CHAPTER - 1

INTRODUCTION
## CHAPTER 1
### INTRODUCTION

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1.01 INTRODUCTION

Science and technology have moulded the destiny of mankind, right from the invention of the wheel, production of fire and metals, alloys and paper to the development of gunpowder, steam engine and lately harnessing the energy of the atom. Iron and steel are increasingly being phased out in favour of plastics.

The large variety of polymers used today, e.g., rubbers paints, adhesives, films, membranes, automobile parts to name a few, are derived from petroleum. Only a small percentage of polymers used today are bioderived. The reason behind this is that natural polymers have an arbitrary structure and structural modifications or manipulations are not easy to come by.

The properties of a polymer greatly depend upon the individual atoms and functional groups on the polymer. The synthesis of polymers from simple chemicals derived from petroleum afford the potential to produce enormous range of products with the desired properties. For example, when we consider the polymers used in medical science, the materials required should be body compatible, soft and wet and do not deform under stress. These materials should also show response to external changes. Scientists have been successful in preparing such materials called as polymer gels.

Polymer gels consist of an elastic crosslinked network and a fluid occupying the interstices of the network. Conventionally, when the fluid is oil, the polymer gel is called as a lipogel or an organogel and when the fluid is water, the term ascribed to it is hydrogel.
Thus, hydrogels are water swellable, partially crosslinked polymeric structures. They are prepared by simple reaction of one or more monomers or by association bonds like hydrogen bonds and strong van der Waals' interactions between polymeric chains [1]. In recent years, there has been a virtual explosion of research and development on hydrogels in the consumer oriented field. Interestingly, one can trace the origin of the applicability of hydrogels to the early press releases of the US Department of Agriculture (USDA) during the 1970's [2-5].

Recently, excellent reviews on hydrogel applications have been published. Osada and Gong [6] have extensively reviewed the biomedical applications of hydrogels. Stimuli responsive hydrogels which show photochromic, electrochromic and photovoltaic behaviour have been reviewed for their applications as energy conversion or chemomechanical materials in this review. Earlier reviews like the classical book by Andrade [7] reviewed the biomedical applications of hydrogels till 1975. These were followed by Gross [8], Mack and coworkers [9], Roorda et al. [10], Kalal et al. [11], Pillai et al. [12] and Heitz et al. [13], where different aspects like synthesis, structure of hydrogels and their characterization have been presented.

1.02 APPLICATIONS OF HYDROGELS

There has been a burgeoning awareness during the last thirty years about many advantages of using polymers where they were previously considered unsuitable. A great deal of research has gone in to create polymers to cater the demands for these
specialized applications. Much of the modern technology would have been impossible without their use [14]. These polymers have a unique confluence of properties for a specific application and this is what makes them speciality polymers.[15]

Hydrogels play an important role as biomaterials probably due to the large amount of water imbibed by them and the lack of interactions between the swollen hydrogel boundary and the dissolved biopolymers and cellular elements. Holly and Refojo [16] have compared the properties of poly (2-hydroxyethyl methacrylate) or (poly 2-HEMA) with those of biosurfaces and found many similarities. Their increasing use in biomaterials is evident by the large number of products involving hydrogels in biomedical applications.

Andrade et al. have reported the use of poly HEMA hydrogels prepared by radiation technique for artificial heart components [17]. Hoffman et al. also have prepared radiation grafted hydrogels from various monomers for applications in blood tissue compatible materials, artificial heart components and kidney prostheses [18-23]. Hydrogels as blood compatible interfaces have been proposed by Kearney et al. [24]. Meaburn et al. have reported the use of poly HEMA hydrogels as burn dressings [25]. Several other workers have reported hydrogels as promising materials for burn dressings [26-35], contact lenses [36] and enzyme and cell immobilization [37-41].

Crosslinked polymer gels which switch on and switch off the supply of drug or biomolecules have been developed by Hoffman and
coworkers [42, 43]. Similar gels were reported by Kim et al. prepared from N-isopropylacrylamide and butyl methacrylate [44, 45] for modulated drug delivery.

Apart from the biomedical applications, these polymers are also being used as urban flood control agents, artificial snow, in-pocket warmers, ice substitutes in food industry, sealents in construction industry and communication systems and fire extinguishing agents [46]. On the domestic front, the largest market for hydrogels lies in diapers, sanitary napkins and adult incontinence briefs [47-53].

Marchetti and Cussler [54] have used hydrogels for concentration of heat sensitive biomolecules. A Japanese patent describes hydrogel toys that swell to large volumes on immersion in water [55].

A promising application of hydrogels lies in their use as water retainers in soil. Hydrogel granules in soil, absorb rain or irrigation water and form millions of reservoirs from which the plants can derive water as and when needed during the absence of rains [56,57,58]. Many commercial hydrogels are available for agronomical applications.

1.03 ORIGIN OF HYDROGELS

Although their evolution as hydrogels occurred around the 1970's, synthetic water absorbent polymers can be found in literature as early as 1938. W. Kern described the synthesis of copolymers of acrylic acid with divinyl monomers [59]. Eliot synthesized a crosslinked carboxymethyl cellulose capable of
water absorption [60] followed by Reid in 1968, who reported the synthesis of polysaccharide based water absorbents [61]. In 1954, F. Bayer obtained a British patent on carboxylate ion based polymer, swelling 500 times in sodium bicarbonate [62]. Markus patented a synthesis method for swellable polyelectrolytes using magnesium sulfate [63]. Synthetic polymers for fire extinguishing were patented by the Dow Chemical Company. These were gels of crosslinked poly (potassium acrylate) [64,65]. The advent of non ionic hydrogels was brought about by Union Carbide with its poly (ethylene oxide) crosslinked by radiation [66]. Acrylic hydrogels were found to be useful in domestic purposes according to Harmon [67] and Harper [68,69].

The mid seventies witnessed a number of patents based on agronomy applications of hydrogels. The USDA patented a super absorbent polymer called as "Super Slurper". This polymer was typically a saponified product of starch grafted (poly) acrylonitrile. A trivial name HSPAN was assigned to this class of hydrogels which was an abbreviated form of hydrolysed starch grafted poly acrylonitrile. This polymer was supposed to absorb thousands of grams of water per gram of polymer [70-74].

