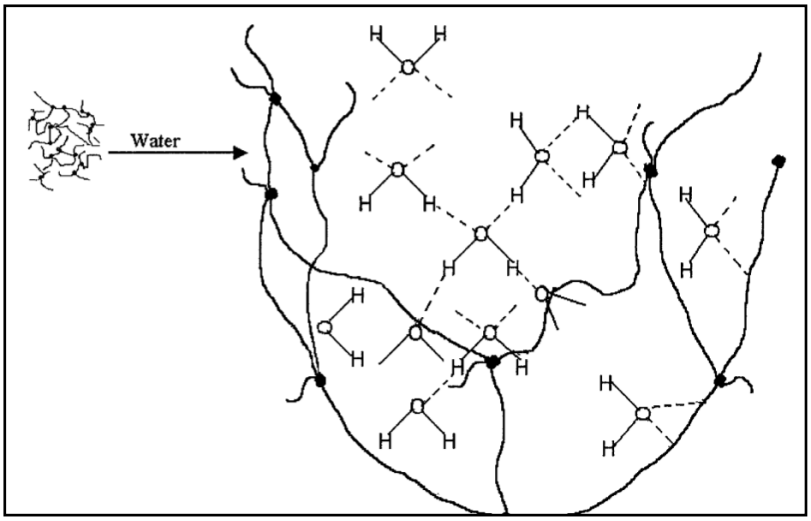


Fig 2.3 (a): swelling and 3-D network formation of hydrogels [8]

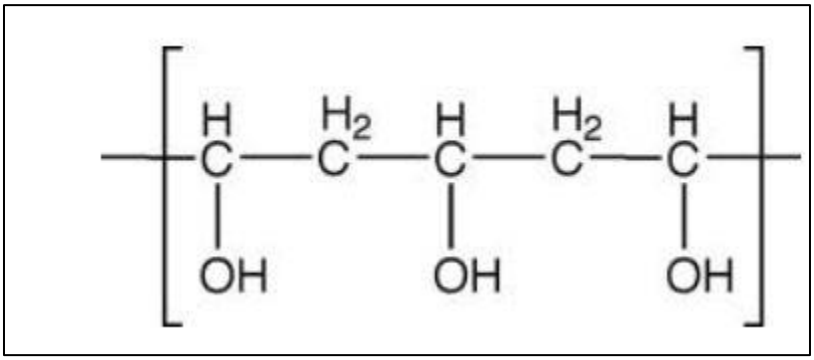


Fig 2.3 (b): Structure of PVA [9]

2.4 ACRYLAMIDE

Poly(acrylamide) (PAAm) is an important and hydrophilic polymer for preparation of hydrogels. The common method to synthesis of PAAm hydrogels is the free radical crosslinking copolymerization of AAm monomer with multifunctional vinyl monomers. PAAm hydrogels and their derivatives are the subject of many studies. PAAm hydrogels have proven capability of water absorption and

biocompatibility with physiologic body fluids. The application of PAAm hydrogels in controlled release of agrochemicals and bioactive is already reported.[18]

2.5 MALEIC ANHYDRIDE

Maleic anhydride has been used in coatings, adhesives, detergent additives, cosmetic additives, dispersants, enzyme carriers, and ion exchange resins. Polymers having pendant hydroxyl functional groups can react easily with the carbonyl carbon of maleic anhydride to attach the maleic acid (MA) group onto the polymers. The method of using maleic anhydride as the carrier for incorporating vinyl groups into polymers has several advantages over conventional methods of vinyl group attachment. First, the water or solvent solubility of the resulting hydrogel precursors is enhanced with an increase in DS(degree of substitution) as opposed to the decrease in water solubility and swelling ratio of hydrogels that are based on acrylic acid and its derivatives. This is because each substitution opens an anhydride ring of maleic anhydride and results in one free carboxylic acid group available at the substituted chain end. This carboxylic group is able to enhance the solubility of a polymer. Second, the functionality of a polymer is preserved, irrespective of the DS. This is because the consumption of one hydroxyl functional group of a polymer used for the attachment of a MA group will be compensated by the generation of one free carboxylic functional group. The newly available carboxylic acid functional group can then be used in any further incorporation of drugs or other bioactive agents. Third, the hydrophilicity of hydrogels is increased with the DS. Contrary to the hydrogels prepared by conventional methods using acrylic acid or its derivatives, an increase in hydrophilicity of MA-based hydrogels would also be expected to increase their swelling ratio.[19]

2.6 HYDROGELS IN AGRICULTURE-

Superabsorbent polymers in agriculture can be used as retaining materials in the form of seed additives (to aid in germination and seedling establishment), seed coatings, root dips, and for immobilizing plant growth regulator or protecting agents for controlled release. Moreover, some hydrophilic polymers such as polyacrylates could also be used to remediate the sandy soil contaminated with heavy metals and improve the plant growth by reducing the metal solubility and decreasing their concen trations in the shoots.

Many kinds of supersorbent hydrogels were prepared from synthetic and natural polymers; the following four types of them have so far been developed as agricultural polymers: (1) starch–graft copolymer (obtained by graft polymerization of polyacrylonitrile onto starch followed by saponification of the acrylo- nitrile units); (2) crosslinked polyacrylates; (3) crosslinked polyacrylamides; and (4) crosslinked acrylamide–acrylate copolymers containing a major percentage of acrylamide units.

The supersorbents were prepared by graft copolymerization, crosslinking polymerization, and other hydrophilization and water insolubilization. This polymer is not contaminated with foreign additives and loses its ability to dissolve in its customary solvents, and its mechanical properties are improved. Acrylamide prepared by -radiation and successfully used as carriers of agrochemicals and soil conditioners for sandy soil plantation.

Relatively low cost, high reduction of irrigation- induced erosion and soil loss, ease of use, and integration make polyacrylamide (PAAm) the best management practice worth looking into by any agricultural operation. Because PAAm tends to coil in aqueous systems, it needs an ionic charge instead of a neutral one to enhance intramolecular electrostatic repulsion responsible for polymer chains extension. Most of the hydrogels marketed for agriculture come from the ionic hydrogels, which represent a recent advance in polymer technology for crop protection.

agricultural uses as soil conditioners and seed additives. The factors affecting the hydrogel swelling properties, including nature of polymer, irradiation doses, polymer crosslinking density, and copolymer compositions, were studied. The ability of such hydrogels to enhance the sandy soil water retention and aid in corn (Zea mays) emergence and performance was investigated.[10]

Recently, hydrogel-based pesticide release devices have become very popular. They consist of a pesticide in a polymer network in the form of a microcapsule or granule. Such systems exhibit many advantages, including controlled or slow release of the core active ingredient (AI) — leading to longer application intervals, reduction in dosage, stabilization of the core AI against environmental degradation (light, air, humidity, and micro-organisms), reduction in mammalian toxicity and human mucous-membrane irritation, reduction in phytotoxicity, reduction in evaporation and leaching, reduction in environmental pollution and drift, increase in the

number of target organisms, and ease of handling of the toxic materials. However, a proper design of the encapsulation system is very important to achieve the desired release characteristics.

In order to obtain optimal performance for the microencapsulated products, time-dependent or site-species release is desirable. Thus, it is important to develop various functional microcapsules from stimulus-responsive hydrogels that are species to target organisms/sites. For example, pressure-, temperature-, pH-, light-, enzyme-, and ion-responsive polymers are desirable. Hydrogels have the requisite features and because of the ability to tune their properties, they are often called 'smart' or 'intelligent' polymers. These technologies have been developed mainly for pharmaceutical applications, but such technologies can also be applied for pesticide release with some modification. For agricultural applications, formulation methods are easier than those applied for drug delivery, making the end-product commercially viable.

To achieve the desired controlled release characteristics, some naturally occurring, cheaply available, biodegradable, and environmentally friendly matrices have been used. Most of the hydrogel-based formulations involve cross-linking of the matrix in the presence of active agents, or emulsication followed by separation of microspheres without wasting the solvent. The present review is not concerned with the various methods used to prepare the polymeric controlled-release (CR) pesticide formulations, rather it is about the different classes of hydrogels that have been used in the literature for CR applications. The CR pesticide formulations have become more popular because the degradation of the active agent can be alleviated. This results in a longer residual activity, resulting in a longer interval between applications. A typical case is the stabilization of biopesticides by micro- encapsulation. There is also a report of the micro-encapsulation of biopesticides using a pH-sensitive polymer that provides protection to the pesticide until the polymer is broken down by the high pH in the insect gut. Several applications of coated granules have also been developed for seedling box applications, wherein the granules are coated with polymers to give a longer residual activity, thereby preventing phytotoxicity. Since the granules are applied to the seedling boxes, i.e. close to the target, less of the formulation is needed to control the insect pests.

Since CR formulations prevent leaching of the active agents, they can be used successfully for fertilizer encapsulation, which has great signicance in agriculture where rainfall is heavy. In dry-land areas or in dry-farming practice, a signicant amount of urea is lost due to decomposition under intense sunlight and heat, with subsequent losses in the environment as a gas. This can be prevented if urea is encapsulated or derivatized. Various modes of loss of urea have been explained in our previous review. The present review addresses technological developments which have occurred over the past few decades in the area of hydrogels for the CR of pesticides[11].

CHAPTER 3

EXPERIMENTAL WORK

3.1 APPARATUS REQUIRED

1. Beaker 100ml
2. Spatula
3. Glass rod
4. Whatman filter paper
5. Measuring cylinder
6. Aluminum Foil
7. Petri plates
8. Test tubes
9. Pipette 20 microliter

3.2 EQUIPMENT REQUIRED

1. Magnetic Stirrer
2. Autoclave
3. Weighing balance
4. Laminar air flow
5. Incubator
6. Hot air oven
7. Water bath

3.3 MATERIALS REQUIRED:

1. Acrylamide (AAm) – Acrylamide extra pure i.e 99% pure of Srichem with molecular weight 71.08 and molecular formula C_3H_5NO with melting point 83-86^oC is taken to conduct the experiments.

2. Maleic Anhydride(MAh) - Maleic anhydride with 99 % purity from Loba chemie with molecular weight 98.06 and molecular formula $C_4H_2O_3$ having melting point 50-53 ^oC and sulphated ash maximum up to 0.05%

3. Polyvinyl alcohol (PVA) – Polyvinyl alcohol (cold) from central drug house is taken to perform the experiment. This polymer is white crystalline powder/flakes/granules having molecular formula $(C_2H_4O)_n$ and average molecular weight 85000 to 124000
   Solubility: 4% solution in cold water is clear and colorless
   Viscosity (4% aqueous solution at 20 ^oC) : 23-38 cP
   Degree of hydrolysis : 86 – 89%
   Maximum impurity limit of ash : 0.75%

4. N,N'-Methylenediacrylamide (N,N'MBA)- N,N'-Methylenediacrylamide (for synthesis) from Merck is used as a cross-linker in synthesizing the hydrogel . This compound have molecular weight of 154.17g/mol and molecular formula $C_7H_{10}N_2O_2$ with purity upto 98%.

5. Potassium persulphate (KPS) - This compound used is of Qualikems having molecular weight 270.31 and molecular formula $K_2S_2O_8$ with chloride amount not more than 0.04% and purity is 98%.This compound plays the role of initiator in the reaction.

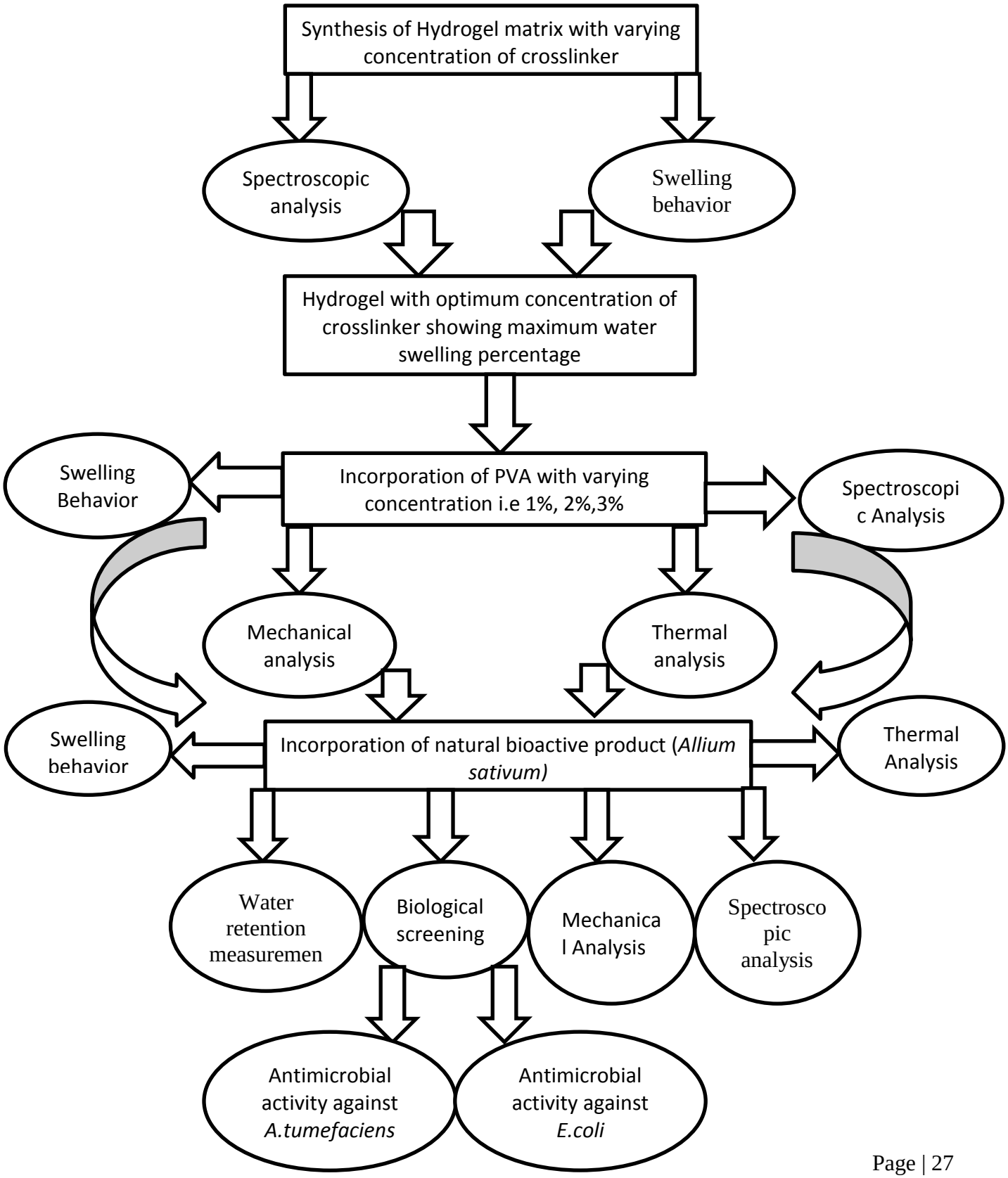
6. Garlic juice (G)- The garlic cloves were peeled off and washed thoroughly in order to remove the impurities and are wiped off removed the excess water. Grinding and filtration is then done to obtain the garlic juice (No water is used while grinding).

7. Biological Substrate:

(a) *Agrobacterium tumefacians*- *A. tumefaciens* is an alphaproteobacterium of the family Rhizobiaceae, rod-shaped, Gram-negative soil bacterium which includes the nitrogen-fixing legume symbionts. Unlike the nitrogen-fixing symbionts, tumor-producing *Agrobacterium* species are pathogenic and do not benefit the plant. The wide variety of plants affected by *Agrobacterium* makes it of great concern to the agriculture industry. The strain was obtained from Biotechnology Department, Delhi Technological University, Delhi.

(b) *E.coli*- It is a gram-negative, facultatively anaerobic, rod-shaped, coliform bacterium of the genus Escherichia. Most *E.coli* strains are harmless, but some serotypes can cause serious food poisoning in their hosts, and are occasionally responsible for product recalls due to food contamination. The strain was obtained from Applied Chemistry Department, Delhi Technological University, Delhi.

