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Semi-IPN poly(AAm-co-MAPTAC)-Chitosan Hydrogels: Synthesis, Characterization and Investigation of Their Potential Use as Nitrate Fertilizer Carrier in Agriculture

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ABSTRACT

Poly(acrylamido-co-3-methacrylopropyl trimethyl ammonium chloride)-Chitosan semi-IPN hydrogels were prepared by free-radical polymerization of the monomer acrylamide (AAm) and the cationic comonomer 3- methacrylo propyl trimethyl ammonium chloride (MAPTAC) with N,N-methylene bisacrylamide (BAAm) as the crosslinker in presence of chitosan, which is also cationic natural polymer. The swelling properties were investigated by using gravimetric method, whereas morphological structure and mechanical performance of the hydrogels were identified by employing scanning electron microscopy (SEM) and uniaxial compression machine, respectively. Potassium nitrate was used as the model fertilizer and its loading and release experiments were carried out with conductimetric measurements. All the results indicated that both cationic MAPTAC units and chitosan were strongly influenced the gel properties from pore structures and swelling properties to nitrate loading and release % values due to the repulsion forces formed between the positive charges in MAPTAC and chitosan, as well as the interaction between these ionic groups and water molecules. The new semi-IPN hydrogels exhibited good slow nitrate release, better swelling and improved mechanical performances in especially some composition . Thus it can be concluded that the new semi-IPN hydrogels have a potential to use them as a nitrate fertilizer carrier. Especially the further investigations performed with A-1M-0.05C hydrogel in soil media revealed that the hydrogel at this combination can be evaluated as one of the promising materials which can be safely used as controlled fertilizer release system..

Keywords:
Hydrogel; Acrylamide; MAPTAC; Controlled fertilizer release.

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INTRODUCTION

Hydrogels, which are formed by chemical or physical crosslinking of hydrophilic polymers via covalent bonds or physical interactions (hydrogen bonds, ionic interactions etc.), were first introduced to the literature by Wichterle ve Lim in 1960. The researchers were succesful in developing poly(hydroxyethyl methacrylate) hydrogels with soft structure as an alternative to poly(methyl methacrylate), which had been used in fabrication of contact lens and was not much comfortable because of its hard structure [1]. After this study, the number of works on hydrogels has increased rapidly and the various hydrogels having both synthetic and natural structure such as poly(acrylamide), poly(acrylic acid), poly(N-isopropyl acrylamide), poly(vinyl alcohol), chitosan, gelatin and alginate etc., were prepared using different types of monomers, co-monomers and crosslinkers [2-9]. Hydrogels are attractive materials because of their soft structure, high water uptake capacities, (in some cases they absorb water thousands of times their own dry weights), biocompatible structures, easily biodegradation and easily production. Due to the mentioned advantages, hydrogels have being used in various fields such as medicine, pharmacy, food, environment, mechanical and civil engineering and they offer several solutions for different applications [10-12]. Although hydrogels have many beneficial properties, their use in some applications, especially in which mechanical stability are required, are restricted because of their soft and fragile structures and especially their easily degradation in wet state. In order to overcome these negative sides and to gather the beneficial properties of various chemical subtances in one material, several strategies have been proposed. The techniques of blending, copolymerization with hydrophobic monomers and preparation of semi and full interpenetrating networks (semi or full-IPN) were successful in obtaining the hydrogels having desired properties [13].

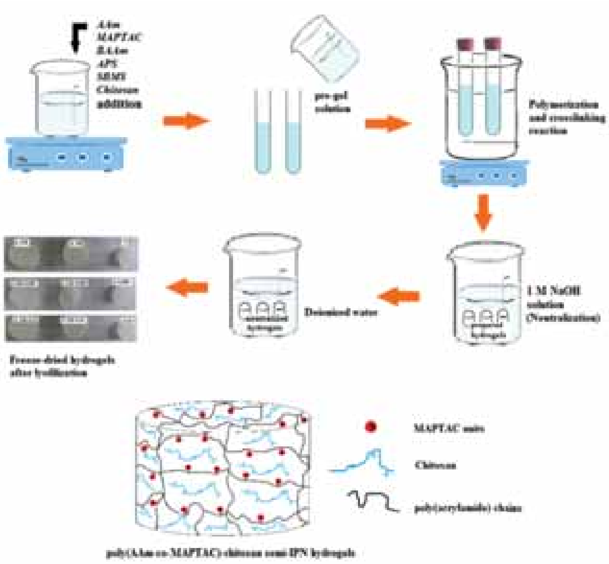

Figure 1. Synthesis schema of the poly(AAm-co-MAPTAC)-chitosan semi-IPN hydrogels