Sumikagel, a product of Sumitomo Chemical Company was prepared by copolymerization of vinyl acetate and methyl acrylate. On saponification of the polymer the resultant mass was swellable, though it remained insoluble in water due to the presence of crystalline regions of poly (vinyl alcohol). The product was claimed to be flexible and transparent [75,76].
Literature reveals a series of commercial products put in the market. Prominent amongst them are Gelguard from the Dow Chemical Company reported in 1966 [64], Viterra, a nonionic hydrogel from Union Carbide [77] in 1976 followed by DWAL, in 1978 [78] produced by the Dow Chemical Company. This polymer was expensive and had other inadequacies because of which the production of DWAL was phased out in 1985. The National Starch and Chemical Co. put forward Permasorb absorbent [79] while in 1983, Kurary Company Ltd., introduced Ki-Gel which was a poly amine crosslinked poly (isobutylene co-maelic anhydride) [80].

Other developments include hydrogels for cell culture substrates, in a patent by Union Carbide in 1990 [81] by Anderson. A Polish patent by Penczek [82] describes hydrogels synthesized from water soluble epoxy resins and poly amines. Enzyme digestible hydrogels by Park [83,84] from albumin as well as chitosan based hydrogels containing N-acetyl-D-glucosamine chains by Pangburn et al. [85] have been put forward.

Tubular specimens of hydrogels of poly (ethylene oxide) star polymers [86] and even guar gum based hydrogels [87] have been put forward for biomedical applications.

Poly urethane based hydrogels using Bipol/Hypol in aqueous acetone solutions have been reported by Hahn [88] and N-vinyl pyrrolidone hydrogels by free radical polymerization by Wolf [89]. Hydrogels have been found to have applications in ink jet recording according to a patent by Artherton [90]. Injectable polysaccharide cell hydrogels have been reported by Griffith et al. for reconstitutive procedures [91].
Hydrogels are characterised by a pronounced affinity for water due to their chemical structure. They do not dissolve in water but swell moderately. Basically absorbent polymer science is an extrapolation of water dispersible polymer technology. Thus when a xerogellent i.e., a hydrogel polymer in its dry state, is placed in water, the same forces responsible for dissolution of water soluble polymers become active. Since the polymer cannot dissolve, it appears to take up water and swell.

Absorbency results due to the presence of water loving polar groups present along the polymer chains. Often called as water solubilizing groups, strong interactions between these polar groups like -COO\(^-\), -OH, -CONH\(_2\), -SO\(_3\)\(^-\) etc. and water, provide the driving force responsible for the entry of water molecules into the polymer matrix. However, the swelling or water absorption does not continue infinitely. Swelling is controlled or limited by forces that restrict the expansion of the matrix, for example chain mobility or flexibility and a network structure. Factors that govern hydrogel swelling are listed in table 1.01.

Cohesive forces like hydrophobic interactions and increased crosslinking density are countered by dispersive forces like high hydrophilicity, osmotic potential etc. When these forces exactly balance each other, an equilibrium is established. A hydrogel can

7
TABLE 1.01 Factors affecting hydrogel swelling [92]

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<thead>
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<th>Disfavour swelling</th>
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<td>Dispersive forces</td>
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<td>Hydrophobic groups</td>
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<tr>
<td>Low crosslinking density</td>
<td>High crosslinking density</td>
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<tr>
<td>High chain mobility</td>
<td>Low chain flexibility</td>
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<tr>
<td>High free volume</td>
<td>Low free volume</td>
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<tr>
<td>Osmotic potential</td>
<td>Dipole-dipole interaction</td>
</tr>
<tr>
<td>Electrostatic repulsion</td>
<td>Presence of foreign ions in fluid</td>
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fig. 1.1 SEM of a poly acrylamide hydrogel at 5800 X magnification.
no longer absorb more fluid and this value is referred to as the equilibrium water uptake, absorbency or water holding capacity of the hydrogel under a given set of conditions. Fig.I. 1 shows a scanning electron micrograph of a swollen hydrogel polymer. Distinct are the large vacant areas where water can be accommodated, leading to high water absorption.

The swelling of hydrogels has been the object of thermodynamic analysis. Considering the physicochemical aspects responsible for swelling, the entropy or free energy factors need to be accounted for. When the polymer is in its dry state (xerogelent), all the chains are arranged in the most entropically favoured manner. When water molecules enter the polymer matrix, as shown in Fig. I. 2 the mass swells. Randomly oriented chains are stretched and reorganized. An ordered arrangement thus results in lowering the entropy of the system, which is not desirable and a force resisting this reordering comes into picture. When this force is exactly compensated for, or balanced by the osmotic driving force, an equilibrium is said to be established.

If we look closely, this force resisting the reordering is nothing but a factor restricting the chain mobility or flexibility. One of the most important factors that holds the chains together, inhibiting their movement is the crosslinking density. It can thus be clearly seen that higher the crosslinking density, smaller is the tendency of the chains to realign and lower is the water absorption or swelling.
fig. 1.2  Swelling and absorbency of hydrogel polymers.
1.05 EQUILIBRIUM SWELLING THEORY

The process of swelling a polymer is age old. Thousands of years ago, man used the pressure generated by swelling wood, to break large boulders. It was in 1935, that Staudinger first reported the swelling of synthetic polymers in solvents to form two component gels. The physical state of such systems undergoes transitions from a glassy state to a rubbery state and finally a gel state [95]. Thus for a hydrogel, the transitions are from a xerogel to a hydrogel, each state showing its own characteristic sorption kinetics.

The interactions between polymer and solvent have been interpreted in terms of colligative properties of the system, and the Flory Huggins theory [94] has been useful for the prediction of a large number of colligative properties. This theory recognizes the forces of molecular association responsible for the transition of a pure polymer and a pure liquid (solvent) into a solution of a two component system.

A hydrogel polymer swells in water, due to the chemical affinity of the polymers with water. This theory predicts the swelling of hydrogels, utilizing the interaction parameter between the two components. The swelling of hydrogels is limited by thermodynamic factors. It is said that when the restraining force (cohesive force) equals the osmotic pressure, an equilibrium swelling results. This happens when the chemical potentials of water in the polymer phase and the fluid phase are equal. In terms of osmotic pressure, an equilibrium swelling sets in when the net osmotic pressure is zero, as shown in equation 1.1 [94].
\[ \Pi_{\text{ion}} + \Pi_{\text{elas}} + \Pi_{\text{elec}} + \Pi_{\text{mix}} = 0 \quad ......(1.1) \]

Where \( \Pi \) stands for the osmotic pressure contributions due to concentration difference between ions in the gel and solution (\( \Pi_{\text{ion}} \)), elastic response of network (\( \Pi_{\text{elas}} \)), electrostatic interactions (\( \Pi_{\text{elec}} \)) and the tendency of polymer to dissolve in the fluid (\( \Pi_{\text{mix}} \)).