3.4 WORK PLAN


Synthesis of Hydrogel matrix with varying concentration of crosslinker
Spectroscopic analysis
Swelling behavior
Hydrogel with optimum concentration of crosslinker showing maximum water swelling percentage
Swelling Behavior
Incorporation of PVA with varying concentration i.e 1%, 2%,3%
Spectroscopi c Analysis
Mechanical analysis
Thermal analysis
Swelling behavior
Incorporation of natural bioactive product (*Allium sativum)*
Thermal Analysis
Water retention measuremen
Biological screening
Mechanica l Analysis
Spectrosco pic analysis
Antimicrobial activity against *A.tumefaciens*
Antimicrobial activity against *E.coli*

3.5 METHODS

3.5.1 Optimization of Cross-Linker

a) In 10 ml of distilled water, pre-determined amount of AAm is dissolved i.e. 3.55 gms using magnetic stirrer with time duration of 5 minutes.
b) Then, 0.908 gms of MAh is dissolved until all the particles makes the homogeneous solution with distilled water.
c) Different concentration of cross linker i.e. NN'MBA is added to above solution which is formulated in Table 1.
d) A definite amount of KPS (0.0445 gm) is then added and stirred until it makes a homogeneous solution.
e) This solution is then poured into test tubes of 15 ml.
f) The water bath is maintained at 70 °C and these test tubes were kept at 70 °C for 20 minutes.
g) The test tube is then broken and hydrogel is obtained in long cylindrical form which is then cut into approximately 0.5 cm thick buttons.
h) These buttons is immersed in distilled water for 24 hours in order to remove the unreacted chemicals.
i) After 24 hours, these hydrogel buttons are dried under ambient temperature until the constant weight is attained.

Table 1:Different concentration of cross linker

DESIGNATION	FORMULATION	AAm(gm)	MAh(gm)	NNMBA(%)	KPS(gm)
IC(0.1)	P(AAm-MAh)	3.55	0.908	0.1	0.0445
IC(0.5)	P(AAm-MAh)	3.55	0.908	0.5	0.0445
IC(1.0)	P(AAm-MAh)	3.55	0.908	1	0.0445
IC(2.0)	P(AAm-MAh)	3.55	0.908	2	0.0445
IC(3.0)	P(AAm-MAh)	3.55	0.908	3	0.0445

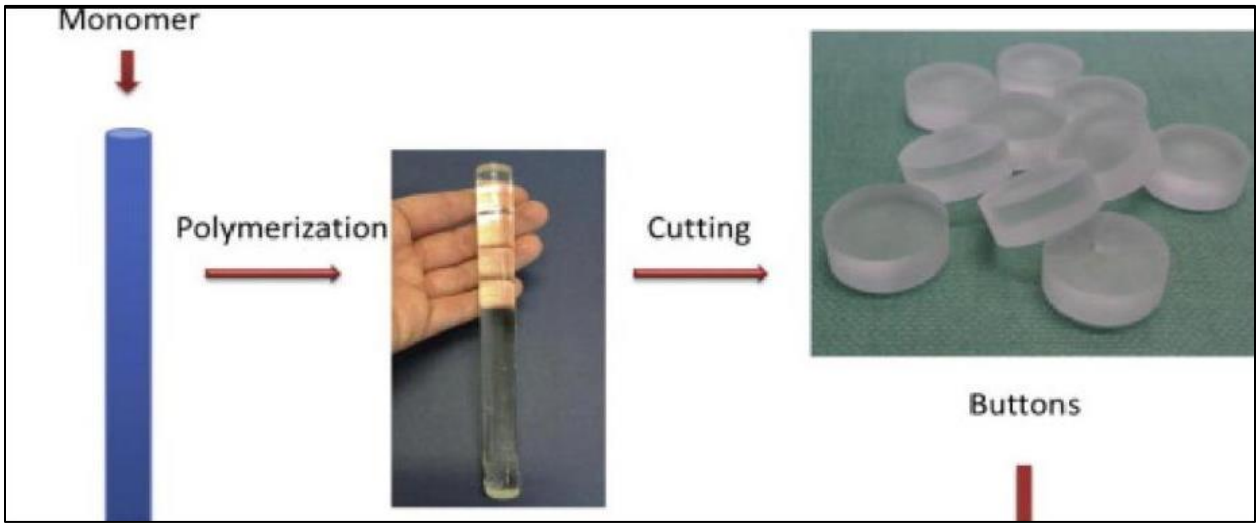


Fig 3.5.1 (a): Diagrammatic representation of preparation of Hydrogel [2]

Fig 3.5.1 (b): Prepared Hydrogel with different concentration of Cross linker

3.5.2 Hydrogel Impregnated with PVA

a) Different concentration of PVA i.e 1%, 2%, 3% of total solution is dissolved in 10ml of distilled water using magnetic stirrer with time duration of 60 to 70 minutes (Table 2).
b) The predetermined amount of AAm (3.55gm) and MAh (0.908gm) is added and stirred well.
c) Then, optimized amount of cross-linker is added to the stirred solution.
d) And finally initiator KPS i.e. 1% of solution is added to solution and stirred until it become homogenous.
e) Again, this solution is then filled in test tube of 15ml and then kept in water bath at the temp of 70°C for about an hour.
f) Test tube is then broken and finally cut into pieces with thickness of 0.5 cm and immersed in distilled water for 24 hours to remove the unreacted chemicals.
g) These are then dried at 25°C for 2 to 3 days.

Table 2:Table representing different concentration of PVA

DESIGNATION	AAm(gm)	MAh(gm)	PVA(%)	NNMBA(%)	KPS(gm)
PVA 1	3.55	0.908	1	0.5	0.0445
PVA 2	3.55	0.908	2	0.5	0.0445
PVA 3	3.55	0.908	3	0.5	0.0445

Fig 3.5.2 (a): Prepared Hydrogel with different concentration of PVA

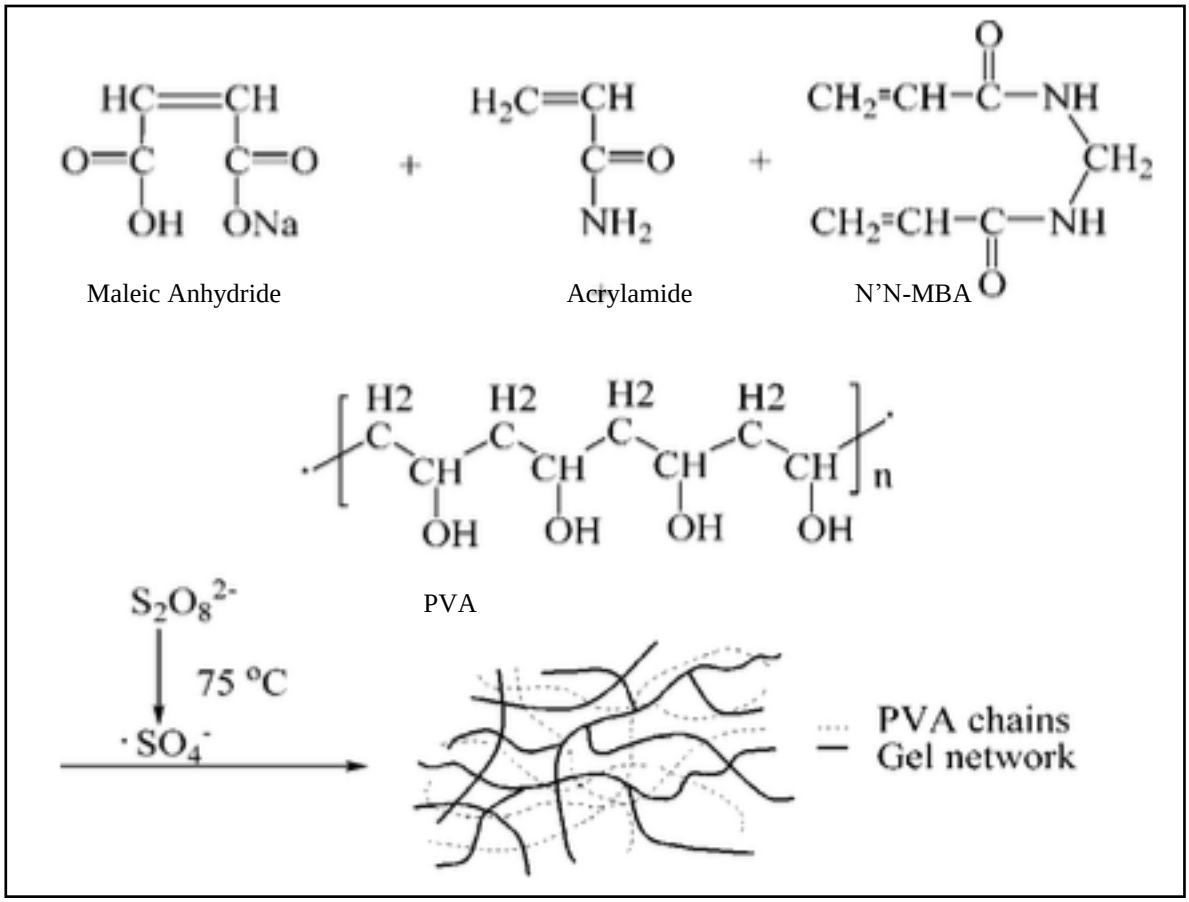


Fig 3.5.2 (b): Reaction mechanism of hydrogel with monomers PVA, MAh, AAm [12]

3.5.3 Providing Antimicrobial Activity To Hydrogel

a) Different concentration of PVA i.e. 1%, 2%, 3% is dissolved in 10 ml of distilled water
b) And then predetermined amount of AAm and MAh is added and stirred
c) The optimized amount of cross-linker is added to the solution and then initiator is added
d) To provide the antimicrobial activity against plant pathogen i.e *Agrobacterium tumefaciens* and against human pathogen i.e *Escherichia coli* (E.coli) fresh garlic juice is added with different concentration (Table 3).
e) Then, this solution is poured in test tube and these test tube is then kept in water bath at temp of 70°C for 1 hour.

Table 3 : Table representing different concentration of PVA and Garlic Juice

DESIGNATION	AAm(gm)	MAh(gm)	PVA(%)	G (%)	NNMBA(%)	KPS(gm)
P1G1%	3.55	0.908	1	1	0.5	0.0445
P1G2%	3.55	0.908	1	2	0.5	0.0445
P1G3%	3.55	0.908	1	3	0.5	0.0445
P2G1%	3.55	0.908	2	1	0.5	0.0445
P2G2%	3.55	0.908	2	2	0.5	0.0445
P2G3%	3.55	0.908	2	3	0.5	0.0445
P3G1%	3.55	0.908	3	1	0.5	0.0445
P3G2%	3.55	0.908	3	2	0.5	0.0445
P3G3%	3.55	0.908	3	3	0.5	0.0445

3.6 CHARACTERIZATION TECHNIQUES

3.6.1 Thermogravimetric analysis-

This analysis is conducted to determine the decomposition temperature or the highest temp upto which material can withstand temperature without degrading. The formed hydrogel undergo thermal analysis. TGA was conducted on PerkinElmer TGA 4000. This experiment was performed under nitrogen atmosphere with 1-2 mg of sample with heating rate of 15°C/min and nitrogen flowing rate is 20ml/min.

Fig 3.6.1 (a): Instrument of TGA

3.6.2 Swelling behaviour-

The swelling behaviour of polymer hydrogel samples are carried out by gravimetric method. The known weight of hydrogel is immersed in distilled water at ambient temperature and then these are hydrogel are taken out at equal interval of time, and then the excess water is soaked with the help of whatman filter paper to minimise the error and this process is done until equilibrium weight of hydrogel is obtained.

The percentage swelling is calculated by following equation-

$P\% = (S_w - D_w)/D_W * 100$

Where S_W - Weight of swollen hydrogel

D_W - Weight of dry hydrogel

P% - Percentage swelling

Analysis of water uptake-

When hydrogel immersed in distilled water, the swelling of hydrogel occurs. This happens when water migrate into the dynamically or pre-existing spaces between the chains of cross linked hydrogel. The phenomenon that come into play is osmosis.[15]

3.6.3 Dynamic Mechanical Analyser-

This experiment is conducted to determined visco-elastic behavior of the material . The sample was in irregularly-shaped cylindrical form . The specimens were approximately 7mm in thickness, 10mm in length, and 10mm in width. The graph is plotted between frequency and time in which fixed strain(quiet small) of the sinusoidal oscillation is given but the oscillation frequency is varied. This test gives storage (G') and loss (G") modulus as the output result which is components of the complex modulus G* as a function of frequency.

i.e. (G* = G' + iG").

Perkin Elmer DMA 8000 is used to perform this experiment.

Fig 3.6.3 (a): Instrument of DMA

3.6.4. Water Retention Measurement-

As discussed in paper of . Kariman M. EL Salmawi [13] 20 gm of dry soil granules are mixed with 0.2 gm of hydrogel. Then 40 ml of distilled water is added to it and is kept in plastic cups of quantity 250ml. These cups are kept at room temperature and is

weighed after every two days. At the same time, the controlled experiment i.e only sand granules and water is also carried out. The percentage of water loss due to evaporation is calculated by following equation

$$\text{Evaporation loss} = [(w_i - w_f)/40] * 100$$

Where, w_f was the initial weight of the beaker containing the hydrogel, w_i was the weight of the beaker without the hydrogel

This experiment is carried out in order to ensure the water retaining capacity of hydrogel when used while cultivation of crops in desert to provide the adequate amount of water. [13]

3.6.5 Fourier-transform infrared spectroscopy (FT-IR)-

The samples of hydrogel crushed and dried to form powder. This sample is mixed with KBr to form pellets. The functional group of prepared hydrogel is analysed by fourier transform infrared spectroscopy on thermoscientific nicolet 380.This study was done in transmittance mode to provide the evidence for formation of P(AAm-MAh), PVA,G hydrogels. This analysis was conducted to understand the reaction occurred between the compounds and crosslinking between the compounds. The IR was taken from 400 to 3000 cm^{-1}.

Fig 3.6.5 (a): Instrument of FT-IR

3.7 BIOLOGICAL SCREENING-

3.7.1 ***Agrobacterium Tumefaciens***- The antimicrobial activity of *Allium sativum* incorporated hydrogel was tested against the *Agrobacterium tumefaciens* . The bacterial culture was obtained from Biotechnology Department of Delhi Technological University. The plates were made by using beef extract 0.3 gm , yeast extract 0.6 gm, peptone 1.5 gm, NaCl 1.5gm, Agar 4.5 gm, in 300 ml of distilled water. 25ml plates were taken in use. This formed mixture is poured in plates and kept aside to solidify. Approximately 106 colony forming units is inoculated on the plates and then using the back of pipette the wells are created so the these dried hydrogel can fit into wells. These plates are then kept in incubator for 24 hours at 25°C. After 24 hours, the zone of inhibition provided by these hydrogels can be seen.

