CONTROLLED RELEASE FERTILIZER FORMULATIONS BASED ON POLYMERS

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CERTIFICATE

This is to certify that the thesis entitled "Controlled Release Fertilizer Formulations Based on Polymers" is an authentic record of the research work carried out by Mr. Joshua Abraham under my supervision and guidance during the period August 1992 to July 1996 in partial fulfillment of the requirements of the degree of Doctor of Philosophy under the Faculty of Science of the Mahatma Gandhi University. The work presented in this thesis has not been submitted for any degree or diploma earlier.

It is also certified that Mr. Joshua Abraham has fulfilled the course requirements and passed the qualifying examination for the Ph.D degree of this University.

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Declaration

I hereby declare that the Thesis entitled ‘Controlled Release Fertilizer Formulations Based on Polymers' is an authentic work carried out by me under the supervision of Prof.V.N.Rajasekharan Pillai, Vice Chancellor, Mahatma Gandhi University, Kottayam. No part of this work had been presented for any other degree or diploma earlier.

Priyadarsini Hills,
10th January, 1997.

Joshua Abraham

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List of Abbreviations

AIBN	Azo-bis-isobutyronitrile
CR	Controlled Release
DAM	Diacetylmonoxime
DDT	Dichlorodiphenyltrichloroethane
DVB	Divinylbenzene
DVB-PAM	Divinylbenzene crosslinked polyacrylamide
DVB-PMMA	Divinylbenzene crosslinked polymethylmethacrylate
EVA	Ethylenevinylacetate co-polymer
FAO	Food and Agricultural Organization of United Nations
Kg/ha	Kilogram / hectare
MAL	Maximum Admissible Level
NNMBA	N,N'-Methylene-bis-acrylamide
NNMBA-PAM	N,N'-Methylene-bis-acrylamide crosslinked polyacrylamide
NNMBA-PMMA	N,N'-Methylene-bis-acrylamide crosslinked polymethylmethacrylate
N	Nitrogen
NR	Natural Rubber
PETA	Pentaerythritol triacrylate
PCUF	Polymer Coated Urea Fertilzers
POCU	Polyolefin Coated Urea Fertilizer
PETA-PAM	Pentaerythritol triacrylate crosslinked polyacrylamide
PETA- PMMA	Pentaerythritol triacrylate crosslinked polymethylmethacrylate
PAM	Polyacrylamide
PMMA	Polymethylmethacrylate
PS	Polystyrene
PVC	Polyvinylchloride
RLCU	Reactive Layer Coated Urea
S & T	Science and Technology
SAC	Scientific Advisory Committee

SCU	Sulphur Coated Urea
SPCU	Silicate and Polymer Coated Urea
TEMED	Tetremethyl ethylene diamine
TSC	Thiosemicarbazide
TTEGDA	Tetraethyleneglycol diacrylate
TTEGDA-PAM	Tetraethyleneglycol diacrylate crosslinked polyacrylamide
TTEGDA-PMMA	Tetraethyleneglycol diacrylate crosslinked polymethylmethacrylate
URM	Urea Rubber Matrices
WHC	Water Holding Capacity

Chapter 1.
Introduction

1.1 Concept of Controlled Release (CR)

The concept of controlled release technology, emerged actively in nineteen sixties, has attracted wide attention over the last two decades. The research and developmental effects in this area are experienced in medical, agricultural and biotechnological fields (Fan and Singh, 1989). The use of drugs, fertilizers, pesticides and herbicides and similar chemically active agents are inevitable to the modern society. However the extensive and unjudged use of these biologically active chemicals have created great alarm among scientists world-wide, because of its adverse impact on the health and environment. The uncontrolled application of these chemicals almost inevitably induces many undesired side reactions in systems which receive them. Controlled release technology finds its potential use in minimizing or avoiding these `side reactions' during the course of action of the active agents by a controlled release of them to the system (Paul, 1976; Fan and Singh, 1989).

Several low molecular weight biologically active agents are in use at present. These agents during their action manipulate the environment around and within us. Hence its efficient, safe and economic use is to be strictly followed for sustaining the environment and human health. The conventional use of these chemicals in biosystems, produces peak and valleys of its concentration within the system in a very short period of time. This necessitates repeated application of these agents to the system in order to maintain its concentration level for performing the function. These periodic applications produce maximum and minimum of active agent concentration in the system. Usually these concentration profile involves harmful and ineffective phases. Thus the efficiency of these chemicals relies on its release to their site of action at the right time and in right quantity (Paul, 1976 ; McCormick, 1987).

Concentration levels of an agricultural chemical or a herbicide in a system, when administered through different modes of conventional (uncontrolled) and controlled manner, are represented in figure 1.1. The upper horizontal line represents the maximum admissible level (MAL) of the herbicide concentration in the system, above which crop damage may takes place, and lower horizontal line represents the minimum concentration level of the herbicide required in the system for the specified action to takes place. In the uncontrolled application of the herbicide (Curve A), the period of action is very short and a part of applied herbicide is wasted, since that is not available in the system at required level. Usually to overcome this shortfall, herbicides are applied at a higher concentration (Curve B). Here the concentration level of herbicide in the system goes beyond the MAL and this results in crop damage. Though the period of effective action is for a longer time, than in case A, damage of the receiving system as well as wastage of chemicals are there.

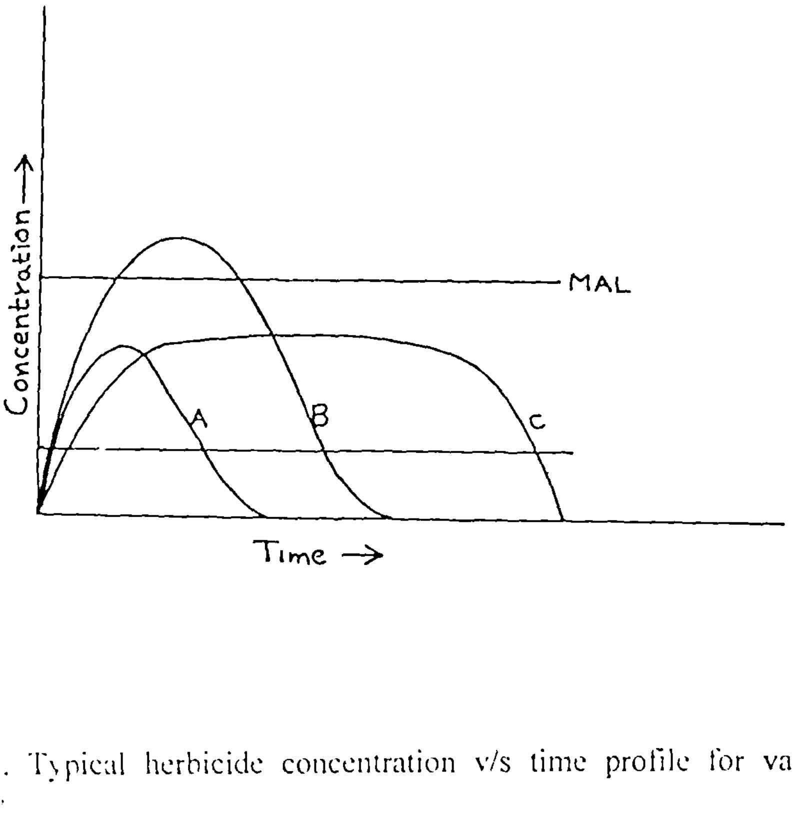


Fig 1.1. Typical herbicide concentration v/s time profile for various modes of delivery

A. *Conventional method of application* B. *Conventional method (overdose)*
C. *Controlled Release method*

The CR formulation delivers the herbicide in right amount (Curve C) and period of action is much longer than in cases A or B ; and an ideal system can maintain the optimum level of concentration of herbicide in the system for an entire crop period. Repeated `B' type application will result in very wide variations in herbicide concentration in the system; sometimes too high, to set in undesired side reactions or too low such that the desired action is not performed. Thus by uncontrolled applications of active agents loss of chemicals and environment pollution due to `side reactions' take place. Neogi and Allan (1974) had illustrated this with a specific example. A pesticide with a half life period of 15 days and with dissipation rate of first order and when a minimum level of 1 mg/day is necessary for effective pest control, if applied by conventional method for a period of action of 50, 100 and 150 days require 10, 100 and 1000 mg respectively ; but if it is released in a controlled manner by a CR formulation it can maintain the minimum required level of 1 mg by continuous supply to restore the amount dissipated, only 3.3, 5.6 and 7.9 mg would be required. Thus considerable amount of costly chemicals can be saved. The losses due to overdoses, usually taking place in conventional application are also minimized, thereby the environment pollution is checked. Moreover the period of action is prolonged with a bare minimum of chemical in the medium. In the application of any active agent to a biosystem, a desirable regime is to release the active agent in a controlled manner and to maintain an optimum level for the required period (Mc Cormick,1987).

Controlled Release (CR) technology is widely made use of in drug formulations in fertility control (Flynn et al 1976), narcotic antagonism (Yolles et al 1976), fluoride for dental purposes (Halpern et al 1976), cancer curing (Yolles et al 1976), and cardiac arrhythmia and to induce hypertension (Chien et al 1976). In the agriculture sector several CR formulations of fertilizers, herbicides, pesticides and pheromones had been developed (Beaton et al, 1967; Shasha and Trimnell, 1989; Schacht et al, 1980; Akelah and Moet, 1990; Kyodonieus, 1980). Major advantages of CR techniques are more efficient utilization of the active agent, possibility of targeting, less frequent administration and reduction in side effects (Fan and Singh 1989).

1.2 Polymers in Controlled Release Technology

Polymers, both natural and synthetic, are very much useful in preparing CR formulations. Most of the drugs, fertilizers, herbicides, pesticides and pheromones are low molecular weight compounds. The tremendous progress in polymer science and technology could make it possible to combine a low molecular active agent species physically or chemically to a polymer through a pre- or post- polymerization reaction. In CR technique the active agent is allowed to release from the polymer-active agent combination over a period of time, most often to a specific target. In physical combinations polymer acts as a rate-controlling device while in chemical combinations it acts as a carrier for the active agent (Akelah and Moet,1990).

Another important advantage of polymeric CR formulation is that the toxic nature of the chemicals are minimized. Many new pesticides are readily biodegradable and highly toxic. For example the organophosphates are very toxic and due to their mobility in air and water, proper respiratory protection measures are inevitable for the persons handling it. Moreover it poses great danger to non-target organisms also. But if it is encapsulated or distributed in a polymer its toxicity will be much reduced, since all the amount does not release at one time. Still another advantage is that the polymer combinations being solids are easy to handle (Neogi and Allan,1974).

The success of CR formulation relies on combining the active agent with the polymer in an economic manner, at the same time maintaining the desired release profile. These are often in opposition and one has to compromise in the ultimate cost/benefit ratio of CR formulations (Paul, 1976). However there are many new classes of polymers which can be effectively employed in CR formulations. The efficiency of CR formulations depends on the following polymer properties : (Paul, 1976).

1) Solubility and distribution characteristics with the active agent.
2) Solubility and distribution characteristics with the environmental agents.

3) Compatibility with the environment. It should be non-toxic.
4) Compatibility with the active agent. It should not produce undesirable products.
5) Stability in the environment. It should not degrade during the course of action. Preferable if degraded after the desired function is over. The degraded products should not harm the environment.
6) Mechanical properties. It should be in a suitable physical form to be easily administered to the system.
7) Ease of fabrication.
8) Cost.

The sought-after release profile from a CR system is the steady state release of active agent, or a zero-order release mechanism kinetically. The attraction of such a system is that the rate of release is not affected by the amount of active agent released or not released at any moment (Paul, 1976). However, many of the CR formulations do not fall under this category. Depending on the rate controlling mechanism involved, the CR systems can be classified into several classes. According to Fan and Singh (1989) the major release mechanisms involved in CR formulations are

1) Diffusion

2) Erosion or Chemical reaction controlled.

3) Swelling

4) Osmosis

1)Diffusion - Controlled Systems

Here the rate determining step is the diffusion of active agent through the polymer. The polymer-environment fluid interaction is practically nil, or polymer is seldom affected by the environment factors. Mainly two categories of diffusion - controlled devices are employed in CR formulations.

a) Reservoir Systems

Here the active agent and polymer are physically combined or active agent is encapsulated in a spherical or cylindrical polymeric device. Micro, macro or nano encapsulation co-acervation and spray encapsulation are well-developed techniques and are employed in drug delivery systems (Speieser, 1976). Active agent releases out to the environment by diffusion, through the micropores of the capsule walls. Ethylene-vinylacetate co-polymers, silicone rubber, polyethylene and polyurethane are commonly used to fabricate such systems (Fan and Singh, 1989).

b) Monolithic systems

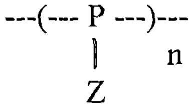
Here the active agent is either dispersed heterogeneously or dissolved in the polymer. The polymer can be biodegradable or non-biodegradable. The dissolved or dispersed active agent releases out by diffusion. If interaction is possible between polymer and environment fluid, release may takes place by leaching also in addition to diffusion. If a soluble additive is incorporated in the polymer matrix, the environmental fluid can easily penetrate the matrix by dissolving the additive and interconnected channels will be formed, through which the release would be easy. These type of physical combinations need not be influenced by structure of the active agent or polymer. Hence this technique has a general applicability. A wide variety of active agents can be incorporated with a broad range of polymers to prepare CR formulations. Polymer matrix of silicone rubber, ethyl cellulose and hydroxypropyl cellulose are widely used in this category (Akelah and Moet,1990; Fan and Singh 1989).

2.a) Erosion- or Chemical Reaction- Controlled Systems

The active agent is physically immobilized in the polymer matrix and release occurs only by the erosion of the polymer. In an ideal system polymer matrix undergo surface erosion, releasing active agent at a rate proportional to the erosion rate. If erosion rate is constant and the matrix dimensions remains unchanged a zero order release rate can be achieved. Poly(vinyl pyrrolidone) and co-polymers of lactic and glycolic acids are used in preparing such systems (Fan and Singh, 1989).

B) Chemical Reaction Controlled -Systems

The active agent is chemically bonded to the polymer either by a covalent or ionic bond. The active agent is incorporated either as a pendant group in the polymer chain or in the polymer backbone itself. Chemical modification of the pre-formed polymer with a desired active agent lead to a polymer with the active group present as a pendant (fig 1.2). Polymerization of active monomers may lead either to polymers with active agent as repeat units (fig 1.3) or polymers that contain active agents as pendants. Positively or negatively charged active agents combine with ion exchange resins to form poly salt resinates (Akelah and Moet,1990). Pendent chain complexes with agricultural and pharmaceutical active agents had been developed (Harris et al, 1976; Duncan and Kopacek,1984)



$$\text{---}(\text{---}\underset{\underset{Z}{|}}{P}\text{---})_{n}\text{---}$$

Fig 1.2 Active agent attached to polymer as a side chain

$$\text{-----}(\text{-----}P\text{-----}Z\text{-----})_{n}\text{------}$$

Fig 1.3 Active agent in the polymer backbone

P - Monomer unit *Z- Active agent*

From these chemical combinations, active agents are released only when the polymer active agent bond is cleaved, otherwise the polymer is to be degraded. When the active agent is a co-monomeric unit in polymer backbone, release may occur by polymer degradation and in such cases the release follow a zero order kinetics (Akelah and Moet, 1990).

3) Swelling CR System

The active agent is dispersed or dissolved in a polymer matrix, in which it is unable to diffuse to any considerable extent. When the polymer gets into contact with an environment fluid which is compatible with it, swelling takes place and the active agent present in the gel portion of the matrix diffuse out. Poly(hydroxy methylmethacrylate), polyacrylamide and poly(ethylene glycols) are used in such systems (Roorda et al,1986).

4) Osmotic Pumping Systems

In this type of devices the driving force is the osmotic force. Usually such systems consist of a solid and water soluble active agent, which is enclosed by a water - permeable, but active agent-impermeable, polymer membrane with a small opening. Water is transported into the core by permeation and hydrostatic pressure will be built up in the core and subsequently, the dissolved active agent comes out (Fan and Singh, 1989).

Apart from these common techniques, new concepts such as magnetic or ultra sound modulation, viable cell immobilization, microspheres and nano particles and targeted delivery are under thorough research in the CR field (Hsieh and Langer, 1980 ; Koestler,1980; Fan and Singh,1989).

A very wide variety of polymers are utilized in CR technology. Development and innovations in new high-tech class of polymers are one of the primary factors responsible for the very rapid and encouraging development in CR technology, which is not only aiming at preserving the environment but also considering the economic aspects.

1.3 Polymers as Soil Conditioners

Creating a suitable soil media is very essential for effective growth of plants. For increasing food production more `problem soils' (uncultivable soils) are to be made suitable for cultivation. Many soil problems hindering cultivation are tackled to a great extent by the use of soil conditioners. A soil conditioner is defined as any synthetic chemical or chemically modified substance that stabilizes soil aggregates and/or favourably modifies soils' structural or physical properties. Ferric sulphate, triphenyl sulphonium chloride, portland cement, periodates, phosphoric acid, calcium chloride, soap, hexadecanol and various types of polymers are examples (Azzam, 1980 ; Seybold, 1994).

Several synthetic and natural polymeric soil conditioners are now in use to stabilize soil aggregates and to modify favourably the soil physical properties. They can improve water retention capacity and prevent wind and water erosion. Even about thirty years ago `Krilium'- hydrolysed polyacrylonitrile was commercialized as a soil conditioner and was reported to improve soil permeability (Seybold, 1994). However its efficiency varied soil to soil (Quastel, 1953). Polystyrene, foam plastics and styromull are insoluble polymers that are used as soil conditioners to convert heavy clayey soils to air permeable and warm one. Bitumen is another material in this class, employed as emulsions for reducing soil run off and saving water in sub soils. This is particularly useful for tropical rainy zones (Azzam, 1980). Polystyrene based macronet polymers are reported to be potential soil conditioners (Kakoulides et al, 1993). Several soluble polymeric soil conditioners are reported to be effective in reclamating clayey soils. Examples are poly(ethyleneglycols), poly(vinylacetate) and poly(vinylalcohol) (Carr, 1975; Dowdy,1972 and Azzam, 1980). Natural rubber, ethylene vinylacetate co-polymer and polymethylmethacrylate are also reported to be useful as soil conditioners for various purposes (Soong and Yeoh,1974; Azzam, 1980).

Polyelectrolytes are the most distinct class among soil conditioners. Several acrylate/acrylamide polymers and co-polymers are very widely used and are reported to be much useful in improving chemical, physical and agronomical properties of soil. Moreover it is very effective in reclamation of saline and alkaline soils (Allison,1952;

1.4 Polymer - Soil Interactions

The effectiveness of polymers as soil conditioners depends on its ability to interact with soil fractions especially clay. Properties of soil as well as polymer decides the extend of such interactions. Molecular weight, molecular size, type and amount of surface charge and configuration are the major deciding factors of polymers while the soil factors are the type and amount of clay in soil, ionic strength and type of ions.

Also soil pH influence the polymer-soil interactions (Seybold, 1994). The polymer soil ratio also is a very important factor. Adsorption of polymers in soil depends on the type of polymer charge and it decreases in the order cationic > non-ionic > anionic. Non-ionic polymers interacts with clay fraction of soil through Vander Waal's forces. Positively charged polymers are electrostatically adsorbed on negatively charged soil fractions, such as clay or organic matter. Negatively charged polymers get adsorbed to soil through "cation bridges" between polymers and soil anionic groups (Bicerano, Benhur et al 1992; Letey, 1994).

1.5 Polyacrylamide as Soil Conditioner

Polyacrylamide (PAM) is a water-soluble polymer and is one of the most widely used and extensively studied soil conditioners. Several reviews are available on the preparation and usage of PAM (Azzam, 1980; Seybold, 1994; Barvenik, 1994). It is otherwise widely used as a flocculent in potable/waste water treatment, to strengthen paper, as adhesion and flooding agents in petroleum industry, in gel electrophoresis and in textile and soap industry as a thickening agent (Seybold, 1994).

As a soil conditioner anionic polyacrylamide (20% hydrolysed) has been reported to be most effective in stabilizing soil, since in such a condition the polymer chain is maximum extended facilitating maximum adsorption or interaction with clay (Shainberg et al, 1990; Malik and Letey, 1991). Once absorbed desorption of PAM from soil very rarely takes place (Letey, 1994). Soil with stable aggregates favours water infiltration and acts against wind and water erosion. PAM as per reports is a good soil stabilizer and is useful in stabilizing structureless soil and sand dunes (Azzam, 1980; Wallace et al, 1986; Levy et al, 1992; Shainberg et al, 1992 and Nadler et al, 1996). As per Terry and Nelson (1986) aggregate stability of a soil increased from 17 to 80 % upon PAM application. PAM when applied with suitable crosslinking agents such as glyoxal is found to be increasing the stability of soil aggregates and prevents soil compaction and increases soil friability (Azzam, 1980).

Water drops of rain or sprinklers can cause detachment of soil particles and enhances their movement. These detached particles clog at the surface of soil and are usually about 1 to 2 mm thick. This seals the soil surface and drastically reduces water infiltration causing higher runoff and further erosion. Surface-sealing and erosion are greatly controlled by PAM. (Seybold, 1994; Stern et al 1992; Fox and Bryan,1992; Shainberg et al 1990; Zhang and Miller, 1996; Lentz et al, 1992 and Lentz and Sojka, 1994; Wallace and Wallace (c),1986).

As per reports PAM greatly increased the water infiltration rate of a loess type soil from 2 to 23.5 mm/ hour and the rain intake from 12.3 to 64.2 mm in a 80 mm rain. This is very important since soils of semiarid regions are unstable and much loss occurs due to run off in rain storms. PAM is a great promise for such soils (Shainberg et al, 1990 and Azzam, 1980). Smith et al (1990) had reported that an increased erosion and decreased infiltration takes place as the impact energy of rain water drops increased. However an higher infiltration rate and decreased erosion was noticed in PAM applied soil compared to untreated plot. Irrigation efficiency is reported to be much increased when PAM is applied through irrigation water at very low concentration. Water holding capacity of soil is greatly enhanced by the usage of PAM (Terry and Nelson, 1986 and Azzam, 1980).

Growth and yield of many crops are reported to be increased upon PAM application and they include wheat, rice, maize, oats, cereals, barley, cotton, sugarbeets, rye grasses and horse beans (Azzam, 1980 and Stern et al, 1992). Increased dry-matter production and seed lings emergence in tomato, cotton and lettuce upon PAM application were reported by Wallace and Wallace (a & b, 1986). Adequate germination rate was achieved in calcareous silty and sandy loamy soils by PAM treatments. The major reason for these increased growth and yield of crops is due to the improved physical property of the soil and the increased water infiltration and aeration upon PAM application. Delaying dissolution of fertilizers, increasing sorption capacity or favouring the uptake of some nutrients by plants, enhancing soil microbial growth and imparting friability which results in improved rooting are also reported to be the possible reasons for the increased yield on PAM application as per Azzam (1980) in his extensive review on PAM. He also reports that urea and ammonium sulphate were found to be participating in coagulating soil particles when applied along with PAM and behave like long acting fertilizers.

Large quantities of PAM are intensively used to deal with problem soils. The major reason for the widespread application of PAM in Europe was the successful modification of non-fertile, calcareous land near Dijon in France. About 4 % of arable land in Belgium (4000 ha), 5 % in France (20,000 ha) and Germany (20,000 ha) are under PAM application. In Indonesia PAM application could reduce soil erosion from 17,000 Kg/ha to 4000 Kg/ha. Water repellency under citrus trees in Egypt also could be alleviated by PAM application. In Belgium, France and Germany PAM is mainly used as a mulch material in silty soil for promoting germination of sugar beets. By spraying 0.2 % PAM solution the crop yield could be increased by 8 to 10 % (De Boodt, 1975 and Azzam, 1980).

The equatorial and tropical soils which receive very heavy rain due to which the aggregate stability is continuously decreasing and the bulk density increasing. Consequently water intake and storage are reduced and surface run off and erosion greatly increased and heavy doses of fertilizers are required for these type of soils. In situation where heavy dozes of fertilizers are required tillage problems becomes difficult, PAM is a potential soil conditioner. By PAM application erosion can be reduced while aggregation, porosity, aeration, friability, infiltration, storage capacity and fertility can be increased, thus making the soil more sustainable and tillage operations made more easy (Azzam,1980).

In solving food shortage problem, increasing productivity, sustaining the existing arable land and the conversion of `problem soils' to arable one are very important. PAM-like polymers are helpful in sustaining the soil and environment (Wallace and Wallace, 1994). The above discussion points out the importance of soil conditioners in solving the problem.

1.6 Fertilizers and Agricultural Production

The importance of fertilizers in agriculture is well understood erstwhile, and present agriculture production greatly depends on it (Cardarelli, 1976; FAO, 1981). It is believed that fertilizers and pesticides are responsible for the 60 % of the total agriculture production. Fertilizer consumption and production has increased several folds when compared to the nineteen fifties or sixties (FAO, 1985). Russel et al (1989) had formulated a relationship between world nitrogen fertilizer use on cereals (X) and mean world cereal yield (Y) between 1956 and 1985, which is expressed by an equation $Y = 1202 + 13.3\ X$ with $R^2 = 0.983$. This clearly indicates the dependence of crop yield on amount of fertilizer applied. Now fertilizers have turned to be one of the costly input in agriculture. Among the N fertilizers, urea is the most widely used one because of its very high N content, ease of handling and comparatively low cost. It was introduced as a fertilizer in 1935, but its global acceptance and extensive use commenced only from early sixties. Now about 70 % of the total N fertilizer used in Asia is urea. India also consumes substantial amount of urea every year (in 1994, 17 million tons). However, efficiency of urea in soil as per several reports is very low (Gould et al, 1986; Fertilizer Statistics, 1995; Prasad et al, 1971).

1.7 Urea in soil

Often fertilizers and other agro-chemicals are applied in amount far excess than the actual requirements. Cardarelli (1976) is of the opinion that only about 15 % of the applied fertilizer enters the crops. Harper et al (1983) points out that N losses from applied fertilizer varies from 20% to 80%. Food and Agriculture Organisation (FAO) estimates that 40-70 % of the applied fertilizer is lost to the environment (FAO, 1983).

Urea when applied to soil is rapidly hydrolyse to ammonium bicarbonate. This reaction is catalysed by the enzyme 'urease' found in many species of bacteria, fungi and yeast. The ammonium bicarbonate thus produced is subsequently nitrified to nitrite and then to nitrate. The first conversion to nitrite is by the activity of `nitrosomonas' and the subsequent conversion to nitrate is by the activity of `nitrobacter' species of microbes (Gould et al, 1986).

The rapid hydrolysis of urea in soil elevates the pH around the urea granules and results in high concentration of ammonium. This situation is very conducive for ammonia volatilization (Gould et al, 1986). One of the major ways of urea loss is by volatilization as ammonia. The ammonia in high concentration in soil is toxic to germinating seeds. Ammonia volatilization is severe when urea is applied by surface broadcast method especially in hot countries (Greenwood, 1981). The loss of urea as ammonia from flooded rice fields poses very serious problems. Biological denitrification is also, a major mechanism of N loss from rice fields that are urea fertilized. A considerable amount of applied urea-N is lost in the form of ammonia from agricultural fields (Gould et al 1986; Bohlool et al 1992; Fernando and Roberts, 1975).

Leaching is another mechanism by which loss of urea and other ammonium forming fertilizers takes place. Urea is a non-ionic and highly water soluble compound and is susceptible to leaching. It is weakly absorbed in soil. Leaching losses of urea occurs by two processes. Urea leaches as such, and as nitrate, the converted product of it in soil. Nitrate ions are very mobile in soil and easily leach down (Gould et al, 1986). It is reported that most of the unused nitrogen (that is not taken up by plants) from agricultural fields out of the fertilizer application leaches down to ground water sources and contaminate the canals, rivers and lakes. The nitrate ion contamination in drinking water causes serious concern, as it is a suspected agent causing `methaemoglobinaemia' in babies and cancer in adults. Maximum admissible concentration (MAC) in drinking water for nitrogen is 11.3 mg/litre as per the direction of European Economic Community. It is reported that the number of people receiving drinking water outside MAC of nitrate is increasing every year. To solve this problem, one of the suggestions was to eliminate or reduce the use of N fertilizers. If this suggestion is opted and followed, drastic reduction in crop yield will be resulted. The pollution due to nitrate ions in drinking water is often called as a `chemical time bomb' by water scientists (Hepburn et al, 1987).

Another problem encountered in urea application is nitrite ion accumulation in soil which is toxic to plants and cause losses of nitrogen. It is reported that the alkaline pH and high ammonium concentration due to the urea hydrolysis in soil affects adversely the `nitrobacter' species, but not the `nitrosomonas' species of bacteria. Hence the urea to nitrite conversion do take place but subsequent conversion of nitrite to nitrate is inhibited. Due to this nitrite ions accumulate and losses of nitrogen takes place as NO and NO_2. These oxides of nitrogen can cause depletion of the precious ozone layer that protects the earth from radiation hazards. Eutrophication (accumulation of salts) of river estuaries is yet another problem associated with over consumption of urea. This very seriously affects the aquatic biota (Bohlool et al 1992; Sahrawat and Keeney, 1986).

1.8 Scope of the work

The increasing rate of urea production itself is an evidence for its increasing consumption. It is a globally accepted and the most widely used N fertilizer. Prasad (1971) points out, in field studies N recovery of urea and other nitrogen fertilizers is about 50% or below for most of the crops. The other 50 % of soil applied urea and other N fertilizers is simply lost to the environment and creates severe environmental problems as explained earlier. In such situation where an increased food production is a necessity and when that is possible only with the aid of chemical fertilizers like urea, and when serious environment problems arises out of the fertilizer application, it is the major concern of scientific community to increase the efficiency of urea like fertilizers or to minimise the loss of fertilizers to the environment, thus helping the farmers to produce more while sustaining the environment. Ever since the fact that low fertilizer efficiency of urea was recognised, efforts were made to increase its use efficiency and it is still continuing.

CR technology can offer much to solve this problem. It is evidenced by the past work as well as the suggestions made by several agencies. FAO suggests the fertilizer manufacturers to increase the efficiency of fertilizers by the development of CR fertilizers. Organization for Economic Co-operation and Development had proposed to concentrate research on CR fertilizers to alleviate the nitrate ion problem in drinking water. The Scientific Advisory Committee to Prime Minister of India in their report in 1988 says "while on the subject of fertilizers, it needs to be emphasised that by using modern science and technology inputs a significant amount of conservation is possible. Much of the urea that is applied to the soil is lost due to leaching and nitrification. Controlled Release of urea could offer impressive savings, but we have not provided sufficient S & T inputs in this vital area to make this possible" (Hepburn and Arizal, 1988; Gopakumar et al, 1993) .

The physical or chemical combinations of urea with polymers and other materials make it a slow release product and several such formulations are available. The major advantages of such formulations are

1. A metered or slow release of urea to the soil over a period of time is made thereby sustained correction of N deficiency is possible. An increased N uptake by plants results, by which yield is increased. This also reduces the over-consumption of nutrients by crops and a fairly uniform growth of crops is ensured throughout the growing season.

2. As the action of CR fertilizers can be adjusted to sustain for a long time, (better systems can perform the function for the entire crop season) frequency of application can be minimised. Thus less labour cost and less machinery damage to crops results.

3. Losses due to leaching and vaporization are minimized. Thus the use efficiency of urea increases and reduces the environmental pollution considerably (Joyce et al, 1988; Trivedi and Pachayappan, 1979).

Agricultural productivity can not be increased without chemical fertilizers. At the same time fertilizer application should not tamper the environment equilibrium.

Controlled Release Technology is very much applicable to this problem. Proven soil conditioners had been utilized in this study to prepare CR urea fertilizers so that CR property and soil conditioning property are tried to be merged in a single product.

The present study aims to incorporate suitable polymer and fertilizer urea in such a manner that the product have CR property. The selection of polymer was very important since the properties of which is the deciding factor of the CR property of the product. Crosslinked polyacrylamide / polymethylmethacrylate were used for coating urea in the present study. Along with these, the suitability of polymers like polystyrene, poly(vinylchloride), ethylene vinylacetate co-polymer and natural rubber to be used as sealant materials for the coating were evaluated.

Chapter 2

Review on Polymer-Based Controlled Release Agrochemicals

2.1 Polymers in Control Release Agrochemicals

The different classes of polymers viz., elastomers, plastics and fibers are extensively used in agriculture for varied purposes. The major application fields include CR pesticides, herbicides and fertilizers, soil conditioning, plant protection, seed coating and gel planting (Mc Cormick,1984). A number of CR agricultural chemicals had been successfully tested and are commercially available. A detailed list of synthetic and natural polymers used for the preparation of such formulations are given by Kyodonieus (1980). Controlled Release agricultural chemicals other than fertilizers are discussed initially.