On substituting the values of individual terms in equation 1.1, using Flory Huggins theory, we get a comprehensive equation describing the equilibrium swelling of an ionic gel in a pure solvent as:

\[ \ln \left( \frac{1 - \nu_{2,s}}{1 - \nu_{2,r}} \right) + \nu_{2,s} \chi \left( \frac{\nu_{2,s}}{\nu_{2,r}} \right)^{1/3} - 0.5 \left( \frac{\nu_{2,s}}{\nu_{2,r}} \right) + \frac{\nu_{2,s}}{V_m} = 0 \quad .....(1.2) \]

Where \( \nu_{2,s} \) is the polymer volume fraction in the swollen gel, \( \nu_{2,r} \) is the polymer volume fraction after crosslinking, \( \chi \) the solvent polymer interaction parameter, \( \rho_x \) the crosslinking density, \( V_1 \) the molar volume of the fluid and \( V_m \) molar volume of the structural unit, while \( i \) stands for fraction of monomer units that are ionized.

The kinetics of swelling of hydrogel polymers has been described by Khare and Peppas [95]. The mass of water absorbed by a polymer at time \( t \) (\( M_t \)) was found to be a function of diffusion exponent \( n \) as:

\[ M_t = M_0 K t^n \quad ...... (1.3) \]
Where \( M_\infty \) is the equilibrium water uptake and \( K \) is a constant.

A measure of the ability of a polymer to swell is the molecular weight between crosslinks. It is observed that an increase in the molecular weight between crosslinks, increases the swelling or water absorption capacity of the polymer. Peppas and Peppas [96] have derived models that predict the swelling of polymers, utilizing the molecular weight between crosslinks. Equations (1.4) and (1.5) describe the swelling of lightly crosslinked anionic and cationic hydrogels respectively.

\[
\frac{V_1}{4l} \left[ \frac{f \: \nu_{2,s}}{\bar{v}} \times \frac{K_a}{10^{-pH + K_a}} \right]^2 = \left[ \ln \left( 1 - \frac{\nu_{2,s}}{\nu_{2,r}} \right) + \frac{\nu_{2,s} + \chi_1 \nu_{2,s}^2}{2} \right] +
\]

\[
\left[ \frac{V_1}{\bar{v} \: M_c} \right] \left[ 1 - \frac{2 \bar{M}_c}{M_n} \right] \nu_{2,r} \left[ \left\{ \frac{\nu_{2,s}}{\nu_{2,r}} \right\}^{1/3} - \frac{1}{2} \left\{ \frac{\nu_{2,s}}{\nu_{2,r}} \right\} \right] \ldots 1.4
\]

\[
\frac{V_1}{4l} \left[ \frac{f \: \nu_{2,s}}{\bar{v}} \times \frac{K_a}{10^{-pH-14 + K_a}} \right]^2 = \left[ \ln \left( 1 - \frac{\nu_{2,s}}{\nu_{2,r}} \right) + \frac{\nu_{2,s} + \chi_1 \nu_{2,s}^2}{2} \right] +
\]

\[
\left[ \frac{V_1}{\bar{v} \: M_c} \right] \left[ 1 - \frac{2 \bar{M}_c}{M_n} \right] \nu_{2,r} \left[ \left\{ \frac{\nu_{2,s}}{\nu_{2,r}} \right\}^{1/3} - \frac{1}{2} \left\{ \frac{\nu_{2,s}}{\nu_{2,r}} \right\} \right] \ldots 1.5
\]
Where, \( V \) stands for molar volume of swelling agent, \( I \) the ionic strength of swelling agent, \( f \) the fraction of ionizable groups on the polymer, \( \nu_2 \) the polymer volume fraction in the swollen hydrogel, \( \nu \) the volume of dry polymer (xerogel), \( K_a \) the dissociation constant, \( pH \) the ion concentration in swelling agent \( \chi \), is the polymer solvent interaction parameter, \( M_c \) is the average molecular weight between crosslinks, \( M_n \) the average molecular weight of initial polymer and \( \nu_2^r \) the polymer volume fraction in the relaxed network.

The judicious use of this equation requires prior knowledge of the various parameters like \( M_c, \chi, K_a \) etc. However, the beauty of the model lies in its capacity to predict swelling values of polymers in different solvents, at various \( pH \) values and degree of ionization of the hydrogel polymer. Knowing the swelling value, one can easily derive the values of crosslink density, \( M_c \) and \( M_n \), which change with the structure and chemical nature of the polymer, thus going a long way in elucidating structure activity relationships in hydrogel systems. Different types of crosslinking are shown in fig. I.3 [97].

1.06 CLASSIFICATION OF HYDROGELS

Polymeric materials presently being used as hydrogels are expressed in literature by a variety of names. Prominent amongst these are xerogellant, superabsorbent polymer (SAP), hydrocolloid [98], water swellable polymer, super sorber and aqueous gelling agent. Similarly hydrogels are classified by a number of different ways. Attempts have been made to classify...
fig. 1.3 Different types of crosslinking possible in hydrogel polymers.
hydrogels depending upon their method of preparation, physical features, ionic or polar charges and mechanical characteristics. As shown in Table 1.02, different classes of hydrogels are in use today.

Dave et al. [99] have classified them according to interactions of hydrogels with water as either discrete or continuous and cited examples of each type of hydrogel. This is essential to establish methodology of characterizing hydrogels, since most of the methods of assessing their physical properties hold good only for one type of hydrogel.

1.07 MONOMERS USED IN HYDROGEL SYNTHESIS

Polymeric hydrogels consist of macromolecules which are crosslinked to form a network structure or a three dimensional matrix. A limited number of monomers have been polymerized or copolymerized to obtain a large variety of hydrogels. Some of the common monomers used, are described here.

