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## **FIXATION OF UREA TO POLY (ACRYLAMIDE-MALEIC ACID) AND NITROGEN RELEASE BEHAVIOUR OF THE PRODUCT – A COMPARISON WITH UREA AND CONTROL**

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### **Abstract**

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The growth and yield from green chilli *Capsicum annuum* plants in presence of a newly prepared slow-release N-fertilizer was investigated. The slow-release fertilizer was prepared by covalently immobilizing urea on a biodegradable polymer matrix consisting of acrylamide (AAm) and maleic acid (MA). The resulting product, abbreviated as P (AAm-MA) U was characterized by FTIR and NMR spectral analyses, thin layer chromatography measurement and elemental analyses. Results showed that P (AAm-MA) U contained 32.85% N and the solvency in aqueous media reduced by 297 times as compared to urea. To clarify the performance of P (AAm-MA) U in agriculture, a comparative study was then carried out on the growth of green chilli plants using urea and control (without N-fertilizer) as the basis. P (AAm-MA) U showed improved yield in terms of average plant size over the cultivation period. The N release behaviour in soil during cropping and plant uptake of N suggested that P(AAm-MA)U can be used as slow-release N-fertilizer.

*Key words:* slow-release, N-fertilizer, P(AAm-MA)U, control, chilli plants

### **Introduction**

Urea is one of the most widely used N-fertilizers. The popularity of urea as the principal source of nutrient in agriculture is based on its low cost of production (Liu et al., 2006). However, inefficient and indiscriminate use of urea often creates serious environmental pollution (Akelah, 1996; Al-Zahrani, 2000) as well as economical loss. The environmental pollution is mainly due to high solubility and volatility of urea which is responsible for high surface run off with rain

or irrigation water, leaching and vaporization. Therefore, it has created enormous interest among the researchers to develop new technology that would help to overcome the limitations of applying urea.

Since the early 1970's, in order to overcome the limitations of urea in agricultural use, researchers are trying to prepare slow/control-release fertilizers (Brown et al., 1966; Miner et al., 1978; Mengel et al., 1987; Shoji et al., 1992; Zhou et al., 1996; Jarosiewicz et al., 2003; Guo et al., 2006). The pur-

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pose of most of these works is to develop materials that would supply nutrients to plants continuously in the form and quantity that are required at each stage of growth for optimum crop production, which itself is determined by the genetic potential of plants (Oertli, 1980). Despite considerable researches in the area, the application of slow/control-release fertilizer is facing problem because of high production cost. It has also been reported that release rate of nutrient in soil is affected by the soil condition and environment (Shaviv et al., 2003).

In this research we are trying to concentrate on the preparation and application of slow-release fertilizers that would be suitable in the sub-tropical and flood prone regions. In our previous works (Rahman et al., 2008; Rahman et al., unpublished), we had reported the preparation and application of poly(acrylic urea) (PAU) and poly(methacrylic urea) (PMAU), two different types of slow-release fertilizers based on homo-polymers of acrylic acid and methacrylic acid, respectively. In this part, a copolymer matrix, P(AAm-MA), comprising acrylamide (AAm) and maleic acid (MA), was used for the covalent fixation of urea. We named this product as P(AAm-MA)U. Here AAm is a N containing monomer and MA is a dibasic acid. The purpose of selecting these monomers was to increase the N content in the fertilizer product. In the application phase, relative growth responses of green chilli '*Capsicum annuum*' plants were studied in presence of P(AAm-MA)U, urea and control (without N-fertilizer), respectively. The release behaviour and plant uptake of N were also measured during cropping.

## Materials and Methods

### Materials

MA and AAm (LOBA, Chemica, India) both synthesis grade, were recrystallized from distilled water at low temperature and kept in the refrigerator. Potassium persulfate (KPS) of reagent grade from LOBA, Chemica, India, was recrystallized from distilled water at low temperature. Thionyl Chloride (BDH, England), commercial grade urea [ $\text{NH}_2\text{CONH}_2$ ], NaOH,  $\text{H}_2\text{SO}_4$  and  $\text{Na}_2\text{S}$  were used

without further purification. Distilled deionized water was used for each measurement. Other chemicals were of analytical grade.

### Instruments

Melting/molten temperatures of PMAU and urea were measured on a Gallenkamp apparatus without any correction. IR Spectrophotometer (Shimadzu, FTIR-8900, Japan) and NMR Spectrometer (Bruker 400 MHz Ultra Shield™ NMR, Switzerland) were used for obtaining IR spectra (KBr) and  $^1\text{H}$  NMR spectra ( $\text{D}_2\text{O}$ ) respectively.