Crops and livestock are produced in a hostile environment comprising approximately of 50,000 species of fungi, 30,000 species of competing weeds and over 10,000 species of insects, in addition to the grain devouring birds and rodents (Cardarelli,1976). The biologically active chemicals have been very effective in suppressing the undesirable weeds and insects, thereby in an increased food production. However the use of such chemicals should not create any adverse effect on man and his environment. For example use of DDT, a pesticide with very long life is undesirable since its residue enters the food chain. On the other hand pesticides with very short lives do not serve the purpose. Moreover these materials are susceptible to leaching by rain water, removal by evaporation or by rapid biodegradation into inactive components. These lost chemicals contaminate the ground water and are a threat to aquatic and wild life. In such cases large excess of these costly active chemicals are applied grossly to compensate the losses. In situation like this the CR technology can offer much to save the costly chemical and the environment, more over the desired action can be prolonged. Many of the active biological agents are effective at very low concentrations. Different CR formulations having varied release profile had been synthesized by incorporating these chemicals either physically or chemically to polymers (Cardarelli,1976; Neogi and Allan, 1974).

2.2 Physical Combinations of Polymers and Active agents

The pre-requisite of a CR physical combination is that the polymer and active agent should not unnecessarily react. Several physical combinations of polymer-pesticide and polymer-herbicide are commercially available and many are under experimental stage (Cardarelli, 1980 a). For CR formulations plastics are preferred to elastomers due to its comparatively low cost and ease of processabilty. The solubility of an active agent in plastics is difficult due to the strong interchain forces. Consequently a diffusion-dissolution mode of agent release is rather difficult to achieve. A major factor affecting release is porosity or free volumes within the matrix of the plastic material, the magnitude of which is controlled by the processing conditions and incorporated additives (Rogers, 1977).

Several pesticides like sevin, dimethoate, ethyl trithion, methyl trithion, diazinon, malathion, chloropyriphos and temephos can be incorporated in plasticized poly(vinylchloride) to obtain CR products (Cardarelli, 1980 a). Chloropyriphos can be combined with polyethylene which can control mosquito larvae for about 18 months by one application itself (Miller et al, 1973). Tributyl tin flouride in a poly-thene modified ethylene vinylacetate co-polymer is used as a CR molluscicide (Cardarelli, 1980 a). Polythene-paraffin mixture combined with insecticide `dichlorvos' has long term effective vapour release (Bogard, 1975). It has been reported that active release is possible for over 160 days when 2,3,6 trichloro phenyl acetic acid combined with polyethylene (Harris, 1973).

Antifouling agents like trialkyl and triaryl organo tin compounds can be incorporated in a variety of elastomers like natural rubber, styrene butadiene co-polymers, ethylene-propylene-diene terpolymers, polyacrylonitriles, polyisobutylenes and polyurethanes. Several organo phosphates, halogenated hydrocarbons and carbamates can be incorporated with elastomers. Temephos/ethylene propylene diene combination had been reported to be a very effective CR pesticide against mosquito larvae (Cardarelli, 1980, b). As early as in 1969, a natural rubber based herbicide formulation containing butoxy ethanol amine ester of 2,4 dichloro phenoxyacetic acid was developed and found effective against aquatic weeds (Cardarelli,b1980, Thompson, 1974).

Apart from the distribution or dissolution of active agents in polymer matrix, there are other methods like micro or macro encapsulation of active agents using polymers for the preparation of CR products. Interfacial polymerization is the widely used technique for microencapsulation. This method is rather attractive, both operationally and economically since water is the continuous and storage phase. Condensation polymerization reactions yielding polyamide, polyester, polyurea, polyurethane, polycarbonate and polysulfonamide can be very well utilized to prepare CR formulations. In such cases the active agents are dissolved in the oil phase along with monomeric species. Crosslinking of the polymer wall yields durable and storage stable capsules (Lowell et al 1977 ; Koestler, 1980). An encapsulated pesticide methyl parathion in crosslinked polyamide-polyurea is marketed under the trade name `Penncap-M'. Microencapsulated pesticides like ethyl parathion and diazinon are under field evaluation. Several controlled release pheromone formulations are also synthesized by microencapsulation. Pheromones are highly expensive and volatile and are used to disrupt the mating activities of insects, thus preventing from the insect population build up (Beroza et al, 1973 ; Carde et al, 1975). Much research is continuing in the utilisation of starch to be used as a polymer matrix for CR agrochemicals (Shasha, 1980).

2.3 Chemical Combinations of Polymers and Active agents

The active agent is chemically attached to the polymer through a covalent or ionic bond. Bio-degradable and non-bio-degradable polymers can be utilised to prepare such combinations. Essentially the biocide and the polymer should contain functional groups which are reactive to each other. The substrate-biocide bond should be such that it may be cleaved by the environmental processes more readily than any other bond in the active agent. Amide, ester and anhydride linkages are very successfully utilised in CR combinations and systems with high percentage of the active agent can be prepared by this method (Allan et al, 1980; Harris, 1980).

2.3.1 Bio-degradable Systems

Biocides having carboxylic acid groups (such as phenoxy carboxylic acids) and the natural polymers having a number of hydroxyl groups such as cellulose, chitin, lignin, starch, alginic acid and lignocellulose had been successfully combined to prepare CR formulations. Heating carboxylic acid herbicides to their melting point and allowing to react with natural polymers yield covalently condensed CR products (Allan et al, 1980). Combinations of phenoxy herbicide acids with natural polymer, aminopolysaccharide chitosan (fish waste) having reactive amine and carboxylic acid groups is an example for amide linkages in CR formulations. CR hebicides by the combination of 3, 6-dichloro-o-anisic acid and fish waste were found to be five times more effective than the free herbicide (Allan et al, 1980). Chitosan is a promising natural polymer for the CR formulations(Allan et al, 1978). Polysaccharides like cellulose, chitin, amylose and amylopectin were found to be useful natural polymers for the CR formulations of 2,4-dichlorophenoxyacetic acid and metribuzin (McCormick et al, 1981). CR formulation of kraft lignin and propachlor have been successfully prepared by Wilkins and Blackmore (1987). Similarly it is reported that rice husk lignin can be combined with 2,4-dichlorophenoxyacetic acid (Kenawy et al, 1992). A review on application of lignin in CR formulations is given by Wilkins (1983). Chemical combination of 2,4-dichlorophenoxyacetic acid and corn starch is also an example of such formulation (Kenawy et al, 1992).

2.3.2 Polymers with Pendant Substituents

Two different synthetic methods are followed in formulating such systems. One method is the polymerization of the active agent containing monomers. The other is functionalization of a pre-formed polymer, thereby the active agent is attached to the polymer system (Harris, 1980; Mathew and Pillai,1993).

2.3.3 CR Formulations by Polymerization of Functional Monomers

The biocides containing reactive functional groups such as carboxyl (-COOH), hydroxyl (-OH), sulfhydryl (-SH) and amino (-NH2) groups can be converted to polymerisable derivatives (Harris, 1980). For example vinyl derivatives of pesticides having carboxyl acid group can be easily prepared by mercuric acetate-sulphuric acid catalysed reaction of the acid with vinyl acetate. Here the acidic H of pesticide is replaced by the vinyl group of acetate (Feld et al, 1975; Harris and Post (a & b), 1975).

Similarly, polymerisable derivatives of pesticides containing acid groups can be prepared by a reaction with alcohols having a vinyl group (Harris and Post, 1974; Harris, 1980). Such functional biocide monomers can be polymerized by bulk, solution or emulsion methods. The vinyl ester of 2,4-dichlorophenoxy acetic acid can be bulk polymerized using free radical initiator azo-bis-isobutyronitrile (AIBN). Solution polymerization method is employed to prepare the co-polymer of 2-acryloxyethyl 2,4-dichlorophenoxy acetic acid and methacrylic acid. Emulsion polymerization is also employed to prepare high molecular weight species of 2,4 dichlorophenoxy acetate (Harris, 1980; Wilkins, 1976).

Co-polymerization of herbicidal monomers and hydrophilic co-monomers were also reported. Co-polymer of vinyl 2,4 dichlorophenoxy acetate and trimethyl amine methacrylamide is an example. Increased release of herbicide is obtained as the hydrophilic co-monomer content increased.(Kenawy et al 1992; Harris et al 1976).

Crosslinked polymers synthesized using pentaerythritol triacrylate as crosslinking agent when used in CR formulations showed an almost constant release rate. Acrylate, methacrylate and acrylamide derivatives of the herbicide, biguanide, are also reported and methacrylate and acrylamide species are more resistant towards hydrolysis than acrylate species. It is possible to synthesize covalently or non covalently bound biguanide systems to various cross linked polyacrylamide films, having different release profile (Kenawy et al, 1992).

2.3.4 ***CR Formulations by Functionalization of Pre-formed Polymers***

Functionalization of pre-formed polymers can also be employed to formulate CR products. By this method a pre-formed polymer is modified to contain the active biocide species. Essentially the polymer and the biocide species should have reactive functional groups. As in the polymerization of biocide monomers, hydroxyl and carboxyl groups containing polymers and biocides are easily combined by this method.

Pesticides containing acid groups are converted to more reactive acid chlorides, which can react with polymers containing pendant hydroxyl or amino groups. Acylation of synthetic and natural polymers are possible in this manner (Neogi, 1970; Wilkins, 1976; Allan et al, 1971 and Allan et al, 1977). In a similar manner pesticides having hydroxyl groups can react with polymers containing pendant acid chlorides. Several synthetic polymers are reported to be prepared by this type of esterification (Harris, 1980). Polymers having pendant hydroxyl groups are also reported to be reactive towards pesticides having reactive aldehyde group (Schacht et al, 1977).

Certain molluscicides are now prepared in combination with polymers to obtain CR products. In such systems an "attractant" can also be incorporated, so that snails are attracted by the genus specific `attractant' and will be perished, due to the action of toxicant. Copper(II) is very effective against snails and its efficiency is reported to be increased when incorporated with an ion exchange resin as a substrate to hold it. Copper sulphate can be incorporated with styrene-butadiene rubber also and is found to be effective against shistostomiasis (Kenawy et al, 1992).

Some marine organisms continuously settle on the submerged surface of hulls of ships, submarines and buoys and this fouling creates very serious problems including reduced speed, increased fuel consumption and destroy the anticorrosive coating. Conventional biocides application against fouling is effective only for a short period. Several organo metallic polymers that have CR properties are found to be effective against fouling. Hydrophilic co-polymers consisting of 8-quinolinyl acrylate and acrylamide for the same purpose had been synthesised (Kenawy et al, 1992).

2.4 Controlled Release Fertilizers

An ideal fertilizer supplies the nutrient required for optimum plant growth during the entire growing season and has reasonable cost/benefit ratio and minimum adverse effect on environment (Gandeza et al, 1991). Three widely accepted practices in order to enhance the efficiency of N fertilizers are *(a)* employing slow or CR fertilizers *(b)* following cultural practices such as deep placement and incorporation of fertilizers with soil *(c)* inhibition of microbial activity to minimize conversion of ammonium ions to nitrate ions and /or urea to ammonium ions. Slow or CR is a newer method and formulation of ideal fertilizers based on this technology has been attempted by many research groups.

Slow or CR property for fertilizers is achieved mainly by two methods: (1) Coating or encapsulating the fertilizer in water insoluble or sparingly soluble and inert materials. (2) Synthesizing fertilizer with slow dissolution as in the case of condensing urea with various aldehydes (Beaton et al, 1967; Prasad et al, 1971). Several polymers of synthetic and natural origin and many inorganic substances have been found useful for coating fertilizers (Gandeza et al, 1991; Yeoh and Soong, 1977 ; Hepburn and Arizal, 1988; Srivastava and Bhowmik, 1976). Release of fertilizers from these coated granules is mainly associated with one or more of the following mechanisms such as (a) water vapour entering the core dissolving the fertilizer and coating bursts due to internal osmotic pressure build up. (b) degradation of coating by microbes or other environment agents and subsequent penetration of water in to the core through the degraded portion, dissolution of the fertilizer and subsequent emission. (c) movement of water to the inner core, dissolution of fertilizer and subsequent evolution of the solution to outside controlled by micropores of the coating. Disadvantage of the first two mechanisms is that once the coating membrane bursts or degrades fertilizer release will be very fast. The third mechanism is very much useful in slowing down the release of fertilizers as water enter to, the core through tiny pores and subsequently fertilizer comes out to the soil. Here the rate of release is rather steady comparing to other types and in some case the rate is found to be gradually declining. Usually temperature influences the rate of release of such systems. As temperature increases pressure builds up in the core, subsequent release also is accelerated. However this is beneficial for the plants, since as temperature increases, plant absorption of nutrient also increases. Thus the system can adjust somewhat the available nutrient in soil as per the plant requirement. In such type of systems usually the release is independent of pH and microbial activity. Several materials are used for such coating. Resin, plastic, lac, silica, sulphur, natural rubber, polyolefin, starch and gypsum were reported to be used for preparing CR urea fertilizers (Prasad et al, 1971; Skogley and King, 1968; Brown et al, 1963; Ahmad et al, 1963; Dhanke et al 1963; Kyodonieus, 1980;Shasha,1980; Gandeza, 1991).

One of the first commercialized and extensively studied slow release fertilizers is sulphur-coated urea (SCU). Urea granules uniformly coated with sulphur followed by a wax coating to seal any pores or cracks of the first coating is found to have slow release property. The efficiency of the product depends on size of the urea prill or granules and the thickness of coating (Rindt et al, 1968; Trivedi and Pachaiyyappan, 1979).

The release from SCU has been reported to take place by one or more of the following mechanisms. (1) Bio-degradation of either wax or sulphur or both coatings. (2) Conversion of amorphous polymer sulphur to crystalline form results in the creation of cracks and pores in the coating. To reduce the microbial attack on coating sometimes microbicidal agents like coal tar is added. Environmental parameters like temperature and moisture can also influence the release rate. Other parameters which affect the release rate are thickness of coating, placement of the granule and time of contact with soil (Allen et al, 1971; Prasad et al 1971; Gould et al, 1986). There are several reports on the field performance of SCU. It is found to be very effective for turf and forage grasses (Allen et al, 1971; Gould et al, 1986). It is reported that when high amount of uncoated urea is supplied to burmuda grass turf, it merely destroyed the turf, whereas ammonium nitrate caused moderate burning of the foliage while SCU caused no damage. Similarly application of uncoated urea at 112 kg/ha to corn seedlings, destroyed it while SCU at the same rate caused no damage (Prasad et al, 1971). SCU is also reported to be an excellent N source for ornamental plants in pots. Experiments on corn indicated that on sandy-loam and loam soils where irrigation practices were carefully adjusted to prevent leaching losses, corn yield and N recovery with a single application of SCU was on par with three split applications of uncoated urea (Prasad et al , 1971). Single application of SCU resulted in more yield and more evenly distributed forage and protein than due to three split applications of ammonium nitrate and nitric phosphate. Observations were similar in crops like sugar cane, citrus and rice (Gould et al, 1986).

The major disadvantages of SCU are (1) the sulphur coating, as not very abrasion resistant may crack during shipment. (2) Sulphur oxidising organisms metabolizes S to produce sulphuric acid, hence soil acidification may take place. (3) Inclusion of biocide in wax coating is necessary, otherwise rapid microbial attack on the sulphur coating occurs and results in fast dissolution of urea. However, this enhances the cost further. (4) In countries like India where sulphur is being imported, the manufacture of SCU is difficult.

2.5 Controlled Release Fertilizers Based on Polymers

Plastics as well as elastomers were used to prepare CR urea fertilizers. Urea is either coated with polymer or distributed in a polymer matrix. Polyethylene, polystyrene, ethylene-propylene co-polymer, ethylene-vinyl acetate co-polymer, natural rubber and starch have been successfully used for the formulation of CR urea fertilizers (Brown et al, 1966; Ahmed et al, 1963; Gandeza et al 1991; Hepburn et al, 1987, Savant et al, 1983). As early as in nineteen sixties the concept of CR was tried and practised in the fertilizer field. Dhanke et al (1963) reported that placing fertilizers in polyethylene capsules effectively controlled the release of fertilizers.

Korean Advanced Institute of Science and Technology in collaboration with International Fertilizer Development Centre, had developed several batches of Silicate and Polymer Coated Urea (SPCU) and they had observed satisfactory results for their product on rice (Savant et al, 1983). Their coating procedure involved coating urea granules initially with sodium silicate and then with a polymer latex using fluidised bed technique. Three types of SPCU were prepared with high, medium and slow release rates. The dissolution rate was adjusted by varying the thickness of coating. The polymer latex used for coating was prepared with styrene, 2,ethylhexyl acrylate and acrylic acid. The SPCU granules retained 2 - 10% of urea two months after application in soil, and this portion of N will be available to plants only after the maximum N requirement stage is over. Nitrogen losses due to NH_3 volatilization, leaching and denitrification is lower for SPCU and it is reported to be superior to uncoated urea (Savant et al, 1983).

An experimental fertilizer called Reactive Layer Coated Urea (RLCU) had been developed by International fertilizer development centre (Christianson, 1988). Coating procedure involves placement of urea granules in a rotating drum, heating and spraying with diphenyl methane diisocyanate. This reacts with NH_2 groups of urea and forms a `reactive layer coating' which have excess unreacted NCO groups. On this coating hot aromatic polyester polyol was sprayed and allowed to react with the free NCO groups to form a water insoluble sealing layer. Uniformly sized urea granules were taken for the process, thus regulated the thickness of coating to obtain relatively uniform product. The material was yellow in colour and was free flowing. The coating was reported to be hard and abrasion resistant. The rate of release was affected by coating thickness, temperature and to a lesser extent by soil moisture. As coating thickness increased, rate of release decreased. The mechanism of urea release from RLCU is reported to be by the movement of water vapour through the coating, because of the high osmotic gradient existing between the fertilizer and soil due to the high humidity in soil. The water vapour dissolves the urea in RLCU and comes out by diffusion. It is also reported that soil pH and microbial activity were not influencing the release rate of RLCU (Christianson, 1988).

Polyolefin-coated urea fertilizer (POCU) was developed in Japan (Gandeza et al 1991). Several types of POCU with varying release rates are reported to be commercially available in Japan. The coating is primarily a blend of polyolefin type resin, ethylene vinylacetate co-polymer and polyvinylidine chloride as major components. Moisture permeability of this resin coating depended on temperature and this property is reported to be achieved by incorporation of inorganic fine powder of talc, silica and metal oxides with the polymer coating. By varying resin/talc ratio different products with different dissolution rate could be obtained. The release mechanism of this product involves movement of water into the granule by osmotic potential, dissolution of urea and diffusion of urea solution through the coating. Release primarily dependent on temperature,. For every 10°C rise in temperature, N dissolution from the granules doubled. POCU is considered as a CR nitrogen fertilizer since N release is controlled by the moisture permeability of the coating which in turn is controlled by temperature. Release was reported to be less sensitive to soil pH and soil moisture. (Gandeza et al; 1991).

Starch, natural rubber and poly ethylene vinylacetate have been used as a matrix for the preparation of CR fertilizers either by dissolution and/or distribution . Otey et al (1984) describes the preparation of starch-urea blends. The method yielded granular products with comparatively higher rates of release and will be useful for crops which needs N at a faster rate. Natural rubber had been used to produce slow release fertilizers by Yeoh and Soong (1977). Their method of preparation involved blending of nitrogen, phosphorous, potassium and magnesium fertilizers with natural rubber solution in toluene and extruding fertilizer-rubber blends and cutting to small pieces after drying by passing hot air. These granules were coated first with a rubber solution and then with a combination of rubber solution and pre-vulcanized concentrated latex. In order to enhance drying they had incorporated propylene glycol with the latex concentrate. To avoid sticking together, small amounts of clay was added to the coated fertilizer. Rubber solution was preferred to latex in preparing the blend since high concentration of fertilizer salts coagulated in the latex which resulted in non-uniform dissolution of fertilizers. This encapsulated fertilizer released nutrients gradually and more evenly and better growth was obtained for rubber plants, compared to the conventional fertilizers. Coated fertilizers with thicker coating were less hygroscopic and had lower release rate. This fertilizer was reported to be suitable for sandy soils were nutrient retention is low and leaching problems are maximum (Yeoh and Soong, 1977; Soong et al, 1977).

Another natural rubber based slow release fertilizer had been formulated by Hepburn et al (1987). Here instead of coating fertilizer granules with polymer, it is distributed in a polymer matrix (natural rubber). The advantage of a flexible matrix is that it is less vulnerable to excessive impact of abrasion during shipment and handling. Rubber was cold masticated and then activators, accelerators and sulphur were added. Afterwards urea was added along with processing aid-urea sealant and dispersed in the matrix. Polyethylene plastic waste / an aromatic oil (dutrex 729) / oleic acid / microcrystalline wax / additional masticated rubber were used as processing aid cum urea sealants. It is reported that the crosslinking influences the rate of release of fertilizer from the matrix. The crosslinking process was aided by zinc oxide, stearic acid, tetra ethyl diuram disulphide and 2, mercapto benzthiazole. For easier incorporation of urea in rubber at higher temperatures, microcrystalline wax was found to be useful. They had evaluated the product by leaching experiments and found that as urea content of the product increased rate of release also increased. The processing aids at concentration of 10 % or below increased the rate of release and at higher concentrations the rate of release was comparatively low. The dissolution rate of this product is influenced by temperature positively. However, some problems regarding the processing are still existing to be refined. The Urea -Rubber Matrices (URM) even at higher application rates like 500 Kg/ha did not adversely affect the seed germination while prilled urea at 300 Kg/ha itself affected severely the seed germination. The release of urea from URM was mainly by diffusion. The microbial decay of rubber matrices was also reported to be a factor involved in dissolution mechanism. Another factor affected release of urea was root penetration of the URM (Hepburn and Arizal, 1988; Hassan et al, 1990; Hepburn and Arizal, 1987).

Several naturally occurring materials were also found to be effective in coating fertilizers. Lac and gypsum are such materials. Srivastava and Bhowmik (1976) had made use of shellac for coating fertilizer urea. As shellac absorbs moisture due to the presence of five hydroxyl groups in its molecule they had reacted it with rosin, so that four hydroxyl groups were esterified and used for coating urea. Urea granules were made moisture free and tumbled with linseed oil. To the oil smeared hot urea granules resin powder was added. The resin melted and spreads over the granules. Recoating was done with oil and resin powder by the same procedure. Soap stone powder was used as a conditioner. A third coating again with the oil and resin powder was done. To this three times coated urea, coal tar as a microbicide was added and tumbled. Thereafter a final coat using paraffin wax was done to seal all cracks, pores and uncovered portions of urea granules during the resin coatings. The product was reported to be free flowing and dry and uniformly coated.

As the price of rosin rised up another method of coating using lac alone was reported by Bhowmik (1980). Here `Kirilac' a by-product of lac industry which is of no commercial value was utilized. Kirilac an insoluble mass is formed by the reaction between hydroxyl and carboxyl groups of shellac molecules during its manufacture.

Another coated fertilizer, gypsum coated urea had been reported by Jayalekshmi Aiyyar (1989). Urea and finely powdered gypsum were mixed in a pan and water sprayed to the mixture. By adjusting temperature and moisture a uniform coating was obtained. Thereafter a binding agent which polymerize on contact with gypsum was sprayed on to the granules, thus converting gypsum coating to a hard shell. Ammonia volatilization losses from gypsum coated urea was lower than prilled urea. Gypsum contains sulphur and calcium, that are important plant nutrients, is reported to be a potential agent for coating fertilizers.

Controlled release zinc fertilizers had been formulated by Joyce et al (1988). Here the zinc fertilizers were distributed in a polymer matrix and extruded. Ethylene vinyl acetate (EVA) and low density polyethylene (LDPE) and their blends were used as the polymer matrix.

Another approach of making CR fertilizers is to use water absorbing polymers as a carrier for fertilizer solutions. Smith and Harrison (1991) had carried out experiments on acrylate, vinyl alcohol and starch based polymers that can be expanded in fertilizer solutions. Apart from the above mentioned examples of controlled or slow release fertilizers a number of potential patented products are there. This brief review brings out the major development occurred in the field of CR fertilizers over the past few decades. World-wide the importance of CR chemicals especially fertilizers is felt and it is a thrust area of research. However commercialized products are very few due to several reasons, including the cost factor. Hence efforts are being continued by several groups in this field.

An agriculture based economy prevailing nation, India, now having the second largest population in the world has to produce more food and fiber for which application of fertilizers is a must. The high cost and environmental problems associated with application of fertilizers at very high rates makes it justifiable to continue research on CR fertilizers as pointed out by the Scientific Advisory Committee to the Prime Minister of India.

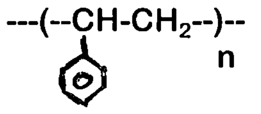
In India urea is produced and consumed in very large quantities. `Surface broadcasting' method is followed in most of the cases hence losses are very high. Our effort was to evolve suitable systems that can regulate the dissolution of urea to soil, thereby increasing the efficiency and minimizing the pollution. The polymers that are used are proven soil conditioners, it will be useful for generating favourable soil physical condition for better plant growth.

Chapter 3
Materials and Methods

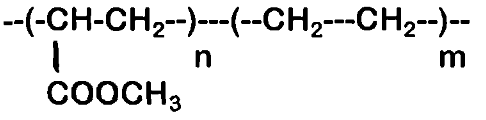
3.1 Introduction

Urea fertilizers when coated with suitable polymers, Controlled Release (CR) properties can be achieved. The crosslinked polymers being more stable and having a net structure is more useful for coating purpose. In this study two crosslinked polymer backbones viz polyacrylamide (PAM) and polymethyl methacrylate (PMMA) were used separately for coating fertilizer urea. Using the crosslinking agents divinylbenzene (DVB), N,N'-Methylene-bis-acrylamide (NNMBA), tetraethyleneglycol diacrylate (TTEGDA) and pentaerythritol triacrylate (PETA), four different crosslinked systems each in polyacrylamide (PAM) and polymethyl methacrylate (PMMA) backbones were prepared and used for coating urea fertilizer.

Along with crossilinked polymer certain sealants were also employed for coating. Polystyrene (PS), polyvinylchloride (PVC), natural rubber (NR) and ethylenevinylacetate co-polymer (EVA) were used separately along with paraffin wax as sealants in each of the four crosslinked polymer systems of PAM and PMMA. These four sealants were used separately along with paraffin wax in each of the four crosslinked polymer systems of polyacrylamide (PAM) and polymethylmethacrylate. The structure of the sealants used are shown in fig 3.1.

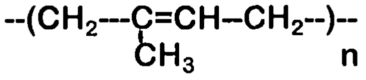


Polystyrene



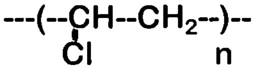
$$--(-\underset{COOCH_3}{CH}-CH_2--)_n---(--CH_2---CH_2--)_m--$$

Ethylenevinylacetate co-polymer



$$--(CH_2---\underset{CH_3}{C}=CH-CH_2--)_n--$$

Natural rubber



$$---(--\underset{Cl}{CH}--CH_2--)_n--$$

Polyvinylchloride

Fig 3.1. Structure of sealants used

Method of preparation of Polymer Coated Urea Fertilizers (PCUF) and their evaluation for slow release properties are described. For all the experiments urea granules and sealant solutions used were prepared as described below.

Polystyrene used in this study was waste packing material widely known by the trade name 'thermocol'.

3.1.1 Preparation of Urea Granules

Urea granules used in this study was of fertilizer grade and were made moisture free before using by placing it in an oven at 80° C for 2-3 hours. To obtain uniform size the granules were passed through a 2mm sieve and those retained by the 1mm sieve were separated and were used for the study.

3.1.2 Preparation of Sealant Solutions

The sealant solutions were prepared by dissolving paraffin wax / PS / NR / EVA or PVC in minimum quantity of $CHCl_3$. Thermocol (PS) was instantaneously soluble in $CHCl_3$. NR and EVA could not be easily dissolved in $CHCl_3$. EVA was allowed to swell in $CHCl_3$ overnight, thereafter with continuous shaking and slight warming it could be dissolved. NR could also be dissolved in similar manner, but a longer time was required. Another method of dissolving NR was swelling it in toluene and making a viscous solution by vigorous shaking. Subsequently required amount of this solution was diluted and used for the coating purpose. PVC used was in the powder form and was easily soluble in $CHCl_3$ with slight warming.

3.1.3 Destabilization of Monomers

Before using for reactions monomers that were stabilized by inhibitors were destabilized by treating it with sodium hydroxide solution, washed with distilled water and finally dried over sodium sulphate.

Free radical initiated solution polymerization method was used to prepare the crosslinked polymer. Selection of solvent was very important, since in ionic solvents such as water or alcohol urea dissolves and coating could not be carried out. After experimenting with several solvents, chloroform was selected as the solvent, which is a nonsolvent for urea and solvent for the co-monomers used.

Before carrying out the coating procedure, it was confirmed whether the co-polymerization of acrylamide/methylmethacrylate and the ~~other~~ crosslinking agents (DVB, NNMBA, TTEGDA and PETA) takes place in chloroform and whether urea do interfere or inhibit the reaction

3.2 Materials Used

The chemicals used and the manufactures are listed below.

Material	***Suppliers***
Acrylamide	Sisco Research Laboratories, Bombay
Azo-bis-isobutyronitrile	Aldrich Chemical Co,Ltd, England
Calcium Chloride	EMerck India Ltd, Bombay.
Chloroform	EMerck India Ltd, Bombay.
Diacetylmonoxime	Aldrich Chemical Co,Ltd, England
Divinylbenzene	Aldrich Chemical Co,Ltd, England
Ethylenevinylacetate co-polymer	Polyolefin Industries, Bombay
Magnesium Oxide	Central Drug House, Bombay
Methylmethacrylate	Kemphasol Chemicals, Bombay
N,N'-Methylene-bis-acrylamide	Sisco Chem Industries, Bombay
Natural Rubber	Rubber Research Institute of India
Orthophosphoric acid	E Merck India Ltd, Bombay.
Paraffin Wax	E Merck India Ltd, Bombay.
Paradimethyl aminiobenzaldehyde	E Merck India Ltd, Bombay.
Pentaerythritol triacrylate	Aldrich Chemical Co,Ltd, England
Polystyrene	Waste packing material (thermocol)
Polyvinylchloride	IPCL, Baroda
Potassium persulphate	E Merck India Ltd, Bombay.

Sulphuric acid	E Merck India Ltd, Bombay.
Tetramethyl ethylenediamine	Sisco Research Lab, Bombay
Tetraethyleneglycol diacrylate	Aldrich Chemical Co,Ltd, England
Thiosemicarbazide	Aldrich Chemical Co,Ltd, England

3.3 Preparation of Polymer Coated Urea Fertilizers (PCUF) Based on Crosslinked Polyacrylamide.

3.3.1 Preparation of PCUF based on Diviylbenzene-crosslinked Polyacrylamide (DVB-PAM) Systems.

Structure of DVB crosslinked PAM is shown in figure 3.2. Co-monomers acrylamide (2.21g) and DVB (0.38 mL) were dissolved in $CHCl_3$ (25 mL), containing the initiator azo-bis-isobutyronitrile (AIBN) (0.1 g). Moisture free fertilizer grade urea granules (25 g) were added to the solution. The temperature of the system gradually raised to $40^{\circ}C$ using a water bath. After some time another initiator tetramethyl ethylene diamine (TEMED) (0.2mL) was added to hasten the polymerization reaction. As the polymerization reaction started, the polymer formed and get deposited on the surface of urea granules. As this process was proceeding the sealant solutions were added in small volumes.

$CHCl_3$ solutions of TC/NR/EVA or PVC (1g) and wax (1g) were added to the reaction mixture and the contents were properly stirred with a magnetic stirrer or manually with a glass rod. Overhead stirrer could not be used since it breaks the coating formed over the urea surface. The reaction allowed to continue for about an hour and gradually the solvent evaporated. As the solution became more and more viscous, use of magnetic stirrer became difficult. Hence mixing and stirring using a glass rod was preferred during later periods, and the stirring continued till all the solvent was evaporated, so that an even coating could be obtained. The four products thus prepared were spread over a petry dish and allowed to dry in an oven at 60-70 $^{\circ}C$ for 2 to 3 hours. Thereafter it was cooled to room temperature and re-coated using same materials of the initial coating. The products appeared to be non-tacky and free flowing.

3.3.2 Preparation of PCUF based on NN'-Methylene-bis-acrylamide - crosslinked Polyacrylamide (NNMBA - PAM) Systems.

The structure of NNMBA-PAM is shown in figure 3.2. The procedure of coating was similar to the DVB-PAM systems. Acrylamide (2.21 g) and NNMBA (0.23 g) were dissolved in $CHCl_3$ (25 mL) which contained AIBN (0.1 g) as initiator. To dissolve NNMBA in chloroform slight warming and stirring were required.

Moisture free urea granules (25 g) were added and temperature was raised to 40°C. Careful stirring was required since very vigorous stirring may rupture the coating, more over the urea granules itself may get broken. As the reaction started, polymer formed and get deposited on the urea granules. While this process was going on, sealant solutions were added. TC/NR/EVA or PVC (1 g) solution and wax (1 g) solution were added in small volumes. The mixture was carefully stirred and the solvent gradually evaporated. The four coated products were spread over petry dishes and dried in an oven at 60-70°C. The dried products were re-coated using same materials used in the primary coating.