3.7.2 Escherichia coli- The antimicrobial action of *Allium sativum* incorporated hydrogel was assessed against *Escherichia coli* by cup diffusion technique. These plates is filled with Luria broth agar media which is made by taking 2gm luria broth(LB) and 1gm agar in 100ml of distilled water. Roughly 106 colony forming units (CFU) of the microorganism *E. coli* were inoculated on Luria broth (LB) agar plate, and after that different concentration of hydrogel containing garlic were added to the well presented in Luria broth agar plate. A response blend having PVA incorporated hydrogel was put in the well in the Luria broth plate and refined under the same condition as the control test. All the Luria broth plates were hatched at 37°C overnight. After incubation period, the plates were observed to see the zone of inhibition provided by the sample hydrogels. [14]

CHAPTER 4

RESULTS AND DISCUSSION

4.1 THERMOGRAVIMETRIC ANALYSIS

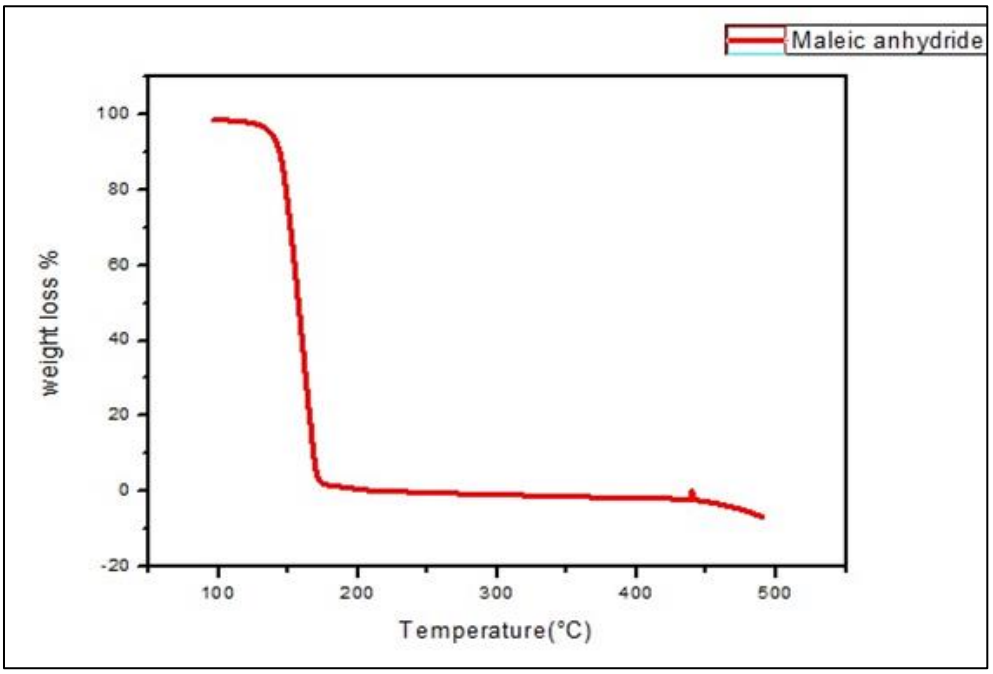


Fig 4.1(a): maleic anhydride TGA graph

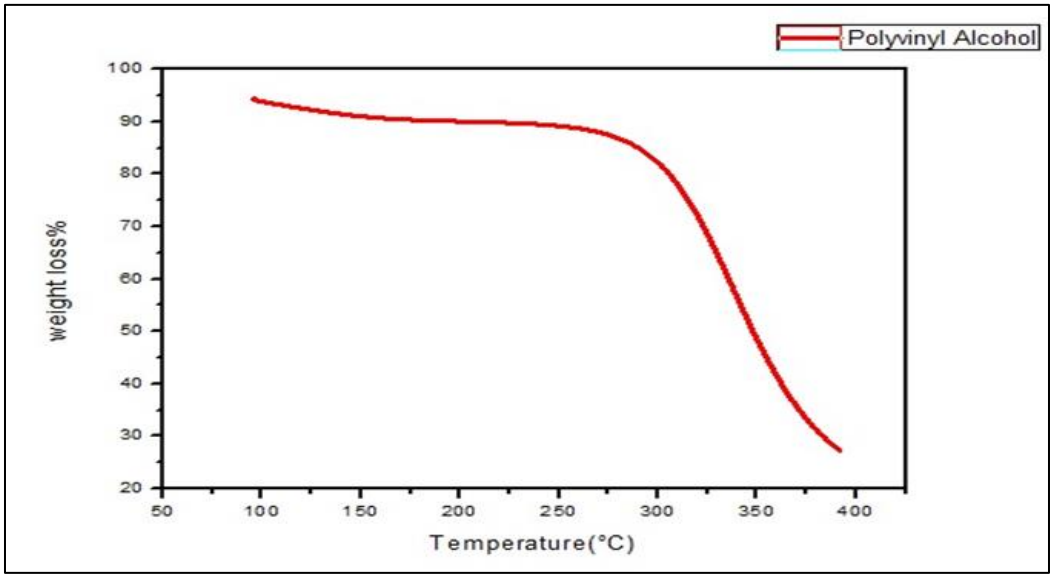


Fig 4.1(b): Polyvinyl Alcohol TGA graph

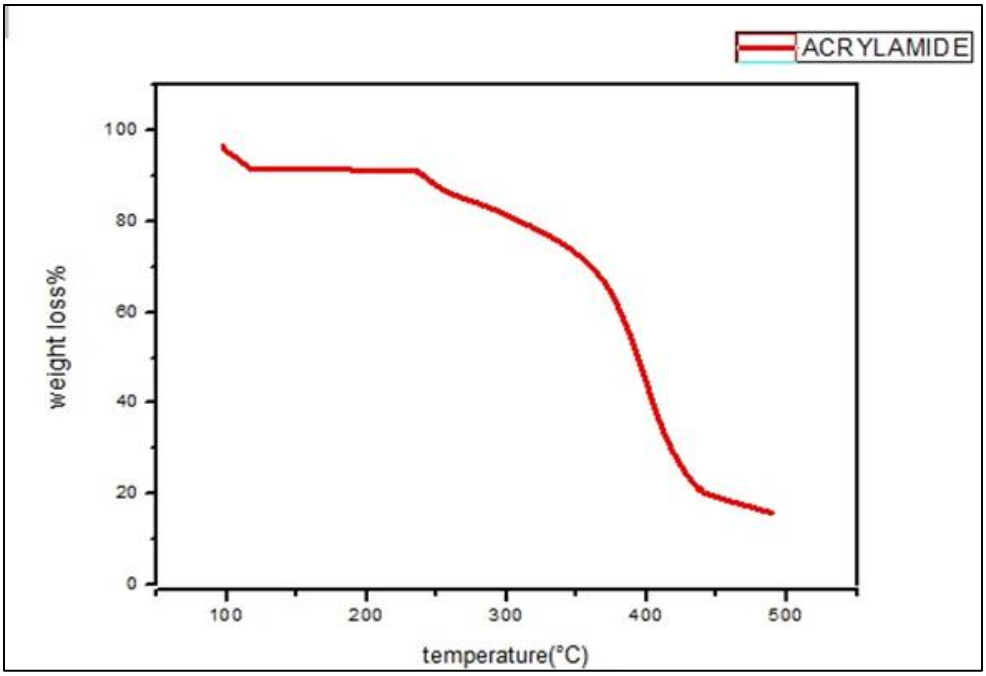


Fig4.1(c): Acrylamide TGA graph

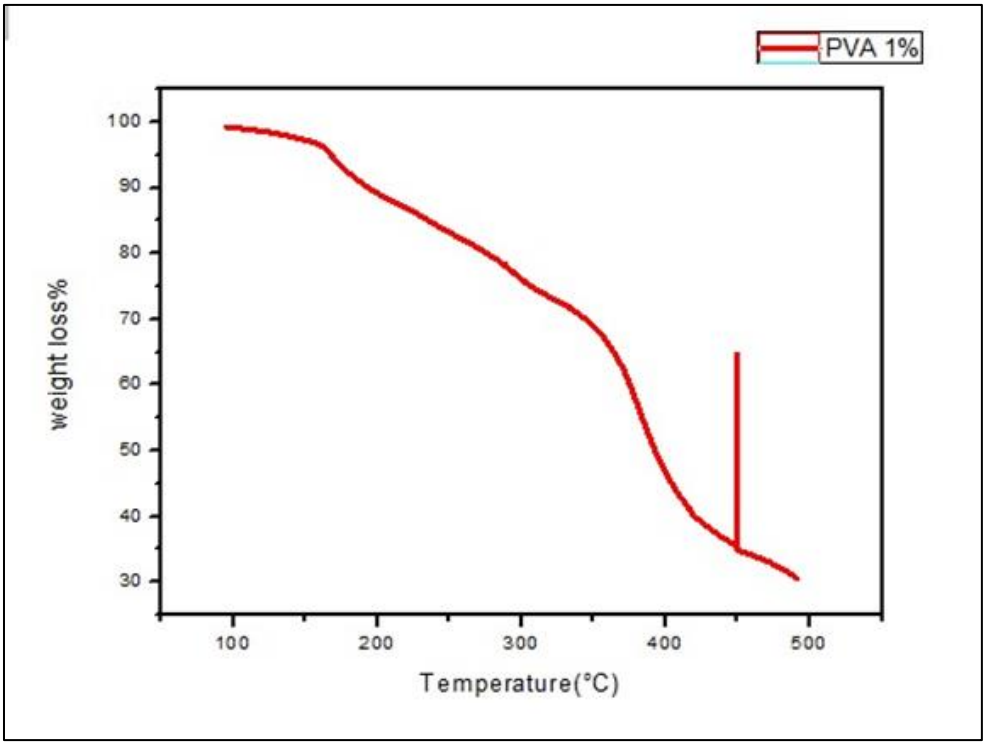


Fig4.1(d): PVA 1%,MAh 0.908gm, AAm 3.55 gm

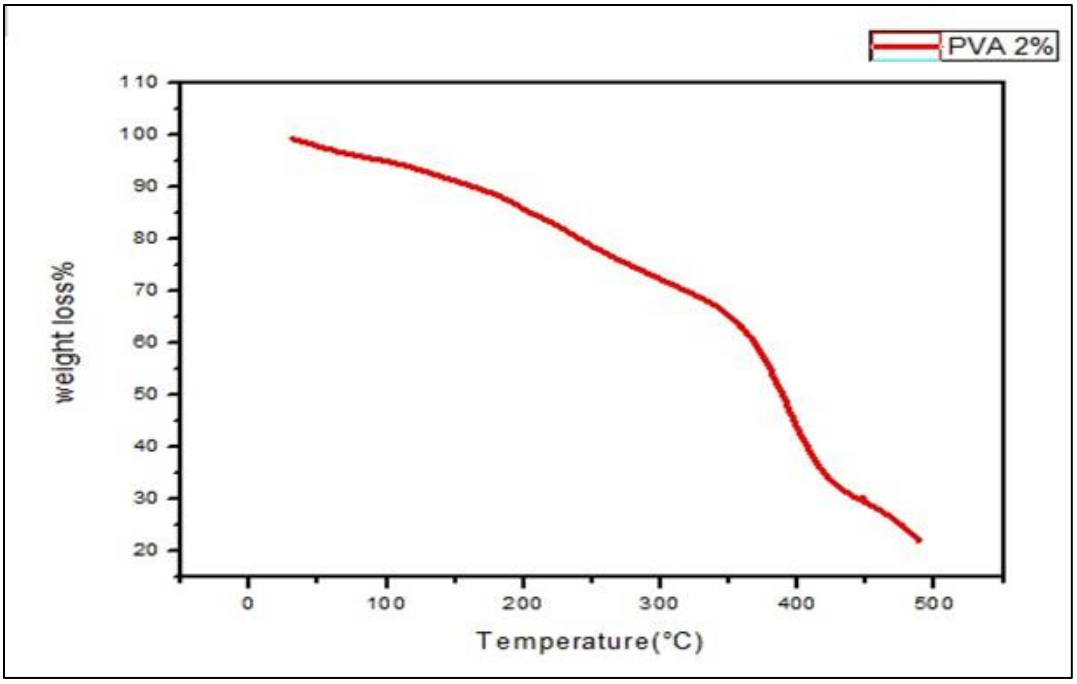


Fig4.1(e): PVA 2%,MAh 0.908gm, AAm 3.55 gm

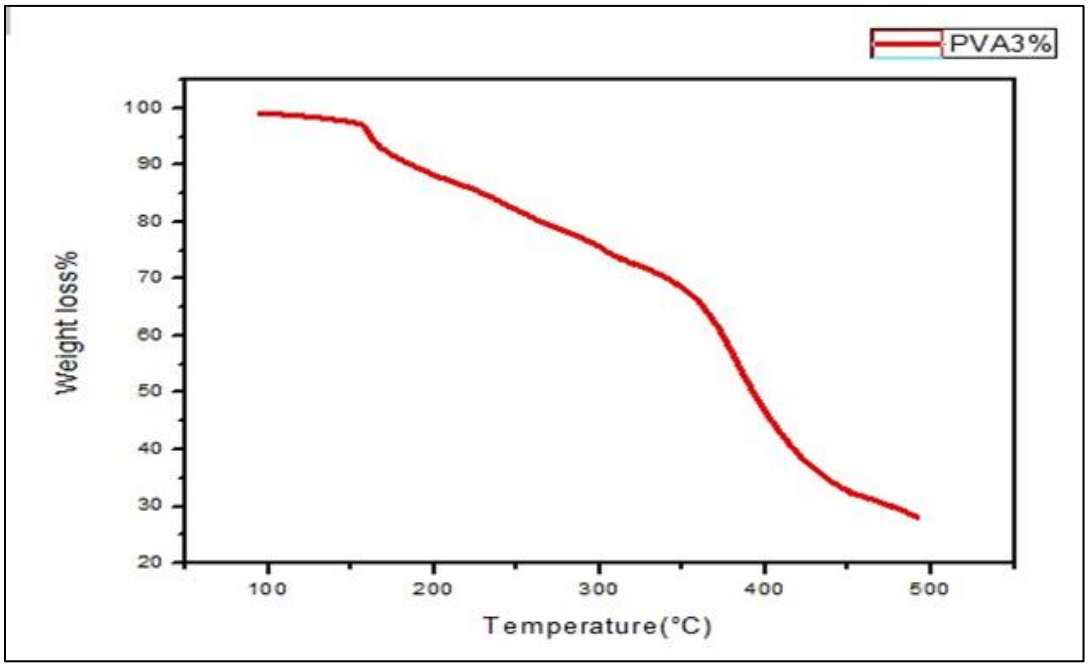


Fig4.1(f): PVA 3%,MAh 0.908gm, AAm 3.55 gm

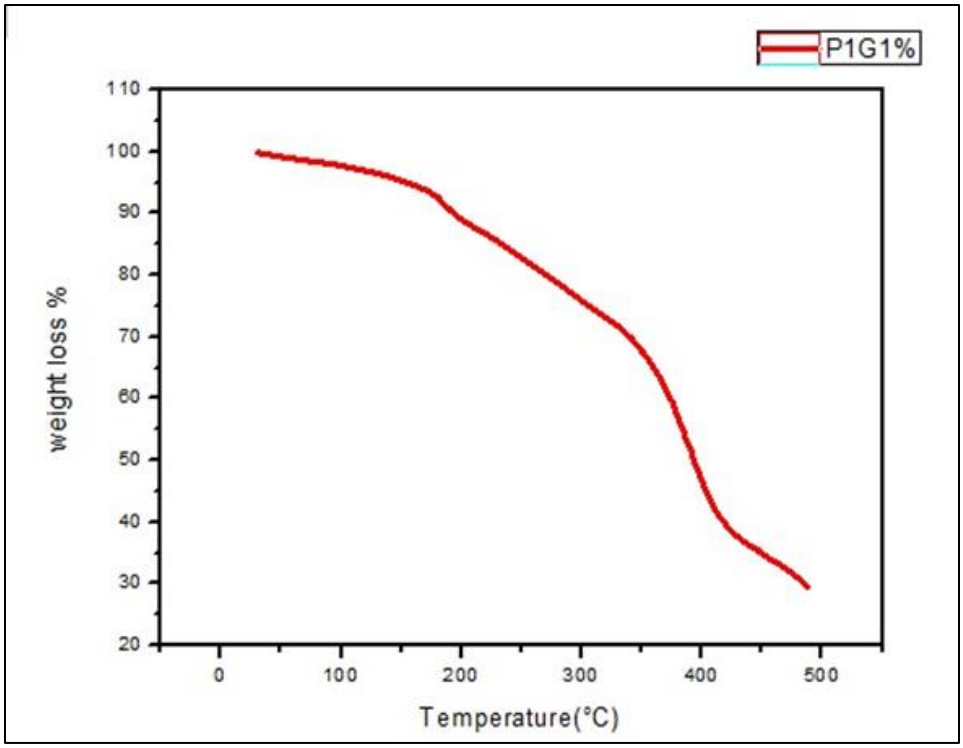


Fig4.1(g): PVA1%, Garlic juice 1%,MAh 0.908gm, AAm 3.55 gm

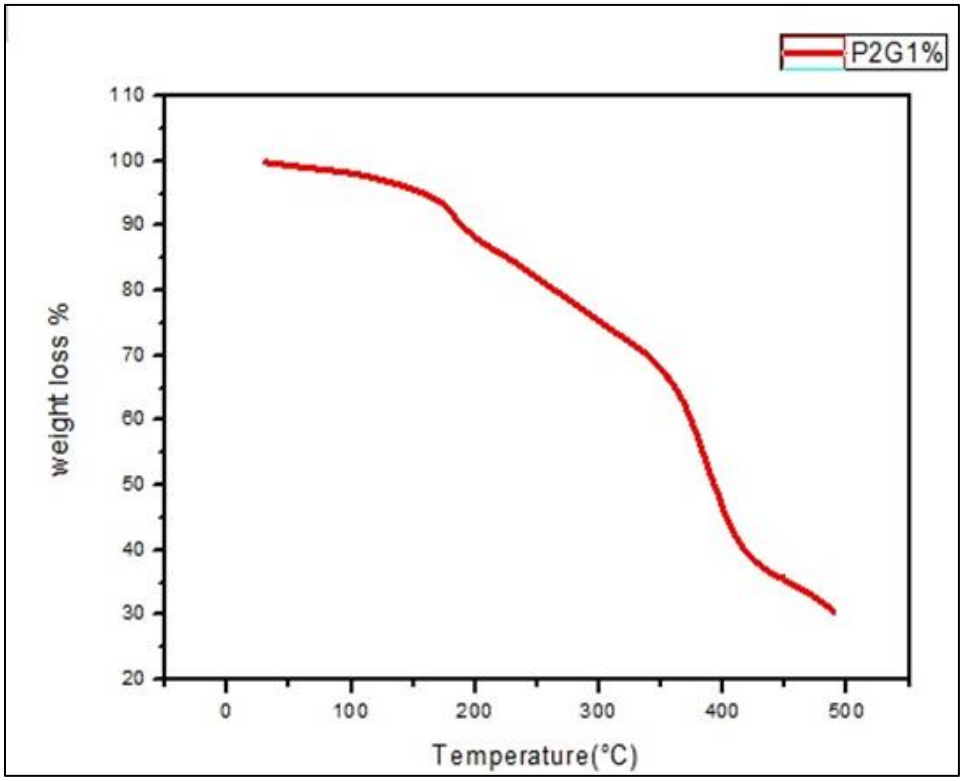


Fig4.1(h): PVA2%,Garlic juice1%,MAh 0.908gm, AAm 3.55 gm

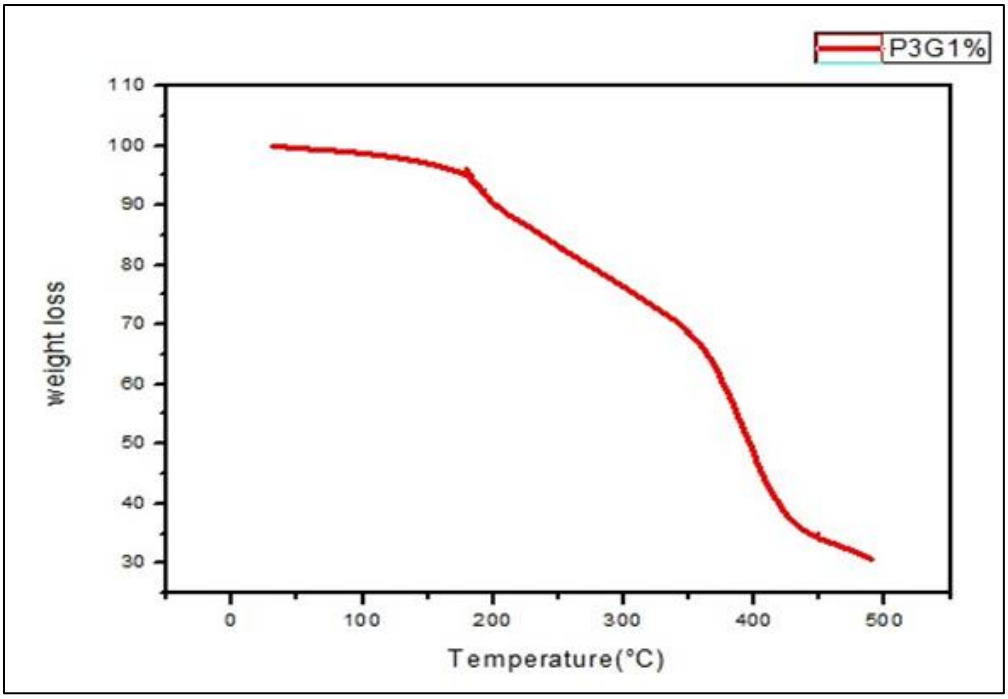


Fig4.1(i): PVA3%,Garlic juice1%,MAh 0.908gm, AAm 3.55 gm

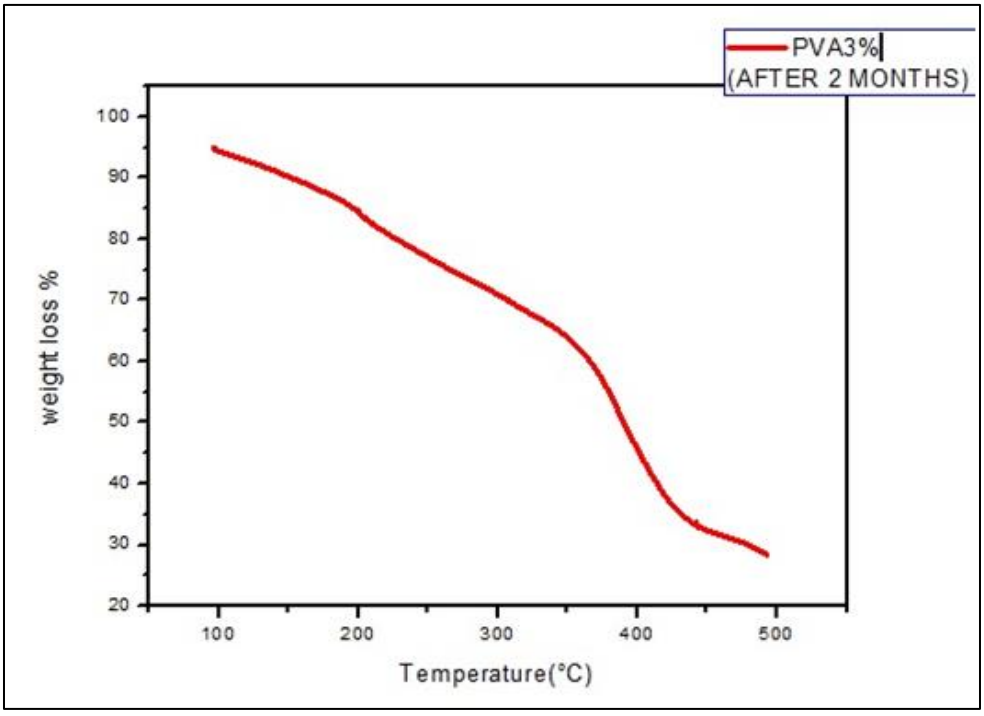


Fig4.1(j): PVA 3% MAh 0.908gm, AAm 3.55 gm(after two months)

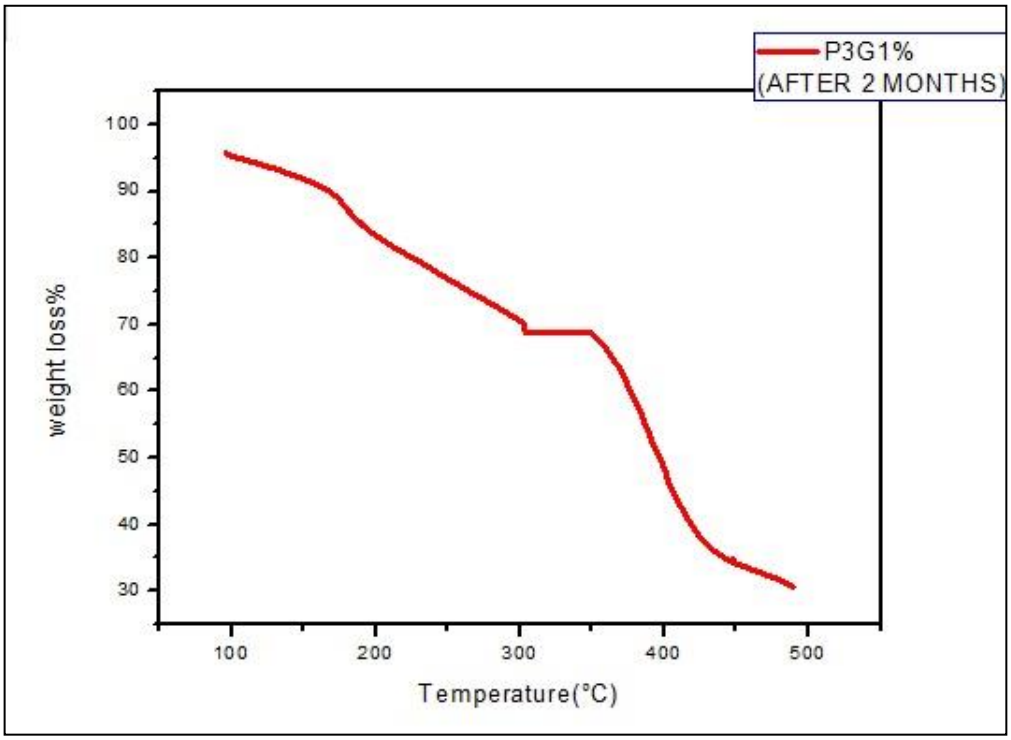


Fig 4.1.(k): PVA 3%,Garlic juice 1%,MAh 0.908gm, AAm 3.55 gm (after two months)

TGA method is basically used to identify decomposition temperature and range of its stability. The maleic anhydride in fig (a) shows that its first drop is at 50°C to 100°C which signifies the loss of moisture from the compound and then there is sharp bend which shows decomposition from 150°C to 175°C and attained the stability from 175°C to 500°C before complete decomposition.

In TGA of polyvinyl alcohol in fig (b), the loss of moisture is predicted from 100°C to 300°C is shown by first dip in graph and complete decomposition take place after 400°C

The acrylamide TGA fig (c) shows that from 100°C to 250 °C stability is attained. After that the loss of moisture from acrylamide takes place from 250°C and along with it decomposition also occur and complete decomposition takes place after 450°C.

In all other TGA graphs fig (d), fig(e), fig(f), fig(g), fig(h), fig(i) of hydrogel shows the same pattern of decomposition . the loss of moisture occur from 50°C to 100°C. Hence in this as the temperature is increased the decomposition increases .But there is linear decomposition from 150°C to 300°C which shows the loss of volatile compounds and again a sharp dip shows abrupt decomposition which continues to 500°C before complete decomposition.