Semi-IPN hydrogels, which are one of the abovementioned techniques, are formed by combination of two different types of polymers, one of which is in network form and the other one is in a linear form [14]. The works on semi-IPN hydrogels have proved that this type of hydrogels increase mechanical strength of wet hydrogels and reduce degradation rates [15]. According to the literature, it is noticed that polysaccharides have been mainly used as linear polymer for production of semi-IPN in these studies [16]. Polysaccharides offer several solutions for particularly the fieds in which biocompatible and nontoxic materials are preferred, such as medicine, food etc. The natural structure of polysaccharides and the environmental sensitive swelling properties of the synthetic hydrogel network can be gathered with the abovementioned semi-IPN hydrogels. The reason that the most widely used polymers in preparation of semi-IPN hydrogels are polysaccharides can be explained with their abundance, low cost, reneweability and suitable for chemical modifications.

Chitosan, which is one of the most known polysaccharides, is a cationic natural polymer formed by bonding N-acetyl-D-glycosamine units with β-(1 → 4) glycosidic bonds and obtained by deacetylation of chitin, which is produced from insect shells [16]. Chitosan is one of the attractive materials due to both its natural structure and pH dependent swelling behavior owing to their high number of amine groups. In most of the works involving semi-IPN, in which chitosan was used as a linear polymer, it was searched that the release of anionic drug, protein and insulin release [17-20], and also removal of humic acid from waste water [21].

Although various semi-IPN hydrogels having chitosan as a linear polymer have been widely studied, it was no noticed a research on a semi-IPN structure formed by combination of cationic poly[acrylamide-co-(3-methacryolypropyl) trimethyl ammonium chloride] (poly(AAm-co-MAPTAC) network and chitosan polymer. Therefore, in present study, it was aimed at preparation of poly(AAm-co-MAPTAC)-Chitosan semi-IPN hydrogels and estimated that both the ammonium and amine groups in MAPTAC and chitosan, respectively would create synergy in several properties of the hydrogel. It can also be stated that the other prediction was that the amine groups in chitosan would be more active in big pores like in poly(AAm-co-MAPTAC) network than in nonionic ones. Moreover it was thougth that introducing chitosan polymer into the poly(AAm-co-MAPTAC) structure may help increment in the mechanical stability of the hydrogels without the need of increasing crosslinker content.

On the other hand it was investigated that the potential use of these novel hydrogels as a controlled release fertilizer material, which is the one of the most popular applications of the hydrogels, recently. As it is well known that hydrogels are used in agricultural applications as a fertilizer and pesticide carrier and enable these agrochemicals to release into soil gradually and thus they are named as controlled-release fertilizer (CRF). In conventional agricultural applications, fertilizers which are placed near to the roots of plants, undergo quickly dispersion and dissolvation with irragation before the plant has benefited sufficiently. This fact which cause to overdose fertilization leads to both the over consumption, thus high cost and damage to plant [22]. For this reason in especially last decade the number of the investigations on CRF has increased rapidly. In this context, various polymeric hydrogels such as polyacrylamide, poly(N-hydroxymethyl acrylamide-co-acrylic acid), chitosan, gelatin and gelatin-poly(acrylamide)-gelatin IPN hydrogels have been examined with many studies, which proved that controlled release of fertilizer was achived by using these polymeric hydrogels [23-27]. However there is still need of further studies on developing and designing new different formulations for CRF production, because some of the abovementioned studies are lack of some informations for example release rates in soil media and mechanical stability measurements of CRF materials, which is also vital because it is required that the material must keep its structural integrity up to release of the fertilizer in the carrier finish. The abovementioned lacks motivated to study also the controlled release fertilizer of these hydrogels. In this work, nitrate was used as fertilizer, because it was estimated that the high number of cationic groups in the semi-IPN hydrogels would increase the nitrate loading and also decrease the release rate of the hydrogels.. Moreover, it was expected that these hydrogels would exhibit not only good loading and release behavior for nitrate fertilizer but also sufficient mechanical strength owing to their semi-IPN structure.