3.3.3 Preparation of PCUF Based on Tetraethyleneglycol diacrylate-crosslinked Polyacrylamide (TTEGDA - PAM) Systems.

The structure of TTEGDA-PAM is shown fig 3.2. Acrylamide (2.21g) and TTEGDA (0.41 mL) were dissolved in $CHCl_3$ (25 mL). The initiator used was AIBN (0.1 g) and was dissolved in the solvent prior to the addition of monomers. Moisture free urea granules were added and temperature raised to 40°C slowly using a waterbath. The co-polymer formed get deposited on the surface of urea granules. During this stage sealant solutions were added in small volumes. TC/NR/EVA or PVC (1 g in $CHCl_3$) solutions and wax (1 g in $CHCl_3$) were added. The solvent gradually evaporated and the products were spread on petry dishes and dried in an oven at 60-70°C. The products were re-coated using same amount of monomers and sealants.

3.3.4 Preparation of PCUF Based on Pentaerythritol triacrylate-crosslinked Polyacrylamide (PETA - PAM) Systems.

The structure of PETA-PAM is shown in fig 3.1. Using PS/NR/EVA or PVC as sealants four PCUF were prepared. Procedure of coating was similar as in the former cases. Acrylamide (2.21 g) and PETA (0.5 g or 0.41 mL) were dissolved in $CHCl_3$ (25 mL) in which AIBN (0.1 g) dissolved in it. Moisture free fertilizer grade urea granules (25 g) were suspended in the solution and the temperature raised to 40°C, with constant stirring. When the polymerization reaction set in the net structured polymer formed and encapsulated the urea granules. The sealant solutions of TC/NR/EVA or PVC (1g in $CHCl_3$) and wax (1g in $CHCl_3$) were added in small portions. The contents were carefully stirred and the solvent was allowed to evaporate gradually. The four coated products were dried in an oven at 60-70°C and re-coated using the same materials.

3.4 Preparation of Polymer Coated Urea Fertilizers (PCUF) Based on Crosslinked Polymethylmethacrylate (PMMA) Systems.

Polymethylmethacrylate (PMMA) being more resistant towards environmental factors such as air, water, temperature etc. and more hydrophobic in nature, it was utilized to formulate CR urea fertilizers. Properties of PMMA can also be varied when crosslinked with different types of crosslinking agents. The crosslinking agents used in the PAM systems were used in PMMA systems also. DVB being very much hydrophobic in nature, DVB crosslinked PMMA may be a very effective system against moisture. In order to adjust proper hydrophobic-hydrophilic behaviour and the polymer morphology other crosslinking agents were viz. NNMBA, TTEGDA and

PETA were also used. The sealants used were also same as in the PAM systems viz. PS / NR /EVA or PVC along with paraffin wax.

3.4.1 Preparation of PCUF Based on Divinylbenzene-crosslinked Polymethylmethacrylate (DVB -PMMA) Systems

The structure of DVB-PMMA is shown in fig 3.3. Free radical initiated solution polymerization was used for the preparation of the polymer. Co-monomers methylmethacrylate (MMA, 2.54 mL) and DVB (0.30 mL) were dissolved in $CHCl_3$ (25 mL) containing AIBN as initiator (0.1 g). Moisture free fertilizer grade urea granules (25 g) were suspended in the solution. The temperature of the system was raised to 40°C using a water bath. Continuous stirring was employed. After some time the initiator TEMED (0.5 mL) added. The formed polymer encapsulated the urea granules and the sealant solutions of PS/NR/EVA or PVC (1g) and wax (1g) in $CHCl_3$ were added in small volumes. The reaction allowed to continue for some time and then the solvent was evaporated. When the solvent was almost separated the coated products were dried in an oven and again re-coated using the same materials. During the process of drying occasional shaking was required to separate out the granules which were sticked together. After drying, the product was free flowing and coating appeared to be rigid.

3.4.2 Preparation of PCUF Based on NN'-Methylene-bis-acrylamide-crosslinked Polymethylmethacrylate (NNMBA - PMMA) Systems

The structure of NNMBA-PMMA system is shown in figure 3.3. Monomers MMA (2.54 mL) and NNMBA (0.19 g) were dissolved in $CHCl_3$ (25 mL) containing initiator AIBN (0.1 g). To dissolve NNMBA slight warming of the solution and stirring were required. Moisture free fertilizer grade urea granules were added to the $CHCl_3$ and the temperature raised to 40°C using water bath with constant stirring. The formed polymer encapsulated the urea granules. Sealant solutions of PS/NR/EVA or PVC (1 g) and wax (1g) in $CHCl_3$ were added in small volumes. The reaction continued for 1-2 hours and the solvent gradually evaporated. The four coated products were dried in an oven at 60-70°C and re-coated with the same materials used for initial coating.

3.4.3 Preparation of PCUF based Tetraethyleneglycol diacrylate-crosslinked Polymethylmethacrylate (TTEGDA - PMMA) Systems.

The structure of TTEGDA-PMMA is shown in figure 3.3. Methyl methacrylate (2.54 mL) and TTEGDA (0.34 mL) were pipetted out into the solvent $CHCl_3$ (25 mL). Moisture free urea granules (25 g) were added to the solution. The temperature of the system raised to 40°C using a water bath. PS/NR/EVA/PVC (1 g in $CHCl_3$) and wax (1g in $CHCl_3$) were added in small volumes. After few hours the coated products were dried in an oven at 60-70°C and re-coated with the same materials of initial coating.

3.4.4 Preparation of PCUF Based on Pentaerythritol triacrylate-crosslinked Polymethylmethacrylate (PETA - PMMA) Systems

The structure of PETA-PMMA system is shown in figure 3.3. Following the similar procedure in the former cases the PETA-PMMA systems were also prepared. Monomers MMA (2.54 mL) and PETA (0.31 mL) were dissolved in $CHCl_3$ (25 mL). AIBN (0.1 g), the initiator was dissolved in $CHCl_3$ prior to the addition of monomers. Moisture free urea (25 g) suspended in the solution and the temperature raised to 40°C gradually. Polymer formed and encapsulated the urea granules. PS/NR/EVA/PVC(1 g) and wax (1 g) solutions were added in small volumes. The products were dried in an oven and re-coated with the same materials of initial coating.

3.5 Evaluation of Polymer Coated Urea Fertilizers (PCUF)

3.5.1 Determination of Urea Content in PCUF.

Urea content in all the samples of PCUF prepared were evaluated. Coated fertilizers were weighed out accurately and crushed. The urea extracted using distilled

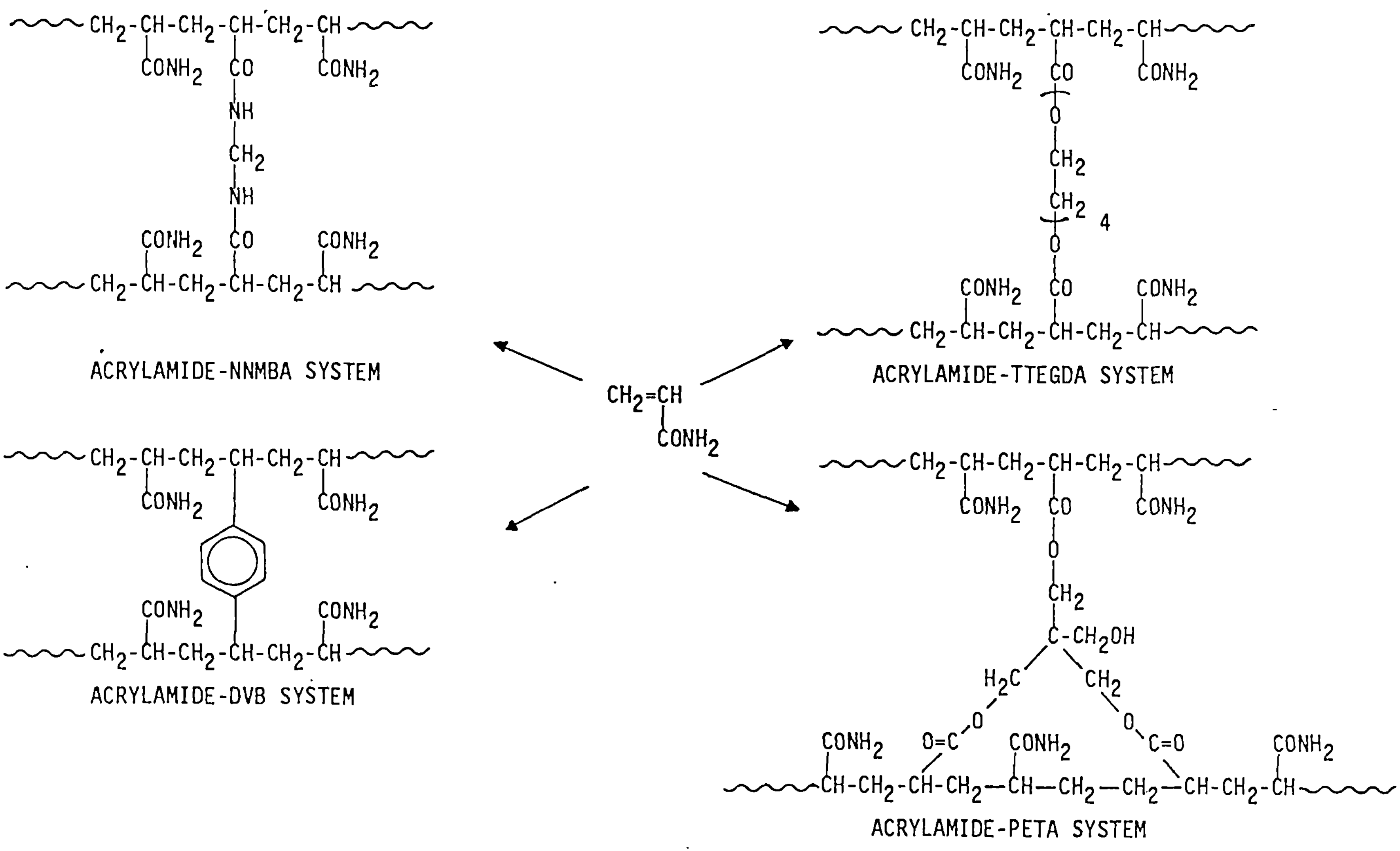


Fig 3.2 Crosslinked poly(acrylamide) systems for coating urea

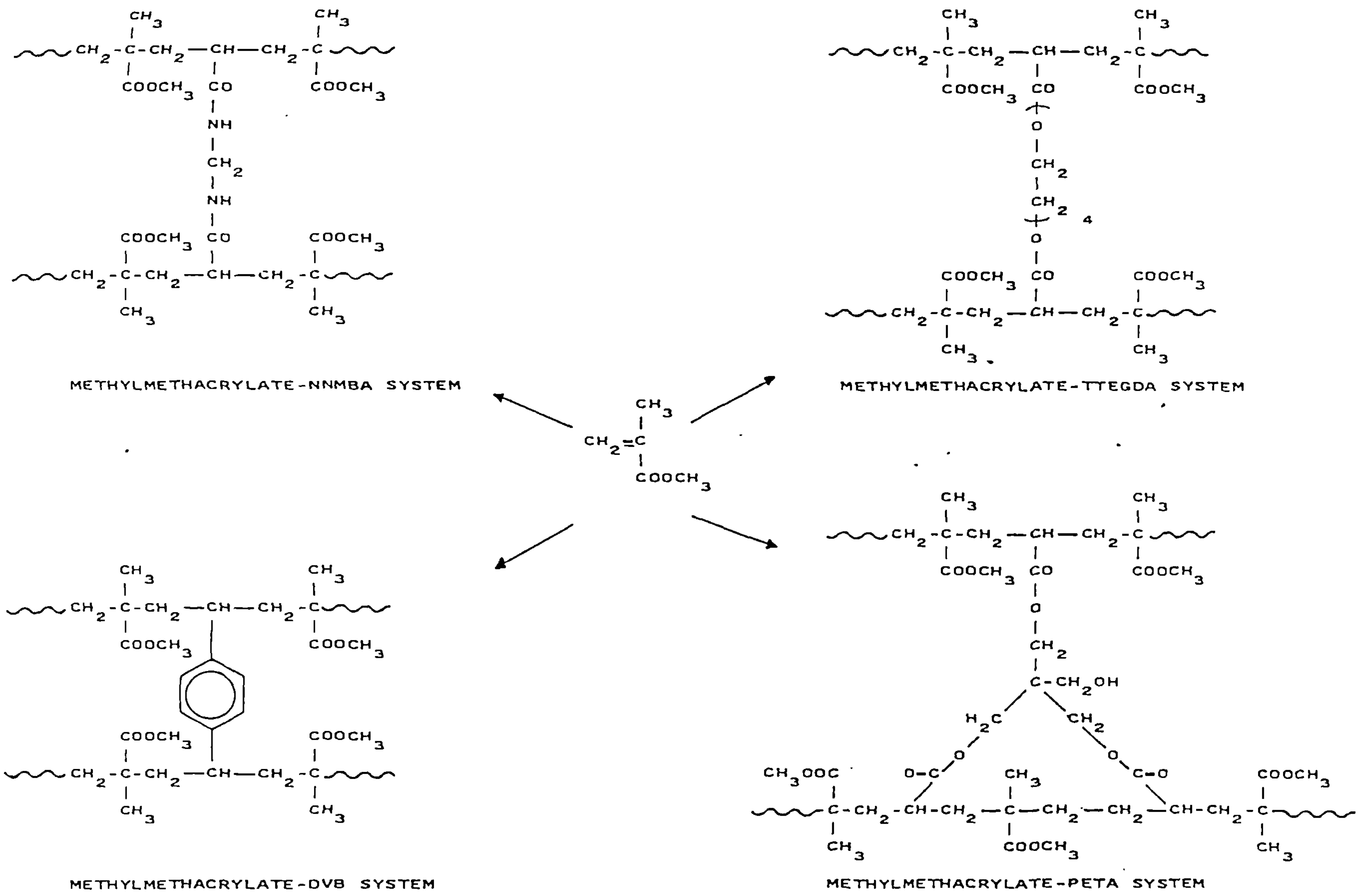


Fig 3.3 Crosslinked poly(methylmethacrylate) systems for coating urea

water quantitatively. Using p-dimethylaminobenzaldehyde method (Watt and Crisp, 1954) urea was estimated.

Urea Stock solution : Urea (0.214 g) dissolved in pre-boiled distilled water (1000 mL). This stock solution contains 100 micro gm / mL urea-N.

Urea Colour agent : P-dimethylaminobenzaldehyde (2 g) dissolved in 95 % ethanol (100 mL) and con. HCl (10 mL) added and mixed well.

Method : An aliquot of the extract upto 15 mL containing 100 to 2500 microgm/mL urea-N was transferred to 25 mL standard flasks. 10 mL colour agent added and made up. Well mixed and allowed the colour to develop. After 10 minutes absorbance was measured at 420 nm using spectrophotometer (Hitachi model 200-20).

3.5.2 Soil Characteristics

The soil used for the experiments were collected from the experimental area of Rubber Research Institute of India. The soil dried in the air and sieved (2 mm). Following analysis were carried out to find its textural class and chemical composition.

pH : Soil was well mixed with water in the ratio 1:10 and after 30 minutes the pH was measured using a pH meter.

$[NH_4]^+$*-N* (ammoniacal -N): By Kjeldahl's method the ammoniacal-N was determined. Soil (10 g) was extracted using $CaCl_2$ solution (0.01 M, 100 mL). An aliquot of the extract treated with MgO (0.5 g) and the mixture was steam distilled . Ammonia was quantitatively evolved and was absorbed in boric acid (4 %, 5 mL) and titrated against HCl (0.02 N).

$CaCl_2$ solution had been reported to be a good extractant for various fractions of soil-N and was used in this study due to its low cost and easy availability (Houba et al. 1990 ; Fox and Piekielek, 1978 ; Houba et al 1986).

Textural Class : To estimate the different fractions viz. sand, silt and clay, mechanical analysis by the international pipette method was carried out (Piper, 1944).

Water Holding Capacity (WHC) : This is a parameter to assess the capacity of a soil to store water. The amount of water held by a soil between 0.3 (Field capacity) and 15 (Wilting coefficient) atmospheric pressure is called available water content. This is the portion of water available to the plants. The water held above 15 bar pressure cannot be absorbed by the plants and held below 0.3 bar will run out of the soil due to gravitational pull. Using a pressure plate apparatus WHC of the soil was determined.

3.5.3 Leaching Studies

The leaching studies were carried out in a PVC tube of 30 cm length and 90 mm diameter. One end of the column was sealed by a PVC sheet and through its centre a glass tube of 5 cm length was fixed in such a manner that all drained water could come out through it. The other end of the glass tube was connected to a flexible plastic tube of 10 cm length. A small amount of glass wool was placed above the glass tube, at the bottom of PVC tube, to prevent soil from coming out. The soil in the tube was consolidated by gentle tapping and equilibrated by passing 0.01 M $CaCl_2$ solution several times. The solution was allowed to drain out completely. About 50 g soil was taken out from the top of the column . PCUF granules at the rate of 400 Kg N / ha (200 mg N / Kg soil) was weighed and placed on top of the column and covered using the 50 g soil taken out earlier. The columns were covered using polythene sheets. Blank (without any fertilizer) and control (with uncoated urea) experiments were also carried out. Three replications were carried out for each treatment. The soil columns were fixed vertically on a wall. After the fertilizer addition at different time intervals, viz. on 1st, 2nd, 7th, 14th, 21st, 28th and 45th days the soil columns were leached using 0.01 M $CaCl_2$ solution (100 mL). The solution was added in small portions of 10 mL at a time. The drained solutions were collected and made upto 100 mL and analysed for ammoniacal-N and urea-N. The analysis of ammoniacal-N was by Kjeldahl's method of distillation as explained in section 3.5.2. Urea-N estimated by p-dimethylaminobenzaldehyde colourimetry (Watt and Crisp, 1954) using a spectrophotometer (Hitachi model 200-20) as explained in section 3.5.1. In cases were urea concentrations were very low (< 20 micro gm / mL) in extracts diacetyl monoxime-thiosemicarbazide method was used for the estimation (Onken and Sunderman, 1977). The values of ammoniacal-N and urea-N of blank experiments (of different time intervals) were deducted from the corresponding values of PCUF and control experiments.

3.5.4 Urea estimation by Diacetylmonoxime - thiosemicarbazide method

Diacetylmonoxime solution :

Dissolved diacetyl monoxime (2.5 g) in distilled water (100 mL).

Thiosemicarbazide solution :

Dissolved thiosemicarbazide (0.25 g) in distilled water (100 mL) .

Acid reagent

Mixed 85 % orthophosphoric acid (300 mL) and con. Sulphuric acid (10 mL) and diluted to 500 mL using distilled water.

Colour agent :

Prepared immediately before use by adding Diacetylmonoxime solution (25 mL) and thiosemicarbazide solution (10 mL) to acid reagent (500 mL).

Urea Standard solution

Urea (0.214 g) dissolved in pre-boiled distilled water (1000 mL). 10 mL of the solution diluted to 100 mL using pre-boiled distilled water. Diluted solution contained 10 ppm urea-N.

Method : 0, 1, 4, 7 mL aliquots of urea standard solution transferred to 50 mL volumetric flasks. This represented 0, 10, 40, 70 ppm urea-N solutions. Adjusted the volume to 10 mL. Colour agent (30 mL) added and mixed well. Placed the flasks in an oven at 120 °C for 30 minutes. The contents rapidly cooled and made up to the volume using distilled water. Colour intensity measured at 525 nm using spectrophotometer (Hitachi model 200-20). From the soil extract a suitable aliquot (10 mL) transferred to 50 mL volumetric flask and colour developed and absorbance measured.

3.5.5 Incubation Experiments

The soil used for incubation experiment was the same soil type used in the leaching experiment. On the basis of leaching experiment, from each polyacrylamide and polymethylmethacrylate systems out of the four coated fertilizers, two with better slow release profile were selected for the incubation study. The soil was sieved (2 mm) and air dried. Water holding capacity of the soil (WHC) was determined. PCUF at the rate of 400 Kg/ha was well mixed with soil (100 g). Distilled water was added to bring the WHC of the soil to 50 %. To maintain the same moisture content in the soil through out the study, the container with the soil sample were weighed once in every three days and water were added if necessary. Blank (without any fertilizer) and control (with uncoated urea) experiments were also carried out. The soil were incubated at room temperature ($28\underline{+}2^{o}C$) for different time intervals. For each incubation period different soil samples with PCUF were kept. All the experiments were triplicated. After each incubation period viz. 2, 7, 14, 21 and 28 days the soil was extracted using 0.01 M $CaCl_2$ solution. The soil used for incubation was completely transferred to a bottle and shaken with 0.01 M $CaCl_2$ (200 mL) for three hours. The PCUF were floated after shaken for some time and were crushed using glass rod so that all the urea present inside the granules were dissolved in the solution. Afterwards it was allowed to settle and the supernatant liquid were either centrifuged or filtered and the filtrate was analysed for ammoniacal-N and urea-N. The estimation of ammoniacal-N was carried out by Kjeldahl's method as described in section 3.5.2. Urea-N by colourimetry (p-dimethyl amino benzaldehyde method) as described in section 3.5.1. In cases where urea concentration was very low Diacetylmonoxime-thiosemicarbazide method was used for the estimation as described in section 3.54. Urea-N and ammoniacal-N content of blank experiments were estimated, averaged and deducted from the corresponding values of PCUF and control experiments.

3.6 Statistical analysis of data

Leaching experiments:

PCUF based on each crosslinked polymer system were treated as a group and they were compared among themselves and with uncoated urea (control) to assess slow release behaviour. The ammoniacal-N, urea-N, total-N (the sum of ammonical-N and urea-N) and cumulative total -N values at different time intervals of each crosslinked system give a picture on the slow release behaviour and they were statistically analysed. Here the sealants in each crosslinked polymer system were taken as one factor and time as the second factor, which influences the dissolution rate. For statistical interpretation the percentage nitrogen released in the form of urea or ammonium through leaching were calculated and subjected to analysis of variance for a two factorial completely randomized design (2 FCRD). The combined effect of these two factors on release of urea could be analysed.

In another approach the different crosslinking agents and sealants were considered as the two factors which affected the release rate. (The two polymer systems viz. PAM and PMMA were treated separately). At each specified leaching period the data were subjected to analysis of variance using 2FCRD. The effect of these two factors on release of urea could be examined by this approach.

Incubation experiment

Two coated fertilizers selected out of the four from each crosslinked polymer system based on the leaching experiment, were compared among themselves and with control for their slow release character.

The values of ammoniacal-N and urea-N of the PCUF and control were subjected to analysis of variance for a two factorial completely randomized design.

3.7 Matrix Type Controlled Release Fertilizers by Distribution of Urea in NNMBA-crosslinked Polyacrylamide

Since urea is soluble in water, so also are the monomers NNMBA and acrylamide, solution polymerization technique was employed for the distribution of urea molecules in crosslinked polyacrylamide matrices. Different crosslinking densities were employed in the system to study the effect of crosslinking on the release properties. Four different crosslinking densities were employed. The amount of monomers and urea taken for the preparation were as shown in table 3.1.

Table 3.1 Weight of monomers and urea taken for preparing matrix type CR fertilizers

Crosslinking density (mol %)	Acrylamide (gm)	NNMBA (gm)	Urea (gm)
5	2.7010	0.3083	10.0
15	2.4167	0.9250	10.0
25	2.1324	1.5417	10.0
35	1.8480	2.4584	10.0

Monomers, acrylamide and NNMBA were dissolved in distilled water (100 mL). Urea crystals were added and dissolved in the water. Free radical initiator, potassium persulphate (0.2 g) dissolved in distilled water (10 mL) and added to the monomer solution. The temperature of the system gradually raised to 70°C using a water bath. The content were well stirred using an overhead stirrer. The prepared gel were dried in an oven at 80°C. The dried gel were made to pieces using a mortar and pestle, and sieved using 1mm and 2mm sieves.

Uniform sized particles (1mm-2mm) of the four products were separated and utilized for further studies. Urea-N content of the products were estimated and their slow release character were studied by incubation experiment.

3.7.1 Urea-N content

The polymer based fertilizer particles were accurately weighed into a stoppered conical flask and pre-boiled distilled water (100 mL) added and kept overnight. Using a glass rod the swollen gels were made to pieces and the contents were vigorously shaken for two hours. Filtered and the filtrate were estimated for urea-N by thiosemicarbazide or p-dimethylaminobenzaldehyde method (Watt and Chrisp, 1954)

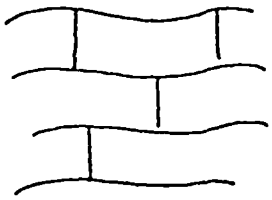
3.7.2 Incubation study

The prepared polymer based urea fertilizers were well mixed with soil (2 mm, 100 g) at the rate of 1000 ppm and incubated for different periods of time (10, 20 and 30 days). Water holding capacity of the soil was determined and 50 % WHC was maintained throughout the study by weighing and adding distilled water if necessary. After each incubation period the soil samples with fertilizers were extracted using 0.01 M $CaCl_2$ (200 mL)solution and urea-N estimated as described in section 3.5.1 or 3.5.4. Control (un-coated urea) and blank (no fertilizer) experiments were also carried out. All the experiments were triplicated. The data were subjected to analysis of variance for a two factor completely randomized design.

Chapter 4
Results and Discussion

The use of polymers in Controlled Release (CR) technology is well established. Through chemical modification of polymers their properties can be adjusted to perform specific functions. The polymers used to prepare the CR formulations should be chemically and mechanically stable throughout the period of its action (Paul, 1976). The physical properties of a polymer depend on whether the system is linear or crosslinked. A linear system is one which is having a continuous long chain of monomeric units and is soluble in suitable solvents, whereas the cross-linked polymers are macroscopically insoluble in usual solvents, but capable of solvation in good solvents. The nature of crosslinking agent affects the rigidity, flexibility and hydrophobic-hydrophilic character of the polymer (Mathew and Pillai, 1993). In crosslinked polymers, chains are interconnected and have a net structure as shown in figure 4.1. Crosslinked polymers being more stable and having a net structure must be more useful for coating purpose.

Monomer + Crosslinking agent ------>



net- structured polymer

Fig 4.1 Structure of crosslinked polymer

Three difunctional crosslinking agents and one trifunctional crosslinking agent were separately used to crosslink polyacrylamide and polymethyl methacrylate. Divinylbenzene (DVB), a difunctional crosslinking agent when introduced in a polymer backbone, rigidity and hydrophobic character can be imparted. Another crosslinking agent tried was tetraethylene glycoldiacrylate (TTEGDA) a difunctional monomer with very flexible and hydrophilic nature. N,N'-Methylene-bis-acrylamide, another difunctional crosslinking agent used, is in between DVB and TTEGDA regarding the flexibility / rigidity nature and hydrophobic/hydrophilic character. Another crosslinking agent tried was pentaerythrytol triacrylate (PETA). It is a trifunctional monomer and can form peculiar three dimensional network co-polymer. Thus using the crosslinking agents DVB, NNMBA, TTEGDA and PETA, four different crosslinked systems each in polyacrylamide (PAM) and polymethyl methacrylate (PMMA) backbones were prepared and used for coating urea fertilizer.

The proven polymeric soil conditioners polyacrylamide (PAM) and polymethylmethacrylate (PMMA) are utilized as the main polymeric backbones for coating. Several CR pesticides based on crosslinked polymers are reported and some of them have, DVB, NNMBA and PETA as the crosslinking agents (Kenawy et al, 1992). These three and another one, tetraethyleneglycol diacrylate (TTEGDA) were used as crosslinking agents in this study so that different properties could be imparted to the polymer backbone.

Among the sealants used polystyrene (PS) and polyvinylchloride (PVC) are plastics with rigid nature while ethylenevinyl acetate co-polymer (EVA) and natural rubber (NR) are elastomers with flexible nature. PS, NR and EVA are also used as soil conditioners for different purposes. The polymeric soil conditioning materials are utilized to prepare CR urea formulations so that soil conditioning and CR properties are merged in a single product. Since proven soil conditioners are used here, this study confined to CR aspect only.

During preparation of polymer coated urea fertilizers (PCUF) it is observed that in presence of urea, polymerization of acrylamide and methylmethacrylate takes place. Urea did not inhibit the reaction. Free radical initiated solution polymerization technique had been employed to prepare the co-polymers. Chloroform can be used as a solvent to carryout the reaction. The polymer formed during the reaction got deposited on the surface of urea granules.

4.1 Characterisation of Polymer Coated Urea Fertilizers (PCUF) - IR Spectroscopy.

IR spectrum of urea and one coated fertilizer system from each of the crosslinked systems were taken before and after the leaching of urea. IR spectrum of urea showed the characteristic absorptions of N-H of the amide group at 3456 cm-1, and 3344 cm-1 and C=O group at 1676 cm-1, 1628 cm-1 and at 1600 cm-1. The coated fertilizer system showed the characteristic absorptions of the polymer chain and urea with intense peaks of N-H bond at 3300-3400 cm-1 region and of C=O bond at 1600 cm-1 region . After the urea leached out from the coated fertilizer systems based on polyacrylamide the intensity of N-H and C=O bands have greatly diminished. In the case of coated fertilizers based on polymethylmethacrylate after leaching the N-H band had disappeared and the intensity of C=O band had decreased. In case of NNMBA-PMMA system (after urea was leached) a weak band of N-H is observed which is due to the N-H of NNMBA.

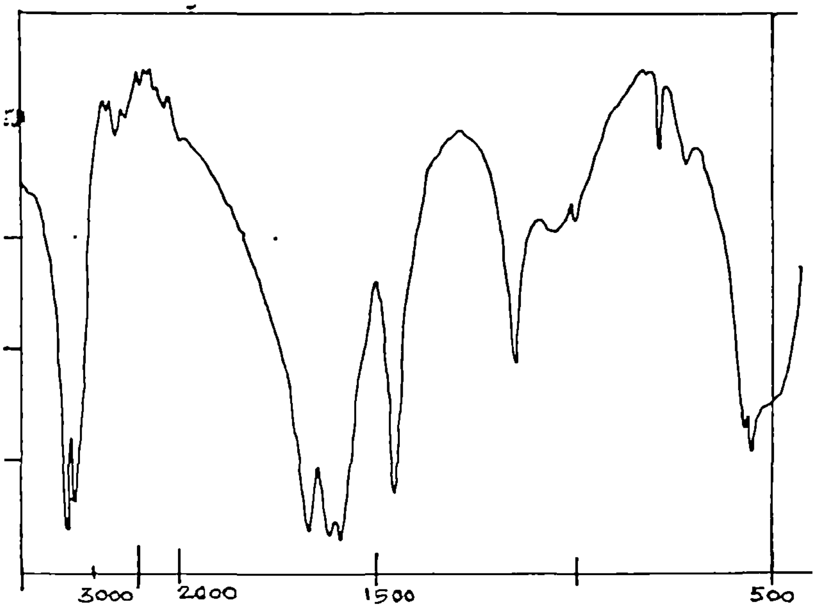


Fig 4.1.1,IR spectrum of urea

Urea (KBr) 3456 cm-1 , 3344 cm-1 (N-H), 1628 cm-1, 1600 cm-1 (C=O)

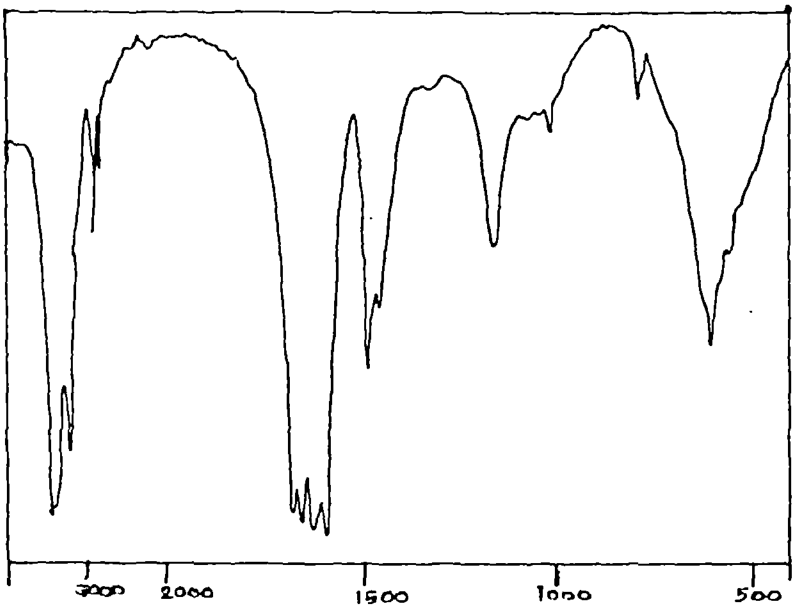


Fig 4.12,IR spectrum of Urea encapsulated DVB-PAM-PVC System.