The TGA of PVA 3% and PVA3G1% shown by fig(j) and fig(k) is done after 2 months and its shows as the time increase the is no change in decomposition pattern hence the degradation of hydrogel after 2 months doesn't occur.

Also, the complete decomposition doesn't occur before 500°C in all hydrogels just like the decomposition doesn't occur in monomer. Hence stability is maintained just like the monomer.

4.2 SWELLING BEHAVIOUR

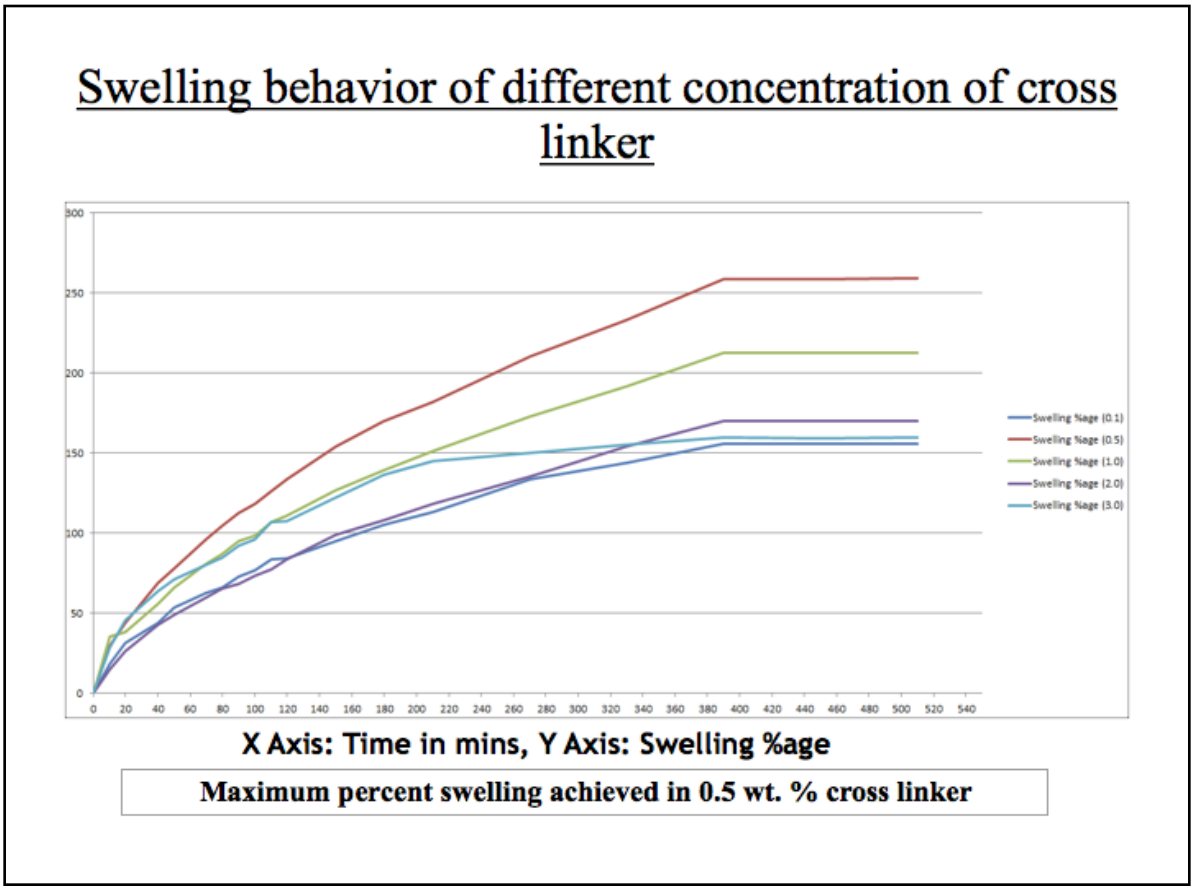


Fig 4.2 (a): Swelling behaviour of different concentration of cross linker

In figure 4.2 (a), the optimization of cross linker is observed by swelling behavior of different concentration hydrogel. 0.5wt% of N,N'MBA is optimised among IC(0.1) to IC(3). Thus the optimum crosslinking occur to 0.5wt% i.e maximum swelling of 1092% is obtained with 0.5% of N,N'MBA for IC(0.1)to IC(3) and when concentration of N,N'MBA is increased, the network structure become more and more denser with decrease in swelling capacity as the space of accumulation of water reduces. This happened as more and more cross linking groups are incorporated which cause decrease in hydrophilic groups resulting decrease in swelling behavior. Also, the mobility of polymer chains decreases and this lowers the swelling behavior of hydrogel. It is exceptional to take note of that a minute amount of cross linker cause drastic changes from liquid state to gel state during the synthesis of hydrogel. If cross linker is absent during the synthesis, the product formed is linear polymer chains with non-consistent jelly like

texture. However, with increase concentration of cross linker from 0.1wt% to 3wt%, the firmness of hydrogel increased and its elasticity decreased due to formation of cross-linked structure. But there is always an optimum value from where this rule is applicable .As the IC(0.1) doesn't come under optimum value it shows firm and less elastic nature as compared to IC(0.5) and the graph between cross linker concentration and elasticity shows in inverted parabolic.

In fig 4.2(b), For enhancing the water absorption capacity, the more hydrophilic group is introduced in the polymeric chain. As PVA has -OH group making it to be more hydrophilic. When swelling behavior results were taken in account, it was found that PVA 3% has maximum swelling as it has more amounts of PVA hence more hydrophilic groups .The network of hydrogel structure become sparser resulting in increase in swelling capacity. This is due to incorporation of more amount of polyvinyl alcohol which resulted in increase in hydrophilic group number and swelling. Moreover the PVA enhances the mobility of polymeric chains and thus higher the swelling of hydrogels. It is important to note that only a very small addition of PVA brings abrupt transition from hydrogel with PVA and without PVA during examination of swelling behavior of hydrogel. It was observed that absence of PVA in the polymerization recipe resulted into low swelling behavior as with use of PVA the swelling characteristics increases 200%.(without PVA swelling percentage was 459% and addition of PVA it is 1409%).
However, with decrease in PVA concentration from 3wt% to 1wt%, because hydrophilic group decreases swelling behavior also decreases.