1.07.1 Acrylic or Methacrylic monomers

The basic structural unit can be summarized as:

\[
\begin{array}{c}
\text{H} \\
\text{R} \\
\text{C} - \text{C} \\
\text{H} \text{ COOR'}
\end{array}
\]

The global market of super absorbents is dominated by acrylic acid \((R, R' = -H)\). Other monomers like methacrylic acid \((R = -\text{CH}_3 R' = -H)\) and their derivatives are often used. Amongst
<table>
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<tr>
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<tr>
<td>Interactions with fluid [99]</td>
<td>o Discrete</td>
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<tr>
<td></td>
<td>o Continuous</td>
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<tr>
<td>Polar or ionic charges [100]</td>
<td>o Neutral</td>
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<td></td>
<td>o Anionic</td>
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<td>o Cationic</td>
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<td></td>
<td>o Zwitterionic or amphiphilic</td>
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<tr>
<td>Method of preparation</td>
<td>o Homopolymeric</td>
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<td></td>
<td>o Copolymeric</td>
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<tr>
<td></td>
<td>o Multipolymeric</td>
</tr>
<tr>
<td></td>
<td>o IPN [101]</td>
</tr>
<tr>
<td>Mechanical and chemical structure [102]</td>
<td>o Affine networks</td>
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<tr>
<td></td>
<td>o Phantom networks</td>
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<tr>
<td>Physical structural features [103]</td>
<td>o Amorphous</td>
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<td></td>
<td>o Semi crystalline</td>
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<tr>
<td></td>
<td>o Hydrogen bonded</td>
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<tr>
<td></td>
<td>o Supermolecular network</td>
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<td>o Hydrocolloidal aggregates</td>
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the hydrogel forming derivatives of acrylic and methacrylic acid
are the hydroxy alkyl esters of which, 2 - hydroxyethyl
methacrylate (HEMA) [104, 105] is of paramount importance
especially for the biomedical applications [106-108]. HEMA (R =
-CH₃ and R' = -CH₂-CH₂-OH) gives homogeneous, transparent and
pliable gels which are stable to chemical reactions like acid
hydrolysis [109], but suffer from a drawback of low mechanical
strength and an equilibrium water uptake, thermodynamically
limited to 40% [110]. The hydrophilicity of HEMA based hydrogels
can be increased by incorporating ether groups. Comonomers like
5- hydroxy -3- oxapentyl methacrylate (1) have been copolymerized
with HEMA by Ratner and Hoffman [111]. Vacik et al. copolymerized
HEMA with methacrylic acid (MAA) [112] to obtain highly porous
absorbents. The incorporation of weak acid groups results in an
increased polarity and favour swelling [113]. Strong acid groups
like sulphonic acid -SO₃H show enhanced hydrophilicity. Huglin
and coworkers [114] copolymerized HEMA with neutralized 2-sulfoxy
ethyl methacrylate (2) while cationic hydrogels using 2- (N, N-
diethylamino) ethyl methacrylate (3) have been reported by
Kossmehl et al. [115].

Other hydroxyalkyl methacrylates like hydroxy propyl
methacrylate, glycerylmethacrylate have also been studied. A
detailed review has been published by Witcherle et al. [116],
which describes different hydroxy alkyl methacrylates used in
hydrogel synthesis.
Amide functional group containing monomers.

Hydrogels containing amide functionality are not restricted to a low water uptake like HEMA hydrogels, and give optically clear and transparent hydrogels. However, they are weak mechanically and lack hydrolytic stability. Acrylamide based hydrogels can easily be prepared by solution polymerization of the monomer in presence of a crosslinking agent. Alternatively, gels can be produced by crosslinking the polyacrylamide chains using γ-rays, as mentioned by Burillo and Ogava [117]. Another method for synthesizing polyacrylamide gels containing low percentage of poly acrylonitrile and poly acrylic acid has been put forward by Kudela et al. [118], by polymerizing acrylonitrile in ZnCl₂ solutions, followed by careful hydrolysis of the nitrile groups to yield amide and carboxylate groups. Similar procedures have been reported in the literature [119-121]. A number of studies have been done to observe the hydrolysis of acrylamide and methacrylamide polymers [125-127]. The results have been interpreted in terms of hydrolytic stability or incorporation of ionic charges on the polymer chains due to hydrolysis.

Weiss and coworkers [125] have reported the synthesis of crosslinked polyacrylamide and studied the effects of kinetics of polymerization on the membrane properties of the gels. Extensive work has been done on the environment sensitivity of these gels. Amide based hydrogels have been reported to show phase changes associated with variations in temperature [126-130], electric field [131-137], solvent [138], pressure [139] and
intensity of incident light [140]. Amongst others are studies on swelling of amide based hydrogels by Piculell et al. [141], who reported copolymers of acrylamide with ethylene oxide, Kyoung and Jim on acrylamide-co-styrene copolymers [142], Hooper et al. on quarternary ammonium salts copolymerized with acrylamide [143] and Cohen et al. [144] who studied the morphology of these hydrogels in detail.

1.073. Vinyl Pyrrolidone based Hydrogels

N-vinyl pyrrolidone (NVP) (4) is a lactum substituted with a vinyl group. NVP yields polymers that are soluble in water and many other organic solvents. Aqueous solutions of poly NVP have been found suitable for oral or intravenous delivery with complete safety [145]. However, hydrogel synthesis using only NVP is not easy, as it requires a very high percentage of crosslinking agent to render it insoluble or impart hydrogel properties. A study by Davis [146] reports as high as 20% crosslinking agent required for NVP hydrogels suitable for drug delivery. NVP is thus more often utilized for increasing the hydrophilicity of hydroxy alkyl methacrylates [147-150]. NVP has also been copolymerized with ionogenic comonomers like acrylic acid [151] and quarternary ammonium ion salts [152] in a U.S. patent.

NVP has evolved an ideal candidate as a hydrophilic monomer in covalent surface grafting systems. Yasuda and Refojo [153] and Laizier and Wajs [154] have reported radiation grafted NVP hydrogels for biomedical applications. Nonpolar materials like
Polyethylene [155], poly methylmethacrylate [156], poly urethane and cellulose acetate [157] have been rendered hydrophilic by NVP grafting.

1.074. Hydrogels based on Polyvinyl Alcohol (PVA)

PVA, obtained by hydrolysis of polyvinyl acetate is a water soluble polymer, which yields hydrogels when crosslinked by crosslinking agents like glutaraldehyde [158-161], dicarboxylic acids [162], 2,4-toluene diisocyanate [163], epichlorohydrin [164]. etc. PVA also forms hydrogels by thermal treatment. Immelman, et al. [165-167], have reported interchain ester formation by thermal treatment of poly (vinyl alcohol)-poly (arylether sulfone) gel membrane. Radiation crosslinking has also been reported for synthesis of PVA hydrogels [168,169].