DVB-PAM-PVC + Urea (KBr). 3400 cm-1 (N-H of Urea. PAM), 1600 cm-1, 1624 cm-1,1650 cm-1, 1675 cm-1 (C=O Urea. PAM)

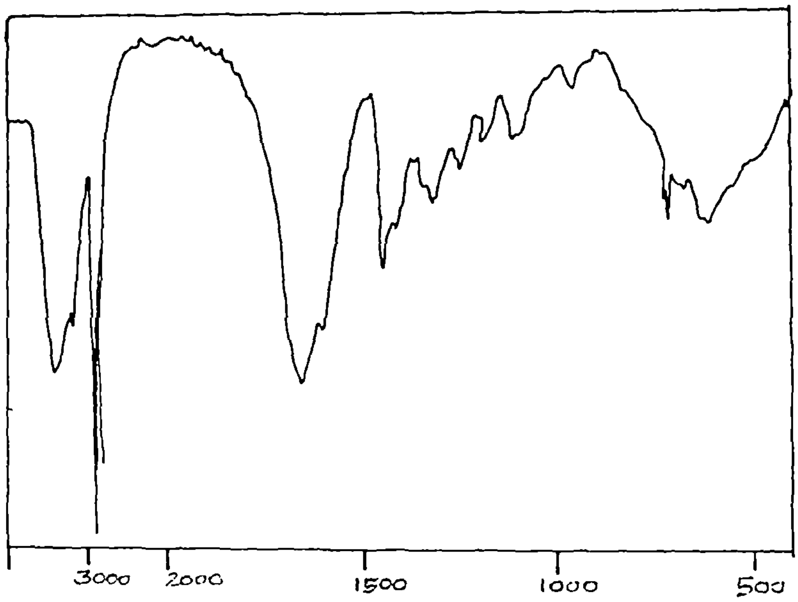


Fig 4.13,IR Spectrum of DVB-PAM-PVC System

DVB-PAM-PVC (KBr) 3424 cm-1 (N-H of PAM), 1667 cm-1, 1603 cm-1 (C=O of PAM)

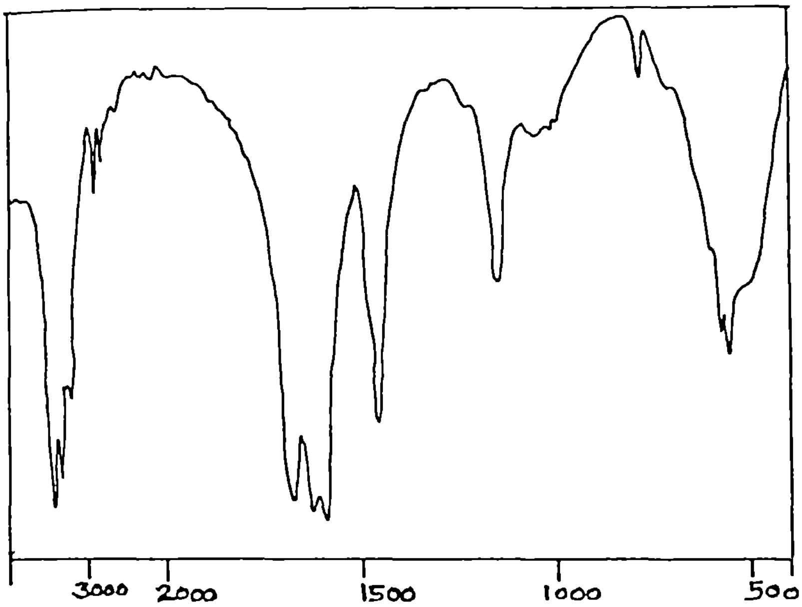


Fig 4. 14, IR Spectrum of NNMBA-PAM-EVA + Urea System

NNMBA-PAM-EVA + Urea (KBr) 3420 cm-1 3340 cm-1, 3230 cm-1 (N-H of urea, PAM, NNMBA), 1600 cm-1, 1622 cm-1, 1678 cm-1 (C=O of urea, PAM and NNMBA)

Fig .4.15,IR Spectrum of NNMBA-PAM-EVA System

NNMBA-PAM-EVA (KBr) 3425 cm-1, 3220 cm-1 (N-H of PAM, NNMBA), 1738 cm-1 (C=O of EVA), 1660 cm-1 (C=O of PAM, NNMBA)

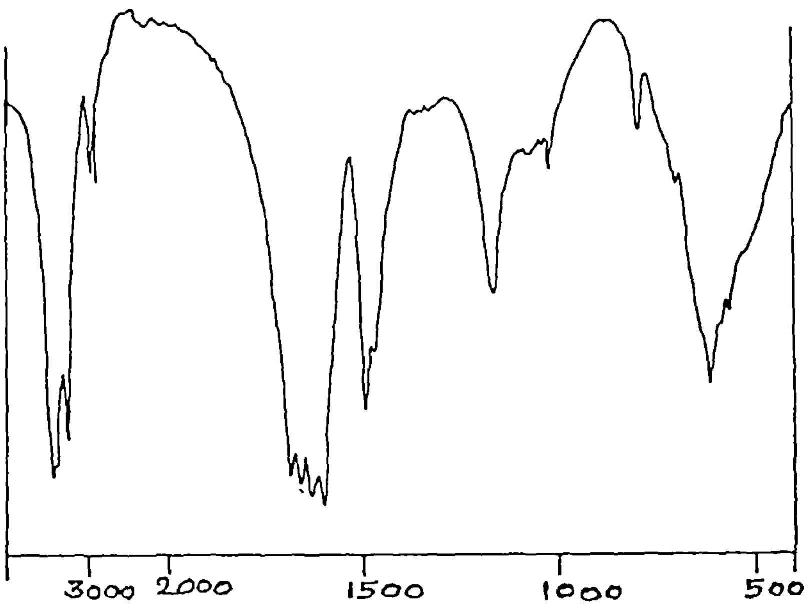


Fig 4.16 IR Spectrum of TTEGDA-PAM-PS + Urea System

TTEGDA-PAM-PS + Urea (KBr) 3420 cm-1, 3200cm-1 (N-H of Urea, PAM), 1600 cm- 1, 1624 cm-1, 1650 cm-1, 1670 cm-1 (C=O of PAM, TTEGDA)

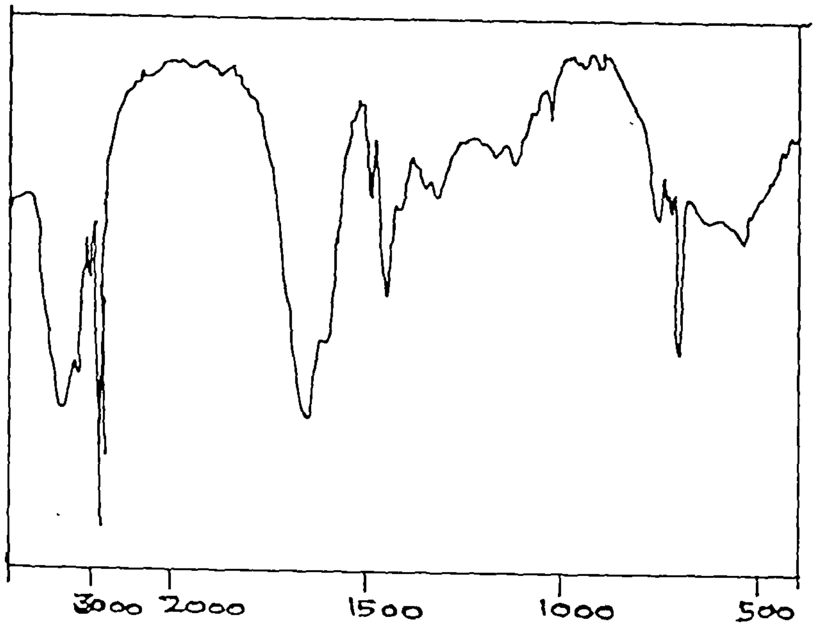


Fig 4.17 IR Spectrum of TTEGDA-PAM-PS System

TTEGDA-PAM-PS (KBr), 3400 cm-1, 3200 cm-1 (N-H of PAM), 1660 cm-1 (C=O of PAM and TTEGDA).

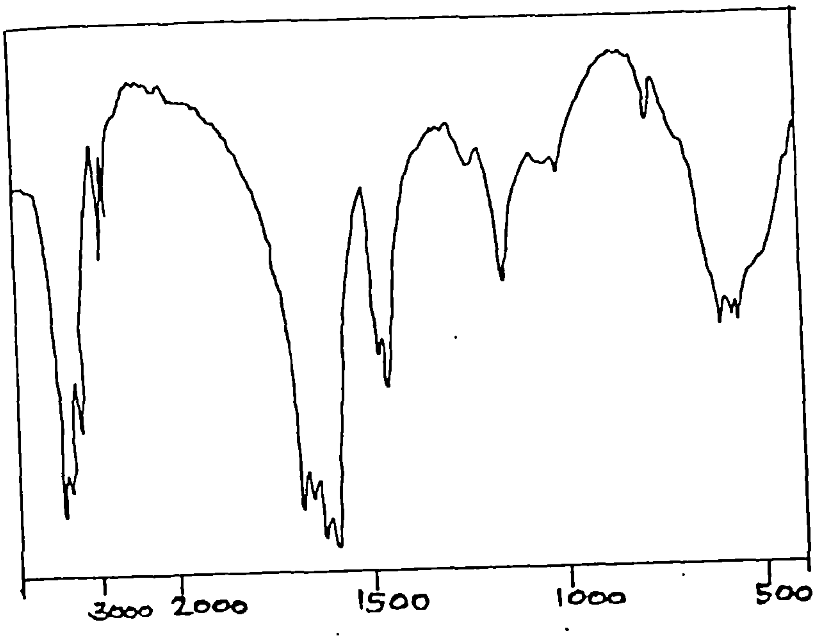


Fig 4.18, IR Spectrum of PETA-PAM-EVA + Urea System

PETA-PAM-EVA + Urea (KBr) 3420 cm-1, 3340 cm-1, 3220 cm-1 (N-H of PAM and Urea), 1600 cm-1, 1624 cm-1, 1650 cm-1 (C=O of Urea, PAM, PETA)

Fig 4.19, IR Spectrum of PETA-PAM-EVA System

PETA-PAM-EVA (KBr) 3430 cm-1, 3200 cm-1 (N-H of PAM), 1732 cm-1 (C=O of PETA, EVA), 1660 cm-1, 1616 cm-1 (C=O of PAM)

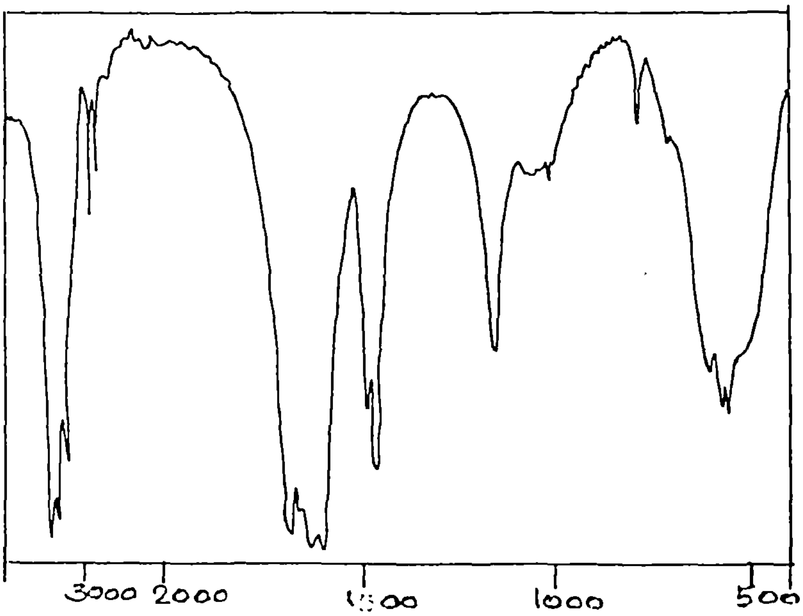


Fig 4.1.10, IR Spectrum of DVB-PMMA-NR + Urea System

DVB-PMMA-NR + Urea (KBr) 3430 cm-1, 3360 cm-1 (N-H of Urea), 1660 cm-1, 1622 cm-1, 1678 cm-1 (C=O of Urea, PMMA)

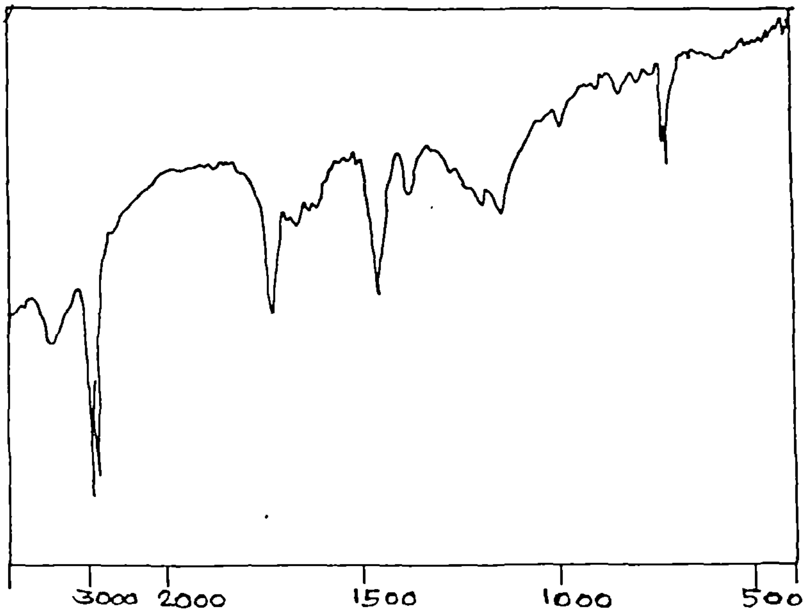


Fig 4.1.11, IR Spectrum of DVB-PMMA-NR System

DVB-PMMA-NR (KBr) 1724 cm-1 (C=O PMMA), 720 cm-1 (benzene ring of DVB).

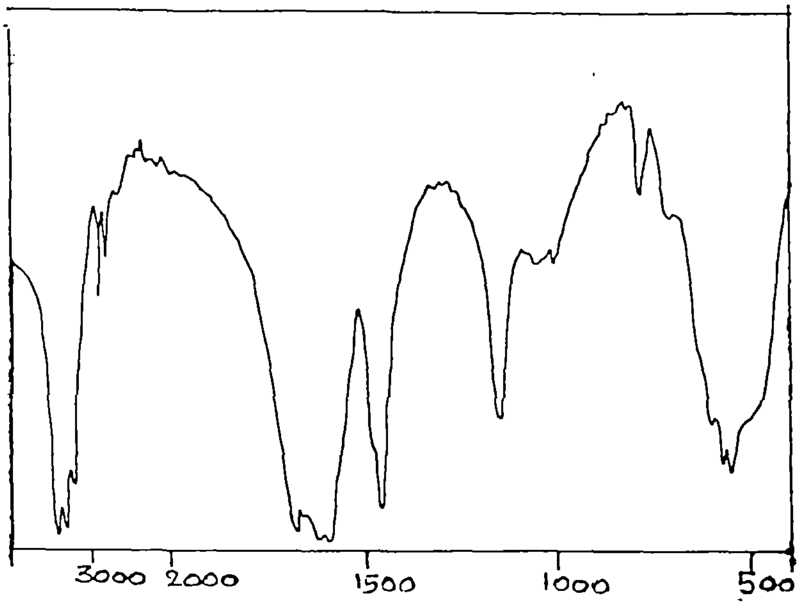


Fig. 4.1.12 NNMBA-PMMA -EVA + Urea System

NNMBA-PMMA -EVA + Urea (KBr) 3450 cm-1, 3350 cm-1 , 3230 cm-1 (N-H of Urea, NNMBA), 1600 cm-1, 1624 cm-1, (C=O of Urea, NNMBA)

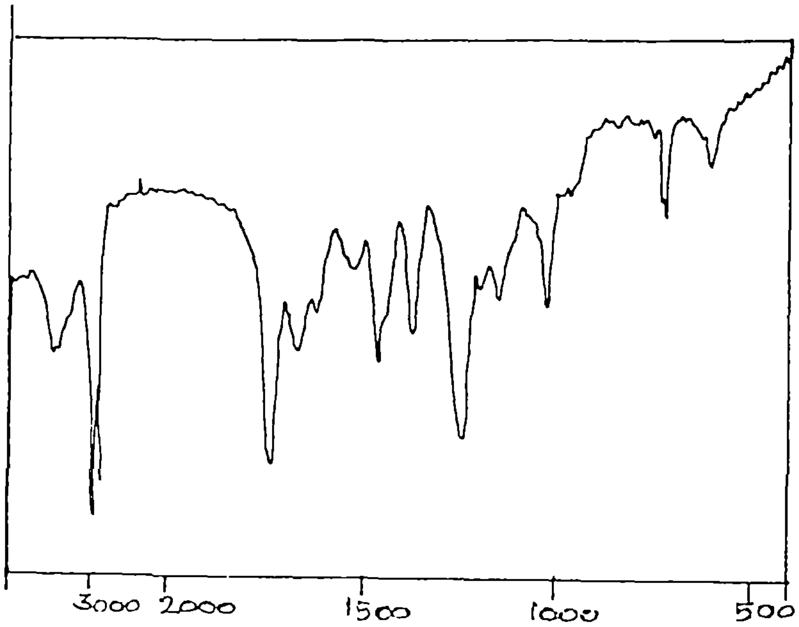


Fig 4. 1.13 IR Spectrum of NNMBA-PMMA-EVA System
NNMBA-PMMA-EVA (KBr) 3440 cm-1, 3360 cm-1 (N-H of NNMBA),1734 cm-1 (C=O of PMMA, EVA), 1660 cm-1, 1619 cm-1 (C=O of NNMBA)

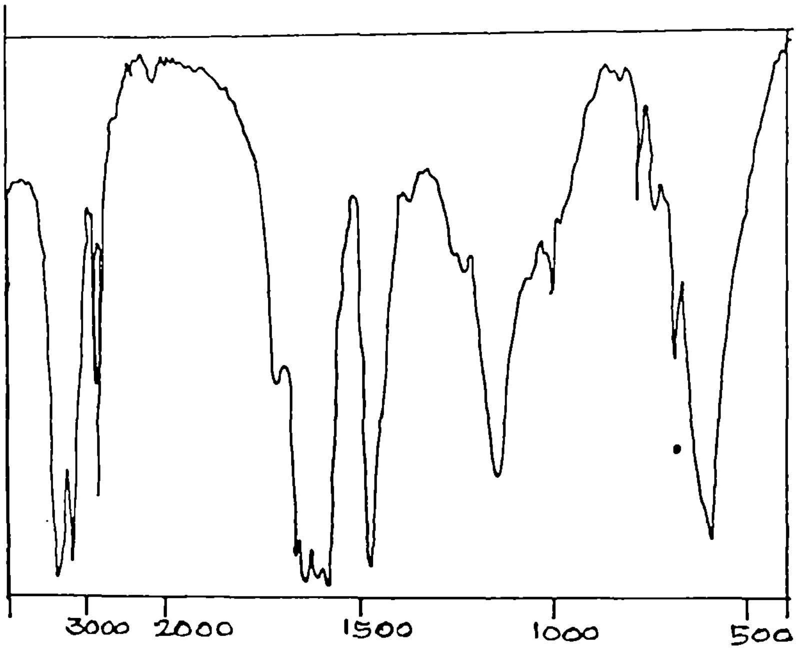


Fig 4.1.14, TTEGDA-PMMA-PS + Urea System.

TTEGDA-PMMA-PS + Urea (KBr) 3392 cm-1, 3216 cm-1 (N-H of Urea), 1718 cm-1 (C=O of PMMA, TTEGDA), 1673 cm-1, 1651 cm-1, 1600 cm-1 (C=O of Urea).

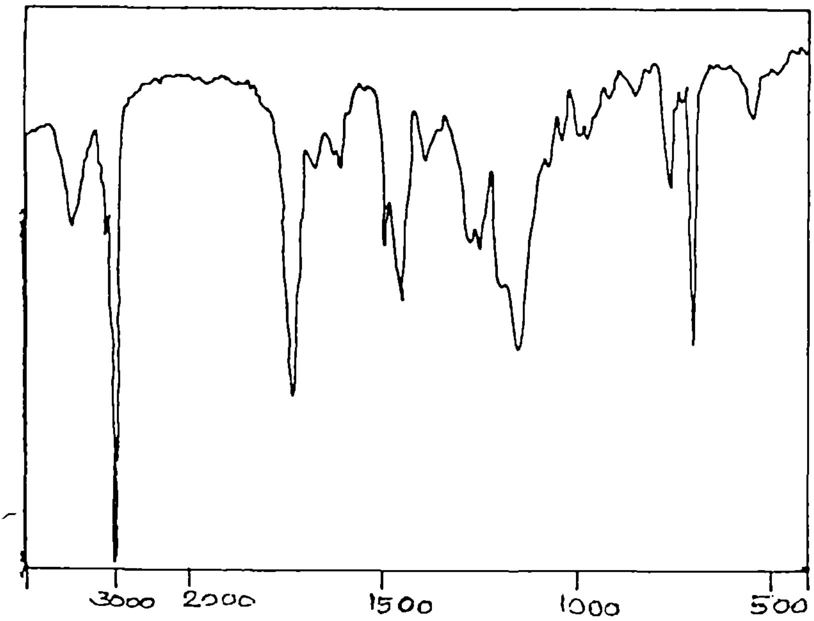


Fig 4.1.15, TTEGDA-PMMA-PS System.

TTEGDA-PMMA-PS (KBr) 3030 cm-1 (C-H of Polystyrene), 1724 cm-1 (C=O of PMMA, TTEGDA), 1664 cm-1, 1622 cm-1, 1600 cm-1 (C=O of TTEGDA), 697 cm-1 (aromatic ring of Polystyrene)

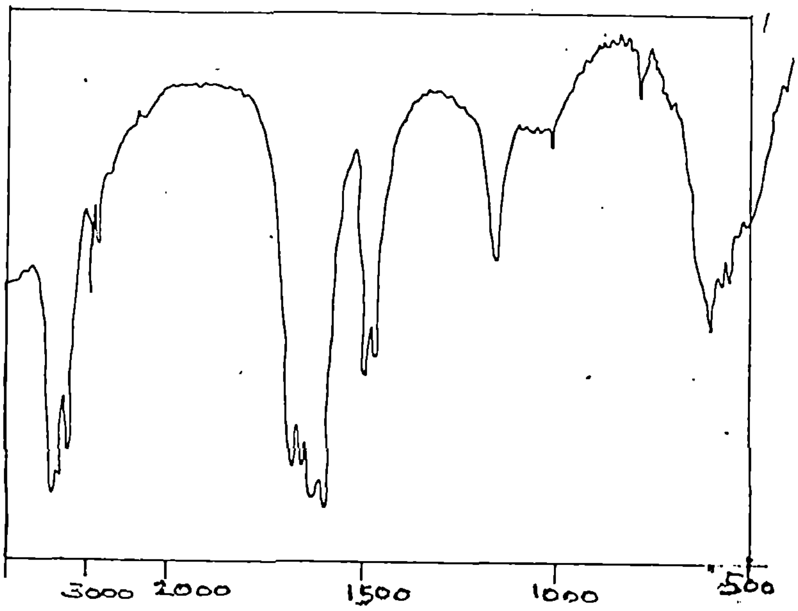


Fig 4.1.16,IR Spectrum of PETA-PMMA-PVC + Urea System

PETA-PMMA-PVC + Urea (KBr) 3420 cm-1, 3350 cm-1, 3230 cm-1 (N-H of Urea), 1674 cm-1, 1650 cm-1, 1624 cm-1, 1600 cm-1 (C=O of Urea, PETA)

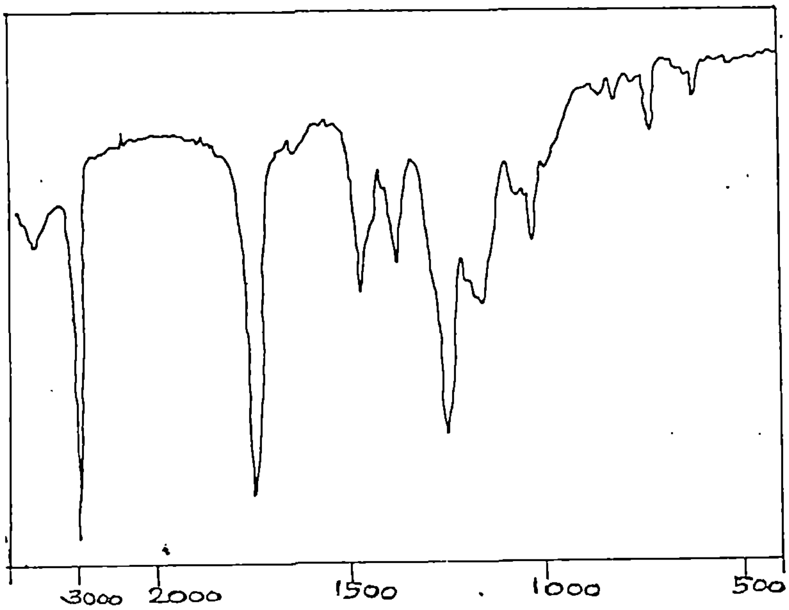


Fig 4.1.17,IR Spectrum of PETA-PMMA-PVC System.

PETA-PMMA-PVC (KBr) 1730 cm-1 (C=O of PMMA, PETA)

4.2 Urea Content in Polymer Coated Urea Fertilizers (PCUF).

The percentage of urea in coated fertilizers based on different crosslinked PAM systems are described in table 4.1. The urea content varies among different formulations in each crosslinked PAM system. This is expected since slight variations were there in the weight of the monomers taken and also the amount of different sealants incorporated in different crosslinked systems might be varied. Among the four coated fertilizers based on DVB-PAM system urea content was maximum for PVC sealant system and least for NR sealant system. Among the NNMBA crosslinked PAM systems the urea content decreased in the order PS > PVC > NR > EVA. In TTEGDA -PAM systems the urea content decreased in the order PVC > PS > NR > EVA and among PETA crosslinked systems it decreased as PVC > PS > NR > EVA. In all the cases urea content was comparatively high when PVC was the sealant, therefore the percentage of coating materials in these systems is lower compared to other systems.

Table 4.1 Percentage urea content in PCUF based on crosslinked polyacrylamide systems.

Sealants	PS	NR	EVA	PVC
Crosslinking agents		Urea	(%)	
DVB	84.1	80.5	83.4	87.1
NNMBA	88.1	81.1	78.5	85.0
TTEGDA	81.6	81.5	77.3	84.5
PETA	82.7	82.3	77.0	87.0

When the elastomers, NR or EVA was used as sealants urea content was comparatively low and hence coating material content was more compared to systems where rigid and hydrophobic sealants viz. PS and PVC were used. Among the systems in which PS was the sealant urea content was lowest in TTEGDA and relatively high in NNMBA system. In systems were NR was the sealant no wide variation in urea content was observed. In cases where EVA was the sealant urea content was comparatively high in DVB system than others. In systems were PVC was the sealant, urea content increased in the order TTEGDA < NNMBA < PETA < DVB.

Table 4.2 gives the percentage urea content of different coated fertilizers based on PMMA systems. Among DVB crosslinked PMMA systems urea content was least when EVA was the sealant and maximum when PVC was the sealant. Among, NNMBA crosslinked PMMA systems urea content increased in the order EVA < PS < NR < PVC. Among TTEGDA crosslinked PMMA systems it increased as EVA < NR < PS < PVC and among PETA crosslinked PMMA systems it increased in the order PS < PVC < EVA < NR. Among the systems were PS was the sealant urea content was almost similar in DVB, NNMBA and PETA crosslinked PMMA systems, but in TTEGDA crosslinked system it was relatively high. Among different crosslinked PMMA systems where NR was the sealant the percentage urea content increased in the order TTEGDA < DVB < PETA < NNMBA and in systems where EVA was the sealant it increased as NNMBA < DVB < PETA < TTEGDA. In systems with PVC as the sealant the urea content was comparatively high in DVB, NNMBA and TTEGDA crosslinked systems. No definite pattern was observed for urea content in different crosslinked PMMA systems.

Table 4.2 Percentage of urea content in PCUF based on crosslinked polymethylmethacrylate systems.

Sealants	**PS**	**NR**	**EVA**	**PVC**
Crosslinking agents		**Urea**	**(%)**	
DVB	83.2	86.7	82.7	90.0
NNMBA	82.8	90.4	79.7	93.1
TTEGDA	85.9	84.2	83.4	87.5
PETA	82.7	87.7	83.3	83.0

Comparatively lower urea content was observed among systems where EVA was the sealant while higher urea content was noticed in PVC systems, in the cases where DVB, NNMBA and TTEGDA were the crosslinking agents. Therefore comparatively higher content of coating materials in EVA systems is noted while lower in PVC systems.

4.3 *Soil Characteristics*

The soil used for the study had following physico-chemical properti

pH	4.85
$[NH_4]^+$ - N	2.181 ppm

Textural Composition

Coarse Sand	49.99 %
Fine Sand	15.62 %
Silt	8.20 %
Clay	22.10 %

Water Holding Capacity (WHC)

Field Capacity	31.73 %
Wilting Coefficient	24.12 %
Available Water Content	7.61 %

4.4 *Results of Leaching Experiments*

Leaching studies were conducted to find the dissolution of urea from coated fertilizers, when subjected to leaching. During the downward movement of leaching solution, the coated fertilizer get into contact with it and dissolution of urea takes place. Urea thus released out of coated granules transformed to ammoniacal form partially or totally. These ions get dissolved in the leaching solution and come out through the leaching column. A part of these ions sometimes get adsorbed in the soil. However this tendency was minimized by equilibrating the soil by passing $CaCl_2$ solution several times prior to the addition of fertilizers. Hence all the exchange sites in soil might have been filled by Ca^{++} ions. Thus it facilitates the urea and ammonium ions to come out through the leaching column. The amount of ammonium and urea in leachate indicate the release properties of coated fertilizers. As the time of contact of urea with soil increases, more conversion to ammoniacal form occurs. Hence the amount of ammonium and urea in the leachate had to be determined. Subsequent conversion of ammonium to nitrite and nitrate forms could also take place, but as the study aims rather in the release of urea from Polymer Coated Urea Fertilizers (PCUF) than the transformations of urea in soil, estimations in leachate were confined to ammoniacal-N and urea-N.

4.4.1 Divinylbenzene-crosslinked Polyacrylamide (DVB-PAM) Systems

Ammoniacal-N and urea-N leached at different time intervals from soil treated with uncoated urea (control) and Polymer Coated Urea Fertilizers (PCUF) based on DVB crosslinked PAM systems were shown in tables 4.3 and 4.4.

Table 4.3 Ammoniacal-N (%) of PCUF based on DVB-PAM systems at different leaching intervals

Systems	PS	NR	EVA	PVC	Control
Time (days)		$[NH_4]^+$ - N (%)			
1	17.53	16.13	12.33	18.70	25.90
2	21.43	21.40	20.07	18.90	36.77
7	21.40	27.20	27.27	24.67	5.53
14	7.47	4.73	5.03	10.13	1.30
21	4.00	2.04	2.57	2.83	0.77
28	1.53	0.63	0.33	1.77	0.37
45	0.37	0.33	0.33	0.27	0.17

Critical Difference (CD) = 1.01

A substantially high amount of ammoniacal-N leached out from the control (uncoated urea) during the initial two days of the experiment and a drastic reduction is noted on 7th and subsequent days, while in all PCUF systems ammoniacal-N content in leachate was very low during 1st and 2nd days and significantly higher values are noted till 21st day (Table 4.3). In the case of control conversion of urea to ammonium was very fast, since all the applied urea was in contact with the soil from the date of application itself. Hence high amount of ammonium was present in the system, susceptible to leaching.

Table 4.4 Urea-N (%) in leachate of DVB-PAM systems at different periods.

Systems	PS	NR	EVA	PVC	Control
Time(days)			Urea	-N(%)	
1	5.37	10.33	10.97	5.43	16.53
2	2.37	1.97	1.73	2.97	4.97
7	1.33	1.63	0.73	0.60	0
14	0.93	0	0	0	0

CD= 0.7

In case of PCUF, the urea, come out from the granules only were converted to ammoniacal form and was susceptible to leaching. The urea-N content in leachate from the control was higher than that from PCUF on 1st and 2nd days (Table 4.4). 7th day onwards no urea could be measured in leachate of control while it was obtained in all PCUF on 7th day and in the case of PS system, on 14th day also.

A portion of urea that is not converted to ammonium form is also susceptible to leaching. In case of control, all the applied urea was in contact with the soil and leached out from the initial day itself, hence high values of urea and ammonium are obtained. Thus a major portion of the applied urea was leached either in the form of urea or ammonium. Later the amount of urea left over were reduced and hence lower values of urea and ammonium were obtained in the leachate. But in Polymer Coated Urea Fertilizers (PCUF) small portions of urea might be released out and a part of the released urea that had not been converted to ammonium form had leached out in the form of urea, that is why a lower value for urea-N. If urea is obtained in leachate for more time the slow release character increases. Thus polystyrene (PS) system is having more slow release property than the other systems (table 4.4).

The total-N value is the sum of ammoniacal-N and urea-N and it gives a more clear picture on the release behaviour of different coated systems (table 4.5).

Significantly lower values for total-N in leachate were observed on 1st and 2nd days for all PCUF systems, while during later periods upto 21st day significantly higher values were noted when compared to control. On 28th day also significantly higher amounts were noted for PS and PVC systems. On 45th day a higher value for total-N is noted in all PCUF, but were not significant statistically when compared to control. These results indicate the general slow release behaviour of the coated systems.