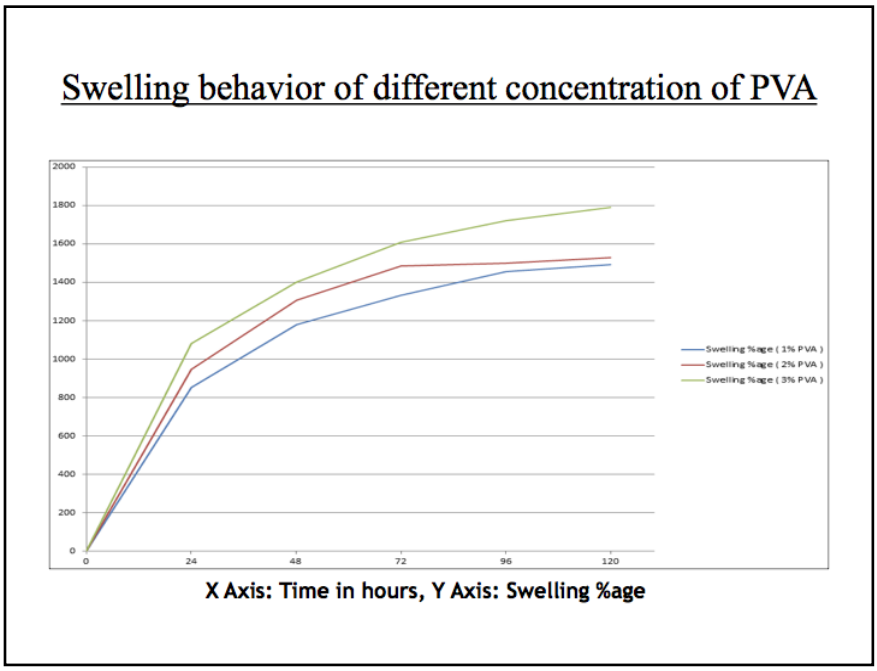


Fig: 4.2 (b): Swelling behavior of different concentration of PVA

4.3 DYNAMIC MECHANICAL ANALYSER (DMA)

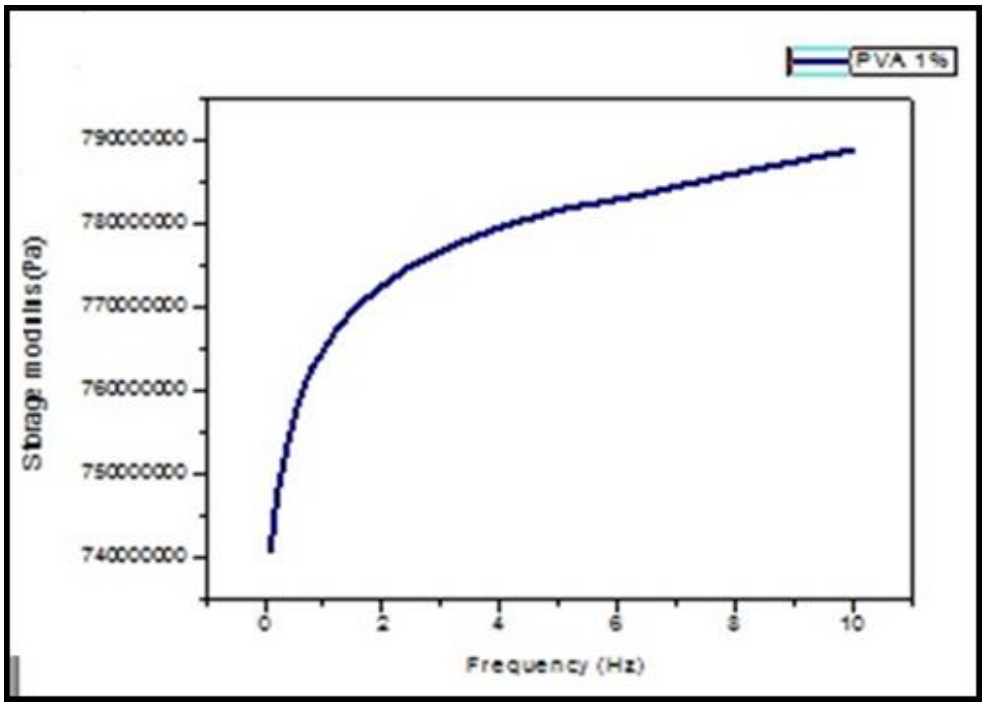


fig 4.3(a): PVA 1%

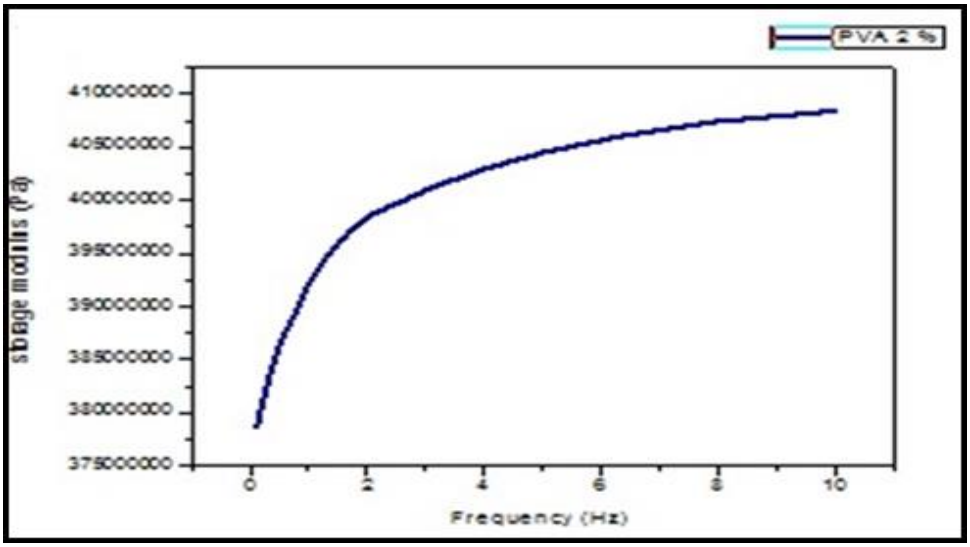


fig 4.3(b): PVA 2%

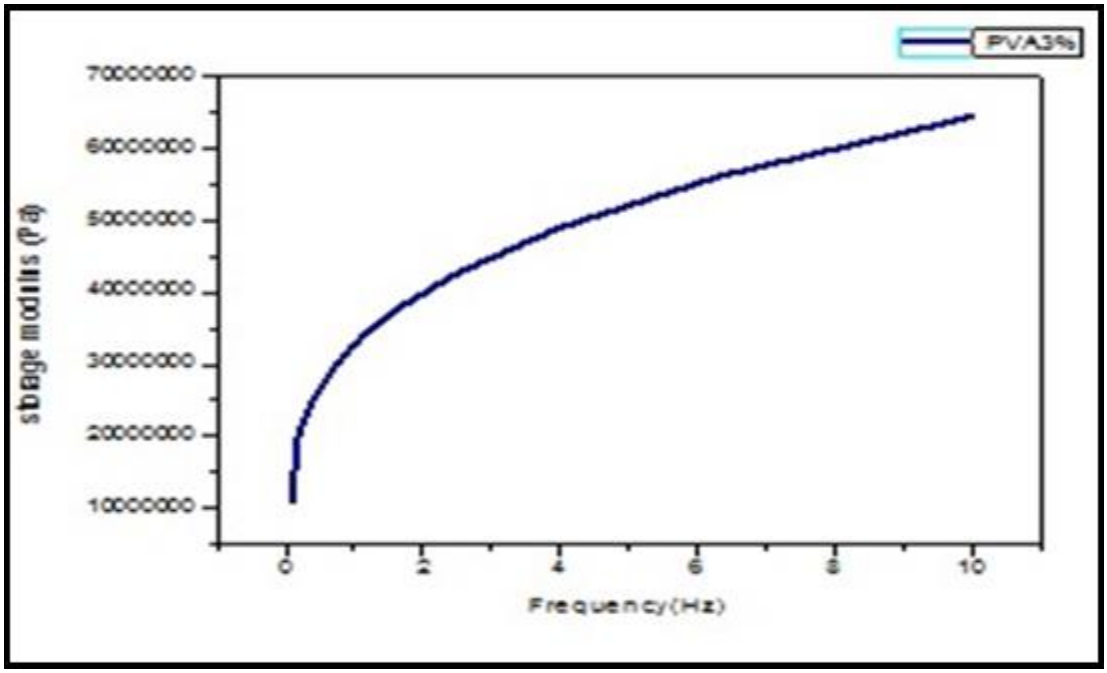


fig 4.3(c): PVA 3%

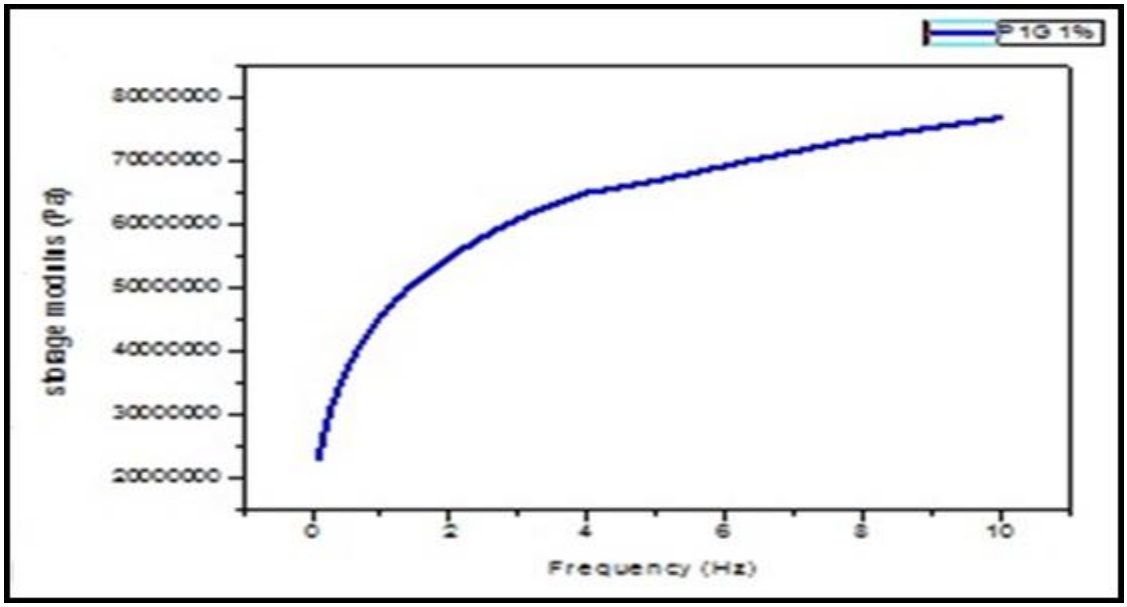


fig 4.3(d): P1G1%

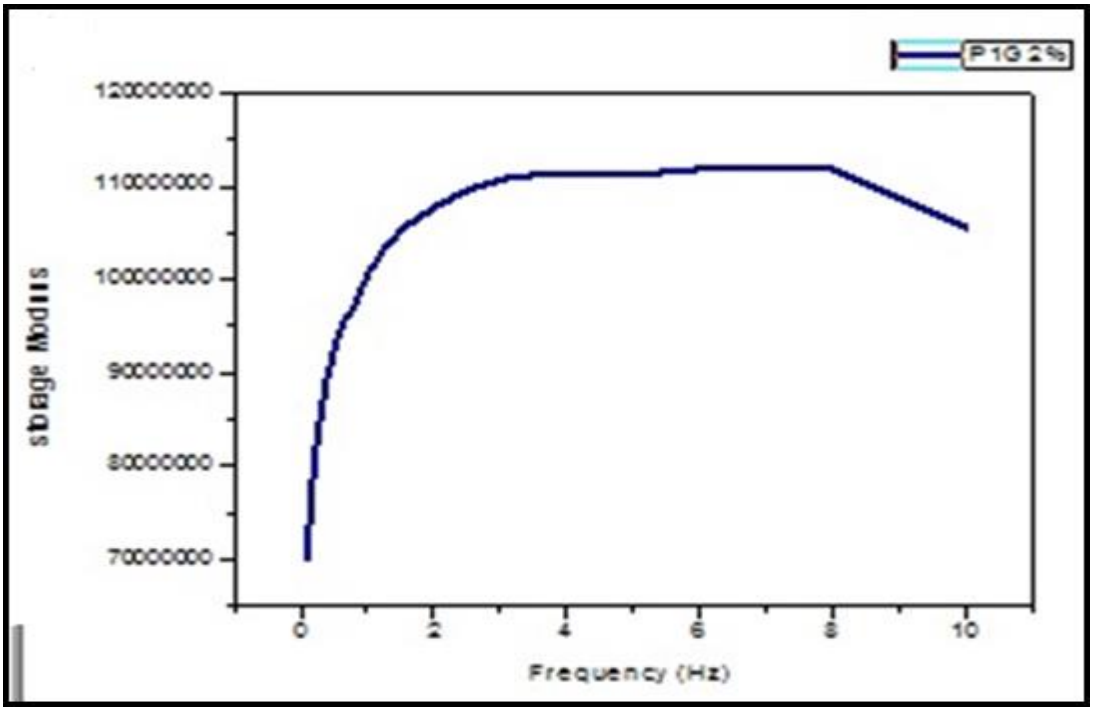


fig 4.3(e): P1G2%

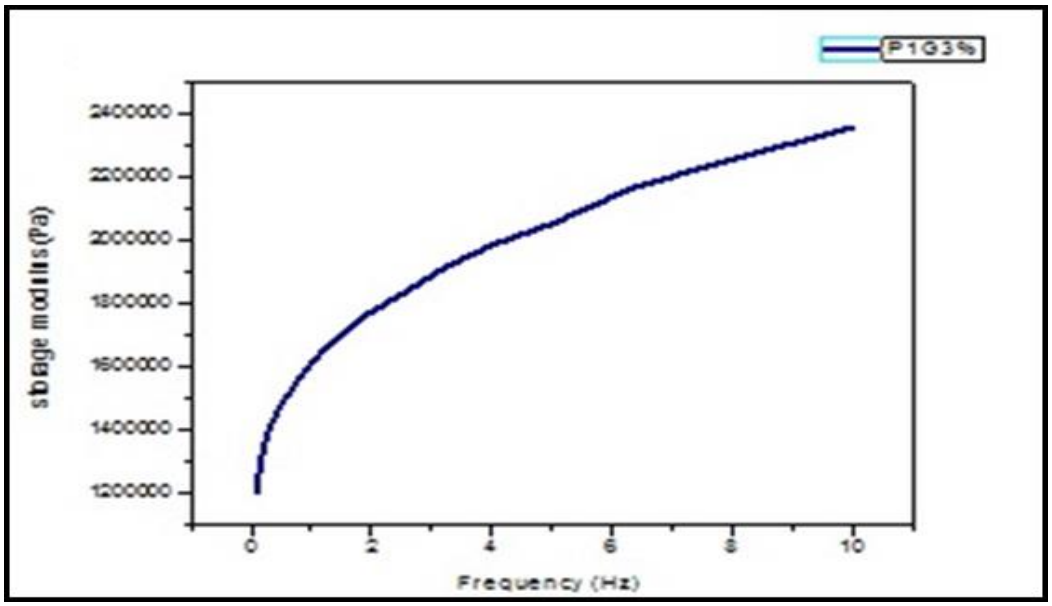


fig 4.3 (f):P1G3%

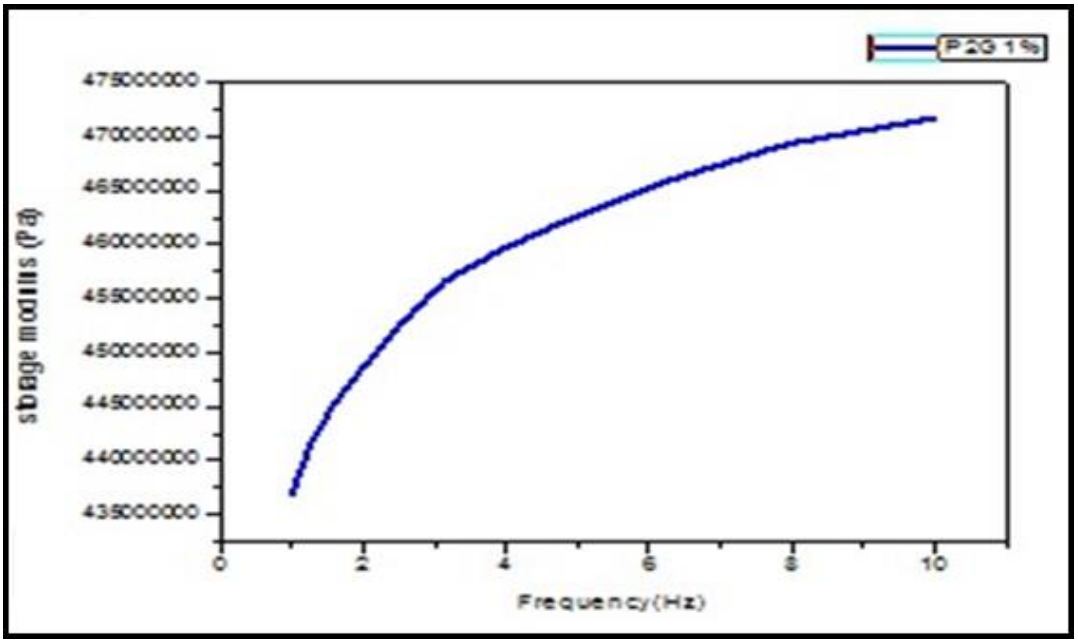


fig 4.3(g): P2G1%

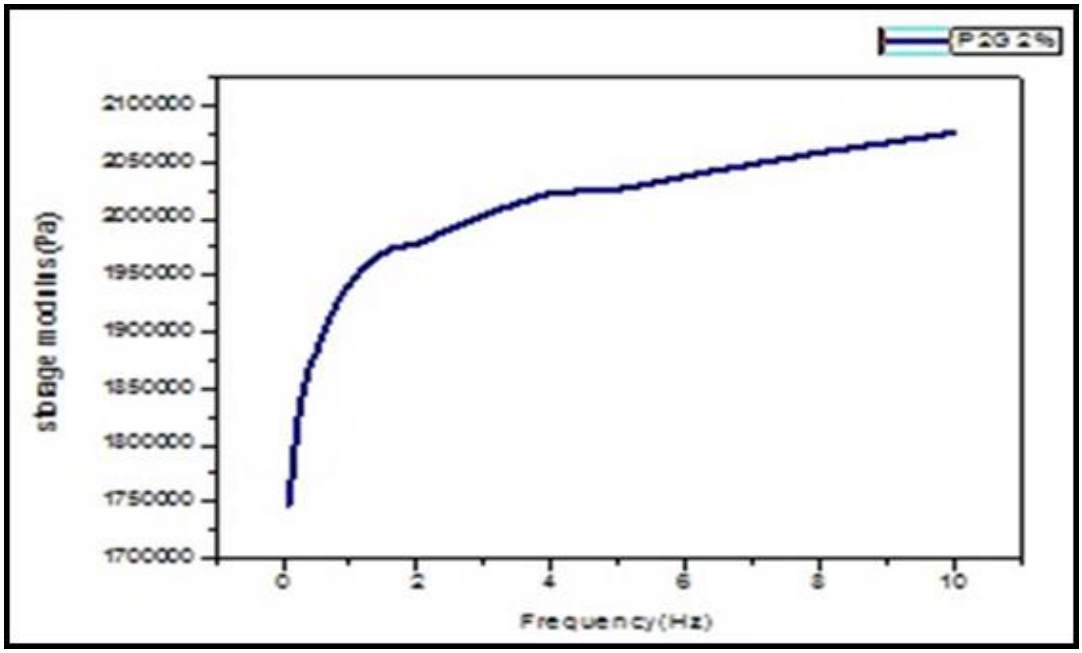


fig 4.3 (h): P2G2%

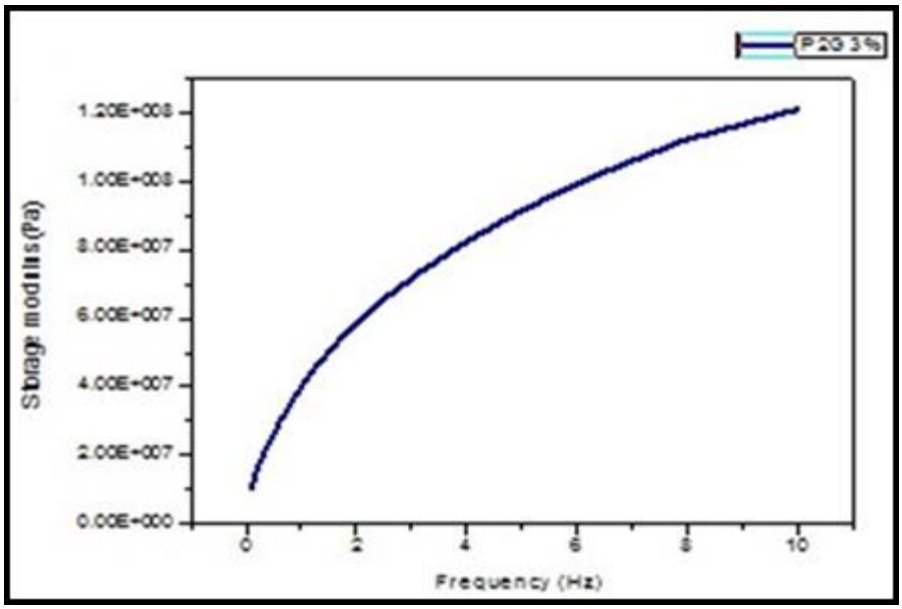


fig 4.3 (i): P2G3%

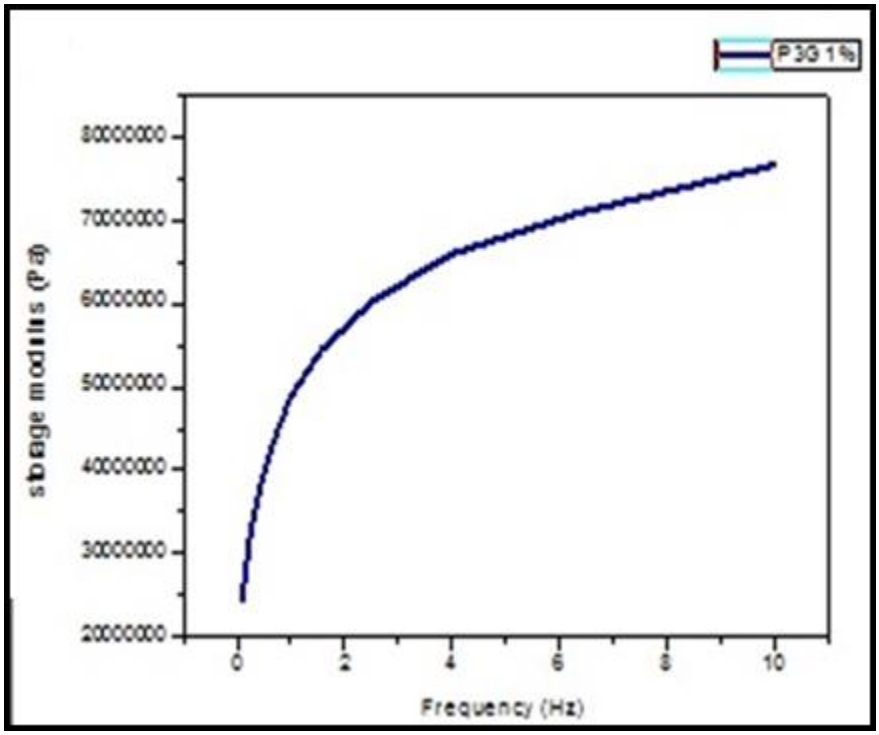


fig 4.3 (j): P3G1%

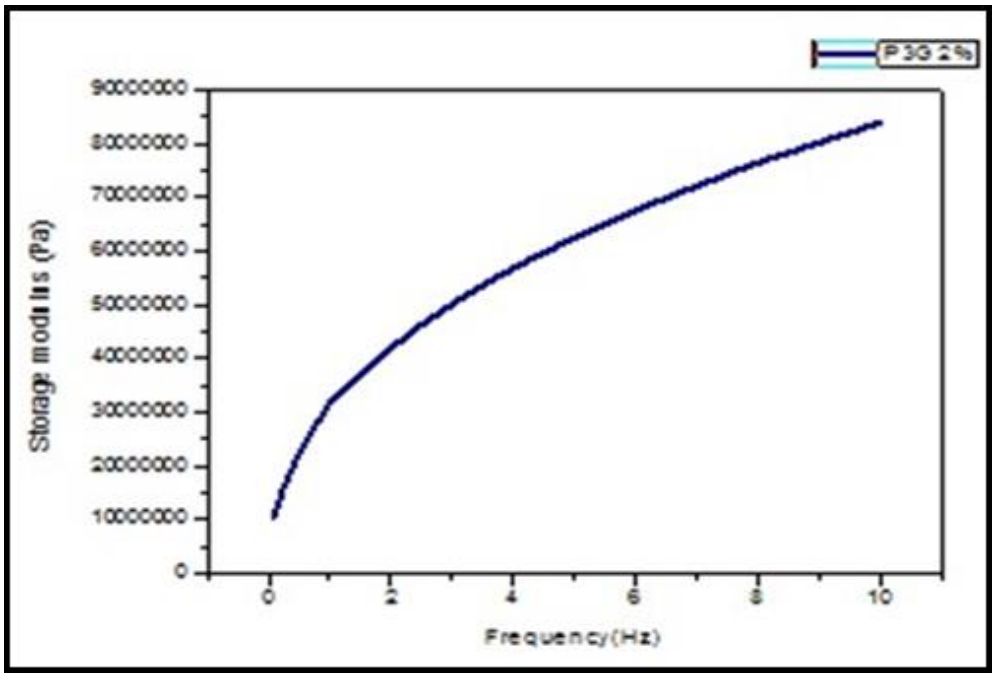


fig 4.3(k): P3G2%

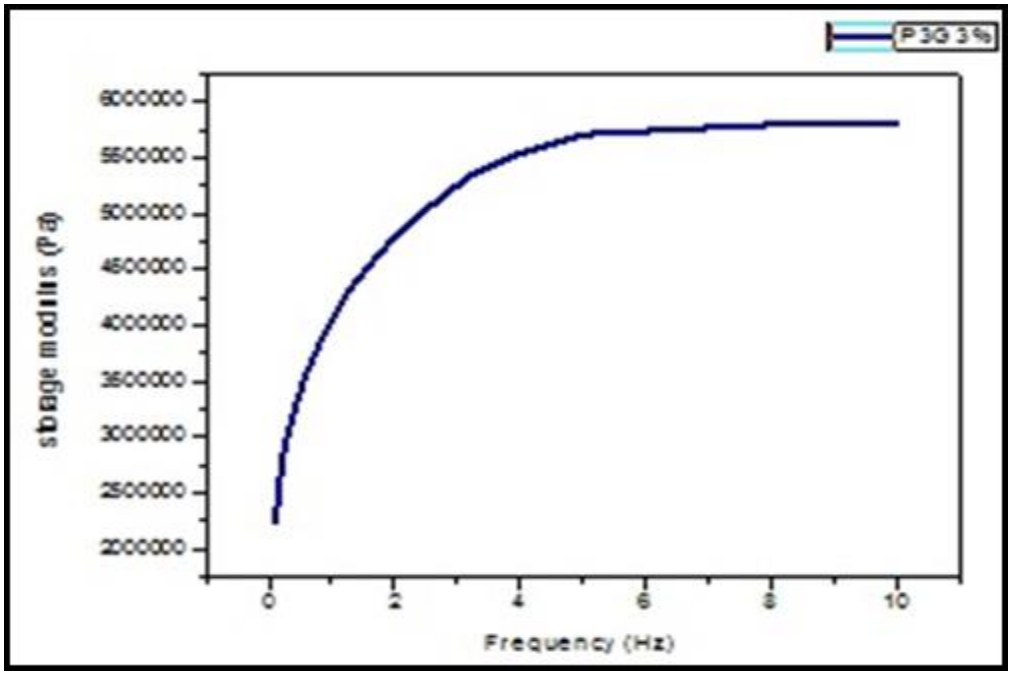


fig 4.3 (l): P3G3%