Applications of PVA hydrogels range from synthetic cartilage joints [168] to hemodialysis membranes [169]. Shiga et al. [170-173] and Nambu [174, 175] have widely reported on PVA hydrogels in biomimetic machinery systems.

1.075. Polyelectrolyte complex Hydrogels

Polyelectrolyte complex hydrogels or PEC hydrogels are formed on crosslinking linear polymer chains by ionic bonds or by coordinate complex formation.

Extensive work has been done on the ligands containing chromium (III) as the metal ion. The gelling of polymer can be controlled using chromium (III) salts, making these gels suitable for profile modification applications [176]. Lockhart et al. have used salts of chromium like Cr(malonate)₃, Cr(acetate)₃ [177]
CrCl₃ or Cr(NO₃)₃ [178, 179]. Others [180-182] have investigated chromium (III) as the crosslinking agent that binds chemically with carboxylate functional groups on the polymer chains. Similar metals like Zinc [183], Copper [184-187], Aluminium [188], Titanium [189], Cobalt and Nickel [187] have been exploited in studies on metal ion crosslinked gels.

A different type of PEC hydrogel consisting of a matrix like polystyrene containing ionic sulfonic acid groups is reported by Woermann using strontium (II) [190] and silver (II) [191] as the counterions for -SO₃ groups. Woerman has also reported poly (phenyl sulfonic acid) gels and studied their viscoelastic properties [192].

Poly (styrene sulfonic acid) hydrogels crosslinked with BF₃ [193] have also been reported. Composite hydrogels from poly (styrene sulfonic acid - co - vinylidene fluoride) [194-197], poly (acrylamide 2- methyl -1- propane) sulfonic acid [198-199], biodegradable PEC gels from chitosan derivatives, poly vinyl sulfate salts [200-206] and hyaluronic acid benzyl ester [207, 208] have also received attention for their membrane properties.

1.076. Other hydrogels

Literature abounds in the vast variety of hydrogels prepared. One can say that any material that can be rendered hydrophilic could be an ideal candidate for hydrogel synthesis e.g., starch, cellulose, lignin, chitosan and many other bio polymers have been used for hydrogel synthesis. Fanta et al. have done pioneering work in developing starch based hydrogels.[2-5].
Acrylonitrile has been grafted on starch obtained from various sources such as corn, cassava etc. Subsequently polymerized and saponified product has been called as HSPAN which shows hydrogel properties [209-217]. Cellulose hydrogels have been reported by Westman and Lindstroem [218,219] who studied their mechanical properties. Gehrke [220] has reported cellulose ether hydrogels and observed their temperature sensitivity. They have observed some relationship between ionic content of such gels and their phase transition temperature. Strumia et al. [221], have studied hydrogels based on acrylic sucrose crosslinked with glutaraldehyde, while kraft lignin hydrogels have been synthesized by Lindstroem and Westman [222] and as superabsorbents by Isao and Namiko [223]. Rao and Jeyanthi have synthesized hydrogels based on collagen p-HEMA and observed them to be nontoxic, biocompatible as well as tolerable when subcutaneously implanted in rats [224].

Nobuyuki et al. have reported hydrogels prepared by depositing glycolipid layer on agar by Langmuir - Blodgett technique [225]. On monitoring the phase transition of this monolayer, the permeability of this hydrogel membrane could be modified. Chitin [226] has been used to prepare a water absorbent fabric. However, chitosan, with its -NH₂ and -OH groups is a better candidate, as chemical modifications using these groups is easily possible. [227,85]. Similarly carrageenan [228] and xanthan [229] hydrogels also find mention in the literature.

Synthetic hydrogels prepared from poly (ethylene oxide-urethane) have been studied for their interactions with water.
Poly urethane hydrogels with enhanced wetting rates have been reported in a US patent [231]. Another US patent describes biomedical applications using these hydrogels [232]. Susumu and Donald [233] have reported segmented poly (ether urethane-urea) hydrogel complexes with LiBr.

Hyderali and Srinivasan [234] have synthesized cinnamyloxy alkyl methacrylate hydrogels. N,N-methylenebis-N-vinyl acetamide crosslinked hydrogels from N-vinyl acetamide find a mention by Akashi et al. [235], while copolymers of HEMA with N,N-dimethyl-N-methacryloxyethyl N-(3-sulfopropyl) aluminum betaine as hydrogels have been put forward by Huglin and Rego [236].

1.08 CROSSLINKING AGENTS USED IN HYDROGEL SYNTHESIS

Hydrogel synthesis involves the preparation of a crosslinked structure. Crosslinking can be done either post polymerization as in radiation crosslinking [117, 153, 154] or may be done by copolymerization of monomers in the presence of a crosslinking agent.

The crosslinking by metal ions has been discussed in earlier section. We have also reviewed chemical reactions, with glutaraldehyde [158, 159], toluene diisocyanate [163], BF₃ [193] for crosslinking and thermal treatments [166, 167] post polymerization.

In another approach to hydrogel synthesis, crosslinking -co-polymerization is carried out using multifunctional monomers. The most widely used crosslinking agents are divinyl monomers i.e.,
monomers containing two vinyl groups that can add across two chains to form crosslinks.

Crosslinking agents like ethyleneglycol dimethacrylate (5, n=1) [237-240], diethylene glycol dimethacrylate (5, n=2) [251], triethylene glycol dimethacrylate (5, n=3) [242], and even multiethyleneglycol dimethacrylates [243] have been reported.

Another versatile crosslinking agent, probably the most widely used is the amide based N,N-methylenebisacrylamide (6) [244-246]. Hydrogels have also been reported by crosslinking N-vinyl pyridine with divinyl benzene [247]. Kojima et al. [248, 249] have reported hydrogels comprising of polymethacrylic acid crosslinked with poly (oxytetramethyl dimethacrylate) (7). Hydrogels for site specific delivery have been reported by Pradney and Copecek [250] using 4, 4-(bismethacryloyl amino) azobenzene (8) as a crosslinking agent. Other crosslinking agents include hexamethylene bis (methacryloyloxy ethylene carbamate) (9), 2-hydroxy trimethylene dimethacrylate (10), 2,3-dihydroxy tetramethylene dimethacrylate (11) [114], also 1,1,1-tris (methacryloyloxy methyl) propane (12) [115], 1,3,5-triacryloyl hexahydro triazine (13) [251-253], methylene bis (4-phenyl isocyanate) (14), allylmethacrylate (15), 2,2'(p-phenylenedioxy) diethyl dimethacrylate (16) and 3, 3-tetramethylene bis (1-vinyl imidazolium diiodide) (17) which have been used to synthesize hydrogels having different properties.
1.09 SYNTHESIS OF HYDROGELS

Hydrogels are water swollen crosslinked polymeric networks, synthesized by reactions between one or more monomers or by association bonds like hydrogen bonding or van der Waals' interactions between polymeric chains. The characteristic properties of hydrogels like equilibrium water uptake, swelling, water retention etc. predominantly depend upon the mode of synthesis and the protocol followed. Many factors like monomer solvent interactions, the concentration as well as type of initiator and crosslinking agent, temperature, nature and reactivity ratios of comonomers and the crosslinking agent and even the method used for drying the product, impart significant contributions to the end product properties.