With the abovementioned aims, a series of hydrogels having acrylamide and 3-methacryolypropyl trimethyl ammonium chloride as a monomer and comonomer respectively and N,N-methylene bisacyrlamide as a cross-linker was synthesized in presence of chitosan and obtained semi-IPN poly(AAm-co-MAPTAC)-chitosan hydrogels with different MAPTAC and chitosan content. These hydrogels were characterized in term of swelling, morphology and mechanical stability via several characterization techniques. The hydrogels were subjected to nitrate loading and release experiments in both of the pure water and in soil. And finally biodegradability of the optimized hydrogel was searched.

MATERIALS AND METHODS

Materials

Acrylamide (AAm), 3-methacrylo propyl trimethyl ammonium chloride (MAPTAC) and N,N-methylene bisacrylamide (BAAm), which were used as main monomer, comonomer and crosslinker, respectively and also chitosan, which was used as linear polymer were all bought from Aldrich Chemicals (Milwaukee, WI,USA). Ammonium peroxydisulfate (APS) and sodium meta bisulfite (SMBS), which were employed as redox initiator pair, were purchased from Merck (Darmstad, Germany). Acetic acid and sodium hydroxide, used for preparation of the hydrogels and also potassium nitrate used for controlled fertilizer release experiments, were supplied by Aldrich Chemicals (Milwaukee, USA). The soil sample was bought from a local market. All the reagents were used as received and deionized water was used throught the experiments and measurements in the study.

Table 1. Experimental conditions of the preparation of the hydrogels.

Hydrogel	AAm(x10^{-2} moL)	MAPTAC (x10^{-2} moL)	BAAm(x10^{-4} moL)	APS(mg)	SMBS(mg)	Chitosan(g)
A	1	0	1.67	5.7	1.9	0
A-1M	0.99	0.01	1.67	5.7	1.9	0
A-2M	0.98	0.02	1.67	5.7	1.9	0
A-0.05C	1	0	1.67	5.7	1.9	0.05
A-1M-0.05C	0.99	0.01	1.67	5.7	1.9	0.05
A-2M-0.05C	0.98	0.02	1.67	5.7	1.9	0.05
A-0.1C	1	0	1.67	5.7	1.9	0.1
A-1M-0.1C	0.99	0.01	1.67	5.7	1.9	0.1
A-2M-0.1C	0.98	0.02	1.67	5.7	1.9	0.1

Preparation of the poly(AAm-co-MAPTAC)-chitosan semi-IPN Hydrogels

Poly(AAm-co-MAPTAC)-chitosan semi-IPN hydrogels were synthesized by employing free radical polymerization in presence of chitosan, using BAAm as crosslinking agent. The synthetic route for the hydrogels was demostrated in Fig. 1. Briefly, AAm and BAAm were dissolved in 10 mL of aqueous acetic acid solution (1% wt.) in turn under magnetic stirring. Then, the comonomer MAPTAC and APS were added to the mixture and continue to mixing. Finally, the reaction was started after pouring chitosan and SMBS into the solution and transferred into air-tight glass tubes. The reaction was carried out in a water bath at 35 °C for 24 h. The resulting hydrogels were cut into the discs that have a approximate length of 1 cm. and immersed and left to neutralization into 1 M NaOH solution for an hour in order to prevent chitosan in the hydrogel from dissolution. After this neutralization, the hydrogels were placed into deionized water for purification and refreshed the water every other day. The fully swollen hydrogels were subjected to lyophilization and referred as A-XM-YC, where X and Y represent the molar ratio of MAPTAC and the weight of chitosan, respectively. The monomer feed according to hydrogel codes was given in Table.1.

Characterization

Swelling tests of the hydrogels were performed in deionized water at room temperature. The water uptake capacities of the hydrogels were determined by gravimetrically. For this, the dry hydrogel samples of which weights were known were immersed in deionized water and allowed to attain the maxiumum swelling degree by following their weights at pre-determined time intervals. During the swelling process the water was refreshed every other day. The percent swelling value was calculated by following equation:

$$S\% = [(m_s - m_d)/m_d] \text{ x } 100 \quad (1)$$

where S%, m_s and m_d show the equilibrium swelling percent, weights of swollen and dry hydrogels, respectively.