### Preparation of P (AAm-MA) U

24 g (0.206 moles) of MA and 6 g (0.084 moles) of AAm were taken in a three necked round bottom flask followed by 200 mL of water and 0.6 g of KPS as initiator. The reaction flask was dipped in a thermostat waterbath and polymerization was carried out for 18 h at  $70^\circ\text{C}$  under a nitrogen atmosphere. 30 g of dried polymeric product, P (AAm-MA) was then dissolved in water. 50 mL of thionyl chloride was added drop-wise over 1 h at low temperature ( $5\text{--}6^\circ\text{C}$ ). After the addition of thionyl chloride temperature was raised to  $70^\circ\text{C}$  and heating was continued for another 2 h. The activated P (AAm-MA) was obtained and the volume of the reaction mixture was reduced simply by heating. 13 g of activated P (AAm-MA) was then taken into 300 mL of ethanol followed by 39 g of urea and 1.5 g of NaOH in a round bottom flask. The mixture in the flask was heated under reflux at  $70^\circ\text{C}$  for 6 h. Finally the product was precipitated from ethanol and washed repeatedly with ethanol to remove any soluble urea or impurities. The preparation of P (AAm-MA) U is shown in Scheme 1.

The product was identified by elemental analysis, TLC measurement, FTIR and  $^1\text{H}$  NMR spectra. The N content was measured by Kjeldahl method (Jeffery et al., 1989). Table 1 shows the physical characteristics of P (AAm-MA) U and urea.

### Soil preparation and fertilizer application

Earthen pots of 24 cm height and 30 cm diameter with a single hole at the centre of the bottom to drain

out excess irrigation/rain water were selected for cropping. Each pot contained 12 kg of soil of sandy loam texture having pH ca. 7.9. Before plantation, soil of each pot was thoroughly mixed with 1.52 g of triple super phosphate (TSP), 0.94 g of muriate of potash (MP) and 0.5 g of gypsum. Three green chilli plants of 18-20 cm height (approximately one month old) were planted in each pot on January 06, 2007. After 30 days of plantation 1.07 g urea and 1.42 g P(AAm-MA)U were applied respectively in urea and P(AAm-MA)U treated pots, at a distance of ca. 2 cm surrounding the plants and at a depth of ca. 2 cm from the surface. The quantities of fertilizers were estimated on the basis of percentage N content in them and the optimum value of nutrient required for chilli plant (Bangladesh Agricultural Research Council Repts. 1997). Four earthen pots were used for each of P(AAm-MA)U, urea and control (without N-fertilizer). Plant height (ground level to the tip of flag leaf) and leaf number were measured during the plant growth from time to time.

During cropping pots were maintained in open air

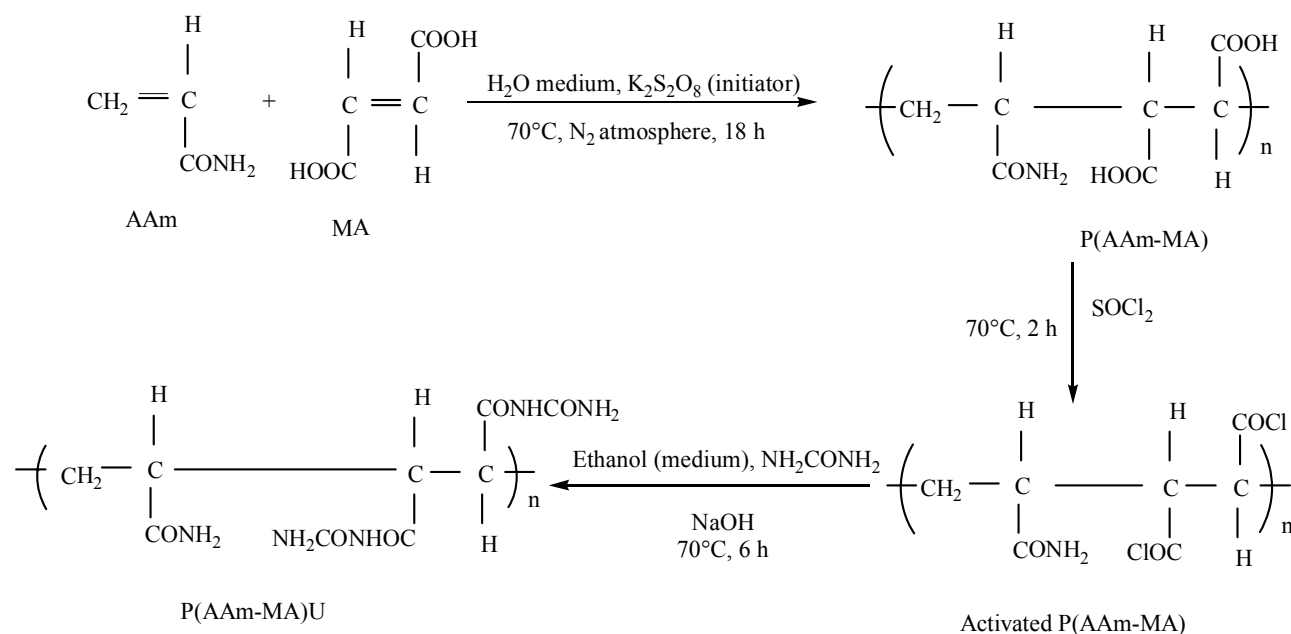
**Table 1**  
Physical properties of P (AAm-MA) U and urea