The different methods used for crosslinking polymerization hydrogel synthesis are outlined below.

1.09.1 Solution Polymerization

One of the often mentioned modes of synthesis is the solution polymerization. Monomers like acrylic acid, acrylamide, methacrylic acid, methylene bis acrylamide etc., are dissolved in a solvent (usually water) and polymerized using appropriate initiators at a given temperature. The product obtained is in the form of a thick viscous rubbery mass. The difficulty in handling this rubbery mass is one of the limiting factors of this method. Again acrylic and methacrylic acid have very high heat of polymerization and temperature control is one of the aspects to be considered from the safety point of view. Usually this is done
either by adding excess solvent or using not more than 70% solution of monomers in the solvent prior to polymerization.

1.092 Suspension Polymerization

Another alternative is to resort to suspension polymerization wherein, an aqueous solution of monomers is suspended in an organic phase such as cyclohexane, hexane etc., together with suspending agents (surfactants) like sorbitan monolaurate, and then free radical initiators added and the mixture polymerized. The merits of this mode of polymerization lie in the ease of handling the product. Also, the precise size and shape of polymer particles can be prepared by judicious use of suspending agents. However, the choice of the right suspending agent, the hydrophilic-lipophilic balance and hydrocarbon phase are the factors that need to be addressed prior to deciding the synthesis strategy. Again the necessity of evaporating the organic phase also adds to the economic calculations.

1.093 Graft Polymerization

Hydrogels can also be prepared by graft polymerizing monomers like acrylonitrile, NVP, HEMA, acrylamide etc., on substrates. Hydrophobic monomers like acrylonitrile have been successfully graft polymerized onto starch. The resultant polymer when hydrolyzed yields a starch grafted with poly (acrylamide - co - acrylic acid) and shows hydrogel properties. Fanta et al. have done pioneering work on acrylonitrile graft polymerization onto starch using ceric ion initiators [209-213]. Bazuaye et al. [254] used a method wherein the starch was pretreated or activated with ceric ion and then reacted with the monomer to be
graft polymerized. This method suffers from limitations of low graft efficiency leading to suppressed hydrogel properties.

All the above mentioned methods are used for hydrogel synthesis and no one method may be considered better than the other. Selection of the right method is thus dependent on desired properties and availability of raw materials.

1.10 PROPERTIES OF HYDROGEL

The characteristic properties of a hydrogel are predominantly dependent on a primary force. This being the hydrogen bonding ability of the constituent functional groups in the polymer with water. Thus, hydrogen bonding ability has a direct influence upon the hydrogel properties like swelling, water absorbency and retention, and moisture sorption. The measurement of water vapour diffusion, permeation and retention, require special techniques due to the unique nature of water, which forms extensive hydrogen bonding with the polar functional groups. It is thus necessary to engineer a polymer in such a way that the juxtaposition of functional groups leads to minimal interaction between them. These polymer sites would then be free to form hydrogen bonds with water, leading to higher sorption and thus show hydrogel properties characteristic of that polymer.

1.11 WATER UPTAKE OR ABSORBENCY

Water absorbency may be defined as the amount of water (deionised) absorbed at equilibrium, per unit weight of dry hydrogel polymer. Expressed in terms of grams of water absorbed
per gram of polymer (g/g), this value is fundamental to the characterization of hydrogels. This value may range between 30 g/g for absorbent based hydrogels (like HEMA hydrogels) to above 1000 g/g for super absorbent hydrogels (eg. prepared from grafted starch). The extent to which permeant molecules are sorbed and their mode of sorption in polymer is a direct consequence of the interactions of polymer functionality and the permeant. The composition of polymers has to be tailored so as to have the maximum dispersive forces so that the chains get separated and the interstitial spaces are occupied by water (permeant) molecules. The absorbency continues depending upon the activity of the permeant within the polymer at equilibrium. Water absorbency is the most important characteristic property of hydrogels and literature reveals many different methods to determine this value. Dave et al. [99] have reviewed different methods to measure the water absorbency for polymers of varying properties and chemical constitution. However, the choice of an appropriate method depend upon the nature of interactions between the polymer and water.

1.12 EQUILIBRIUM SWELLING

The volume expansion of a dry polymer due to penetration of imbibed fluid at equilibrium conditions is called as swelling. The swelling index of a polymer can be expressed as:

\[ S = \frac{100 \text{ (wet weight - dry weight)}}{\text{dry weight}} \] \[ \ldots 1.6 \]
Swelling depends upon the strength and orientation of the interactions between polymer chains. Sorption of fluid plasticises the polymer by breaking these bonds and this opening of the structure leads to a higher permeability. Thus, if the functional groups that interact with the fluid are removed, the swelling due to that fluid would be expected to decrease. On the other hand, if the percentage of noninteracting groups is increased, a similar effect would be seen. In other words, swelling of polymers is expected to be greater in solvents where its affinity for macromolecules is greater than the cohesive forces as well as secondary bonds acting between the polymeric chains that resist the network expansion.

1.13 MOISTURE REGAIN

This is defined as the amount of moisture absorbed by a polymer when it is exposed to a constant moisture stress. It is measured gravimetrically in terms of percentage moisture regained as compared to a completely dry state, or other suitable units like mol/s/m/Pa.

When compared with other solvents water, has a very high cohesive energy density (CED), e.g., methanol has a CED of 810 Kg/dm$^3$ as compared to 2120 kg/dm$^3$ of water. Thus water shows strong interactions with hydrophilic or polar substrates resulting in a diffusion behaviour not shown by other permeants. It is thus obvious that permeation of water vapour varies from polymer to polymer depending upon the nature of interactions,
ease of extension, bending and rotation of bonds. As shown in table 1.03, the moisture regain varies from a fraction to a value in thousands of units, where the chain molecules may be thought to be swimming in a sea of water.