Table 4.5 Total-N (%) of PCUF based on DVB-PAM systems at different leaching intervals

System	PS	NR	EVA	PVC	Control
Time(days)		Total-N	(%)		
1	22.90	26.46	23.30	24.10	42.43
2	23.80	23.37	21.80	21.87	41.73
7	22.73	28.83	28.00	25.27	5.53
14	8.40	4.73	5.03	10.13	1.30
21	4.00	2.03	2.57	2.83	0.77
28	1.53	0.63	0.33	1.77	0.37
45	0.37	0.33	0.33	0.27	0.17

CD =0.87

Among the four coated urea systems, PS and PVC sealant systems show a more sustained slow release character compared to NR and EVA sealant systems. On 14th, 21st and 28th days PS system had significantly higher value for total-N than NR and EVA systems. Similarly on 14th and 21st days PVC system had higher total-N in leachate than NR and EVA systems. Lower total-N values on 1st and 7th days in the case of PS system indicate that the amount of urea released from the system was low initially and at later stages there was higher amount of urea remained in the system, to be released when compared to other systems. Among NR, EVA and PVC systems, total-N values of NR system were high during the initial periods, hence high initial rate of release. In case of PVC system a significantly higher amount of N released during later periods when compared to EVA system hence it has a better slow release profile. The values of cumulative total-N are shown in table 4.6. Cumulative total-N value is maximum for NR system and least for EVA system at the end of the experiment (table 4.6). Therefore the amount of N leached in 45 days was maximum from NR system and least from EVA system. Though cumulative total-N value is lower for EVA system, after 7th day a very sharp reduction in total-N content is noted, when compared to PS and PVC systems. Hence PS and PVC systems were selected for incubation study for further evaluation.

Table 4.6 Cumulative total-N (%) of PCUF based on different DVB-PAM Systems.

Systems	PS	NR	EVA	PVC	Control
Time (days)		Cum.	Total	-N (%)	
1	22.90	26.46	23.30	24.10	42.43
2	46.70	49.83	45.10	46.00	84.17
7	69.43	78.67	73.10	71.23	89.70
14	77.83	83.40	78.13	81.37	91.00
21	81.83	85.43	80.70	84.23	91.77
28	83.37	86.07	81.03	86.00	92.13
45	83.73	86.40	81.37	86.23	92.30

CD = 2.33

4.4.2 N,N'-Methylene-bis-acrylamide-crosslinked Polyacrylamide (NNMBA-PAM) Systems

Ammoniacal-N (%) and urea-N (%) in leachate of four coated fertilizers based on NNMBA-PAM system and control at different time intervals are depicted in tables 4.7 and 4.8 respectively. Ammoniacal-N (%) content in leachate are low during initial periods for all coated systems when compared to control. All systems released higher amounts of ammoniacal-N during later periods therefore from 7th day onwards. This indicate the slow release properties of all coated systems. EVA system is having lower value for ammoniacal-N on 1st, 2nd and 7th days compared to other systems, while higher values are obtained during later periods. This indicates its higher slow release character. PS system have higher ammoniacal-N values on 21st, 28th and 45th days than NR and PVC systems.

Table 4.7 Ammoniacal-N (%) of NNMBA-PAM systems at different leaching intervals

Systems	PS	NR	EVA	PVC	Control
Time (Days)		$[NH_4]^+$-N	(%)		
1	17.67	25.00	17.47	28.40	25.90
2	20.13	19.80	15.87	17.97	36.77
7	20.77	26.23	18.77	21.93	5.53
14	7.80	9.10	5.13	4.03	1.30
21	3.10	0.77	2.87	0.73	0.77
28	1.50	0.83	3.07	0.77	0.37
45	0.77	0.40	1.77	0.30	0.17

CD = 1.30

Urea-N values are shown in table 4.8. In NR and PVC systems urea-N could be obtained till 7th day. In PS system till 14th day, urea-N was noted while in EVA system till 21st day it could be noticed. These observations indicate the better slow release behaviour of PS and EVA based coated fertilizers.

Table 4.8. Urea-N (%) of NNMBA-PAM systems at different leaching intervals.

Systems	PS	NR	EVA	PVC	Control
Time (Days)		Urea-N	(%)		
1	6.37	4.30	7.13	5.97	16.53
2	4.23	3.70	4.63	8.47	4.97
7	2.60	1.33	2.47	0.77	0
14	0.87	0	2.10	0	0
21	0	0	1.43	0	0

CD = 0.97

The total-N (ammoniacal-N + urea-N) gives a more clear picture (table 4.9) on release properties. For all coated fertilizers, total-N values were significantly lower than that of control on 1st and 2nd days and significantly higher values were observed on 7th and 14th days. This indicate the slow release property of coated fertilizers. EVA system is having a higher total-N value on 21st, 28th and 45th days when compared to NR, PVC and PS systems hence a better slow release character.

Similarly PS system has higher total-N value than NR and PVC systems, hence a better slow release profile.

Table 4.9 Total-N (%) values of NNMBA-PAM systems at different leaching intervals.

Systems	PS	NR	EVA	PVC	Control
Time(Days)		Total-	N(%)		
1	24.03	29.30	24.60	34.37	42.43
2	24.37	23.50	20.50	26.43	41.73
7	23.37	27.57	22.17	22.67	5.53
14	8.67	9.10	7.23	4.03	1.30
21	3.10	0.77	4.30	0.73	0.77
28	1.50	0.83	3.07	0.77	0.37
45	0.77	0.40	1.77	0.33	0.17

CD =1.24

The cumulative total-N values of EVA and PS systems were lower than that of NR and PVC systems throughout the experiment (table 4.10). Among PS and EVA systems, latter is having a lower value of cumulative total-N from 2nd day to 45th day. Thus while considering the cumulative total-N values, it is indicated that the sealant EVA could impart better slow release property than the sealant PS in NNMBA-PAM system. Based on these observations, EVA and PS systems were selected for incubation study.

Table 4.10 Cumulative Total-N (%) values of NNMBA-PAM systems at different leaching intervals.

Systems	PS	NR	EVA	PVC	Control
Time(Days)		Cum.	Total-N	(%)	
1	24.03	29.30	24.60	34.37	42.43
2	48.40	52.80	45.10	60.80	84.17
7	71.77	80.37	67.27	83.47	89.70
14	80.43	89.47	74.50	87.50	91.00
21	83.53	90.23	78.80	88.23	91.77
28	85.03	91.07	81.87	89.00	92.13
45	85.80	91.47	83.63	89.30	92.30

CD = 3.71

4.4.3 Tetraethyleneglycol diacrylate-crosslinked Polyacrylamide (TTEGDA-PAM) Systems

Ammoniacal-N (%) and urea-N (%) content in leachate at different time intervals of PCUF based on TTEGDA-PAM system and control are represented in tables 4.11 and 4.12 respectively.

Table 4.11 Ammoniacal-N (%) of TTEGDA-PAM systems at different leaching intervals.

Systems	PS	NR	EVA	PVC	Control
Time(Days)		$[NH_4]^+$	-N (%)		
1	12.90	20.47	15.17	21.47	25.90
2	14.20	19.53	19.73	10.03	36.77
7	15.77	24.67	20.23	22.87	5.53
14	4.17	8.93	8.43	12.03	1.37
21	3.80	1.50	5.87	1.17	0.77
28	3.00	0.37	2.83	0.37	0.37
45	2.87	0.20	0.87	0.30	0.17

CD=0.90

A significantly lower amount of ammoniacal-N (%) was observed for all coated fertilizer systems on 1st and 2nd days, while on 7th and 14th days, a significantly higher amount of the same was noticed when compared to control (table 4.12). In the case of PS system, significantly higher amount of ammoniacal-N was obtained than control on all subsequent days also. Similarly ammoniacal-N values were significantly higher in leachate of EVA system on 21st and 28th days when compared to control. In NR and PVC systems, though not statistically significant a higher amount of ammoniacal-N was there on 21st day. These observations indicate that all coated fertilizers have slow release property.

Urea-N was obtained till 28th day in case of PS system, till 14th day in case of EVA system and till 7th day in cases of NR and PVC systems (table 4.12). This indicates the higher slow release character of PS system over others. EVA system is comparatively better than NR and PVC systems in slow release character.

Table 4.12 Urea-N (%) of PCUF based on TTEGDA-PAM systems at different leaching intervals.

Systems	PS	NR	EVA	PVC	Control
Time (Days)	Urea -N (%)				
1	7.20	6.00	6.13	9.40	16.53
2	6.57	3.90	4.47	7.47	4.97
7	5.17	0.73	4.70	0.70	0
14	2.87	0	1.83	0	0
21	2.13	0	0	0	0
28	0.90	0	0	0	0

CD = 0.80

The total-N values in leachate (table 4.13) show it had considerably lower values for all coated systems on 1st and 2nd days than the control. On 7th day, about four times or more of total-N content in leachate of control was obtained for all coated systems.

Table 4.13 Total-N of PCUF based on TTEGDA -PAM systems at different leaching intervals

Systems	PS	NR	EVA	PVC	Control
Time (Days)	Total -N (%)				
1	20.10	26.47	21.30	30.87	42.43
2	20.77	23.43	24.20	17.50	41.73
7	20.93	25.40	24.93	23.57	5.53
14	7.03	8.93	10.27	12.03	1.30
21	5.93	1.50	5.87	1.17	0.77
28	3.90	0.37	2.83	0.37	0.37
45	2.87	0.20	0.87	0.30	0.17

CD=0.65

Similarly substantially higher amount of total-N content were observed in coated systems on 14th day also. In leachate of PS and EVA systems on subsequent days also a significantly higher amount of total-N was obtained when compared to control.

But NR and PVC systems were not having considerable difference with control on 21st, 28th and 45th days. When PS and EVA systems were compared the former had a significantly lower value for total-N in leachate on 1st, 2nd, 7th and 14th days, while higher values were obtained on 21st, 28th and 45th days.

The cumulative total-N (%) values of different systems are shown in table 4.14. For all coated systems throughout the experiment period, significantly lower values for cumulative total-N (%) was observed and this indicate that all coated systems are having slow release character (table 4.14).

Table 4.14 Cumulative total-N (%) of TTEGDA-PAM systems at different leaching intervals.

Systems	PS	NR	EVA	PVC	Control
Time (Days)		Cum.	Total-	N (%)	
1	20.10	26.47	21.30	30.87	42.43
2	40.87	49.90	45.50	48.37	84.17
7	61.80	75.30	70.43	71.93	89.70
14	68.83	84.23	80.70	83.97	91.00
21	74.77	85.73	86.57	85.13	91.77
28	78.67	86.10	89.40	85.50	92.13
45	81.53	86.30	90.27	85.80	92.30

CD=1.46

Among the four coated systems PS system was having significantly lower values for cumulative total-N than the other three systems, from 2nd day till the end of the experiment. The same trend was observed in EVA system also when compared to NR and PVC systems till 14th day. A higher value for cumulative total-N was observed for EVA system at later stages of the experiment (table 4.14). However, considerably higher values for total-N was noted for the EVA system on 21st, 28th and 45th days (table 4.13) than NR and PVC systems. Considering these factors PS and EVA systems were selected for incubation study.

4.4.4 Pentaerythritol triacrylate-crosslinked Polyacrylamide (PETA-PAM) Systems.

Table 4.15 and 4.16 represent the ammoniacal-N (%) and urea-N (%) in leachate at different time intervals of PCUF based on PETA-PAM system and the control (uncoated urea). As in other polyacrylamide based coated fertilizers, here also significantly lower amount of ammoniacal-N (%) was observed on 1st and 2nd days in coated systems compared to control.

Table 4.15. Ammoniacal-N (%) of PCUF based on PETA-PAM systems at different leaching intervals.

Systems	PS	NR	EVA	PVC	Control
Time (Days)		$[NH_4]^+$ -N (%)			
1	17.70	21.97	14.53	20.53	25.90
2	18.40	21.20	12.97	15.63	36.77
7	24.33	16.63	19.87	23.60	5.53
14	13.30	5.06	12.87	15.43	1.30
21	4.93	2.73	6.90	0.73	0.77
28	1.57	1.20	3.27	0.33	0.37
45	0.33	0.37	1.27	0.30	0.17

CD=1.18

On 7th and 14th days substantially higher amounts of ammoniacal-N in leachate of all coated fertilizers were noticed compared to control. Except PVC system all the other three coated fertilizer systems were having significantly higher values of ammoniacal-N in leachate on 21st day also. EVA and PS systems were having significantly higher ammoniacal-N (%) values on 28th day also. Though PS, NR and PVC systems were having not very high ammoniacal-N content on 45th day when compared to control, EVA system had comparatively more ammoniacal-N. This indicates the higher slow release character of EVA system compared to other systems.

Urea-N was obtained in leachate of EVA system till 14th day while it could be obtained upto 7th day only in case of other systems (table 4.16.) This indicate that

EVA system is having better slow release property than the other systems.

Table 4.16. Urea-N (%) of PCUF based on PETA-PAM systems at different leaching intervals.

Systems	PS	NR	EVA	PVC	Control
Time (Days)		Urea-N	(%)		
1	5.63	5.77	6.93	4.97	16.53
2	1.90	2.80	4.73	2.53	4.97
7	1.07	0.70	2.90	0.77	0
14	0	0	1.07	0	0

CD=0.69

Table 4.17. Total-N (%) of PCUF based on PETA-PAM systems at different leaching intervals

Systems	PS	NR	EVA	PVC	Control
Time(Days)		Total-	N (%)		
1	23.33	27.73	21.47	25.50	42.43
2	20.30	24.00	17.70	18.17	41.73
7	25.40	17.33	22.77	24.37	5.53
14	13.30	5.07	13.93	15.43	1.30
21	4.93	2.73	6.90	0.73	0.77
28	1.57	1.20	3.27	0.33	0.37
45	0.33	0.37	1.27	0.30	0.17

CD=1.18

The total-N values are shown in table 4.17. Here also on initial two days total-N content was significantly lower and on 7th and 14th days it was significantly higher for all coated fertilizers when compared to control. This indicate the slow release property of coated systems. Total-N (%) values were significantly higher for EVA system than other coated systems during later periods. For PS system the same trend was noticed upto 28th day when compared to NR and PVC systems. This points out the better slow release property of EVA and PS systems than NR and PVC systems.

The cumulative total-N (%) values of different coated systems and control are represented in table 4.18. The cumulative total-N values confirms the slow release character of all coated fertilizers. Significantly lower values for cumulative total-N were noticed for all coated systems when compared to control till 45th day.

Table 4.18 Cumulative total-N (%) of PETA-PAM systems at different leaching intervals.

Systems	PS	NR	EVA	PVC	Control
Time (Days)		Cum.	Total	-N (%)	
1	23.33	27.77	21.47	25.50	42.43
2	43.63	51.73	39.17	43.67	84.17
7	69.00	69.07	61.93	68.03	89.70
14	82.33	74.13	75.87	83.47	91.00
21	87.27	76.87	82.77	84.20	91.77
28	88.83	78.07	86.03	84.53	92.13
45	89.17	78.43	87.30	84.80	92.30

CD=3.60

The cumulative total-N value on 45th day indicate, NR and PVC systems were having a lower value than PS and EVA systems, but the amount of total-N released during the initial period of EVA and PS systems were significantly lower than NR and PVC systems (table 4.17).

Moreover in case of NR system a drastic reduction in total-N (%) values were observed after 7th day and in PVC system the same trend was observed after 14th day. Hence due to the better release profile, PS and EVA systems were selected for incubation study for further evaluation.

4.5 Comparison of the Sealants in Different Crosslinked Polyacrylamide Systems

The results of leaching experiments are analysed in another approach. The effect of different sealants and crosslinking agents on release of urea at a particular time interval is analysed. In the former analysis the performance of different sealants in a particular crosslinked polymer system over a period of time was assessed whereas here performance of the four sealants in all the four crosslinked systems at a particular time is analysed. Total N (%) and cumulative total-N (%) values of the PCUF based on the four sealants in the different crosslinked systems of PAM are compared statistically by analysis of variance for a completely randomized design. Total-N values represent the amount of N released from the coated systems at a specific period while cumulative total-N values represent the amount of N released from the systems till the specified time. The release features of all the 16 coated fertilizers based on PAM at each time interval are described.

Total-N values of the initial day of the leaching experiment for the sixteen coated fertilizers based on PAM are given in table 4.19. The lowest value for total-N on 1st day was noted for TTEGDA-PS combination hence it is having the lowest release rate while highest release rate was obtained for NNMBA-PVC combination. Among PS systems, total-N of TTEGDA-crosslinked system was significantly lower than the other crosslinked systems viz. DVB, NNMBA and PETA.

Table 4.19 Total-N (%) values of different PCUF based on PAM on 1st day.

Sealants	PS	NR	EVA	PVC
Crosslinking agents	Total-N (%)			
DVB	22.90	26.40	23.30	24.10
NNMBA	24.03	29.30	24.60	34.37
TTEGDA	20.10	26.47	21.30	30.87
PETA	23.33	27.73	21.47	25.50

CD=1.50

In systems were NR was the sealant DVB, TTEGDA and PETA-crosslinked systems were not significantly different to each other, but NNMBA-crosslinked system was having a significantly higher value for total-N. Among EVA systems total-N content of TTEGDA and PETA crosslinked systems were significantly lower than that of DVB and NNMBA-crosslinked systems. When PVC was the sealant, DVB and PETA-crosslinked systems were having a lower total-N value, hence a lower release rate than NNMBA and TTEGDA-crosslinked systems.

Table 4.20 Total-N (%) values of different PCUF based on crosslinked Polyacrylamide on 2nd day.

Sealants	PS	NR	EVA	PVC
Crosslinking agents		Total	-N (%)	
DVB	23.80	23.37	21.80	21.87
NNMBA	24.37	23.50	20.50	26.43
TTEGDA	20.77	23.43	24.20	17.50
PETA	20.30	24.00	17.70	18.17

CD=1.76

Tables 4.20 and 4.21 represent the total-N and the cumulative total-N values respectively of different Polymer Coated Urea Fertilizers (PCUF) on the 2nd day Among the four PS systems, TTEGDA and PETA-crosslinked systems had significantly lower value for total-N than DVB and NNMBA-crosslinked systems. All the four NR systems were more or less similar with regard to total-N value. In the systems where EVA was the sealant, PETA-crosslinked system was having a significantly lower value while TTEGDA system had significantly higher value. When PVC was the sealant TTEGDA and PETA-crosslinked systems were having significantly lower value than DVB, NNMBA-crosslinked systems.

Table 4.21 Cumulative total-N (%) of different PCUF based on crosslinked polyacrylamide on 2nd day.

Sealants	PS	NR	EVA	PVC
Crosslinking agents		Cum.	Total-(%)	
DVB	46.70	49.83	45.10	46.00
NNMBA	48.40	52.80	45.10	60.80
TTEGDA	40.87	49.90	45.50	48.37
PETA	43.63	51.73	39.17	43.67

CD= 2.69

While cumulative total-N values of 2nd day were (table 4.21) considered PETA-EVA and TTEGDA-PS systems were having significantly lower values than all the other systems. Among PS and NR sealant systems, lowest values for cumulative total-N were noted for TTEGDA and DVB systems respectively. In both EVA and PVC systems, PETA crosslinked system showed lower values.

Tables 4.22 and 4.23 represent the values of total-N (%) and cumulative total-N (%) of 7th day. Among PS systems TTEGDA crosslinked system had significantly lower value for total-N (Table 4.22). In NR systems, PETA crosslinked system had the lowest total-N value and in EVA systems, NNMBA and PETA systems were having almost similar values for the same which are significantly lower than DVB and TTEGDA crosslinked systems. In systems were PVC was the sealant, NNMBA crosslinked system had the lowest value.

Table 4.22 Total-N (%) values of different PCUF based on crosslinked polyacrylamide systems on 7th day.

Sealants	PS	NR	EVA	PVC
Crosslinking agents	Total-N (%)			
DVB	22.73	28.83	28.00	25.27
NNMBA	23.37	27.57	22.17	22.67
TTEGDA	20.93	25.40	24.93	23.57
PETA	25.40	17.33	22.77	24.37

CD=1.10

Table 4.23 Cumulative Total-N (%) values of different PCUF based on crosslinked polyacrylamide systems on 7th day.

Sealants	PS	NR	EVA	PVC
Crosslinking agents	Cum.Total N (%)			
DVB	69.43	78.67	73.10	71.23
NNMBA	71.77	80.37	67.27	83.47
TTEGDA	61.80	75.30	70.43	71.93
PETA	69.00	69.07	61.93	68.03

CD=3.01

The cumulative total-N values of TTEGDA-PS and PETA-EVA systems were similar and were significantly lower than all the other systems as observed on 2nd day. Hence these systems are having lower initial rate. In both NR and PVC sealant systems PETA crosslinking system was having significantly lower cumulative total-N value.

Tables 4.24 and 4.25 give the total-N and cumulative total-N values of different systems on 14th day. As observed on 2nd and 7th days, here also TTEGDA crosslinked system continued to have a lower value for total-N among the PS sealant systems (Table 4.24), which indicate the lower release rate of TTEGDA-PS system during the initial periods.

Table 4.24 Total-N (%) values of different PCUF based on crosslinked polyacrylamide systems on 14th day.

Sealants	PS	NR	EVA	PVC
Crosslinking agents		Total-N	(%)	
DVB	8.40	4.73	5.03	10.13
NNMBA	8.67	9.10	7.23	4.03
TTEGDA	7.03	8.93	10.27	12.03
PETA	13.30	5.07	13.93	15.43

CD=1.23

In NR systems, DVB and PETA-crosslinked systems released lower amount of total-N than NNMBA and TTEGDA-crosslinked systems. For the various crosslinked systems based on EVA sealant, DVB-crosslinked system and systems based on PVC sealant NNMBA-crosslinked system have significantly lower values for total-N (Table 4.25).

Table 4.25 Cumulative Total-N (%) values of different PCUF based on crosslinked polyacrylamide Systems on 14th day.

Sealants	PS	NR	EVA	PVC
Crosslinking agents		Cum.	Total-N	(%)
DVB	77.83	83.40	78.13	81.37
NNMBA	80.43	89.47	74.50	87.50
TTEGDA	68.43	84.23	80.70	83.97
PETA	82.33	74.13	75.87	83.47

CD=3.37

Cumulative total-N values (Table 4.25) justify the better slow release nature of TTEGDA crosslinked system among PS systems. Among NR systems, PETA system had significantly lower value for cumulative total-N as observed on 7th day. Among the EVA systems, NNMBA system had a lower value for cumulative total-N and in PVC systems DVB, TTEGDA and PETA-crosslinked systems were similar and had lower values than NNMBA-crosslinked system.

Tables 4.26 and 4.27 represent the values for total-N (%) and cumulative total-N (%) values of the 21st day. Among PS systems, TTEGDA crosslinked system shows better slow release character. On 21st day it had a significantly higher value for total-N.

Table 4.26 Total-N (%) values of different PCUF based on crosslinked polyacrylamide systems on 21st day.

Sealants	PS	NR	EVA	PVC
Crosslinking agents		Total	-N(%)	
DVB	4.00	2.03	2.57	2.83
NNMBA	3.10	0.77	4.30	0.73
TTEGDA	5.93	1.50	5.87	1.17
PETA	4.93	2.73	6.90	0.73

CD=0.55

Similarly in systems were NR was the sealant, PETA-crosslinked system released a significantly higher amount of total-N (Table 4.26). Among the EVA systems also PETA-crosslinked system had a higher total-N value than other crosslinked systems. Among PVC systems the total-N values were in the order DVB > TTEGDA > NNMBA = PETA.

The cumulative total-N values among PS sealant systems were (table 4.27) in the order PETA > NNMBA > DVB > TTEGDA. The cumulative total-N decreased in the order among NR systems as NNMBA > TTEGDA > DVB > PETA and among EVA systems as TTEGDA > PETA > DVB > NNMBA and among PVC systems as NNMBA > TTEGDA > DVB > PETA.

Table 4.27 Cumulative Total-N (%) released from different PCUF based on crosslinked-polyacrylamide systems on 21st day.

Sealants	PS	NR	EVA	PVC
Crosslinking agents		Cum.	Total-N	(%)
DVB	81.83	85.43	80.70	84.23
NNMBA	83.53	90.23	78.80	88.23
TTEGDA	74.77	85.73	86.57	85.13
PETA	87.27	76.87	82.77	84.20

CD = 3.53

Table 4.28 and 4.29 represents the values for total-N (%) and cumulative total-N (%) on 28th day. In systems were PS was the sealant TTEGDA-crosslinked system had a significantly higher value than other crosslinked systems which were not significantly different to each other. Among the NR systems, PETA-crosslinked system was having a significantly higher value for total-N than other systems. Among EVA systems PETA, TTEGDA and NNMBA-crosslinked systems were having higher values compared to DVB-crosslinked system which was having a very low value of total-N. In PVC systems, DVB-crosslinked system had a higher value than other systems. PETA system was having a very low value

Table 4.28 Total-N (%) values of different PCUF based on crosslinked-polyacrylamide systems on 28th day.

Sealants	PS	NR	EVA	PVC
Crosslinking agents		Total-	N(%)	
DVB	1.53	0.63	0.33	1.77
NNMBA	1.50	0.83	3.07	0.77
TTEGDA	3.90	0.37	2.83	0.37
PETA	1.57	1.20	3.27	0.33

CD=0.28

While cumulative total-N values were considered (Table 4.29), among PS systems TTEGDA system and among NR systems PETA crosslinked system and among EVA systems DVB crosslinked system and among PVC systems PETA crosslinked system were having lower values.

Table 4.29 Cumulative total-N (%) values of PCUF based on crosslinked-polyacrylamide systems on 28th day.

Sealants	PS	NR	EVA	PVC
Crosslinking agents		Cum.	Total-N	(%)
DVB	83.37	86.07	81.03	86.00
NNMBA	85.03	91.07	81.87	89.00
TTEGDA	78.67	86.10	89.40	85.50
PETA	88.83	78.07	86.03	84.53

CD=3.64

In systems were EVA was the sealant, DVB and NNMBA-crosslinked systems were not significantly different while in PVC systems PETA, TTEGDA and DVB-crosslinked systems were also not significantly different to each other.

Tables 4.30 and 4.31 represent total-N (%) and cumulative total-N (%) values of 45th day. Among PS systems, TTEGDA-crosslinked system had comparatively higher value for total-N than the other three systems (Table 4.30).

Table 4.30 Total-N (%) values of different PCUF based on crosslinked-polyacrylamide systems on 45th day.

Sealants	PS	NR	EVA	PVC
Crosslinking agents		Total-	N (%)	
DVB	0.37	0.33	0.33	0.27
NNMBA	0.77	0.40	1.77	0.33
TTEGDA	2.87	0.20	0.87	0.30
PETA	0.33	0.37	1.27	0.30

CD=0.31

All the crosslinked systems were having almost similar values for total-N were NR was the sealant, while among EVA systems, NNMBA-crosslinked system was having a significantly higher value than that of the other systems. When PVC was the sealant, all the four crosslinked systems were more or less similar in total-N value.

Table 4.31 Cumulative total-N (%) released from PCUF based on PAM systems on 45th day.

Sealants	PS	NR	EVA	PVC
Crosslinking agents		Cum.	Total-N	(%)
DVB	83.73	86.40	81.37	86.23
NNMBA	85.80	91.47	83.63	89.30
TTEGDA	81.53	86.30	90.27	85.80
PETA	89.17	78.43	87.30	84.80

CD=3.74

At the end of the leaching experiment on 45th day the cumulative total-N value among the PS systems is lowest for TTEGDA-crosslinked system. In NR systems the lowest value is for PETA-crosslinked system while in EVA systems it is DVB-crosslinked system and among PVC systems it is PETA-crosslinked system are having lower values.

These results indicate that when PS was the sealant, TTEGDA appears to be a better crosslinking agent to obtain prolonged release characteristics. Among NR sealant systems, PETA-crosslinked system and among EVA sealant systems, NNMBA-crosslinked system was found to be having better slow release properties. When PVC was the sealant the effect of crosslinking agent was not significant to the level as it was in other cases. In PVC sealant systems DVB, TTEGDA and PETA-crosslinked systems were more or less similar in the release characters and NNMBA-crosslinked system had a higher initial release rate and higher cumulative total-N value at the end of the experiment. However the study gives only an indication of slow release properties while more confirmatory conclusion can be drawn based on incubation experiments.

4.6 Results of Leaching Experiments of Polymethylmethacrylate Systems

4.6.1 Divinylbenzene-crosslinked Polymethylmethacrylate (DVB-PMMA) Systems.

Tables 4.32 and 4.33 represent the ammoniacal-N (%) and urea-N (%) estimated in leachate at different time intervals. Considerably lower values for ammoniacal-N were obtained for all the coated systems than control on 1st and 2nd days. From 7th day to 45th day a significantly higher amount of ammoniacal-N was obtained for all coated systems than control. This indicates the slow release behaviour of the prepared coated systems. Significantly lower amounts of ammoniacal-N were observed for PS system during initial days compared to other coated systems. Similarly NR system was having significantly lower ammoniacal-N values on 1st, 2nd and 7th days than EVA and PVC systems. From 14th to 45th day significantly higher ammoniacal-N values are observed for PS system compared to other coated systems. NR system was having a lower initial rate of release. This indicates the better slow release character of PS and NR systems.

Table 4.32 Ammoniacal-N (%) of PCUF based on DVB-PMMA systems at different leaching intervals.

Systems	PS	NR	EVA	PVC	Control
Time(Days)		$[NH_4]^+$-N	(%)		
1	6.73	11.10	17.40	15.63	25.90
2	9.93	16.63	18.10	20.10	36.77
7	15.60	19.03	21.70	22.27	5.53
14	12.53	10.27	7.23	11.13	1.30
21	9.40	4.33	3.77	7.07	0.77
28	5.03	2.30	2.60	1.30	0.37
45	3.00	1.83	1.53	2.13	0.17

CD=0.87

Table 4.33 Urea-N (%) of PCUF based on DVB-PMMA systems at different leaching intervals.

Systems	PS	NR	EVA	PVC	Control
Time(Days)		Urea-N	(%)		
1	2.03	8.90	6.60	6.07	16.53
2	3.03	4.30	3.73	3.03	4.97
7	4.63	2.63	2.23	2.03	0
14	1.17	0	0	0	0

CD=0.67

Urea-N was detected in leachate of PS system till 14th day, while in other coated systems it could be noticed till 7th day only (table 4.34). This further substantiates the better slow release character of PS system.

Total-N values indicate (Table 4.34) the slow release property of coated fertilizers further. All coated systems were having significantly lower values for total-N on 1st and 2nd days than uncoated urea (control). On all subsequent days all the coated systems were having significantly higher values for total-N. Among the coated systems, PS system had a more sustained release character than rest of the systems. On 1st, 2nd and 7th days it had significantly lower and on 14th, 21st, 28th and 45th days it had significantly higher total-N values compared to other coated systems. This indicates the better slow release character of PS system. The NR system had a significantly lower total-N on 1st, 2nd and 7th days than EVA and PVC systems. During later periods it had more or less similar values of total-N compared to EVA system. When NR and PVC systems were compared PVC system had a significantly higher total-N values on 14th and 21st days and NR system was having a significantly higher value on 28th day.

Table 4. 34 Total-N (%) values of PCUF based on DVB-PMMA systems at different leaching intervals.

Time	PS	NR	EVA	PVC	Control
(Days)		Total-N	(%)		
1	8.77	20.00	24.00	21.70	42.43
2	12.97	20.93	21.83	23.13	41.73
7	20.23	21.67	23.93	24.30	5.53
14	13.70	10.27	7.23	11.13	1.30
21	9.40	4.33	3.77	7.07	0.77
28	5.03	2.30	2.60	1.30	0.37
45	3.00	1.83	1.53	2.13	0.17

CD=0.67

Cumulative total-N values (Table 4.35) clearly indicated the better sustained release characters of PS and NR systems over EVA and PVC systems. Though definite conclusions were difficult based on total-N values, with cumulative total-N it was possible. Throughout the experiment period PS system had significantly lower values for cumulative total-N than the other three systems. Similarly NR system also had a significantly lower value for cumulative total-N than EVA and PVC systems. The initial release rate of NR system was lower than that of EVA and PVC systems. Based on these observations PS and NR systems were selected for the incubation study.

Table 4.35 Cumulative total-N (%) values of PCUF based on DVB-PMMA systems at different leaching intervals.

Systems	PS	NR	EVA	PVC	Control
Time(Days)		Cum.	Total-N	(%)	
1	8.77	20.00	24.00	21.70	42.43
2	21.30	40.93	45.83	44.83	84.17
7	41.97	62.60	69.77	69.13	89.70
14	55.67	72.87	77.00	80.27	91.00
21	65.07	77.20	80.77	87.33	91.77
28	70.10	79.50	83.37	88.63	92.13
45	73.10	81.33	84.90	90.77	92.30

CD=1.67

4.6.2 N,N'-Methylene-bis-acrylamide-crosslinked Polymethylmethacrylate (NNMBA-PMMA) Systems.

Ammoniacal-N (%) and urea-N (%) content at different time intervals, of NNMBA-PMMA systems are shown in tables 4.36 and 4.37 respectively. Substantially lower values for ammoniacal-N were noticed for all coated fertilizers on 1st and 2nd days than that of control. Moreover on subsequent days significantly higher amount of ammoniacal-N in leachate was noted for PS, NR and EVA systems when compared to control. PVC system had significantly higher ammoniacal-N values on 7th and 14th days than control. This indicates the slow release nature of the formulations. Among coated systems EVA system was having lower ammoniacal-N values till 14th day than all other systems. On 45th day EVA system had a significantly higher value for ammoniacal-N. PS and NR systems were having higher values for ammoniacal-N during later stages compared to PVC system.