Properties	Urea	P(AAm-MA)U
Nature	Granular solid, white colour	Sticky solid, white colour
Solubility, g/100mL, at ambient temp	104	0.35
N content, %/g	46.66	32.85
Melting/Molten temperature, °C	120-125	190-195

with temperature and humidity averaged between 18.1-29.5°C and 55.5-91.58%, respectively and total rainfall was recorded as 198 mm. Watering of the soil was done at the identical level in each pot when the pot was visibly dried.

#### Statistical analysis

The recorded data were analyzed statistically using ANOVA technique following randomized complete



**Scheme 1.** Reactions for the preparation P (AAm-MA) U

block design. The differences among the treatment means were evaluated by Duncan's New Multiple Range Test (DMRT).

## Results and Discussion

FTIR spectra for urea and P (AAm-MA) U are shown in Figure 1. In both compounds broad absorption band due to N-H stretching is observed between 3200-3500  $\text{cm}^{-1}$  and a band due to C=O is appeared between 1600-1700  $\text{cm}^{-1}$ . P (AAm-MA) U gave two absorption signals due to N-H<sub>2</sub> and N-H bending at 1406.00 and 1274.90-1325  $\text{cm}^{-1}$ , respectively, while in urea one such signal due to N-H<sub>2</sub> bending is observed. This is an indication that urea has been fixed to the copolymer matrix. The absorption band due to the alkyl part of P(AAm-MA)U appeared in the range between 1008.7 and 1213.1  $\text{cm}^{-1}$ .

The <sup>1</sup>H NMR spectra for P (AAm-MA) U is shown in Figure 2. The chemical shifts due to amide (-

CONH<sub>2</sub>) and substituted amide (CONH) are observed at 5.64 ppm and 4.324 ppm, respectively. The absence of any chemical shift due to carboxyl group (-COOH) in the region 10.5-12.00 ppm indicates that carboxyl group in the modified polymer matrix is completely eliminated by the substituted amide linkage due to the formation of covalent bond with urea. It was not possible to assign all the chemical shifts appeared in the NMR spectra of P(AAm-MA)U, because macromolecules in solution is expected to have complicated chemical structure resulting from hydrogen bonding among inter or intra molecular chains.

In TLC measurements, both urea and P (AAm-MA) U gave sharp single spots with different R<sub>f</sub> values of 0.918 and 0.824 for urea and P (AAm-MA) U, respectively. This indicates that new compound has been formed due to the fixation of urea with activated copolymer matrix.

The N content in P (AAm-MA) U measured by the Kjeldahl method was 32.85%. Since it is a ran-