1.14 WATER RETENTION UNDER STRESS

The chemical properties of water change once it is bound to a polymer. It can no longer be addressed as water but has to be called as bound or bulk water [93]. Now, when a slab of hydrogel is placed in water and allowed to swell, it will contain bound, bulk as well as free water, which is not bound and may be lost under stress. It is very important to determine the amount of free water present in a hydrogel as this value precludes its applications in areas like agronomy or diapers where the weight of soil aggregates or an infant's weight may induce pressure stress resulting in water loss or in sealent applications where high turbulence may induce loss of free water and prove detrimental to its use. The amount of bound and bulk water can be estimated by many different ways [99] and the difference between the total absorbency and the bound + bulk water gives the free water contained in a gel. Alternatively, the number of polar groups determine the number of water molecules directly bound to the polymer (bound water). The bulk water could be determined by statistical analysis depending on water cluster numbers [256,257]. The sum of those two values, bound and bulk would give the water retained under stress.
Table 1.03. Moisture regain values for certain polymers at 100% Rh and 25°C temperature [255].

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Moisture regain $P \times 10^{-15}$ mol$^{-1}$ m$^{-1}$ s$^{-1}$ Pa$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly (vinyl chloride)</td>
<td>0.50 - 1.50</td>
</tr>
<tr>
<td>Poly (tetrafluoroethylene)</td>
<td>1.00</td>
</tr>
<tr>
<td>Poly ethylene</td>
<td>0.76 - 3.75</td>
</tr>
<tr>
<td>Poly propylene</td>
<td>0.50 - 1.25</td>
</tr>
<tr>
<td>Poly styrene</td>
<td>17.50</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>1839.00</td>
</tr>
<tr>
<td>Poly (vinyl alcohol)</td>
<td>14045.00</td>
</tr>
</tbody>
</table>
1.15 SURFACE PROPERTIES

Swelling and absorbency reflect the internal properties of a hydrogel. However, surface properties are essential for their wettability, biocompatibility and even selectivity. Hydrogels vary in their wettability characteristics. The water content, ionic characteristics and wettability bear influence upon cell adhesion and thrombogenicity. The anionic character of a hydrogel would render it suitable for blood compatibility while cationic character favours cell growth. Hydrogels can change the polarity of their surface [16]. The possibility of changing the polarity of the interface between gel and fluid by means of conformational and orientational changes is of prime importance. Free rotation of C-C bonds, chain rigidity or flexibility and size of macromolecular aggregates is to a large extent responsible for the characteristic properties of a hydrogel.

1.16 RELEASE OF IMBIBED SOLUTES AND FLUID

Polymeric materials were first exploited for their use in sustained release applications about three decades ago. These devices, based on inert plastic materials, have since gained immense attention. In principle, there are three types of controlled release devices available viz. (A) The Monolithic device where the active ingredient is solubilized or dispersed in an inert diffusional barrier (B) The Reservoir type device where the active ingredient forms the core and is surrounded by a non-interacting semipermeable barrier and (C) The Bound device where the active ingredient is bound to the polymer by chemical bonds and its release is modulated by hydrolysis of these bonds by enzymes etc.
Nagy [93] has called gels an intelligent species, capable of communicating with the environment. This communication is sustained primarily by diffusive processes leading to release of imbibed materials in a controlled fashion. The interactions between the polymer, imbibed species and the medium in which it is placed and other factors such as hydrophobic interactions, syneresis, entropy factors, influence of foreign ions, electric field, electromagnetic radiations etc., all play important roles in release of imbibed species. These factors should thus be considered for a proper control of release mechanisms.

Hydrogel controlled release devices belong to the first category and are more preferred due to the ease of preparation, degrees of freedom available to manipulate the polymer structure and hence the properties of the controlled release device. Factors like restriction of using only reactive species in case of bound devices severely limit their applicability. Studies can also be undertaken on release profiles of active ingredients during the glass transition stage, release during structural changes, volume expansion and water absorption.

The release kinetics of active ingredient from the matrix depends on the kinetics of swelling and is a result of the change in magnitude of the rate of polymer relaxation towards the rate of drug diffusion. Controlled release systems release the active ingredient at different rates following either a Fickian transport, Zero order or an anomalous transport. The analysis of release data throw light on the mode of active ingredient transport.
1.17 FLOW PROPERTIES OF HYDROGELS

The dynamic behaviour of polymer solutions and their relation to macromolecular properties is usually investigated in terms of the study of deformation and flow of matter. The rheological studies reveal a direct evidence of normal mode of relaxations in flow and a reflection of dynamical processes at a molecular level.

Many fluids obey the Newton's hypothesis concerning flow of viscous liquids that stress is shear rate and are called as Newtonian liquids.

On the other hand, for several class of fluids, like colloids and dispersed systems, the viscosity changes with a change in the rate of shear. In the study of anomalous viscosity the fundamental parameter is thus the rate of shear. It is necessary to employ instruments where different shear rates are produced. Rotating cylinder type of viscometers like Brookfield, use a cylinder, cup, bob or disc, supported on a wire and rotated at various speeds in a sample. Viscosity is measured by drag of cylinder, cup or bob on the wire.

Orientation of molecular chains, disentanglements and reformation of molecular chains appear to play important roles in anomalous viscosity observations.

1.18 MECHANICAL PROPERTIES OF HYDROGELS

Hydrogels find applications in areas where materials with high permeability, tensile strength and good machinability are required. These properties, alongwith good wettability and
biocompatibility impose strict guidelines for the synthesis of hydrogel polymers. It is thus mandatory that a group of comonomers be polymerized rather than a single or a homopolymer. Hydrogels are thus synthesized by copolymerizing hydrophilic comonomers with a small proportion of lipophilic moiety which imparts tensile strength to the product. e.g., when poly HEMA hydrogels are synthesized, ethyl methacrylate imparts additive strength while methyl acrylate gives pliable hydrogels, suitable for studies on fundamental aspects of rubber elasticity. Thus hydrophilicity together with good mechanical strength is desirable in hydrogels and is achieved by judicious choice of hydrophilic and hydrophobic comonomers or by inducing a physical crosslinking together with covalent crosslinking which can vary the topological aspects of the network.