From the above results, it can be concluded that as frequency increases from 0.01 to 10 Hz the storage modulus also increases. This experiment was conducted at 40°C to resemble the temperature of hot areas.

As the frequency increases, It makes the polymeric chains to freeze giving the stiff behaviour. The storage modulus measures the elasticity or the stored energy given via frequency.

Moreover, different concentration of hydrogels (i.e with garlic juice and without garlic juice) shows same pattern of graphs proving that garlic didn't affect the mechanical properties of hydrogel.

Therefore, these results revealed that storage modulus is directly proportional frequency depicting that the hydrogel formed is of elastic nature, which can be further used in packaging industries.

4.4 WATER RETENTION MEASUREMENTS

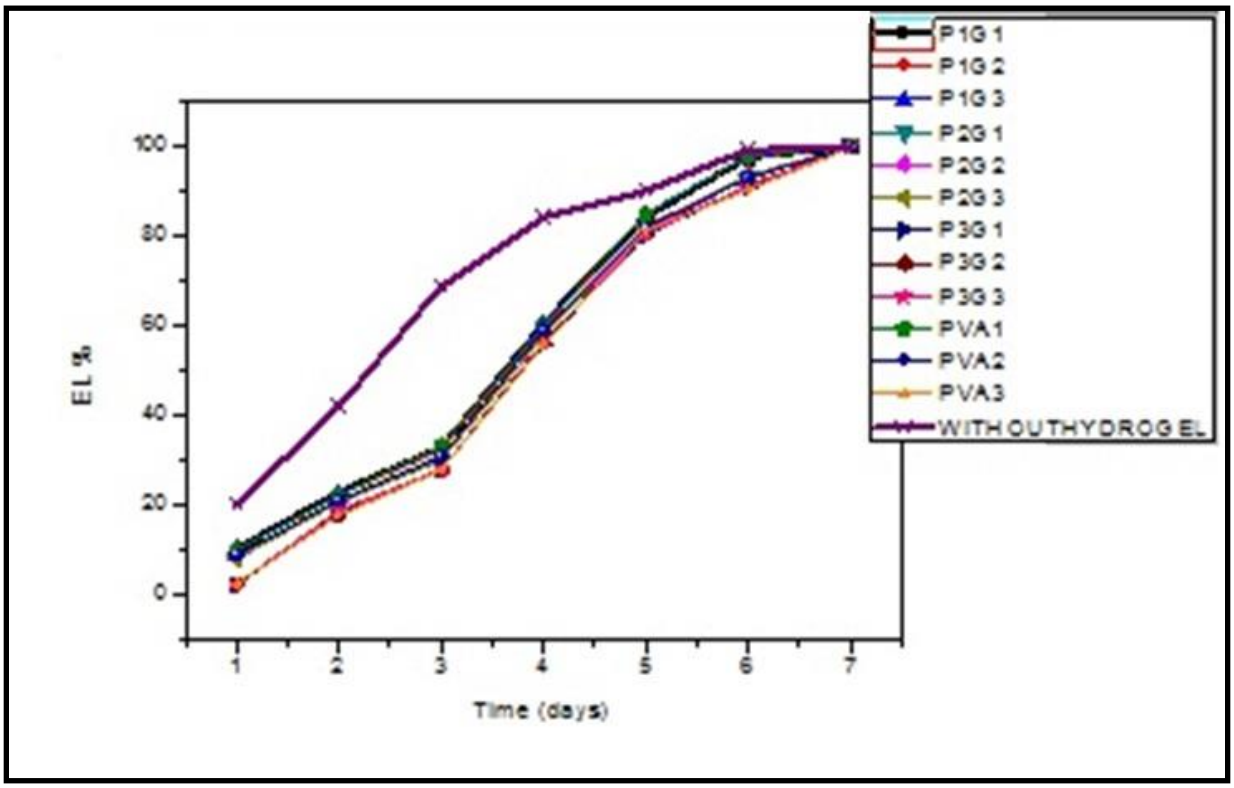


Fig 4.4 (a): comparative study of water retention of hydrogel in soil with no and different concentration of hydrogel