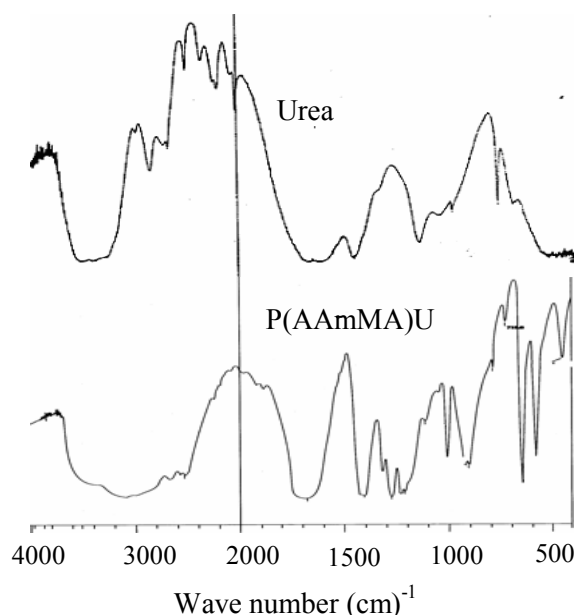


Fig. 1. FTIR spectra of urea and P (AAm-MA) U

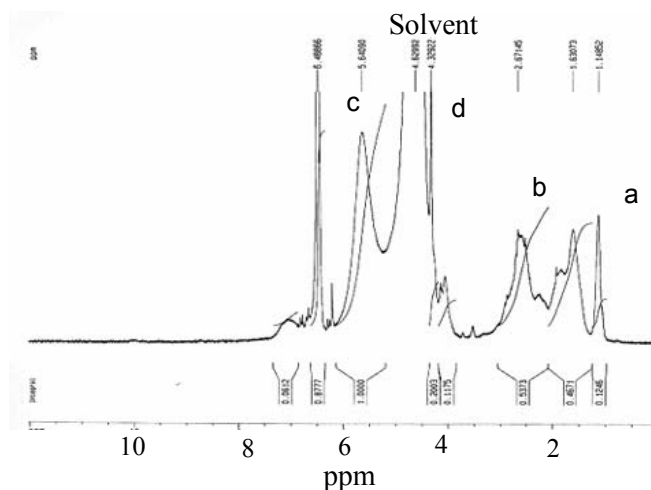
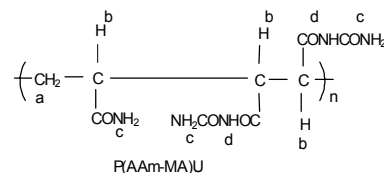
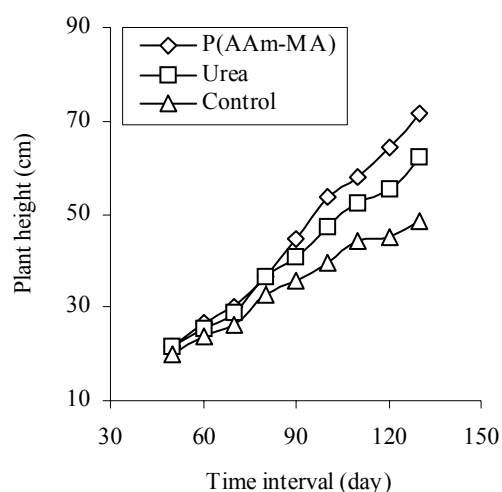
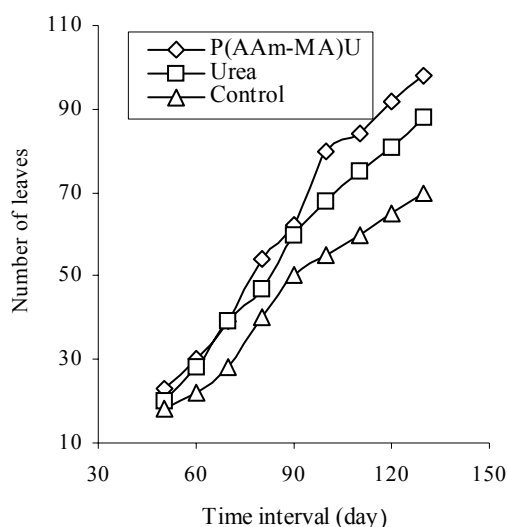


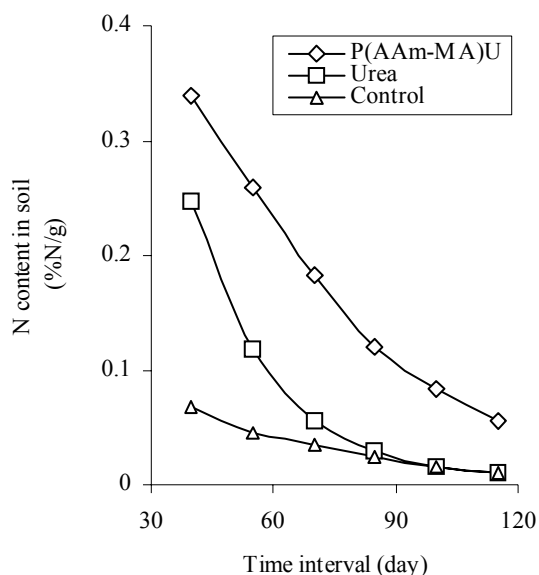
Fig. 2. <sup>1</sup>H NMR spectra of P (AAm-MA) U