Table 4.36 Ammoniacal-N (%) values of PCUF based on NNMBA-PMMA systems at different leaching intervals.

Systems	PS	NR	EVA	PVC	Control
Time(Days)		$[NH_4]^+$-N	(%)		
1	8.67	11.33	2.73	19.23	25.90
2	13.80	16.50	4.23	15.63	36.77
7	17.73	13.03	8.57	21.13	5.53
14	17.76	13.13	12.27	12.87	1.30
21	6.57	9.53	6.57	0.97	0.77
28	4.57	5.77	4.80	0.77	0.37
45	2.23	2.47	4.57	0.37	0.17

CD=0.92

Urea-N (Table 4.37) was detected in leachate of EVA system even on 45th day of the experiment while for PS and NR system it was observed till 7th day and for PVC system the same was noticed on 1st and 2nd days only. This indicate that EVA system is having a better slow release behaviour than other systems and PS and NR systems are better than PVC system.

Table 4.37 Urea-N (%) values of PCUF based on NNMBA-PMMA at different incubation intervals.

Systems	PS	NR	EVA	PVC	Control
Time(Days)		Urea-N	(%)		
1	5.03	7.57	0.60	13.57	16.53
2	3.57	5.70	1.10	5.20	4.97
7	6.57	5.13	2.97	0	0
14	0	0	4.77	0	0
21	0	0	2.00	0	0
28	0	0	1.40	0	0
45	0	0	0.57	0	0

CD=0.72

The total-N values gave (Table 4.38) a more clear picture on release properties. Total-N released from EVA system was significantly lower than that of other systems on 1st, 2nd and 7th days and on 14th day it had significantly higher value than that of NR and PVC systems but was comparable with that of PS system. On 21st day NR system had a significantly higher value for total-N than other coated systems, while EVA system had a higher value for the same than PS system. On 28th and 45th days EVA system had a higher value than all other systems, while the values of PS and NR systems were comparable and were significantly higher than PVC system. Thus EVA system was having a more sustained release character than others. Amount of total-N released from PVC system was high during the initial period and a sudden decrease was noted later. PS and NR systems were comparable in release characters, however, a lower initial release rate for PS system was noticed.

Table 4.38. Total-N (%) of PCUF based on NNMBA-PMMA Systems at different leaching intervals.

Systems	PS	NR	EVA	PVC	Control
Time(Days)		Total-N	(%)		
1	13.70	18.90	3.33	32.80	42.40
2	17.37	22.20	5.33	20.80	41.73
7	24.30	17.17	11.53	21.13	5.53
14	17.77	13.17	17.03	12.87	1.30
21	6.57	9.53	8.57	0.97	0.77
28	4.57	5.77	6.20	0.77	0.37
45	2.23	2.47	5.13	0.37	0.17

CD=0.77

Table 4.39. Cumulative total-N(%) of PCUF based on NNMBA -PMMA systems at different leaching intervals

Systems	PS	NR	EVA	PVC	Control
Time(Days)		Cum.	Total-N	(%)	
1	13.70	18.90	3.33	32.80	42.40
2	31.07	41.10	8.67	53.63	84.17
7	55.37	58.27	20.20	74.77	89.70
14	73.13	71.40	37.23	87.63	91.00
21	79.70	80.93	45.80	88.60	91.77
28	84.27	86.70	52.00	89.37	92.13
45	86.50	89.17	57.13	89.73	92.30

CD=1.62

While cumulative total-N values were considered, it clearly established the better slow release characters of EVA system. Throughout the experiment EVA system had a substantially lower value for cumulative total-N than the other systems, while PVC system had a significantly higher value for the same (Table 4.38). When PS and NR systems are compared except on 14th day a lower value for cumulative total-N was noted for PS system suggesting a better release character for the same. Based on the above observations EVA and PS systems were selected for incubation study.

4.6.3 Tetraethyleneglycol diacrylate-crosslinked Polymethylmethacrylate (TTEGDA-PMMA) Systems.

Ammoniacal-N (%) and urea-N (%) values of TTEGDA-PMMA system are shown in tables 4.40 and 4.41 respectively. Coated fertilizers were having a significantly lower ammoniacal-N value than that of control on 1st and 2nd day. During later periods coated systems were having higher value for ammoniacal-N, when compared to control.

Table 4.40 Ammoniacal-N (%) of PCUF based on TTEGDA-PMMA systems at different leaching intervals.

Systems	PS	NR	EVA	PV	Control
Time(Days)		$[NH_4]^+$-N	(%)		
1	6.43	9.17	13.77	18.47	25.90
2	12.57	17.43	23.03	13.43	36.77
7	10.50	13.50	14.23	21.50	5.53
14	10.27	13.17	9.70	13.17	1.30
21	7.73	9.43	6.40	0.83	0.77
28	6.67	5.63	4.80	0.43	0.37
45	3.80	2.43	1.30	0.33	0.17

CD=0.77

This indicates the slow release behaviour of coated fertilizers. Among coated systems, PS system had a lower value for ammoniacal-N on 1st, 2nd and 7th days than other systems. On 14th day also it had a lower value for the same than NR and PVC systems. During later stages of the experiment it had significantly higher value for ammoniacal-N than the rest of the systems. This indicates the better slow release nature of PS system. The NR system had lower ammoniacal-N value during initial periods and higher values later compared to EVA and PVC systems.

Table 4.41 Urea-N (%) of PCUF based on TTEGDA-PMMA systems at different leaching intervals.

Time	PS	NR	EVA	PVC	Control
(Days)		Urea-N	(%)		
1	1.87	6.03	6.07	13.77	16.53
2	2.70	5.63	4.73	3.97	4.97
7	4.10	2.00	1.93	1.30	0
14	2.17	1.13	0.57	0	0
21	0.73	0	0	0	0
28	0.30	0	0	0	0

CD=0.65

Urea-N was present in leachate of PS system upto 28th day while for NR and EVA systems it was present upto 14th day and for PVC system it was present upto 7th day only (Table 4.41). This indicates the better slow release character of PS system over others. NR and EVA systems are having better release character compared to PVC system.

Table 4.42 shows the total-N in leachate of different systems. The PS system had a distinctly lower total-N values than the other coated systems during the initial periods. At later stages (on 28th and 45th days) it released a significantly higher amount total-N than the rest of the systems. More sustained release of nitrogen from PS system was noticed when compared to other systems. Among NR, EVA and PVC systems the NR system released lower amount of N during initial days and higher amounts at later stages than other systems. Between EVA and PVC systems the former had a better slow release profile since higher total-N values were obtained on, 28th and 45th days.

Table 4.42 Total-N (%) of PCUF based on TTEGDA -PMMA systems at different leaching intervals

Time	PS	NR	EVA	PVC	Control
(Days)		Total-N	(%)		
1	8.30	15.20	19.83	32.20	42.40
2	15.27	23.00	27.73	17.40	41.73
7	14.60	15.50	16.17	22.80	5.53
14	12.43	14.30	10.27	13.17	1.30
21	8.47	9.43	6.40	0.83	0.77
28	6.97	5.63	4.80	0.43	0.37
45	3.80	2.43	1.30	0.33	0.17

CD=0.69

The cumulative total-N values for different systems are shown in table 4.43. PS system distinctly had a better release profile than other systems. It had substantially lower values for cumulative total-N through out the period when compared to other systems. Similarly NR system also had lower values for cumulative total-N when compared to EVA and PVC systems through out the experiment.

Table 4.43 Cumulative total-N (%) values of PCUF based on TTEGDA-PMMA systems at different leaching intervals.

Systems	PS	NR	EVA	PVC	Control
Time (Days)		Cum.	Total-	N (%)	
1	8.30	15.20	19.83	32.23	42.23
2	23.57	38.27	47.57	49.63	84.17
7	38.17	53.77	63.77	72.43	89.70
14	50.60	68.07	74.03	85.60	91.00
21	59.07	77.50	80.43	86.43	91.77
28	66.03	83.13	85.20	86.87	92.13
45	69.83	85.57	86.53	87.20	92.30

CD=1.42

Between EVA and PVC systems the cumulative total-N values of EVA system were significantly lower than that of PVC system. These observations favours the selection of PS and NR systems for incubation study for further evaluation.

4.6.4. Pentaerythritol triacrylate-crosslinked Polymethylmethacrylate (PETA-PMMA) Systems

Tables 4.44 and 4.45 give the ammoniacal-N (%) and urea-N (%) values of PETA systems. As in other coated systems here also significantly lower values for ammoniacal-N were noted for all coated systems on 1st and 2nd days. On 7th, 14th and 21st days higher values for the same was noted when compared to control. This indicates the slow release behaviour of coated fertilizers. Among the coated systems EVA system is having comparatively lower ammoniacal-N values till 7th day and higher values on 14th, 28th and 45th days.

Table 4.44 Ammoniacal-N (%) values of PETA-PMMA systems at different leaching intervals.

Systems	PS	NR	EVA	PVC	Control
Time(Days)		$[NH_4]^+$-N	(%)		
1	16.10	22.00	8.60	16.40	25.90
2	18.47	18.73	12.90	22.13	36.77
7	22.27	28.27	19.90	21.50	5.53
14	13.80	10.13	18.67	11.07	1.30
21	3.90	2.20	3.77	7.90	0.77
28	1.70	1.13	2.73	1.23	0.37
45	0.23	0.30	1.10	0.43	0.17

CD=1.10

Table 4.45 Urea-N (%) of PCUF based on PETA -PMMA Systems at different leaching intervals.

Systems	PS	NR	EVA	PVC	Control
Time(Days)		Urea-N	(%)		
1	4.37	3.00	5.87	4.87	16.53
2	2.93	1.97	4.50	2.00	4.97
7	2.10	1.27	3.10	2.00	0
14	0	0	1.87	0	0
21	0	0	1.07	0	0

CD= 0.81

For EVA system, urea-N could be obtained till 21st day, whereas it was noted till 7th day only for other systems (Table 4.45). This indicates the better slow release character of EVA system..

Table 4.46 gives the total-N leached out from different systems at various time intervals. Total-N values in leachate of EVA system on 1st, 2nd and 7th days were lower and during later periods it was higher when compared to other coated systems. The only exception was on 21st day where PVC system was having a higher value.

Table 4.46 Total-N (%) of PCUF based on PETA-PMMA systems different leaching intervals.

Systems	PS	NR	EVA	PVC	Control
Time(Days)		Total-N	(%)		
1	20.47	25.00	14.43	21.27	42.43
2	21.40	20.70	17.40	24.13	41.73
7	24.37	29.53	23.00	23.50	5.53
14	13.80	10.13	20.53	11.07	1.30
21	3.90	2.20	4.83	7.90	0.77
28	1.70	1.13	2.73	1.23	0.37
45	0.23	0.30	1.10	0.43	0.17

CD=0.84

Table 4.47 Cumulative total-N (%) values of PCUF based on PETA-PMMA systems at different leaching intervals.

Systems	PS	NR	EVA	PVC	Control
Time(Days)		Cum.	Total-	N (%)	
1	20.47	25.00	14.47	21.27	42.43
2	41.87	45.70	31.87	45.40	84.17
7	66.23	75.23	54.87	68.90	89.70
14	80.03	85.37	75.40	79.97	91.00
21	83.93	87.57	80.23	87.87	91.77
28	85.63	88.70	82.97	89.10	92.13
45	85.87	89.00	84.07	89.50	92.30

CD=2.16

Cumulative total-N values help to distinguish further the slow release property of coated systems and are shown on table 4.47. EVA system had significantly lower cumulative total-N values than all other systems upto 28th day of the experiment. This further substantiates the better slow release character of EVA system. PS system had significantly lower cumulative total-N values than NR system upto 45th day and when compared to PVC system except on 1st and 14th days it follows the similar trend. PS and PVC systems are very close in release properties and considering the lower initial rate of PS system it had been selected along with EVA system for the incubation study.

4.7 Comparison of Sealants in Different Crosslinked Polymethylmethacrylate Systems.

The total-N values of the 16 coated urea fertilizers based on PMMA systems on 1st day are shown in table 4.48. When PS was the sealant, TTEGDA and DVB-crosslinked systems recorded very low values for total-N compared to NNMBA and PETA-crosslinked systems. When NR was the sealant, TTEGDA-crosslinked system had the lowest value and PETA-crosslinked system had the highest value for total-N. NNMBA-EVA system recorded the lowest value for total-N among all PMMA systems on 1st day. Among PVC systems, NNMBA and TTEGDA-crosslinked systems were having considerably higher values for total-N. Generally all PVC systems had higher release rate on 1st day.

Table 4.48 Total-N (%) values of PCUF based on different crosslinked PMMA systems on 1st day.

Sealants	PS	NR	EVA	PVC
Crosslinking agents	Total-N (%)			
DVB	8.77	20.00	24.00	21.70
NNMBA	13.70	18.90	3.30	32.80
TTEGDA	8.30	15.20	19.83	32.20
PETA	20.47	25.00	14.43	21.27

CD=1.21

The values of total-N and cumulative total-N for 2nd day were represented in table 4.49 and 4.50 respectively. When PS was the sealant, DVB-crosslinked system had significantly lower value for total-N (Table 4.49) than other crosslinked systems. The values of total-N were in the order DVB< TTEGDA< NNMBA < PETA. Among NR systems the difference was not much. DVB and PETA-crosslinked systems were having comparable values which were lower than NNMBA and TTEGDA-crosslinked systems.

Table 4.49 Total-N (%) of PCUF based on different crosslinked PMMA systems on 2nd day.

Sealants	PS	NR	EVA	PVC
Crosslinking agents		Total	-N (%)	
DVB	12.97	20.93	21.83	25.13
NNMBA	17.37	22.20	5.53	20.80
TTEGDA	15.27	23.00	27.73	17.40
PETA	21.40	20.70	17.40	24.13

CD=0.79

As observed on the 1st day, NNMBA-EVA system was having the lowest total-N value, while highest value was for TTEGDA-EVA system on 2nd day, when all the systems were considered. The total-N values of EVA systems were in the order NNMBA < PETA < DVB < TTEGDA. Among the PVC systems TTEGDA system was having lowest total-N value on 2nd day. The cumulative total-N values gives a better picture on the amount of nitrogen released from different systems (Table 4.50).

Table 4.50. Cumulative Total-N (%) of PCUF based on different PMMA systems on 2nd day.

Sealants	PS	NR	EVA	PVC
Crosslinking agents		Cum.	Total-	N(%)
DVB	21.73	40.90	45.83	44.83
NNMBA	31.07	41.10	8.67	53.63
TTEGDA	23.57	38.27	47.57	49.63
PETA	41.87	45.70	31.87	45.40

CD=1.30

Cumulative total-N values of PS systems increased in the order DVB < TTEGDA < NNMBA < PETA. When NR was the sealant, cumulative total-N values were higher than the corresponding PS systems. Among EVA systems the lowest cumulative total-N value (8.7 %) was noted for NNMBA system and it was the lowest among all the PCUF based on PMMA systems. PVC systems generally had high cumulative total-N values compared to other systems and highest among all the PMMA based systems was noted NNMBA-PVC system.

Total-N (%) and cumulative total-N (%) values of 7th day are shown in tables 4.51 and 4.52 respectively. When PS was the sealant, TTEGDA-crosslinked system had released a substantially lower amount of total-N. Among NR systems also, TTEGDA-crosslinked system recorded a lower value for total-N. The lowest value for total-N among all coated fertilizers was again noted for NNMBA-EVA combination. Among PVC systems, NNMBA-crosslinked system was having the lower value for total-N.

Table 4.51. Total-N (%) of PCUF based on different crosslinked PMMA systems on 7th day.

Sealants	PS	NR	EVA	PVC
Crosslinking agents		Total-	N (%)	
DVB	20.23	21.67	23.93	24.30
NNMBA	24.30	17.17	11.53	21.13
TTEGDA	14.60	15.50	16.17	22.80
PETA	24.37	29.53	23.00	23.50

CD=1.39

Table 4.52 Cumulative Total-N (%) of PCUF based on different crosslinked PMMA systems on 7th day.

Sealants	PS	NR	EVA	PVC
Crosslinking agents		Cum.	Total	-N (%)
DVB	41.97	62.60	69.77	69.13
NNMBA	55.37	58.27	20.20	74.77
TTEGDA	38.17	53.77	63.77	72.43
PETA	66.23	75.23	54.87	68.90

CD=1.39

Cumulative total-N values (Table 4.52) among PS systems were lowest for TTEGDA systems as observed during earlier periods. This indicates the lower initial release rate of the system. Among NR systems also TTEGDA-crosslinked system recorded the lowest value for cumulative total-N as observed earlier. All NR systems had higher cumulative total-N values compared to corresponding PS systems. The lowest value of cumulative total-N (20.2%) among all PMMA based systems was again noted for NNMBA-EVA system. The PVC systems had comparatively higher cumulative total-N values as noted in earlier cases.

The total-N and cumulative total-N values of 14th day are described in table 4.53 and 4.54 respectively. Among PS systems, TTEGDA-crosslinked system during this period also have lowest total-N value. When NR was the sealant, DVB and PETA crosslinked systems were similar and quantity of N released were lower than the NNMBA and TTEGDA-crosslinked systems. In systems were EVA was the sealant DVB-crosslinked system released only 7.2 % N, while TTEGDA, PETA and NNMBA-crosslinked systems released comparatively higher amounts. PVC systems were not having wide variations in the total-N released.

Table 4.53 Total-N (%) of PCUF based on different crosslinked PMMA systems on 14th day.

Sealants	PS	NR	EVA	PVC
Crosslinking agents		Total-	N (%)	
DVB	13.70	10.27	7.23	11.13
NNMBA	17.77	13.17	17.03	12.87
TTEGDA	12.43	14.30	10.27	13.17
PETA	13.80	10.13	20.53	11.07

CD=0.83

A wide variation for cumulative total-N values were noted among PS systems on 14th day. The values were much lower for TTEGDA and DVB-crosslinked systems. The NR systems were having higher cumulative total-N than corresponding PS systems except in the case of NNMBA. Among EVA systems NNMBA-crosslinked system was having the lowest cumulative total-N value of 37.2 % which was the lowest among all the PMMA systems. Comparatively higher cumulative total-N values were noted for PVC systems this time also except in PETA-crosslinked system.

Table 4.54 Cumulative Total-N (%) of PCUF based on different crosslinked PMMA systems on 14th day.

Sealants	PS	NR	EVA	PVC
Crosslinking agents		Cum	Total-	N (%)
DVB	55.66	72.87	77.00	80.27
NNMBA	73.13	71.40	37.23	87.63
TTEGDA	50.60	68.07	74.03	85.60
PETA	80.03	85.37	75.03	79.97

CD=1.64

Tables 4.55 and 4.56 show the total-N and cumulative total-N values on 21st day respectively. Among PS systems, comparatively higher total-N values were noted for TTEGDA and DVB-crosslinked systems. These systems were having lower initial rates and during later periods higher quantities of N were released. Wide variation for total-N values were noted for NR systems. TTEGDA and NNMBA-crosslinked systems were having much higher total-N values on 21st day when compared to DVB and PETA-crosslinked systems.

Table 4.55 Total-N (%) of PCUF based on different crosslinked PMMA systems on 21st day.

Sealants	PS	NR	EVA	PVC
Crosslinking agents		Total	- N(%)	
DVB	9.40	4.33	3.77	7.07
NNMBA	6.57	9.53	8.57	0.97
TTEGDA	8.47	9.43	6.40	0.83
PETA	3.90	2.20	4.83	7.90

CD=0.56

Among EVA systems, NNMBA-crosslinked systems had released highest amount of N. Very wide variation in total-N values noted among PVC systems. Higher values were noted for DVB and PETA-crosslinked systems. Among PS systems cumulative total-N value of TTEGDA-crosslinked system was 59 % only distinctly lower compared to 65.1, 79.7 and 83.9 (%) of DVB, NNMBA and PETA systems respectively (Table 4.56). Among NR systems, TTEGDA and DVB systems were having significantly lower cumulative total-N values than other systems. In systems were EVA was the sealant NNMBA-crosslinked system recorded only 45.8 % for cumulative total-N which was the lowest among all PMMA based coated system on 21st day.

Table 4.56 Cumulative Total-N (%) values of PCUF based on different crosslinked PMMA systems on 21st day.

Sealants	PS	NR	EVA	PVC
Crosslinking agents		Cum.	Total-	N(%)
DVB	65.07	77.20	80.77	87.33
NNMBA	79.70	80.90	45.80	88.60
TTEGDA	59.07	77.50	80.43	86.43
PETA	83.93	87.57	80.23	87.87

CD=1.80

All PVC systems were comparable and were having higher cumulative total-N values than corresponding crosslinkrd systems.

Total-N (%) and cumulative total-N (%) values of 28th day are shown in tables 4.57 and 4.58 respectively. When PS was the sealant, TTEGDA-crosslinked system had released higher amount of N compared to other systems.

Table 4.57 Total-N (%) of PCUF based on different crosslinked PMMA systems on 28th day.

Sealant	PS	NR	EVA	PVC
Crosslinking agent		Total	-N (%)	
DVB	5.03	2.30	2.60	1.30
NNMBA	4.57	5.77	6.20	0.77
TTEGDA	6.97	5.63	4.80	0.43
PETA	1.70	1.13	2.73	1.23

CD=0.47

Among NR systems NNMBA and TTEGDA systems released higher amounts of total-N than DVB and PETA systems. Among EVA systems NNMBA-crosslinked system had higher total-N value than other systems. All PVC systems released a substantially lower amount of total-N compared to other corresponding systems, all less than 1.3 %.

Table 4.58 Cumulative Total-N (%) of PCUF based on different crosslinked PMMA systems on 28th day.

Sealants	PS	NR	EVA	PVC
Crosslinking agents		Cum	Total	-N(%)
DVB	70.10	79.50	83.37	88.63
NNMBA	84.27	86.70	52.00	89.37
TTEGDA	66.03	83.13	85.20	86.87
PETA	85.63	88.70	82.97	89.10

CD=1.19

The cumulative total-N values give the total amount of N released upto 28th day (Table 4.58). Among PS systems, TTEGDA-crosslinked system had lowest cumulative total-N. All NR systems were having comparatively higher cumulative total-N values than corresponding PS systems and among them DVB and TTEGDA-crosslinked systems were having lower values. Among EVA systems, NNMBA-crosslinked system was having the lowest cumulative total-N value of 52 % which was the lowest among all the PMMA systems. All PVC systems were comparable and having higher cumulative total-N values than other systems.

Tables 4.59 and 4.60 represent total-N (%) and cumulative total-N (%) values of 45th day. Among PS systems TTEGDA-crosslinked system released significantly higher amount of total-N than the other systems. This clearly indicates the better slow release nature of the system. In systems where NR was the sealant, NNMBA and TTEGDA-crosslinked systems released significantly higher amount of N than the DVB and PETA-crosslinked systems. In EVA systems NNMBA-crosslinked system released 5.1 % total-N which was the highest among all PMMA systems. In systems were PVC was the sealant, DVB-crosslinked system had released 2.13 % of total-N while other systems released less than 0.4 % only.

Among PS systems, TTEGDA-crosslinked system had the lowest cumulative total-N value of 69.8 %. When NR was the sealant, DVB-crosslinked system was having lowest cumulative total-N value of 81.3 %. Among EVA systems, NNMBA-crosslinked system had a cumulative total-N value of 57.1 % which was the lowest among all PMMA systems.

Table 4.59 Total-N (%) of PCUF based on on different crosslinked PMMA systems on 45th day.

Sealants	PS	NR	EVA	PVC
Crosslinking agents		Total	-N(%)	
DVB	3.00	1.83	1.53	2.13
NNMBA	2.23	2.47	5.13	0.37
TTEGDA	3.80	2.43	1.30	0.33
PETA	0.23	0.30	1.10	0.43

CD=0.35

Table 4.60. Cumulative total-N (%) of PCUF based on different crosslinked PMMA systems on 45th day.

Sealants	PS	NR	EVA	PVC
Crosslinking agents		Cum	Total	-N(%)
DVB	73.10	81.33	84.90	90.77
NNMBA	86.50	89.17	57.13	89.73
TTEGDA	69.83	85.57	86.53	87.20
PETA	85.87	89.00	84.07	89.53

CD=2.10

This clearly indicates that NNMBA-EVA system was having a distinctly lower release rate and a more sustained release profile than all other coating systems. As in previous cases all PVC systems were having comparatively higher cumulative total-N values. Based on the analysis it is indicated that when PS is the sealant, TTEGDA is the better crosslinking agent to obtain better slow release properties. For NR sealant also TTEGDA is the better crosslinking agent while NNMBA also gave comparable slow release behaviour. For EVA sealant NNMBA crosslinking agent is the most suitable and this combination is having the best slow release property among all the PMMA systems. For PVC sealant, DVB and PETA crosslinking agents are better and they have comparable slow release property.

4.8 Results and Discussion of Incubation Experiments

4.8.1 Polymer Coated Urea Fertilizers (PCUF) Based on Divinylbenzene-crosslinked Polyacrylamide Systems

Fig 4.2 and 4.3 represent ammoniacal-N (%) and urea-N (%) at different incubation periods respectively. At all the incubation periods the ammoniacal-N value of PS and PVC systems were much lower than that of control. For control, ammoniacal-N content was 49.7 % on 2nd day and on subsequent incubation periods it were always more than 95 % . On 2nd, 7th and 14th days ammoniacal-N content of PS systems (36.1, 45.9 and 52.6 % respectively) were significantly lower than that of PVC system (43.7, 56.2 and 65.6 % respectively). But on 21st day ammoniacal-N value of PS system (80.3 %) was higher than that of the PVC system (77.4 %). The values of PS and PVC systems were not significantly different on 28th day. Only 25.9 % of urea-N was estimated on 2nd day in control treatment (Fig 4.2).

In both coated systems urea-N was present upto the end of the experiment. This clearly indicated the slow release behaviour of PS and PVC coated systems in soil. Urea content in soil with PS system on 2nd, 7th and 14th days were 60.3, 51.0 and 39.2 % respectively. PVC system was having a significantly higher value for urea-N (18 %) on 21 st day than that of PS system (16.2 %). But the systems were not significantly different on 28th day with respect to urea-N. This indicates that the release of urea from PS system was at a lower rate during the initial period than PVC system.

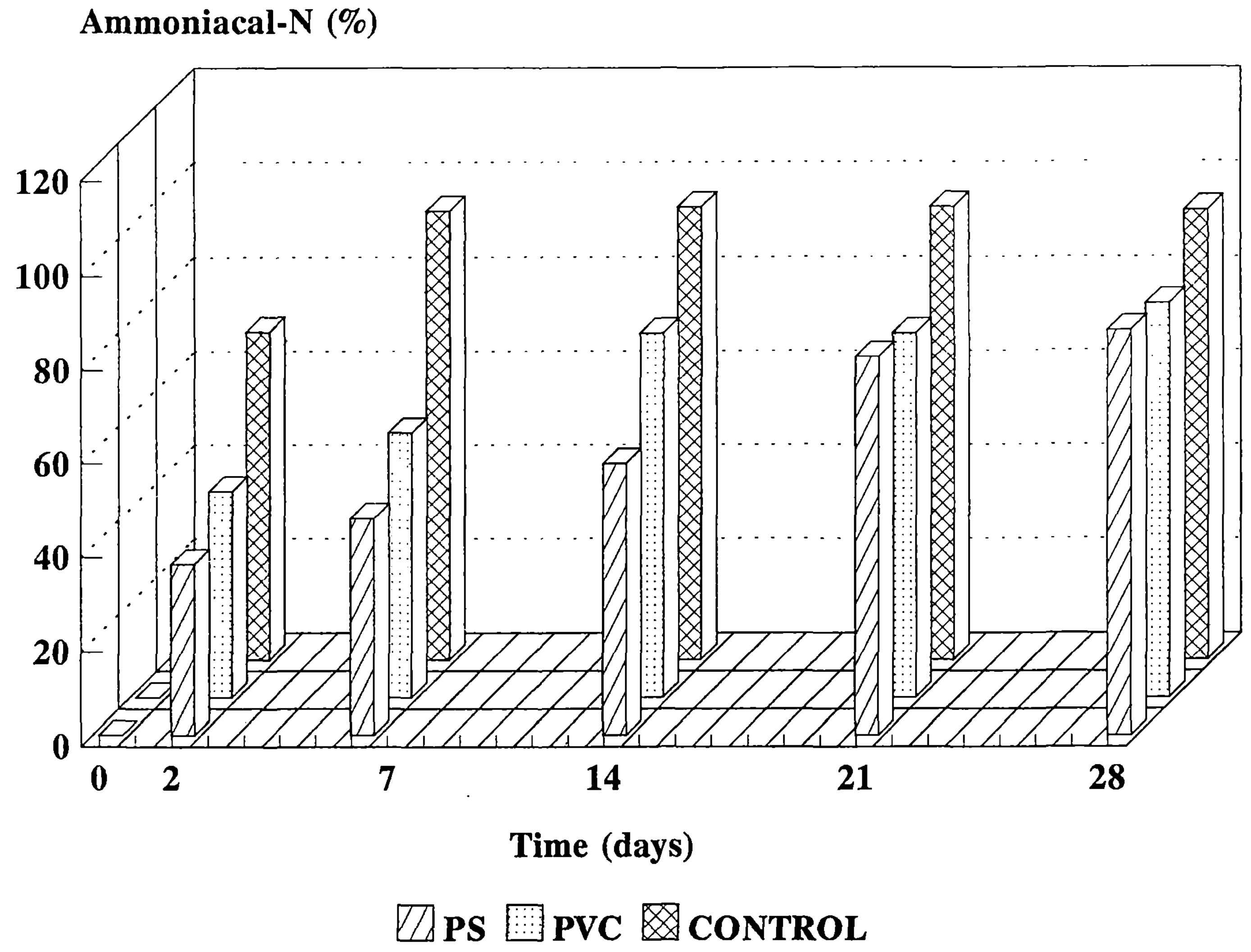


Fig 4.2 Ammoniacal-N (%) at different incubation periods of DVB-PAM systems

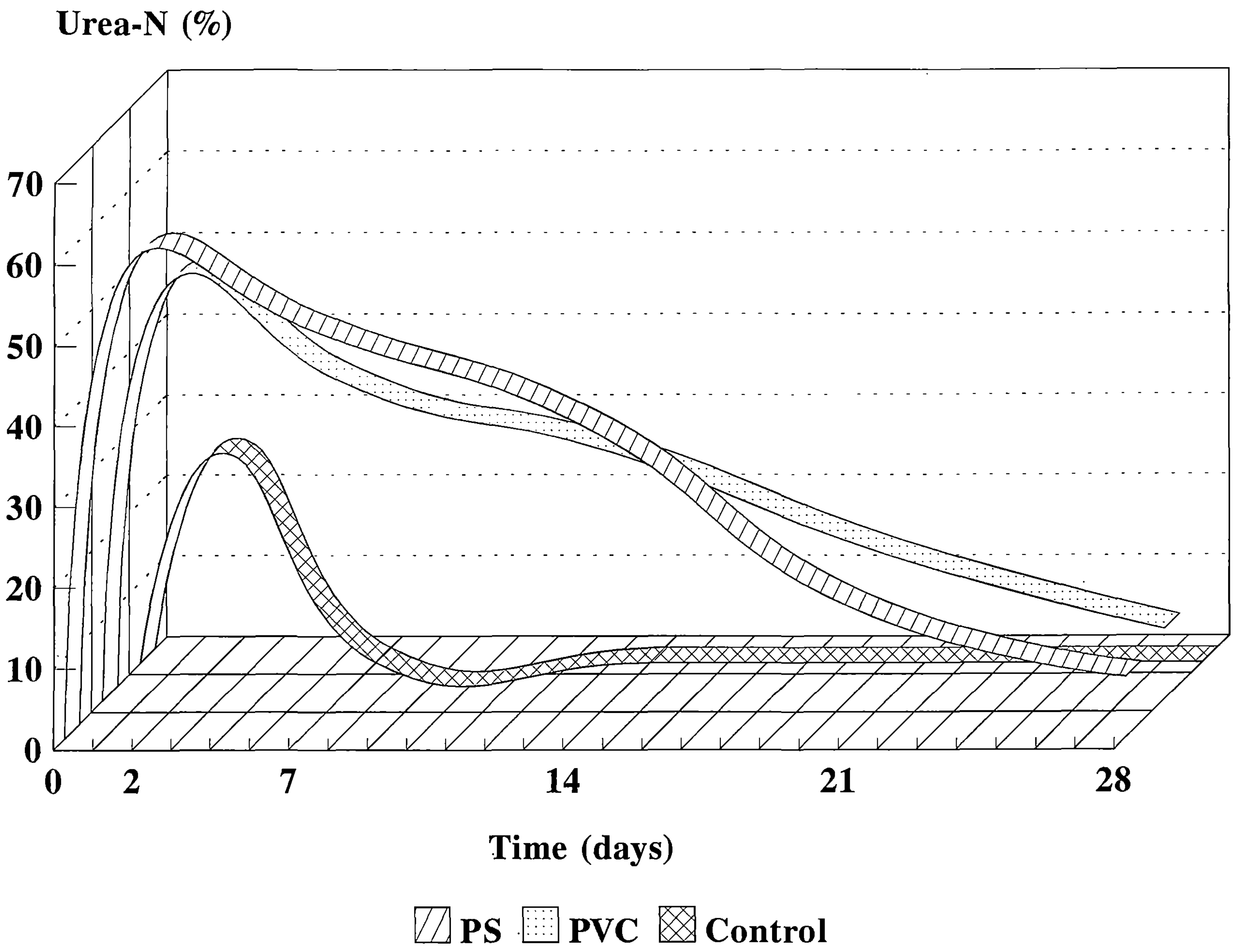


Fig.4.3 Urea-N (%) at different incubation periods of DVB-PAM systems

4.8.2 Polymer Coated Urea Fertilizers Based on N,N'-Methylene-bis-acrylamide-crosslinked Polyacrylamide.

The ammoniacal-N(%) and urea-N (%) content of EVA and PS coated systems and control are shown in figures 4.4 and 4.5 respectively. Both coated systems were having considerably lower values for ammoniacal-N when compared to control. This clearly points out the slow release behaviour of both the coated systems. When EVA and PS systems were compared, EVA system was having distinctly lower release rate than PS system, since considerably lower value for ammoniacal-N was noticed for EVA system through out the incubation period of 28 days, than PS system. Ammoniacal-N (%) values of EVA system were 35.4, 48.4, 52.7, 73 and 83.7 on 2nd, 7th, 14th, 21st and 28th days while for PS system the corresponding values were 51.8, 62.0, 71.1, 84.2 and 87.6.