The results of water retention when evaluated it shows that the controlled one (i.e only water & sand) has more water evaporation rate as compared to those having hydrogels within them. Highest water retention was shown by hydrogel with PVA 3%,G3%, AAm 3.55gm, MAh 0.908gm, Crosslinker 0.5%.The maximum difference in percent of water evaporation loss with hydrogel P3%G3% and controlled is approximately 41%.By addition of hydrogel the evaporation rates decreases with quite good amount which is useful on farmlands which may act as a subminiature of water reservoir which retain water and provide moisture to crops .In this manner, it will provide benefits like increasing the water utilization efficiency, reduction in frequent irrigation and longer time for irrigation cycles.[13]

4.5 FOURIER TRANSFORM-INFRARED SPECTROSCOPY-

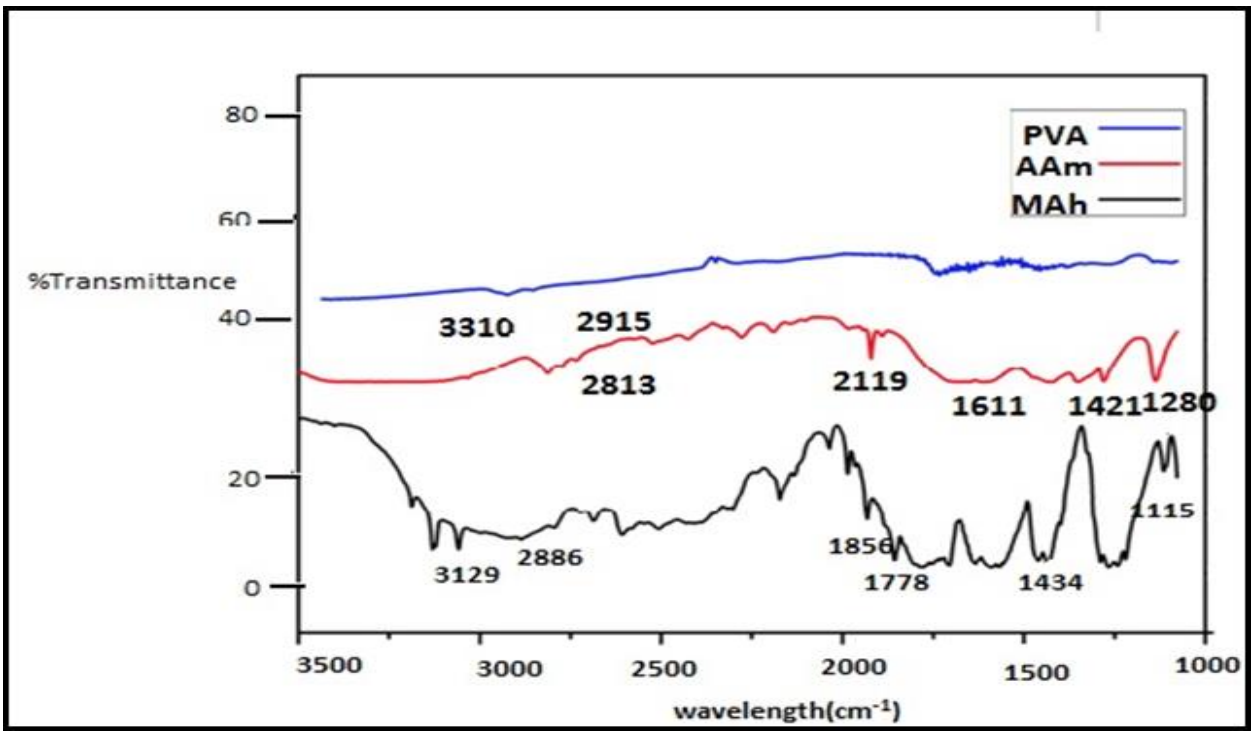


Fig 4.5(a): FTIR graph of PVA, AAm, MAh

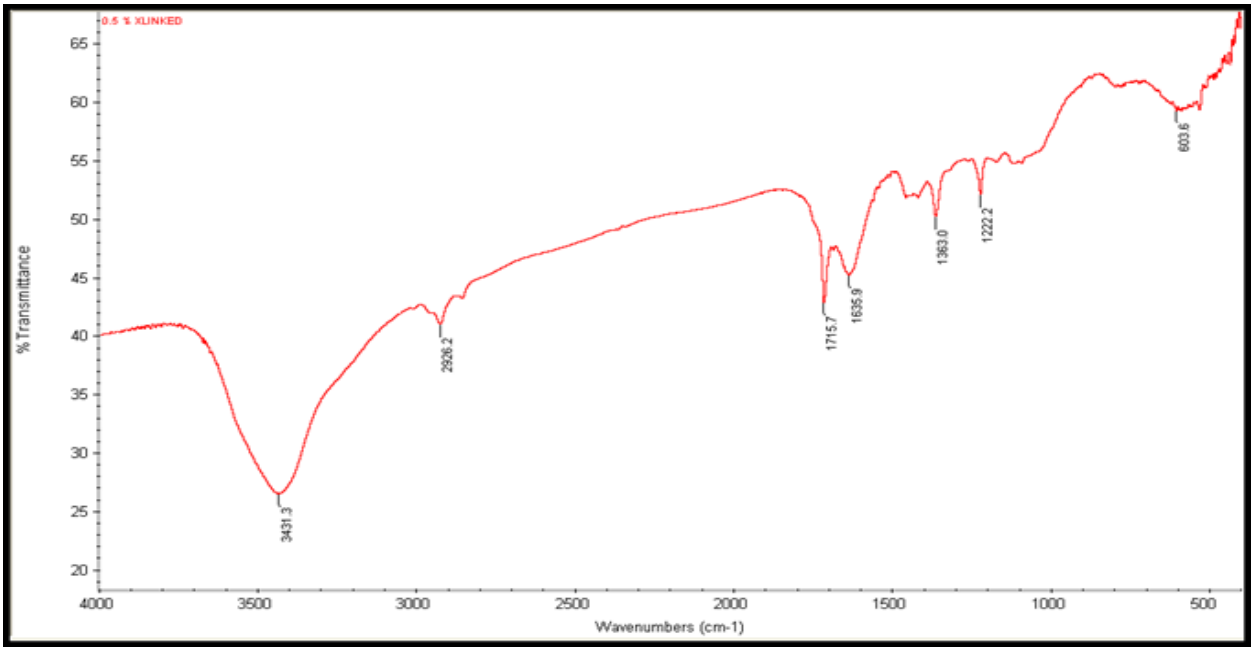


Fig: 4.5 (b): FTIR graph of Hydrogel of P(AAm-MAh) with 0.5% cross linker

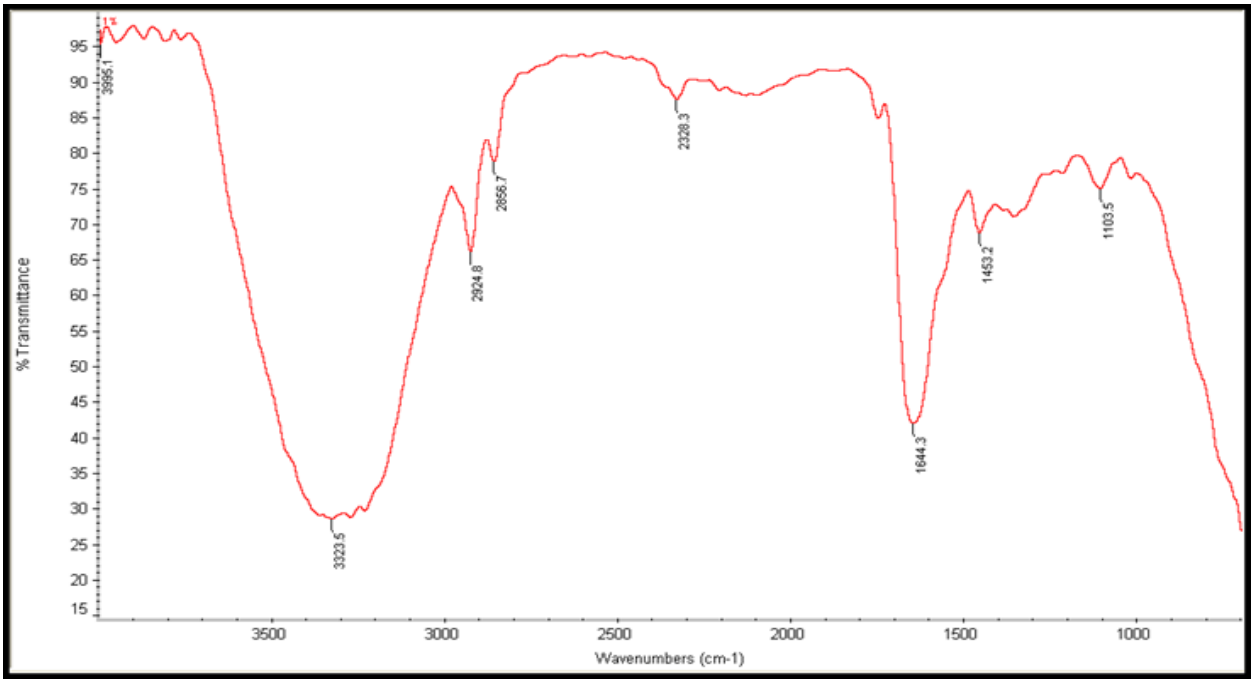


Fig: 4.5 (c): FTIR graph of hydrogel of PVA, P(AAm-Mah) with 0.5% cross linker

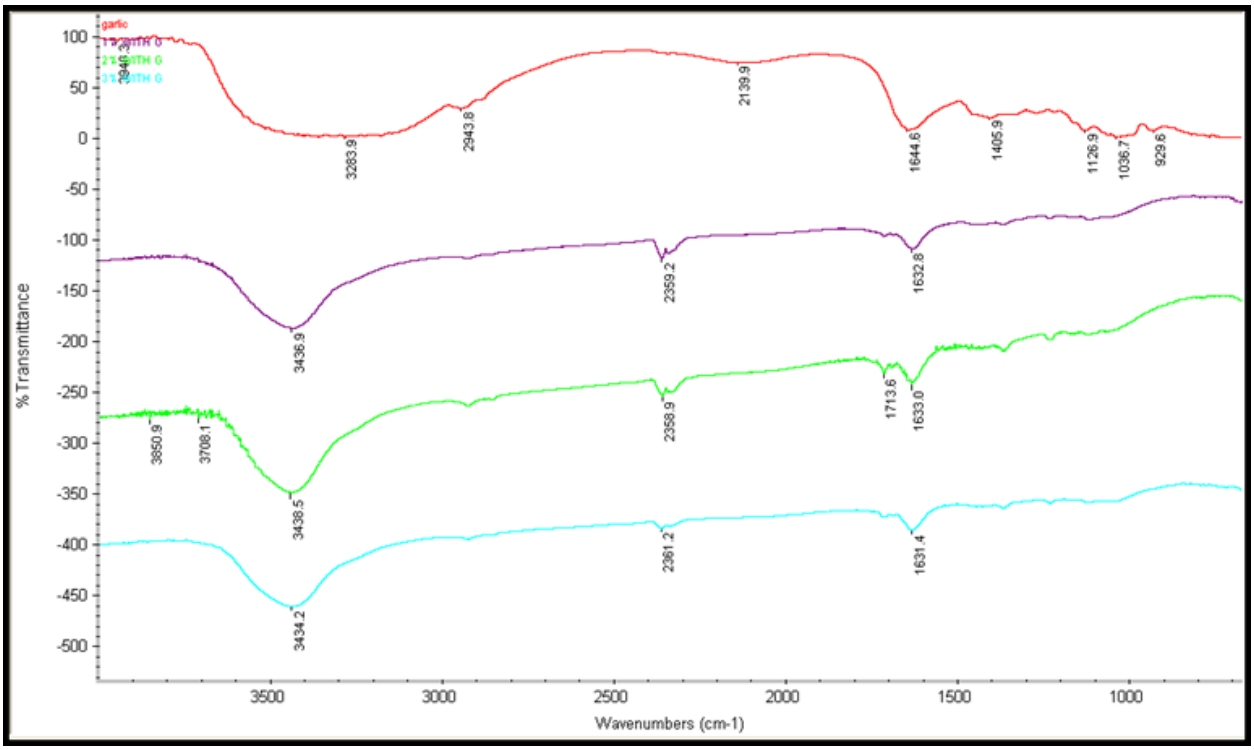


Fig: 4.5 (d): 1. FTIR graph of pure garlic juice, 2: FTIR graph of hydrogel incorporated 1% garlic, AAm, MAh, 1% PVA, 3: FTIR graph of hydrogel incorporated 1% garlic, AAm, MAh, 2% PVA, 4. FTIR graph of hydrogel incorporated 1% garlic, AAm, MAh, 3% PVA

FT-IR spectra of MAh, PVA and AAm were evaluated.

Fig (a) shows the individual spectra of PVA, AAm, MAh

In PVA spectra , the peak at 2915 is due to -CH bond, the stretching vibration bands appearing in the wave-number 3310 cm-1 were due to OH groups .

In Acrylamide spectra, the peak 3319 is due to -NH stretching of acrylamide group, 2813 cm is due to -CH stretching of bond, the peak at 1611 is due to -C=O and that of 1421cm is due to carboxylate group.[12]

In maleic anhydride spectra, the peak at 3129 cm is due to aromatic stretching of maleic anhydride functional group , and that of -C=O is due to two carbonyl group present in maleic anhydride. The peak at 1434 cm is due to -C=C- bond and that of -C-O is coming at 1115 $cm^{-1.}$

In fig (b) FT-IR spectra of MA, and PAA-MA were evaluated, as presented in 0.5% cross linker FTIR.[12]

In these spectra, the stretching vibration bands appearing in the wave-number range 2400-3500 cm-1 were due to NH and COOH groups in PAA-MA hydrogel. [12]

This wide wave-number ranges made it a broad band due to some intramolecular hydrogen bonding in the copolymer. When MAh is introduced into this copolymer, these peaks have increased in its intensity gradually with the increasing of COOH groups of maleic acid. The peak at 1715 cm^{-1} appears and characteristic for carbonyl group (C=O) stretch and for amide (CO-NH2) and carboxylic (COOH) groups absorption.The peak at 2926.2cm^{-1} is due to C-H bond. Cyano group (C-N) on the chains of PAA-MA give absorption band at 1363.0 cm^{-1} while the peak at 1222 cm-1 can be attributed to (C-C) stretching vibration along the copolymeric chain structure. The very important difference, in the result of FT-IR for the prepared hydrogel was seen the vinyl (C=C) which appeared at 1635.9 cm^{-1} streatching vibration for PAA-MA spectrum [3].It is noticed that the peak around 1860 and 1780 cm^{-1} both disappeared confirming that anhydride is converted into acid and hydrogel of P(Acrlyamide-co-maleic acid) has been prepared under given reaction conditions[2].

In fig (c), The hydrogel spectra of PVA AAm, MAh, the peak at 3323 cm^{-1} is due to clubbing of -OH and -NH group and peak at 2924 cm^{-1} and 2858 is result of -CH and -CH2 bond and that of -C=O is at 1644 cm^{-1}. The peak observed at 1453cm^{-1} is due to -CN bond and -C=C- and peak at 1103 cm^{-1} is result of -C-O bond.[12]

This result of FT-IR proves that maleic anhydride is hydrolysed to maleic acid as the peak present due to -C=O at 1856cm^{-1} and at 1778cm^{-1} disappeared when hydrogel spectra was studied and it may also proves that PVA form an interpenetrating network with poly(acrylamide-co-maleic acid) as -OH peak which was in pure PVA was also present in hydrogel spectra. and all the other peak is coming at approximately at same point as in hydrogel of poly(acrylamide -co-maleic acid).[12]

In fig (d) (1) represent the FT-IR spectra of pure garlic extract. The bands at 929 cm^{-1} are assigned to SOS disulfide stretching in proteins.The band at 1036 cm^{-1} is assigned to phenylalanine. The band at 1,136 cm^{-1} is assigned to cellular nucleic acid.The band at 1,405 cm^{-1} is assigned to CH2 stretching of phos-pholipids. The band at 1,644 cm^{-1} is assigned to amide [16]. The peak at 2139 cm-1 is of allicin present garlic responsible for antimicrobial activity. The peak at 3283 cm-1 and 2943cm-1 is due to -OH and -NH group.[20]
The fig (d) (2),(3),(4) represents the spectra of hydrogel incorporated garlic, AAm, MAh, PVA. This figure represent that due to having same group common between several compound used it shows only one peak of that single. The peak at 3430-3440 cm-1 represent the clubbing of -OH and -NH group and 2350-2390cm-1 represent the presence of allicin group of garlic, the peak at 1620 -1640 cm-1 represent the -C=O.group.The FT-IR results also justify that there was no major structural change in the hydrogel polymer.