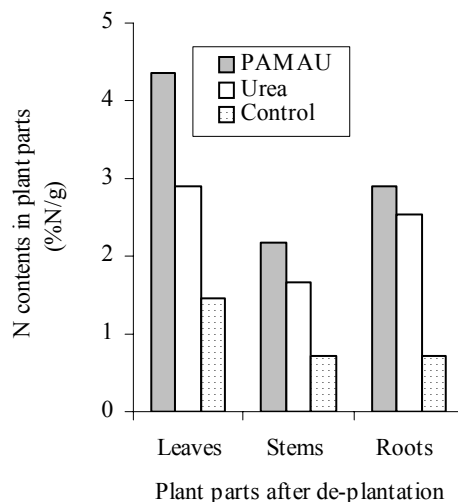
**Fig. 3.** Average plant height at different time intervals for chilli plants in P (AAM-MA) U, urea and control treated pots



**Fig. 4.** Average number of leaves per plant in P (AAM-MA) U, urea and control treated pots at different time intervals during growth



**Fig. 5.** N content in P (AAM-MA) U, urea and control treated soils measured at different time intervals

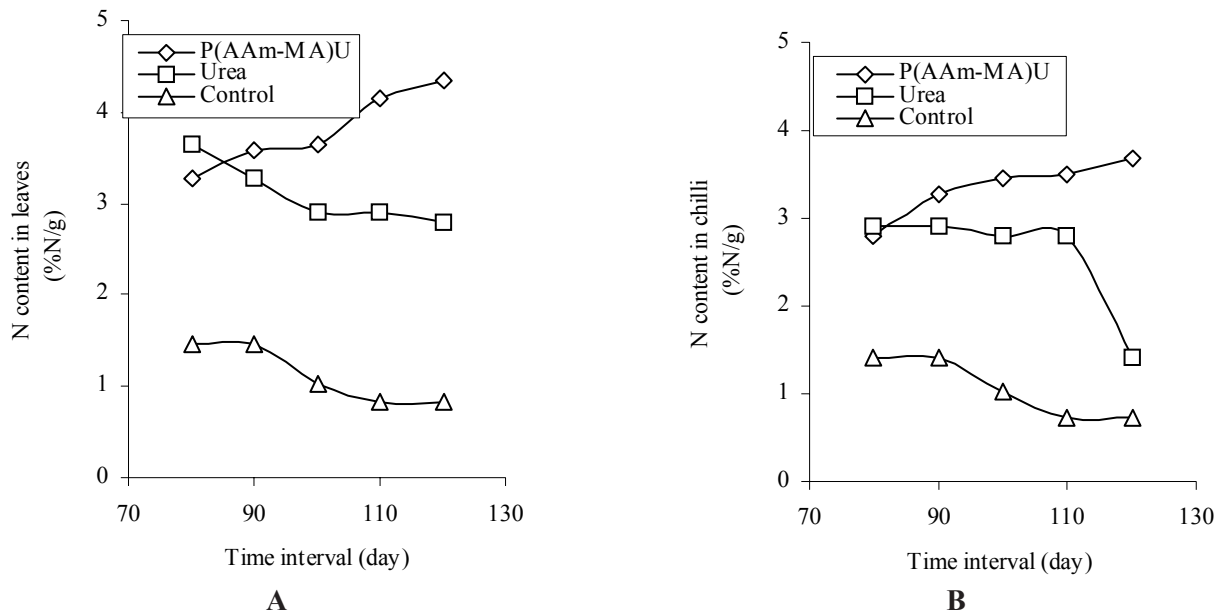


**Fig. 7.** N content in different plant parts obtained from P (AAM-MA) U, urea and control treated soils after de-plantation

dom copolymer having complicated chemical structure the theoretical N content could not be predicted. However, the above elemental and spectral analyses suggest that urea is bonded to the copolymer matrix.