The urea-N values support this inference. Throughout the incubation period, urea-N content was significantly higher for EVA system than PS system. This observation clearly establish the fact that EVA system had a more sustained and lower release character than PS system. At the end of the incubation period on 28th day 12 and 7.1 % of urea-N remained in soil with EVA and PS systems respectively.

4.8.3 Polymer Coated Urea Fertilizers Based on Tetraethyleneglycol diacrylate-crosslinked Polyacrylamide.

Fig 4.6 and 4.7 represents the ammoniacal-N (%) and urea-N (%) of TTEGDA-PAM systems (PS and EVA) were having slow release character since, ammoniacal-N values were much lower compared to control. Among the coated systems PS system was having significantly lower value for ammoniacal-N than that of EVA system upto 21st day. However on 28th day EVA system was having a significantly lower ammoniacal-N value than PS system. The ammoniacal-N (%) content of

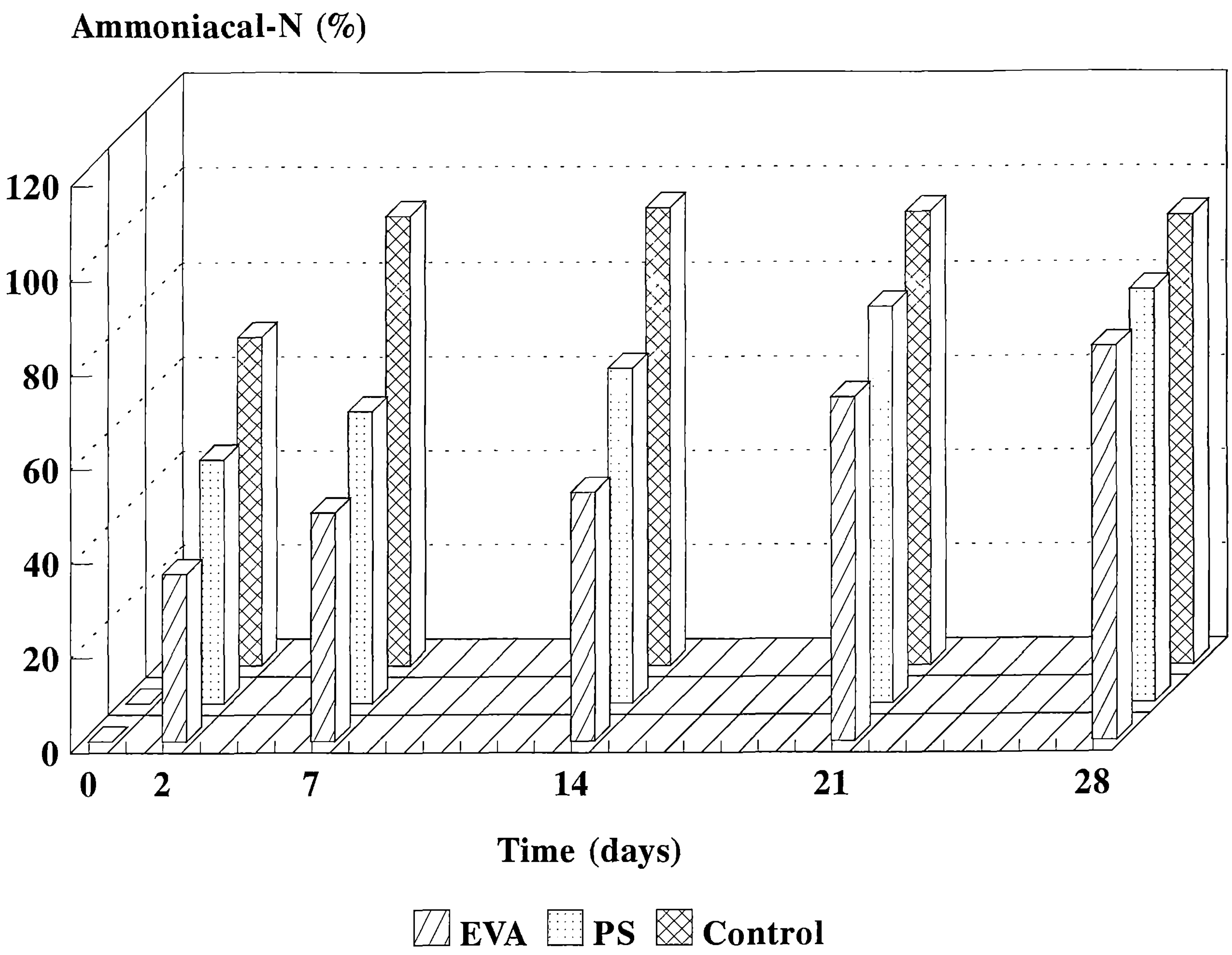


Fig. 4.4. Ammoniacal-N (%) at different incubation periods of NNMBA-PAM systems

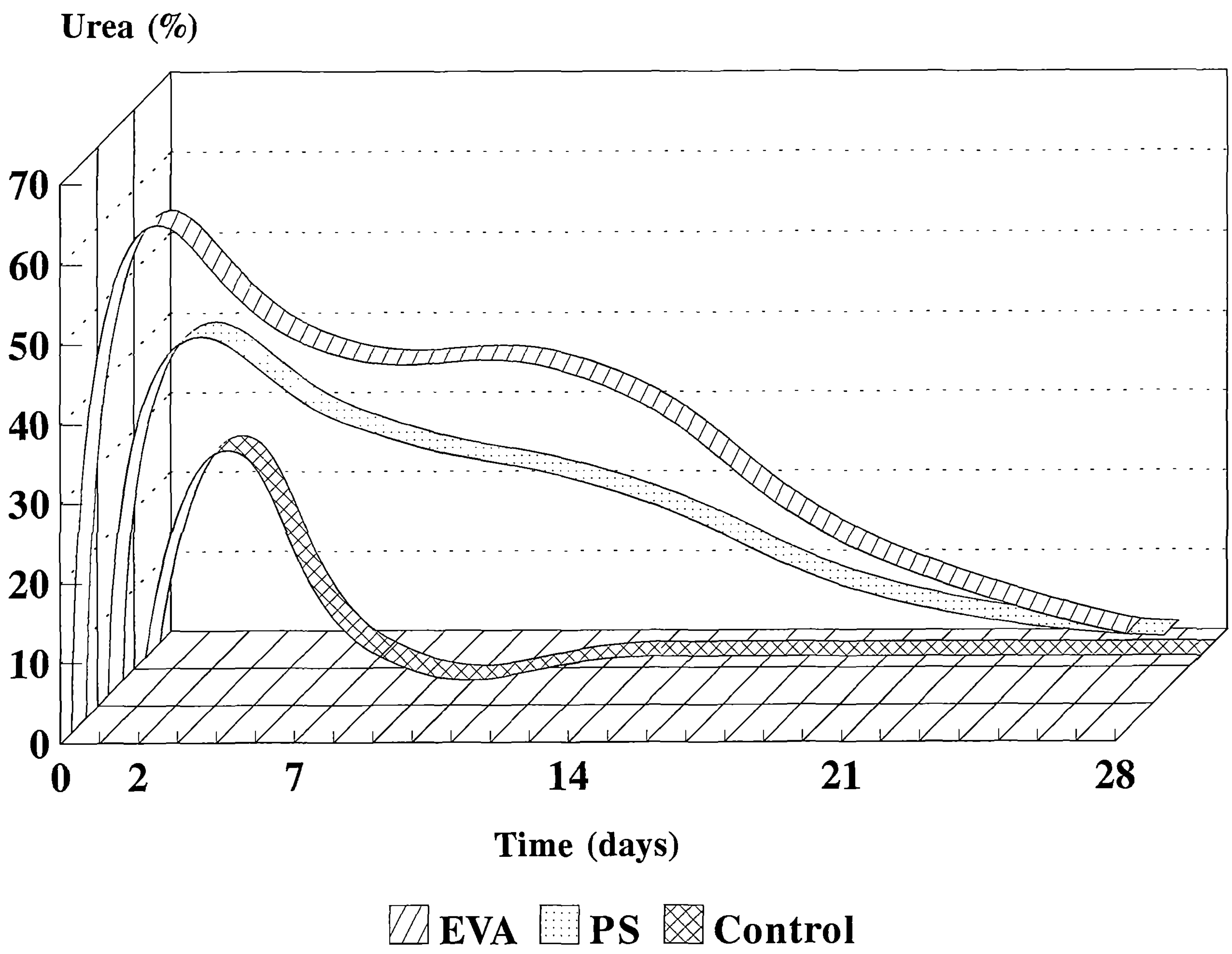


Fig.4.5.Urea-N (%) at different incubation periods of NNMBA-PAM systems

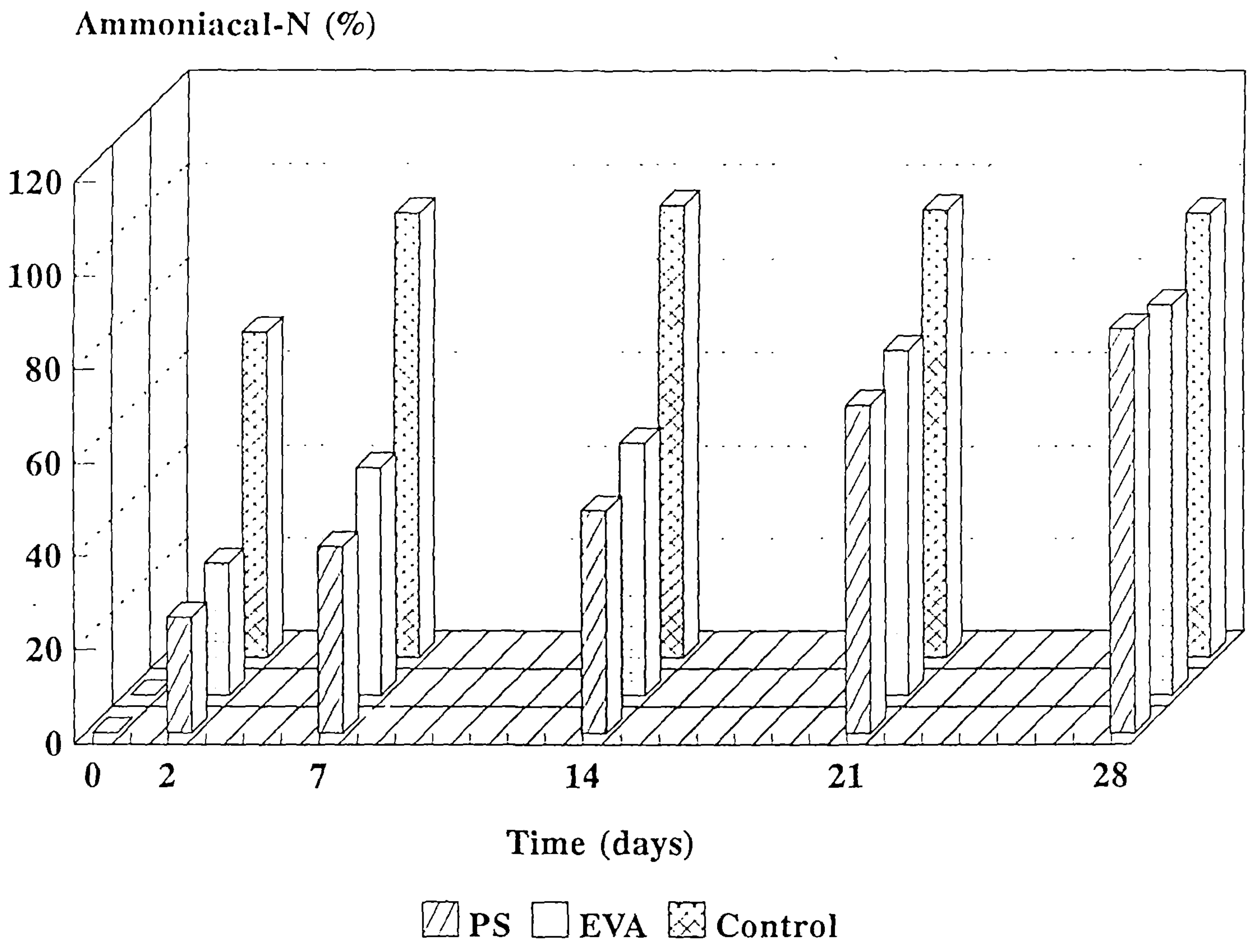


Fig 4.6. Ammoniacal-N(%) at different incubation periods of TTEGDA-PAM systems

Cb: 27

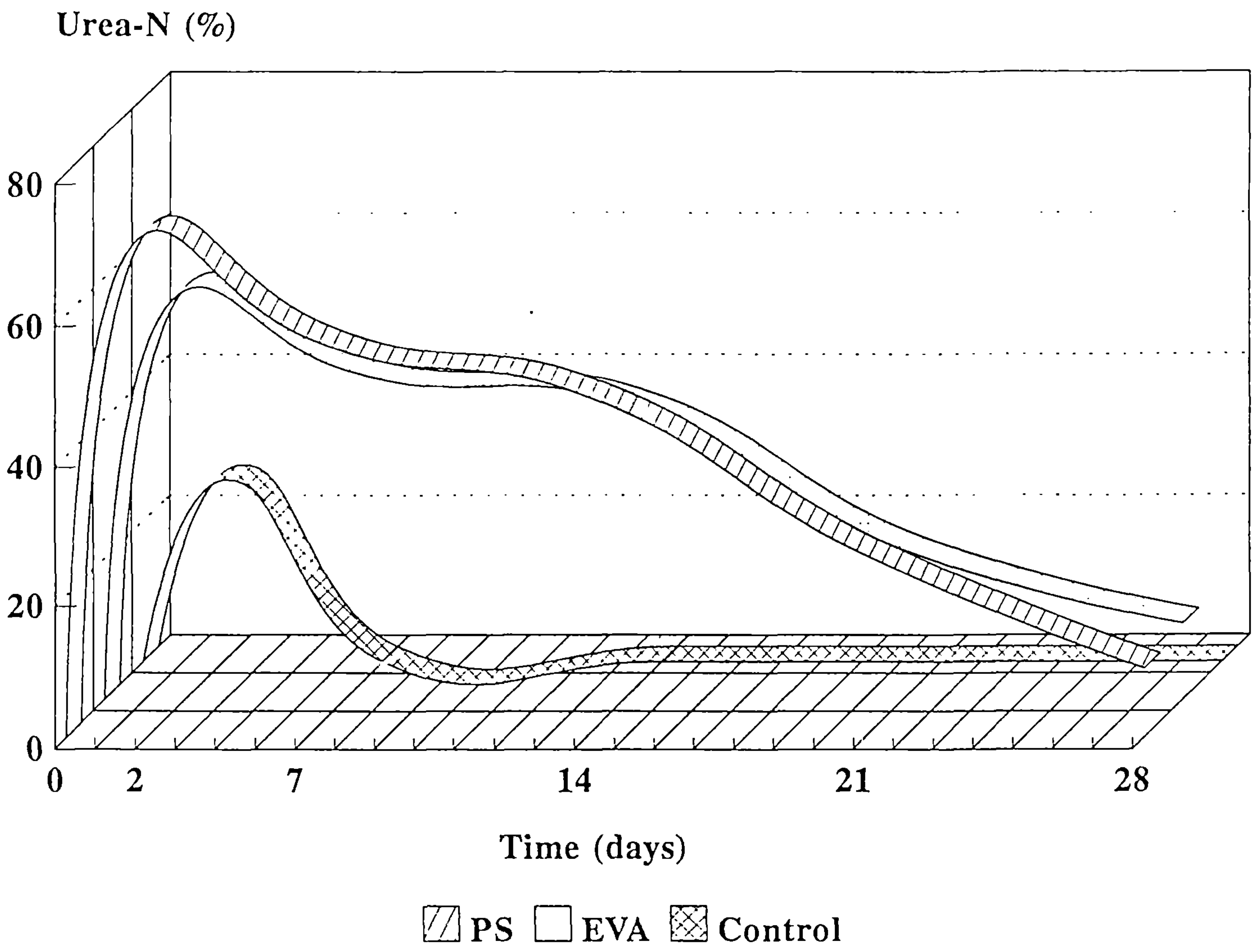


Fig.4.7. Urea-N at different incubation periods of TTEGDA-PAM systems

CD: 1.23

PS system on 2nd, 7th, 14th, 21st and 28th days were 24.4. 39.8, 47.7, 70.3 and 86.7 % respectively while for EVA system the corresponding values were 38.2, 48.9, 57.3, 74.1 and 83.8 %. The difference in ammoniacal-N content between PS and EVA system was very high on initial days compared to that of 28th day. This indicates the lower initial release rate of PS system.

Urea-N of PS system were significantly higher than that of EVA system on 2nd, 7th, 14th and 21st days. On 28th day the PS and EVA systems were not significantly different with respect to urea-N. On 28th day the urea-N values were 9.7 and 10.7 % for PS and EVA systems respectively. This observation made it clear that the PS system has a better release profile than that of EVA system.

4.8.4 Polymer Coated Urea Fertilizers Based on Pentaerythritol triacrylate-crosslinked Polyacrylamide

Fig 4.8 and 4.9 represent the ammoniacal-N and urea-N contents of EVA and PS system, at different incubation periods. Both systems were having significantly lower amount of ammoniacal-N content upto 28th day when compared to control. Among the coated systems, EVA system was having a distinctly lower values for ammoniacal-N than that of PS system. The ammoniacal-N (%) of EVA system were 35.8, 47.1, 56.0, 77.7 and 86.0 while that of PS system were 43.9, 57.1, 64.6, 82.5 and 85.7 on 2nd, 7th, 14th, 21st and 28th day respectively. Thus the quantity of urea released from EVA system were lower than that of PS system upto 21st day and on 28th day the systems were not significantly different to each other with respect to ammoniacal-N.

The urea-N content of EVA system at different incubation periods were much higher than that of PS system. Hence the amount of urea-N remained in the EVA system were much more than that of PS system. At the end of the incubation study on 28th day 13.0 and 10.8 % urea-N remained in the EVA and PS systems respectively. These observations indicate that EVA system have a more sustained release character than PS system.

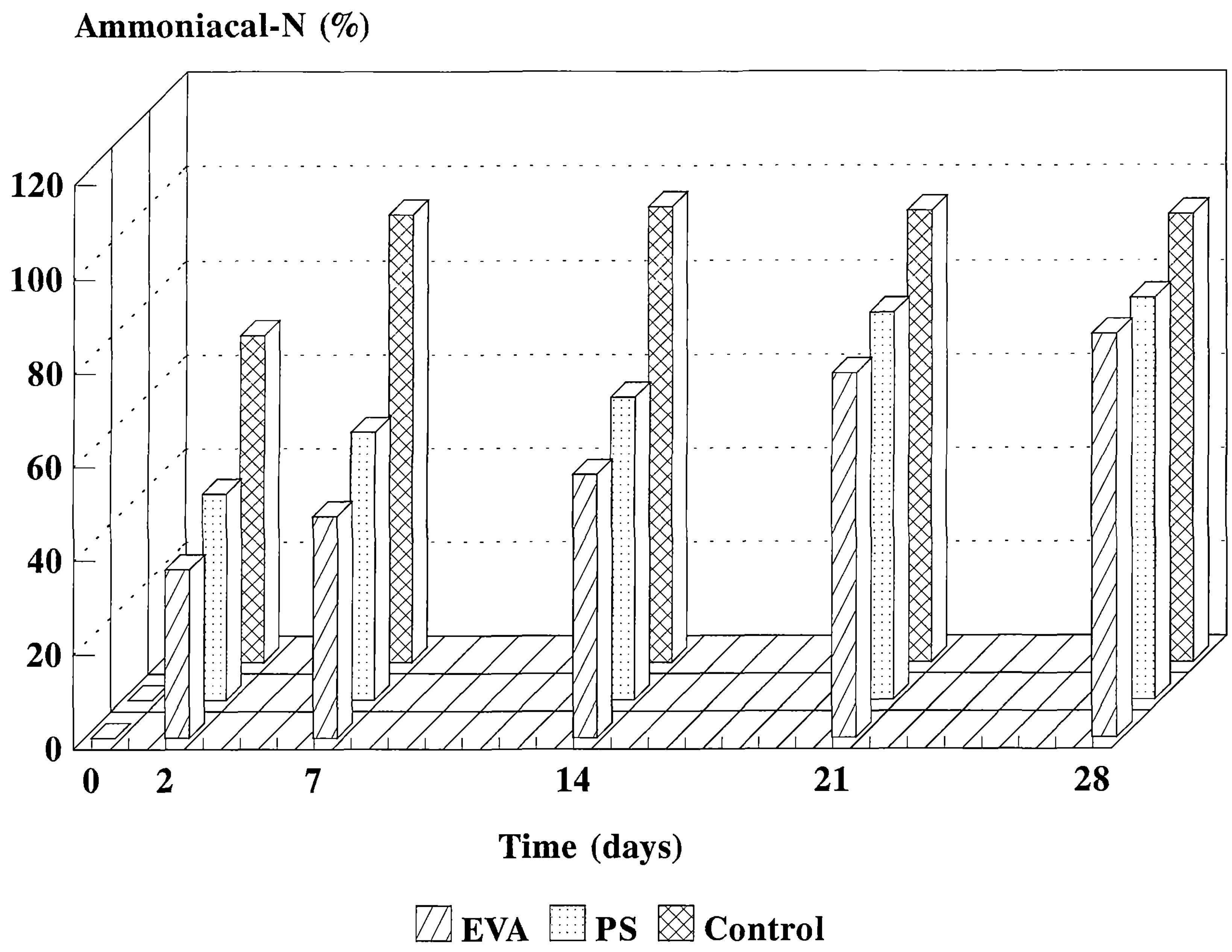


Fig.4.8. Ammoniacal-N (%) at different incubation periods of PETA-PAM systems

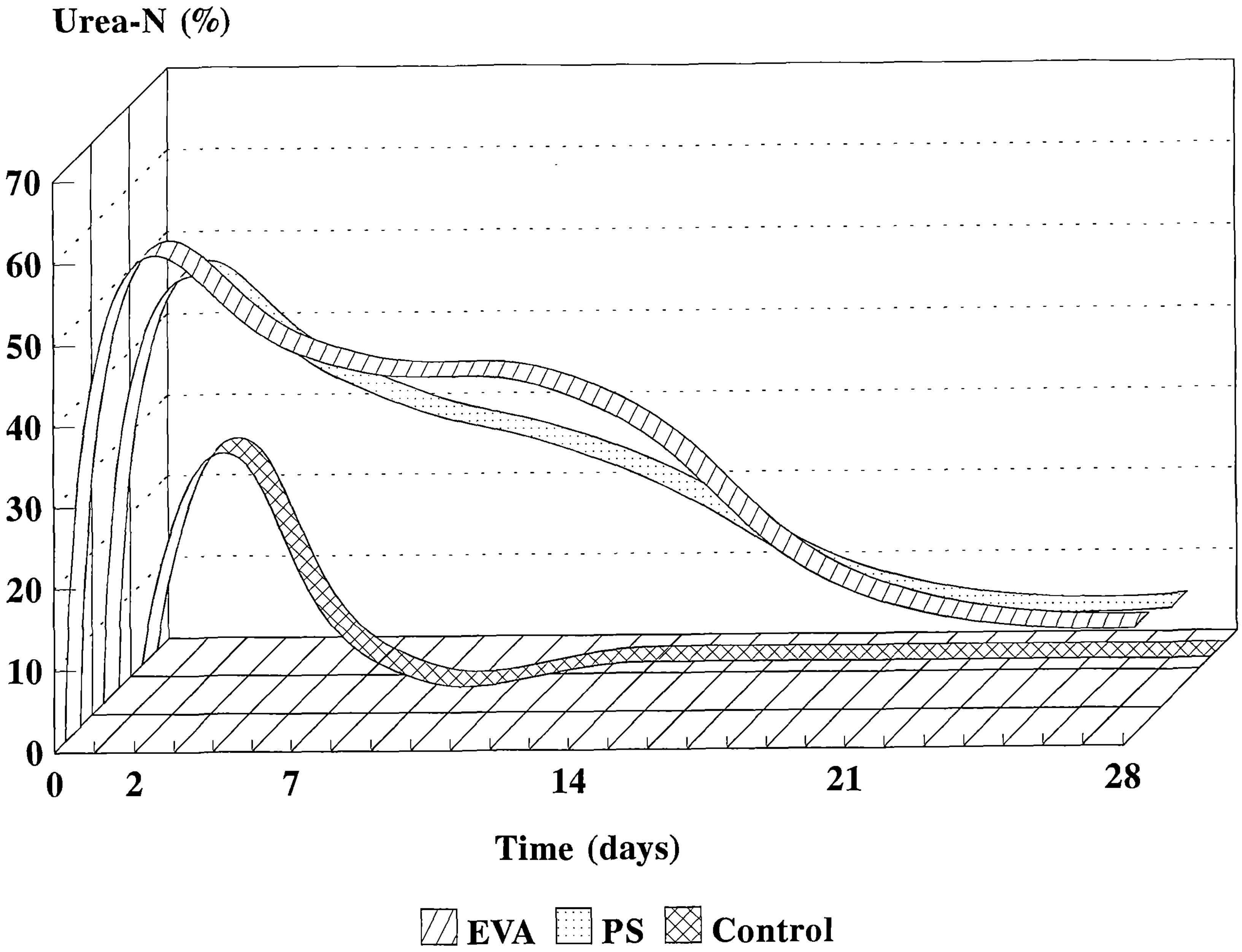


Fig 4.9. Urea-N (%) at different incubation periods of PETA-PAM systems

4.8.5 Polymer Coated Urea Fertilizers Base on Divinylbenzene-crosslinked Polymethylmethacrylate Systems

The ammoniacal-N (%) and urea-N (%) content of PS and NR systems and control at different incubation periods were shown in fig 4.10 and 4.11 respectively. Both coated systems were having considerably lower amount of ammoniacal-N content than control throughout the experiment period. Among PS and NR systems, the former was having significantly lower value for ammoniacal-N (%) than the latter. PS system was having ammoniacal-N (%) values as 25.8, 30.0, 39.9, 54.9 and 65.4 while the values for the same for NR system was 32.2, 46.9, 54.1, 60.4 and 75.9 on 2nd, 7th, 14th, 21st and 28th day respectively.

The amount of urea remained within the PS system were significantly higher than that of NR system throughout the experiment. At the end of the experiment on 28th day PS system was having 30.7 % urea-N while NR system was having 19.4 % only. These observations suggests that the PS system has a lower and more sustained release character than NR system.

4.8.6. Polymer Coated Urea Fertilizers Based on NN'-Methylene- bis-acrylamide-crosslinked Polymethylmethacrylate

Fig 4.12 and 4.13 represents the ammoniacal-N and urea-N content of EVA and PS coated systems and control. Both coated systems are having much lower ammoniacal-N content when compared to that of control, suggesting both systems were possessing slow release character. When EVA and PS systems are compared former is having much lower ammoniacal-N value than that of PS system. In 28 days only less than 50 % of urea had released out from EVA system. The ammoniacal-N (%) values of EVA systems were 12.5, 23.4, 27.7, 37.5 and 46.8 on 2nd, 7th, 14th, 21st and 28th days respectively while the corresponding values of PS system were 33.8, 44.1, 55.6, 62 and 80.4. The EVA system was clearly having a