1.19 WORLD PRODUCTION

Nowadays, polymer science uses a large variety of methods to characterize a polymer, developing data relating to performance of polymer materials to their chemical and physical structure. The characterization and resultant understanding of polymer systems requires contributions from various fields like rheology, electron microscopy, spectroscopy, thermal analysis and physical techniques.

The world production of hydrogel polymers is no doubt increasing. Leading companies were reported to have massive expansion programmes and the world production increased 2800% in less than a decade [267].
fig. 1.4 A plot showing the rise in demand for absorbent polymers worldwide.
Looking at the wide range of applications of hydrogels, it is not surprising that major producers the world over, are going in for massive expansion programmes for hydrogel production (Table 1.04). As is clearly evident from Fig. 1.4, the demand for super absorbent polymers has risen by a phenomenal 3000% in less than a decade [267]. This gives enough reasons to justify massive expansion programme of some of the major manufacturers of hydrogel polymer.

1.20 IMPORTANCE OF STUDYING HYDROGELS FOR AGRONOMY APPLICATIONS

Macromolecular synthesis is based upon pattern recognition and logical reasoning. Chemical interconversions that can reliably be used to buildup complex targets originated by identifying recurrent relationships between reactants and products. Polymer molecules are distinguished from other chemical compositions, fundamentally by their tremendous size. Most of their properties arise due to this size. However, far below the macroscopic size, many of the properties and applications of polymers are influenced by individual atoms and functional groups within the polymer. In a thorough study of structure activity relationship between a polymer structure, its characteristic properties and applications, it is necessary to dwell into the submolecular aspects of chemical composition.
<table>
<thead>
<tr>
<th>Company name</th>
<th>Production Capacity (TPA)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aberdeen Chemicals (USA)</td>
<td>10,000 - 40,000</td>
<td>261</td>
</tr>
<tr>
<td>Allied Colloids (UK)</td>
<td>- 30,000</td>
<td>262</td>
</tr>
<tr>
<td>Hoechst Cleanse sp. chem. (USA)</td>
<td>40,000 50,000</td>
<td>263</td>
</tr>
<tr>
<td>Nippon Shokubai (Japan)</td>
<td>- 1,70,000</td>
<td>264</td>
</tr>
<tr>
<td>Stockhausen (USA)</td>
<td>25,000 50,000</td>
<td>265</td>
</tr>
<tr>
<td>Sumitomo· Seika (Japan)</td>
<td>14,000 22,000</td>
<td>266</td>
</tr>
</tbody>
</table>
Macromolecules that possess open features such as open channels, regular voids and are sensitive to the external environment are both technologically and scientifically challenging.

Mankind has progressed, and so have its needs. The effects of a gargantuan technology progress has led to an increase in world population. Significant achievements in medical and pharmaceutical sciences led to an increase in life spans and decrease in infant mortality. However, our mother earth, with the limited resources, offers limited capacity for such large populations. Food and water are the urgent requirements of the teeming billions. With the national perspective, the food grain demand in India is expected to be around 240 million tonnes by the year 2000 [258]. This means that an additional 64 million tonnes of food grain is to be produced. This is by no means a simple task considering ever decreasing percapita land and water resources. It is reported that only 32.7% of the land under food grain production is under irrigation [259]. Obviously therefore, the improvement in productivity of rainfed areas is of specific concern. This picture portrays the concerns not of India, but of the world over. If a comparison is made of water used in irrigation world over, a rough estimate would indicate that only about 25% of the irrigation water is actually used by the plants. The rest is lost through evaporation. An estimate in 1970 puts evaporation losses in irrigation waters to be a staggering 1460 Km$^3$ as depicted in table 1.05 [260].
TABLE 1.05. The amount of water consumed worldover in 1970 for irrigation purposes [260].

<table>
<thead>
<tr>
<th>Continent</th>
<th>Estimated amount of water applied (Km³)</th>
<th>Estimated consumptive water loss (Km³)</th>
<th>Water Loss. (% of applied)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asia</td>
<td>1400</td>
<td>1100</td>
<td>79</td>
</tr>
<tr>
<td>North America</td>
<td>125</td>
<td>83</td>
<td>67</td>
</tr>
<tr>
<td>Europe</td>
<td>208</td>
<td>129</td>
<td>62</td>
</tr>
<tr>
<td>Africa</td>
<td>108</td>
<td>92</td>
<td>82</td>
</tr>
<tr>
<td>South America</td>
<td>54</td>
<td>46</td>
<td>82</td>
</tr>
<tr>
<td>Australia &amp; Oceania</td>
<td>13</td>
<td>10</td>
<td>77</td>
</tr>
<tr>
<td>World Total</td>
<td>1909</td>
<td>1460</td>
<td>76</td>
</tr>
</tbody>
</table>
This makes it mandatory to look forward towards sustainable agricultural resource management. Practices like drip irrigation systems (DIS) or sprinkler systems are in vogue today. A DIS is thrice as costly as a conventional flood irrigation, as it requires a filtration system at source and an array of tubes or pipes to carry the water. It also requires a pump to drive the water through these tubes. Apart from the cost, plant spacing and topography need to be considered before installation. Randomly distributed and closely spaced crops like rice and wheat cannot use DIS.

On comparison with hydrogel application, through hydrogel granules dispersed in the field below the soil surface, water drips directly onto each plant's root zone. Slowly and steadily, the plant gets the right amount of water at the right time and right place.

Hydrogels can be adopted in poor soil and water quality, as well as difficult terrain. As only the roots are watered, weed proliferation is minimized so is the use of weedicides. If a fertilizer like urea was included in a hydrogel, the roots would directly receive the nutrients and the 25-30% of fertilizer that is usually lost can be saved. It also preserves the soil fertility which other irrigation methods erode through water logging and salination. Hydrogels also improve soil porosity leading to fine textured soils. Labour costs are minimized and
INDIA

175 MILLION HECTARES LAND
UNDER SERIOUS ENVIRONMENTAL
DEGRADATION

6000 MILLION TONNES OF
TOP SOIL ERODED

5.4 MILLION TONNES OF FERTILIZER
LOSEES (N P K ALONE)

TOTAL LOSS ESTIMATED AT ABOUT
Rs. 7000 MILLION

fig. 1.5

Losses due to improper use of natural resources
which demands prudent use of farm management
practices.
watering frequency is decreased. More importantly, it addresses the basic issue of water management. As the use of hydrogels restricts the unnecessary use of water, extending the area under cultivation, using the same amount of water, can meet the growing need of the burgeoning population.