Solubility measurement was carried out in water. As shown in the Table 1, relative to urea solubility of

P (AAM-MA) U was much lower and the dissolution process was also comparatively slower, having taken four days. This slow dissolution and relatively low solubility of P (AAM-MA) U are important parameters to satisfy the requirements of slow-release fertilizer.



**Fig. 6. N content in (A) leaves and (B) matured chilli obtained from P (AAM-MA) U, urea and control treated soils at the interval of 10 days during cropping**

Figure 3 shows the average plant height of chilli plants measured after 50 days of transplantation at an interval of 10 days. In P (AAM-MA) U treated pot the average plant height increased at a faster rate as compared to that in the urea treated pot. In absence of N-fertilizer (control) the plant height increased but relatively at a lower rate. The observed F ratio is greater than the tabulated value at 5% level of significance. This implies a significant difference among the plant heights with the variation in soil treatments. The mean difference values of both P (AAM-MA) U (10.17) and urea (6.03) from control are greater than the values of least significant difference (LSD) at both 5% (3.88) and 1% (5.38) levels of significance. The mean difference value in case of P (AAM-MA) U is comparatively higher than that of urea. Hence P (AAM-MA) U offered a larger plant height relative to urea.

Figure 4 represents the variation in average number of leaves with time after transplantation. In P (AAM-MA) U treated pot average number of leaves increased rapidly as compared to urea treated pot. Since all the plots were maintained under identical environment, it can be assumed that the faster growth of chilli plant in P (AAM-MA) U treated pot is due to the

sustained and slow release of N from the polymer matrix. The observed F ratio is greater than that of tabulated value. The mean difference values of P (AAM-MA) U (17.11) and urea (10.89) from control are greater than LSD values at both 5% (4.57) and 1% (6.23) levels of significance. Moreover the mean difference value of P (AAM-MA) U from urea (6.24) is greater than LSD values at both 5% and 1% levels of significance. Hence P (AAM-MA) U offered a relatively faster growth of plants.

N content in P (AAM-MA) U, urea and control treated soils were measured at various time intervals during the growth of chilli plants. Figure 5 shows the variations of N content in different soils. Before plantation the N content in the soil was 0.09%. After 10 days of fertilizer application P (AAM-MA) U treated soil has the highest N content followed by urea and control. Relatively higher N level in P (AAM-MA) U treated soil may be due to the reduced surface runoff, evaporation and leaching. The mean difference value of P (AAM-MA) U (0.1407) from control is greater than LSD values at both 5% (0.057) and 1% (0.081) levels of significance. Again the mean difference value of P (AAM-MA) U from urea (0.094) is higher than

LSD values at both 5% and 1% levels of significance. Hence this data analysis also indicates that in case of P (AAM-MA) U, N availability in soil is higher than in urea and control treated pots.

The N levels in leaves and matured chillis were measured at different time intervals during plants growth. Figure 6 shows the variations of N levels in leaves and chillis with time. The N contents in leaves and chillis obtained from urea and control treated soils decreased with time whereas from P (AAM-MA) U treated soil they increased. This behaviour may suggest that P (AAM-MA) U has the property of slow-release fertilizer. The statistical analysis shows that the N contents in leaves at different time intervals are not same. The calculated F ratio is higher than the tabulated one. Mean difference values of both P (AAM-MA) U (2.67) and urea (1.98) from control are greater than the LSD values at 5% (0.599) and 1% (0.872) levels of significance. Similarly result is also observed with the statistical analysis of N content in chillis measured at different time intervals.

N levels in different plant parts such as stems, roots and leaves were also measured. The N contents in all three plant parts obtained from P (AAM-MA) U treated soil has relatively higher value as shown in the Figure 7. This result again suggests that the use of urea bonded to copolymer matrix reduced the release of N and hence the loss of N through leaching, volatilization and irrigation water.

## Conclusions

P (AAM-MA)U was prepared in three steps. First, P (AAM-MA) a kind of random copolymer was prepared by solution copolymerization of AAm and MA in presence of KPS initiator. Carboxyl groups in the polymer matrix were activated by chlorination and then reacted with urea. The product was characterized by TLC measurements, elemental and spectral analyses. The performance of P (AAM-MA) U in agriculture was followed by studying the growth of green chilli plants and compared the results with urea and control (without N-fertilizer) under identical condition. Comparative release behaviour of N was also studied by

measuring the N level in soil during plant growth. The results suggested that P (AAM-MA) U improved the growth of plants as well as sustained higher N level in soil for longer time.

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