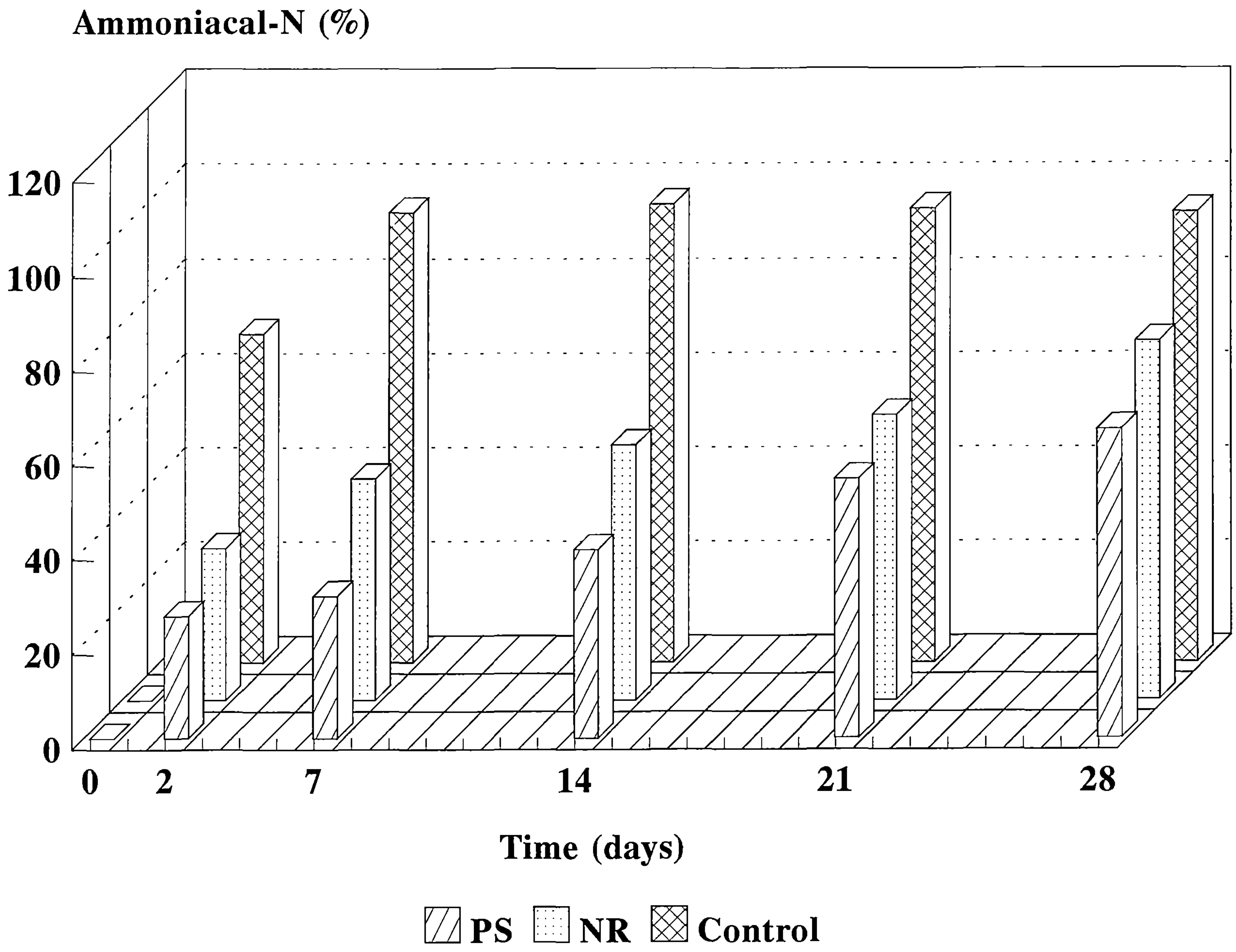


Fig 4.10. Ammoniacal-N (%) at different incubation periods of DVB-PMMA systems

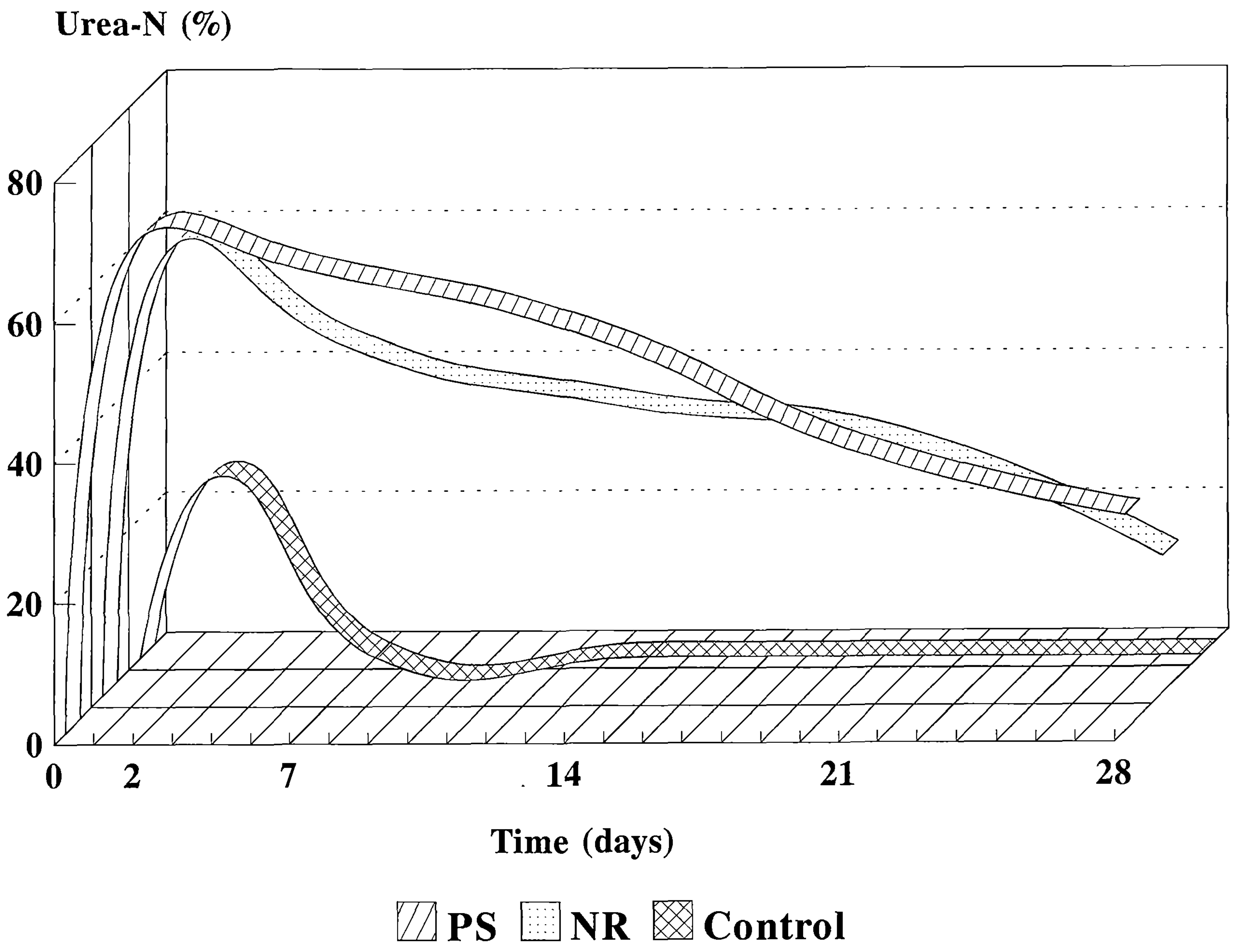


Fig 4.11. Urea-N (%) at different incubation periods of DVB-PMMA systems

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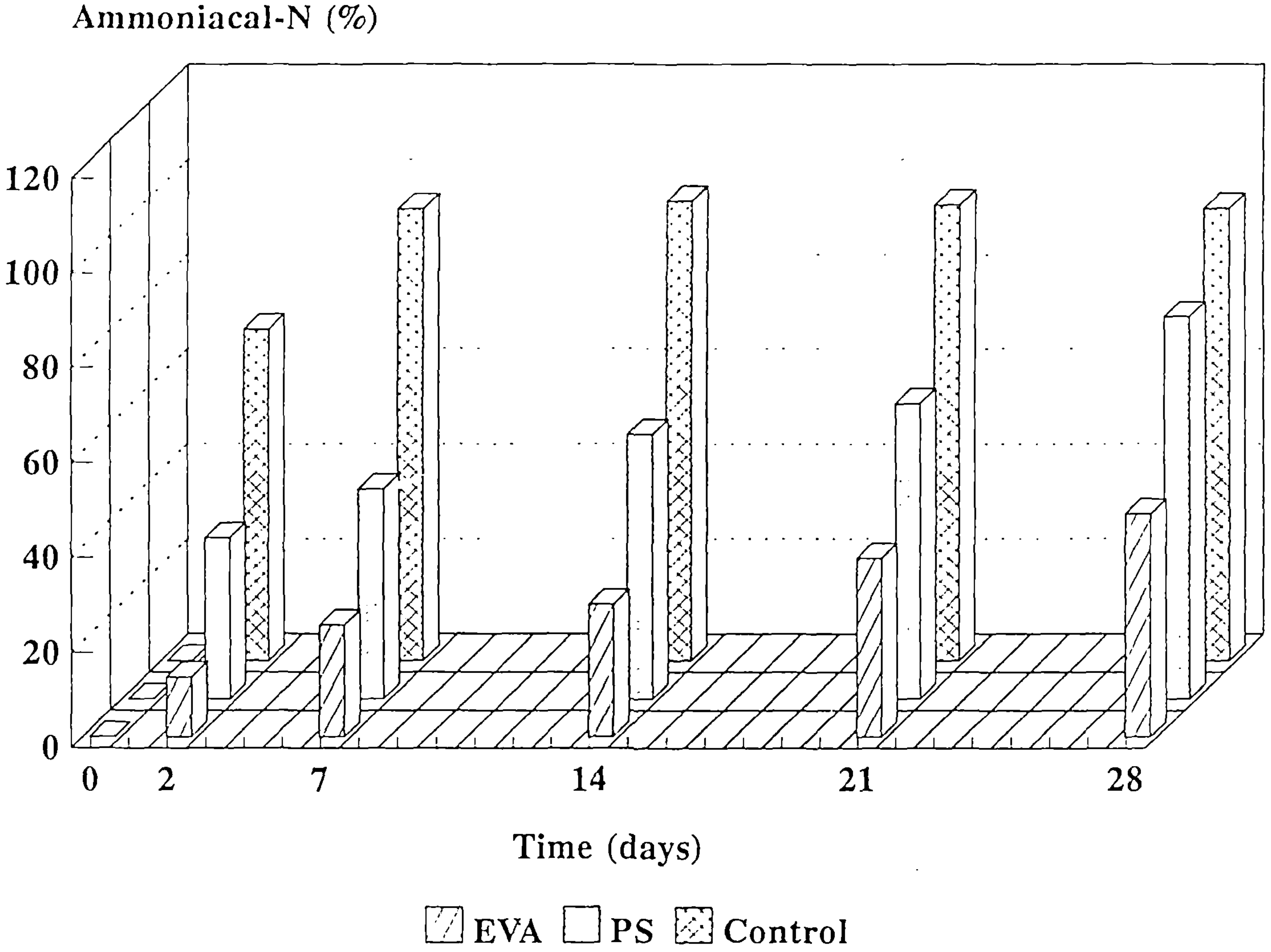

Fig. 4.12. Ammoniacal-N (%) at different incubation periods of NNMBA-PMMA systems

CD = 167

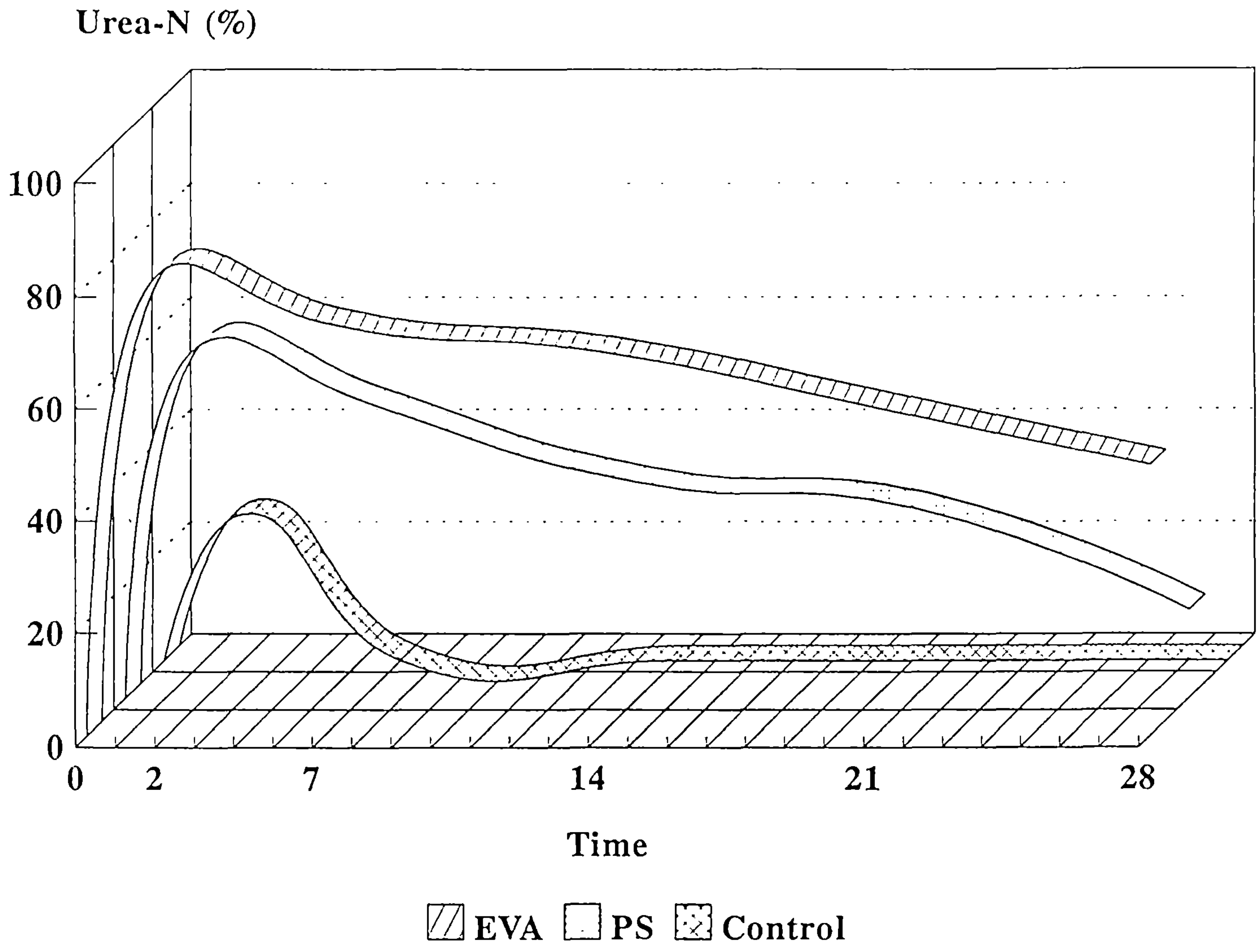

Fig 4.13. Urea-N (%) at different incubation periods of NNMBA-PMMA systems

much lower release rate than that of PS system. This observation is further supported by the urea-N values (Fig 4.12).

At all incubation periods the difference between EVA and PS systems were more than 20 %. At the end of the experiment on 28th day EVA system had 48 % urea-N while PS system had 15.5 % urea-N still to be released. Thus EVA system has a much lower release rate than PS system.

4.8.7 Polymer Coated Urea Fertilizers Based on Tetraethyleneglycol diacrylate-crosslinked Polymethylmethacrylate .

Ammoniacal-N and urea-N of PS and NR systems at different incubation periods were shown in fig 4.14 and 4.15. Both coated systems were having significantly lower for ammoniacal-N than that of control through out the experiment period. Thus both systems possess slow release properties. Among the two coated systems PS system was having significantly lower ammoniacal-N than that of NR system upto 28th day. The ammoniacal-N (%) values of PS system were 23.3, 33.4, 43.4, 53.7 and 63.5 on 2nd, 7th, 14th, 21st and 28th days respectively, while the corresponding values for NR system were 33.7, 48.7, 59.3, 64.3 and 79.4 respectively. Thus the PS system was having a lower release rate than NR system.

Urea-N (%) in soil with PS system at different incubation periods were 63.9, 61.4, 52.7, 42.9 and 32.5 % on 2nd, 7th, 14th, 21st and 28th days respectively while for NR system it were 57.3, 47.7, 34.6, 30.2 and 14.7 %. At the end of the study on 28th day PS system was having more than double the amount of urea-N than NR system. PS system had a lower release rate than NR system.

4.8.8 Polymer Coated Urea Fertlizers Based on Pentaerythritol triacrylate-crosslinked Polymethylmethacrylate.

Ammoniacal-N and urea-N content of EVA and PS systems at different incubation periods are shown in table 4.16 and 4.17 respectively. Both coated systems are having significantly lower ammoniacal-N (%) than control upto 28th day, thus both coated systems possess slow release character. Among the coated systems EVA and PS, the former had a lower ammoniacal-N (%) content through out the experiment period of 28 days. The ammoniacal-N content (%) of EVA system were 36.3, 44.6, 49.8, 55.9 and 77.0 while for PS system it were 47.0, 56.2, 66.7, 73.57 and 82.8 on 2nd, 7th, 14th, 21st and 28th days respectively.

Since the quantity of urea released from EVA system were considerably lower than PS system at different incubation periods, EVA system had a lower release rate than PS system. This observation was further supported by the amount of urea estimated at the different incubation periods (Fig 4.16). EVA system was having a significantly higher urea-N (%) than PS system at all the incubation periods. On 28th day the EVA system had 18.1 % urea while PS system had 13.9 % . These observation suggested that EVA system had a more sustained release profile and lower release rate than PS system.

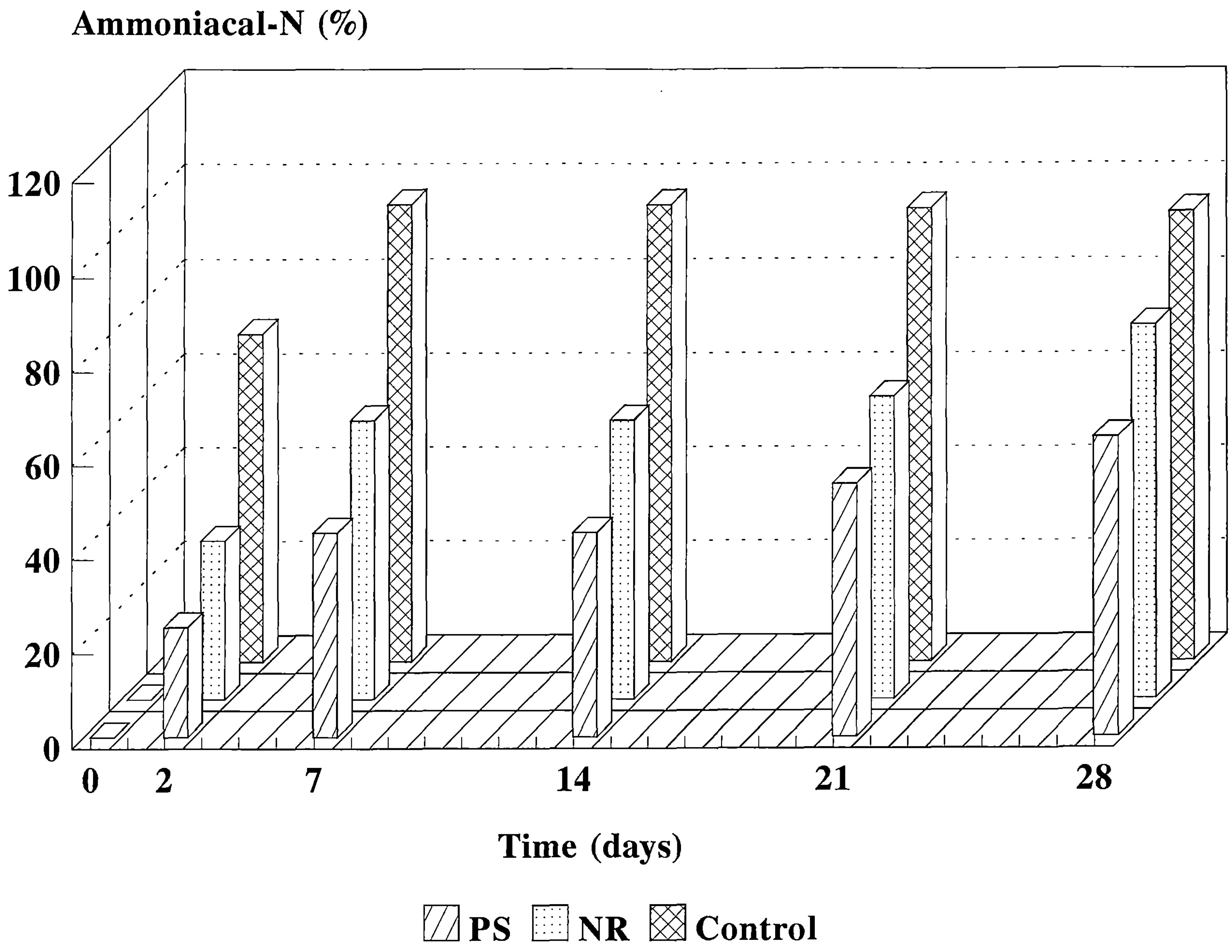

Fig 4.14. Ammoniacal-N (%) at different incubation periods of TTEGDA-PMMA systems

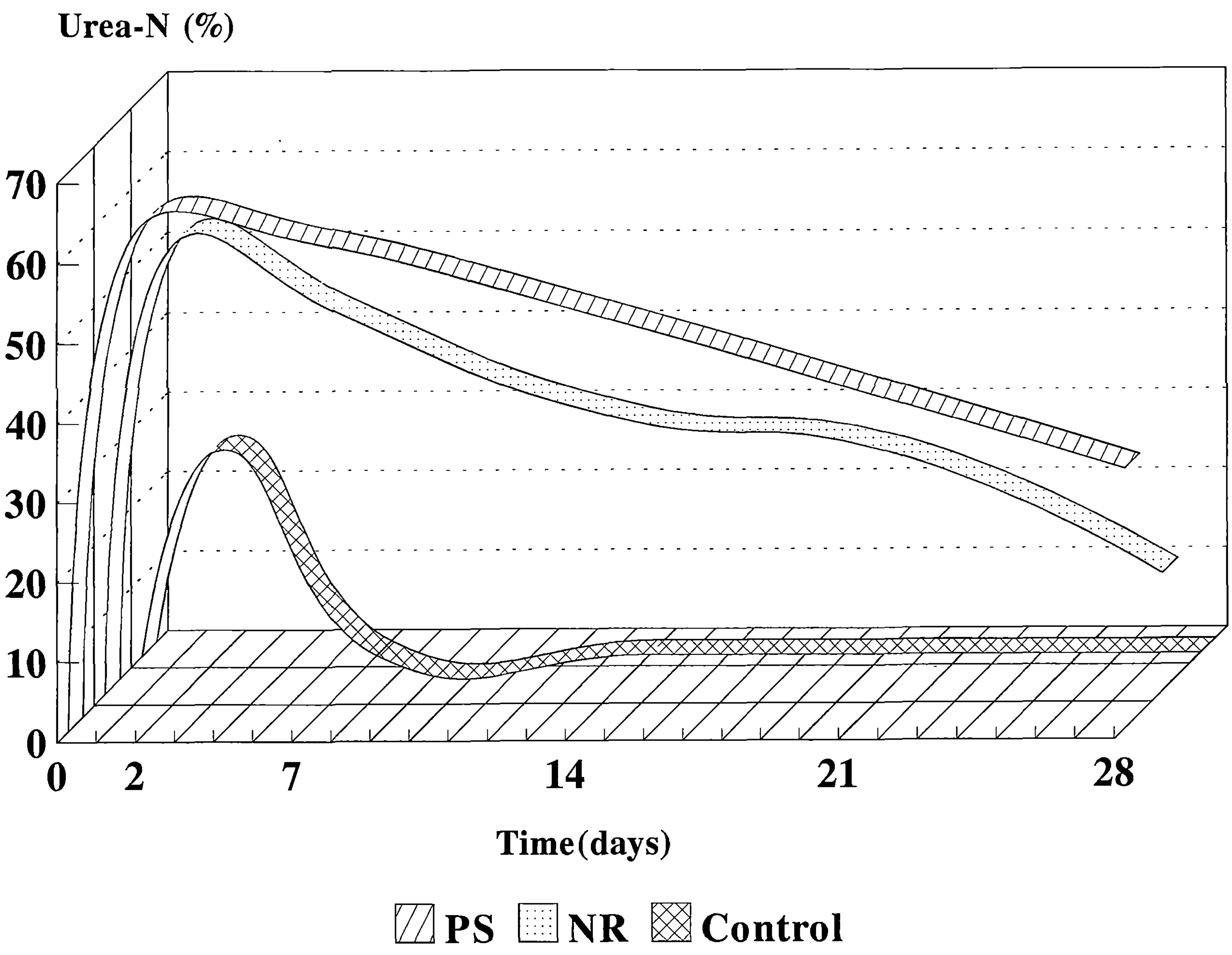

Fig 4.15. Urea-N (%) at different incbation periods of TTEGDA-PMMA systems

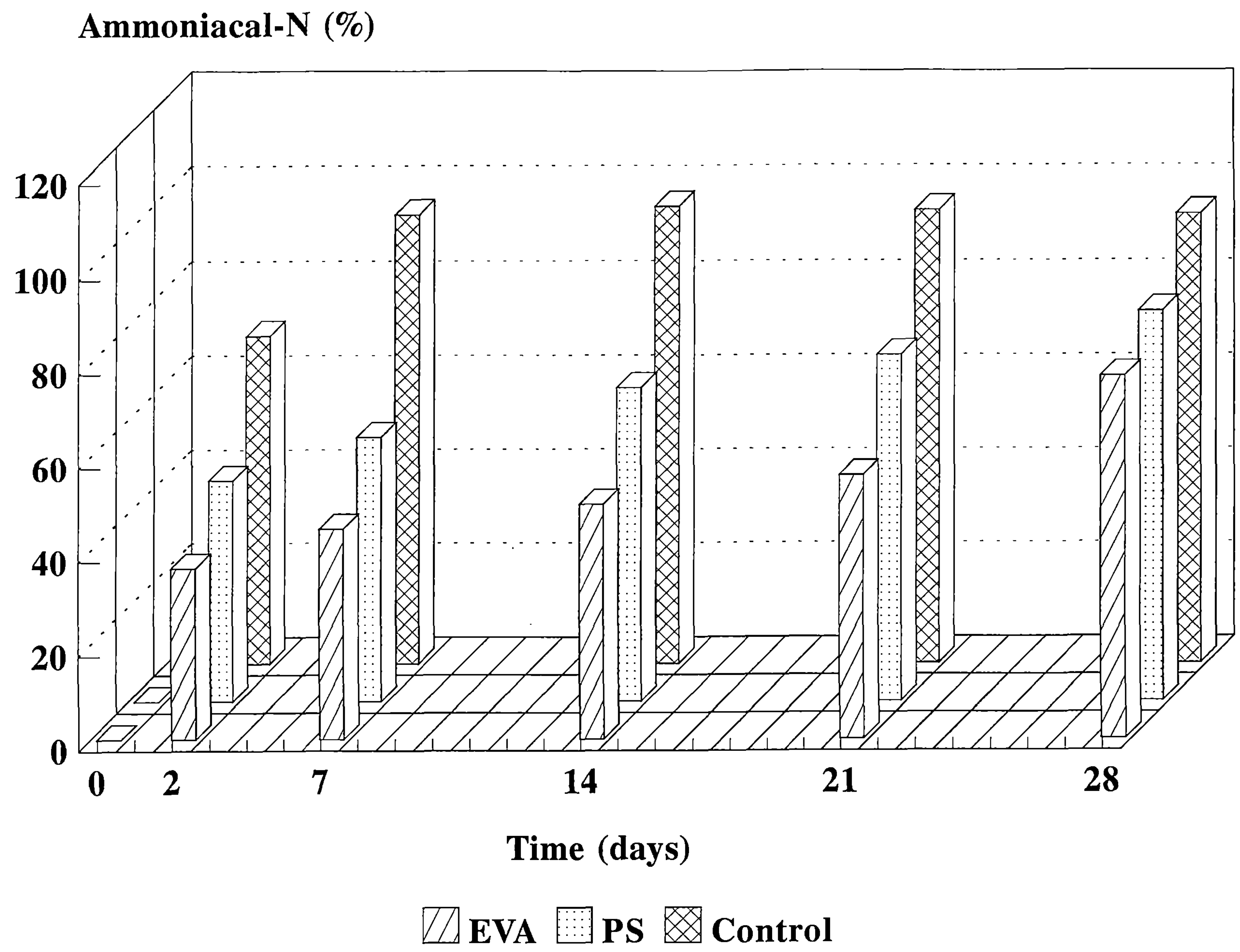

Fig 4.16. Ammoniacal-N at different incubation periods of PETA-PMMA systems

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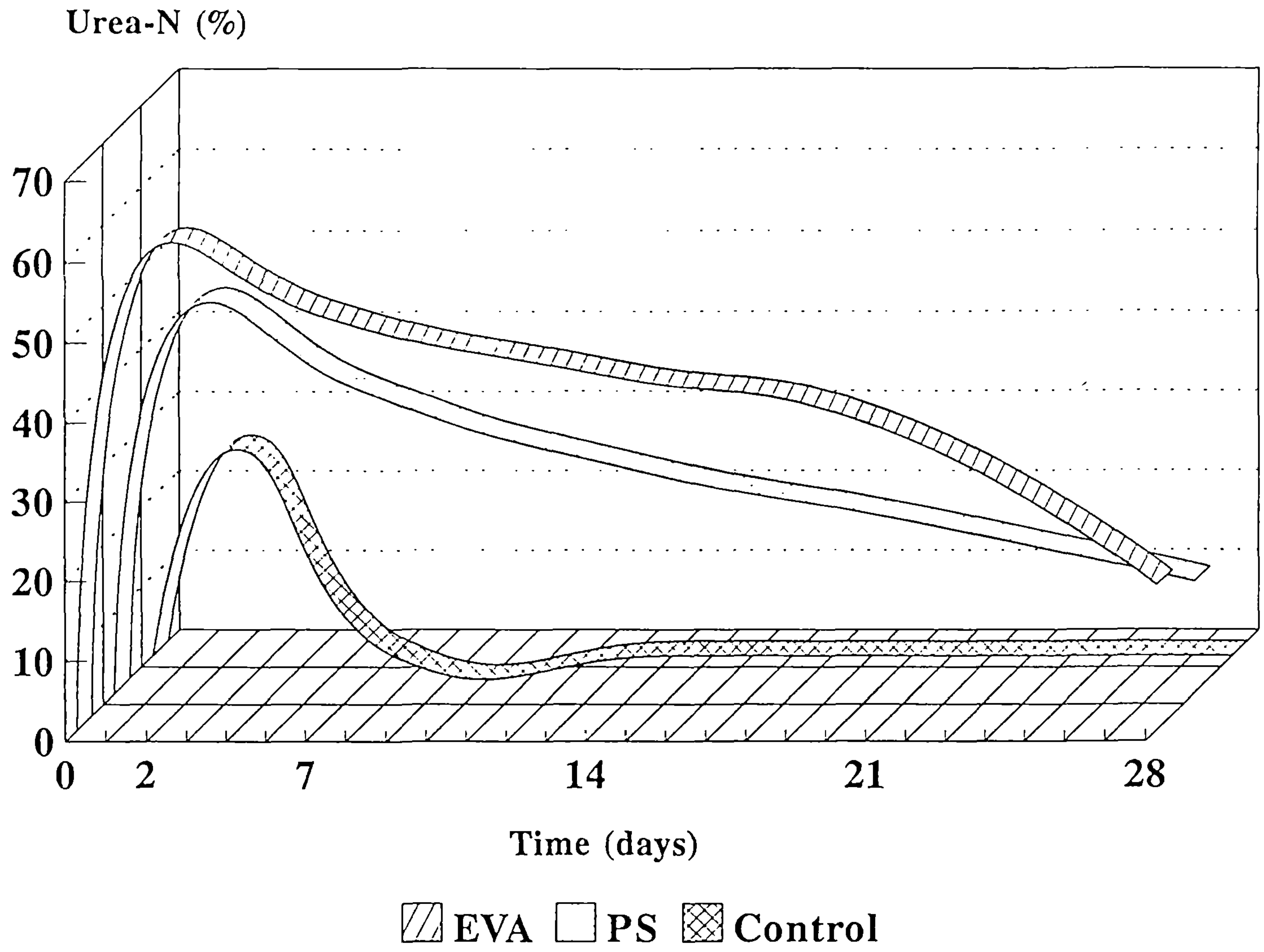

Fig 4.17. Urea-N(%) at different incubation periods of PETA-PMMA systems

4.9 Matrix Type Controlled Release Urea Fertilizers

Distribution of urea fertilizers in a polymer matrix is attempted to obtain CR properties. Smith and Harrison (1990) had worked in similar line. They allowed the hydrophilic polymers to swell in fertilizer solution and afterwards dried and powdered the product. In such cases the fertilizer particles get adsorbed on the surface of the polymer material. Incorporation of fertilizer in the inner parts may not take place. In the present study the polymerization process had been performed in the fertilizer solution itself. Therefore the monomers acrylamide and NNMBA and urea were dissolved in water and allowed the polymers to get polymerized by free radical initiation method. The monomers polymerized in presence of urea, so that a uniform distribution of urea in the polymer matrix took place. The rigidity of the polymer increases as the crosslinking density increases. In the case of hydrophilic polymer like polyacrylamide the swelling character decreases as the crosslinking dens``ity ``increases. Four crosslinking density had been employed viz. 5, 15, 25, 35 mole % to prepare the CR fertilizers.

The results of the incubation experiment is shown in table 4.61.

Table 4.61. Urea (%) content at different incubation period of matrix type fertilizers

Time (days)	Urea-N (%)				
Crosslinking density (mol %)	35	25	15	5	Control
10	40.5	36.73	28.53	24.4	6.3
20	5.83	4.07	1.73	1.33	0
30	1.5	0.2	0.2	0.2	0

CD = 1.14

On 10th and 20th days all the prepared fertilizer systems had significantly higher values for urea-N than control. This clearly indicates the slow release character of the prepared matrix type fertilizers. Evidently as the crosslinking density increased the amount of urea remained also increased. This is expected since the swelling nature of the system decreases as the crosslinking density increases, hence in higher crosslinked systems the swelling might be lower and hence the release also was lower. On 30th day, only 35% crosslinked product had significantly higher urea-N content. This further substantiate the lower release rate of higher crosslinked systems.

Chapter 5

Summary and Conclusion

An attempt is made in the present work to combine polymeric soil conditioners and fertilizer urea so that CR properties and soil conditioning properties were tried to be merged in a single product. Using polyacrylamide or polymethylmethacrylate (PMMA) as the major polymer backbones, and divinylbenzene (DVB), N,N'-methylene-bis-acrylamide (NNMBA), tetraethyleneglycol diacrylate (TTEGDA) or pentaerythritol triacrylate (PETA) as crosslinking agents different CR urea fertilizers were prepared by coating method. In each of the crosslinked systems used for coating polystyrene (PS), natural rubber (NR), ethylene vinyl acetate copolymer (EVA) and polyvinyl chloride (PVC) were separately used as sealants. The prepared fertilizer systems were evaluated for their slow release character by leaching and incubation experiments.

In another approach, by distributing urea in NNMBA crosslinked PAM matrix, CR urea formulations were prepared. By varying crosslinking density, four different formulations were prepared and evaluated for their slow release character by incubation experiments.

While synthesizing the polymer, coating process of urea was carried out. Urea did not inhibit the co-polymerization of AA/MMA and DVB/NNMBA /TTEGDA or PETA . The method may be attractive economically since the two processes are combined and carried out in a single step.

Crosslinked PAM/PMMA can be effectively utilized for coating urea fertilizer. The coated products have CR properties. The release is generally faster in PAM systems than in PMMA systems. Depending on the sealant incorporated, the release rate varies in each crosslinked polymer based fertilizer systems. Among DVB-PAM systems PS and PVC systems had a more sustained or prolonged release profile than NR or EVA systems and among them PS system was having a lower initial release rate. Among NNMBA-PAM systems EVA system had a better slow release profile.

Among TTEGDA-PAM systems PS system was having more slow release character than other systems. Among PETA-PAM systems, EVA system was having a better release profile.

Among DVB-PMMA systems, PS system, and among NNMBA-PMMA systems EVA system were found to have better slow release profile. Among TTEGDA-PMMA systems PS system and among PETA-PMMA systems EVA system has better slow release profile.

In the matrix type CR urea fertilizers prepared it was observed that the crosslinking density affects the release rate. As the crosslinking density increased the slow release character also increased.

Detailed field studies are necessary to assess the improvement in soil physical properties like aggregation stability and water holding capacity by the use of prepared CR fertilizers. Attempts are also to be made in finding cheaper crosslinking agents to be used in PAM / PMMA for coating urea. Further refinement in the process is required in optimizing coating thickness. Moreover the prepared fertilizers are to be tested in various other soil types at varying temperature regimes.

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