4.6 BIOLOGICAL SCREENING

4.6.1 *Agrobacterium tumefaciens*

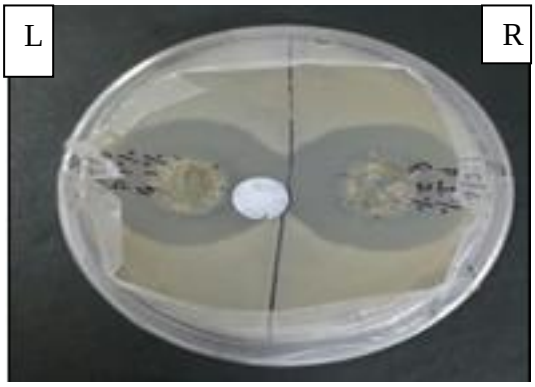


Fig 4.6.1(a): L:P1G1%, R: P1G2% (Growth of inhibition against *Agrobacterium tumefaciens*)

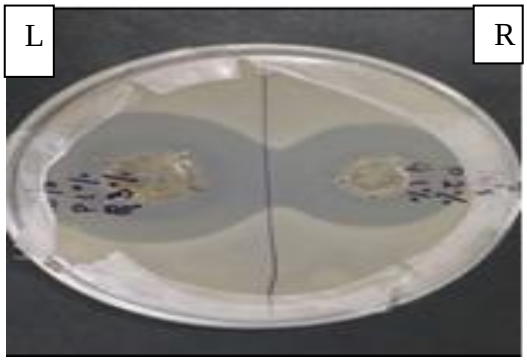


Fig 4.6.1(b): L:P1G3%, R :P2G2% (Growth of inhibition against *Agrobacterium tumefaciens*)

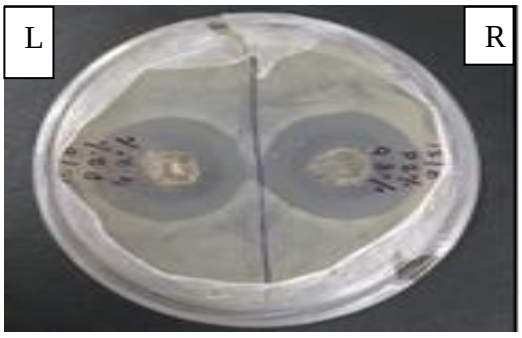


Fig 4.6.1(c): L:P2G2%, R: P2G3% (Growth of inhibition against *Agrobacterium tumefaciens*)

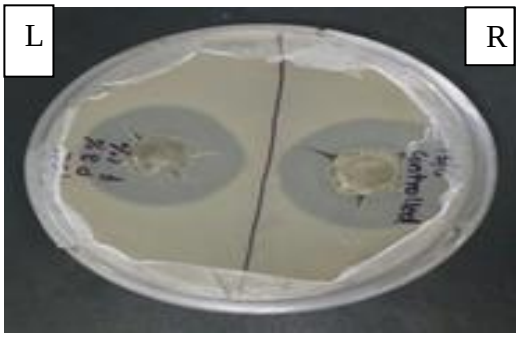


Fig 4.6.1(d): L: P3G1% R: Unloaded drug hydrogel (Growth of inhibition against *Agrobacterium tumefaciens*)

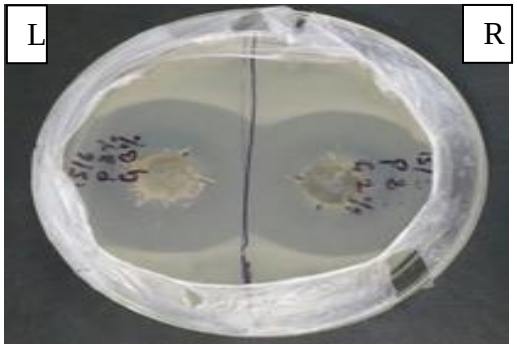


Fig 4.6.1(e): L:P3G3%, R:P3G2% (Growth of inhibition against *Agrobacterium tumefaciens*)

As per the below results antimicrobial test gives the positive results against *Agrobacterium tumefaciens*, thus forming the zone of inhibition of different diameter

In control the disc of pure PVA is taken which shows no inhibition but in figure it seem it has some inhibition that is not inhibition but the hydrogel expands due to which bacteria didn't grow in that part of plate

While other disc loaded with garlic shows the inhibition towards plant pathogen called *Agrobacterium tumefaciens* which usually attack fibrous crops like pigeon pea etc. And it also shows that it mainly rely upon garlic concentration.

Table 4 : Zone of inhibition with different concentration of PVA and garlic against Agrobacterium tumefaciens

DESIGNATION	HYDROGEL DISC DIAMETER(cm)	ZONE OF INHIBITION(cm)
P1G1%	1.5	2.3
P1G2%	1.5	2.4
P1G3%	1.5	3
P2G1%	1.2	2.2
P2G2%	1.2	2.5
P2G3%	1.2	3.1
P3G1%	1.3	2.3
P3G2%	1.3	2.5
P3G3%	1.4	3.1

4.6.2 *Escherichia coli*

Fig 4.6.2 (a): Unloaded drug Hydrogel(Growth of inhibition against *E.coli*)

Fig 4.6.2 (b): P1G1%(Growth of inhibition against *E.coli*)

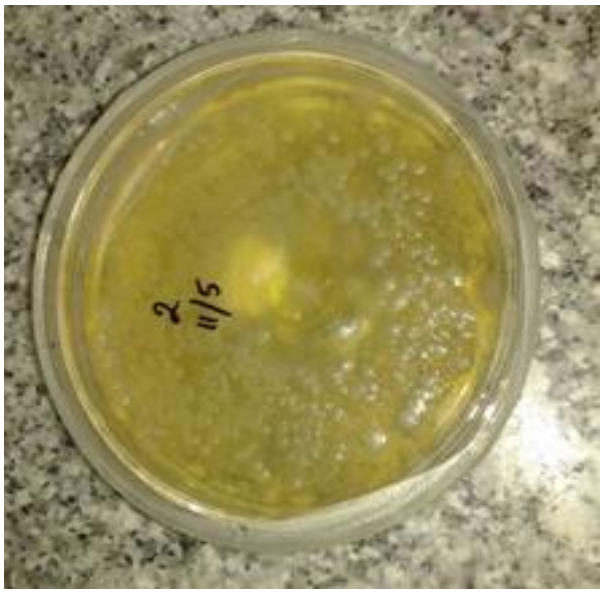


Fig 4.6.2 (c):P2G1%(Growth of inhibition against *E.coli*)

Fig 4.6.2 (d):P3G1%(Growth of inhibition against *E.coli*)

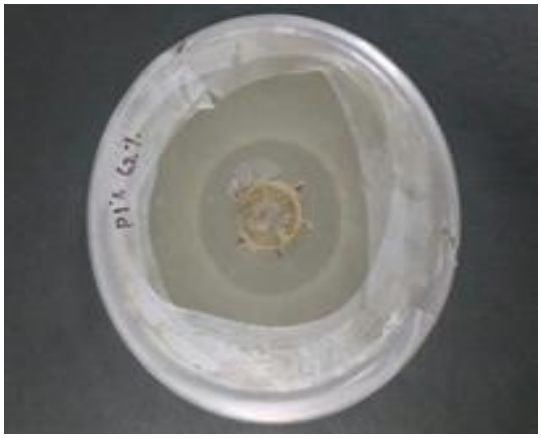


Fig: 4.6.2 (e): P1G2% (Growth of inhibition against *E.coli*)

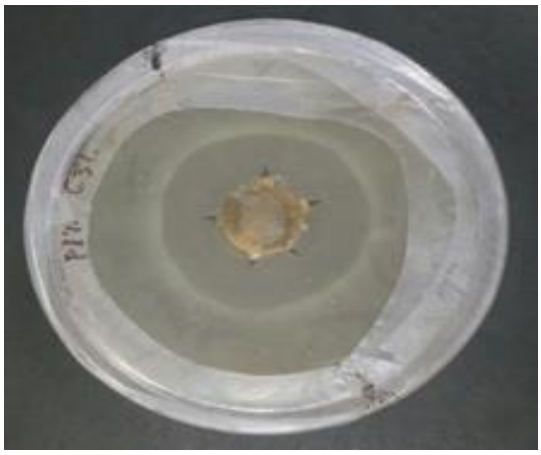


Fig: 4.6.2 (f): P1G3%(Growth of inhibition against *E.coli*)

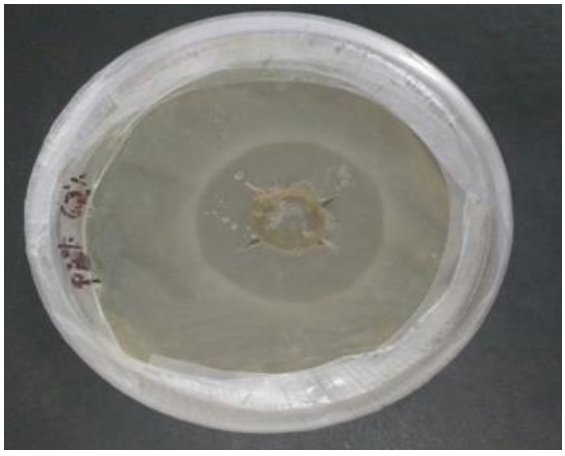


Fig: 4.6.2 (g): P2G2% (Growth of inhibition against *E.coli*)

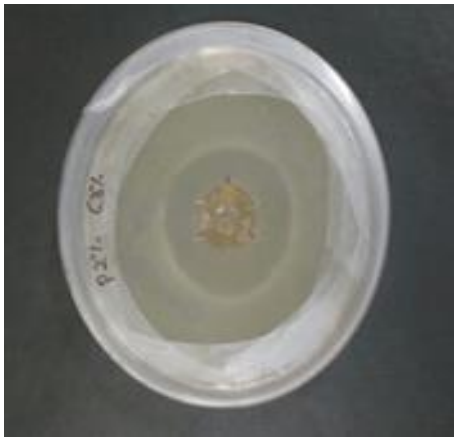


Fig: 4.6.2 (h): P2G3% (Growth of inhibition against *E.coli*)

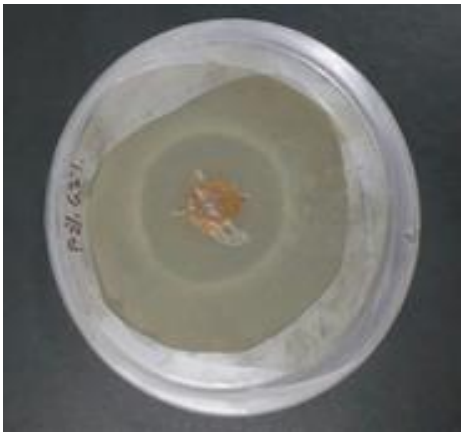


Fig: 4.6.2 (i): P3G2% (Growth of inhibition against *E.coli*)

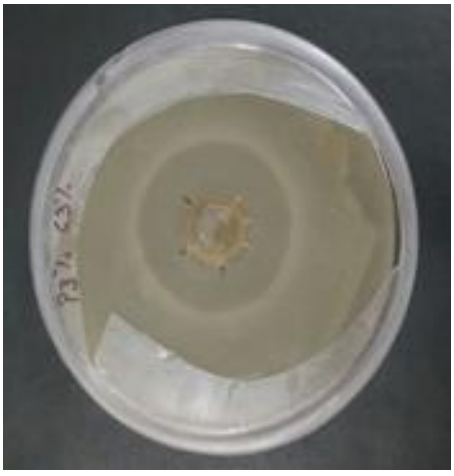


Fig: 4.6.2 (j): P3G3% (Growth of inhibition against *E.coli*)

According to the below mentioned results, antimicrobial activity against *E.coli* gives the positive result and giving different diameters for zone of inhibition. *E.coli* is the common bacteria for urinary infection.

For controlled disc of pure PVA is taken, showing no zone of inhibition, while the *Allium sativum* juice loaded hydrogel clearly shows the zone of inhibition with varying diameters provided by *Allium sativum*.

Table 5: Zone of inhibition with different concentration of PVA and garlic against E.coli

DESIGNATION	HYDROGEL DISC DIAMETER(cm)	ZONE OF INHIBITION(cm)
Controlled	1.5	NO INHIBTION
P1G1%	1.5	0.6
P1G2%	1.5	1
P1G3%	1.5	1.5
P2G1%	1.4	1.7
P2G2%	1.2	2
P2G3%	1.3	1.9
P3G1%	1.5	1.6
P3G2%	1.3	1.8
P3G3%	1.3	1.9

5. CONCLUSION

Indian Economy is largely depend on agriculture, still for one of the most important agriculture input country depends upon rainfall which is uncertain, unreliable and erratic in India. In addition sandy soil is unsuitable for agricultural purpose as the water retention property of sandy soil is very poor.

Also, Pathogenic microorganisms pose a big threat towards food production. Meanwhile, negative impacts on humans and environment are seen by the use of Chemical pesticides. Some experiments have shown that the pesticides can be very toxic to a wide range of soil microorganism. Pesticides can be directly toxic for non-target microorganisms or indirectly by killing or reducing the amount of organisms that are food for others. In some cases both direct and indirect effects are observed.

keeping these points in view, hydrogel is designed which overcome both problems of irrigation by providing regular watering to soil and also providing antimicrobial activity to soil by using *Allium sativum* juice. Being the natural product it doesn't degrade the quality of soil, non- toxic to human health and environment.

The result shown by study of optimisation of crosslinker is the optimized value for N,N'MBA concentration with respect to maximum swelling was 0.5wt% for IC(0.1) to IC(3). Thus the optimum crosslinking conducive to maximum percent swelling (1092%) was obtained with 0.5wt% [N,N'MBA] for IC(0.1)to IC(3) and after increasing [N,N'MBA] the network structure became denser resulting in decrease in swelling capacity. In enhancing the swelling properties based on Maleic anhydride, Acrylamide and polyvinyl alcohol were synthesised by using optimised N,N'MBA as crosslinking agent. The FTIR spectra demonstrated that the AM monomers were successfully cross-linked onto the maleic acid as maleic anhydride is converted into maleic acid in presence of water and polyvinyl alcohol is penetrated between the chains of acrylamide and maleic acid. The effect of reaction parameters, i.e [PVA] on swelling behavior were investigated with optimised crosslinker. The maximum percent swelling (1409%) was achieved under the optimum reaction conditions, which were found to be: 3.55 gm [AAm],

0.908gm [MAh], 3% [PVA], 0.5wt% [N,N'MBA] and 0.0445 gm [KPS]. When the concentration of PVA increased, the percentage swelling of hydrogel increased in comparison to hydrogel without PVA. The percent increased in swelling is approximate to 300%. P(AAm-MAh-PVA) has great potential to improve its antimicrobial activity by incorporating antimicrobial natural agents. Biological screening of hydrogel matrices incorporated with product of natural origin (*Allium sativum*) shows positive results against plant pathogen (*Agrobacterium tumefaciens*) as well as against human pathogen (*Escherichia coli*) without affecting swelling behaviour of matrix.

FTIR confirms the formation of desired hydrogels. From thermal analysis it is found that formed hydrogels remain unaffected from environmental stresses during the period of study of 2 months. The hydrogel with 3% PVA, 3% *Allium sativum* juice, 0.5% crosslinker, 3.55gm acrylamide, 0.908gm of maleic anhydride shows best results amongs all the formed hydrogel as zone of inhibition in this hydrogel against agrobacterium tumefaciens is 3.1 cm while against *E.coli* is 1.9 cm and it also shows highest water retention measurement. The maximum difference in percent of water evaporation loss with hydrogel PVA3%, *Allium sativum* juice3%, and one without hydrogel is approximately 41%.

In Agriculture the formed hydrogel can act as a sub miniature of water reservoir which decrease the irrigation cycle and it also provide antimicrobial activity for protection of crops from pathogens and also reduce the soil pollution, environmental pollution and health problems. The current study can lead to develop a new class of hydrogels that can be a boom for agriculture field.

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