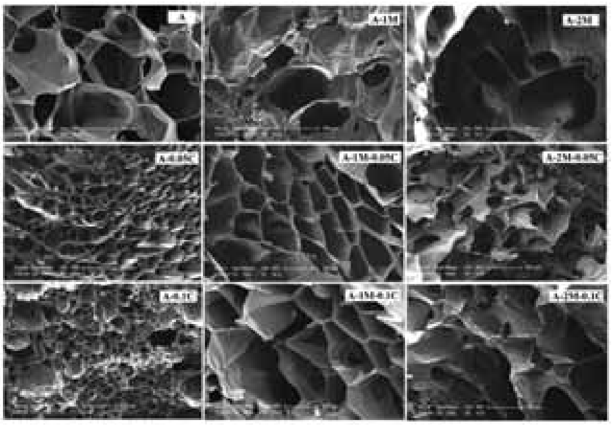

Figure 2. SEM images of the poly(AAm-co-MAPTAC)-chitosan semi-IPN hydrogels. The scale bars are 200 µm

The mechanical strengths of the hydrogels were identified by applying compressing test. The fully swollen samples having 1 cm of the length were subjected to uniaxial compression by using Zwick/Roell Z1.0 universal testing machine (Zwick Gmb&Co.KG,Ulm,Germany) equipped with a 50-N load cell at a compression rate of 3 mm/min. The compression was maintained upto 60% of the deformation rate and the compression force values versus the deformation percentages were monitored.

The pore structure of the freze-dried hydrogels was investigated with SEM technique by using an ESEMFEG/EDAX Philips XL-30 instrument (Philips, Eindhoven, The Netherlands).

Loading and release experiments

Nitrate fertilizer loading capacities were followed by conductimetric measurements, using C65/C66 model conductivity meter (Milwaukee WI,USA). The pre-weighed hydrogel samples were placed into 25 mL of aqueous KNO_3 solution (1% wt.) and allowed to KNO_3 penetration for 48 hour. The KNO_3 loaded hydrogels were then removed from the medium and KNO_3 concentration in the solution was determined from the conductimetric measurements. The loading % KNO_3 was calculated according to the following equation:

$$\text{Loading\%} = [(c_0 - c_d)/(c_0 \text{ x } m_d)] \text{ x100} \quad (2)$$

where c_0 and c_d denote the initial and the final KNO_3 concentrations, respectively, while m_d represents the weight of the dry hydrogel sample.

Release experiments were performed by placing the pre-weighed KNO_3 loaded hydrogels into 100 mL of deionized water. The release KNO_3 amounts were determined by measuring the conductivity of the solution at certain time intervals and calculating using the following equation:

$$\text{Release \%} = [(c_t \text{ x } 0.1)/(m_{KNO3} \text{ x } m_L)] \text{ x } 100 \quad (3)$$

where c_t, m_{KNO3} and m_L show the KNO_3 concentration at certain time intervals, the KNO_3 amount released by the hydrogel and the weight of the KNO_3 in the loaded gel, which determined from the loading experiments.

Release tests were repeated for soil medium with only the hydrogel exhibited good swelling, mechanic, loading and the lowest release rate performance. With this aim, the KNO_3 loaded chosen hydrogel (A-2M-0.05C) samples were weighed and placed into the 100 g of the soil in a beaker by burrying them in tea-bags made of nylon wire mesh. Then 30 mL of deionized water was added and the beaker was covered with a aluminium foil to protect the soil from evaporation and kept at room temperature for 35 days. One of the samples was withdrawn from the soil at every 24 hours and immersed into deionized water for 24 hours. After 24 hours KNO_3 concentrations were determined by conductimetric measurements and used to calculate the % KNO_3 release of the hydrogels in soil media by employing the Eq.3.

Biodegradation tests

The biodegradability test was performed by using the KNO_3 loaded dry A-1M-0.05C hydrogel samples of which weights were ranged between 0.08 and 0.12 g. In this test, dry hydrogels were burried into a soil by inserting in a teabag in order to prevent the hydrogels from as much as any dirt or etc. The container, which was filled with soil, was then covered with aluminium foil to protect the soil from evaporation and kept at room temperature. The samples were taken from the soil and weighed at pre-determined time intervals (7 days). The weight loss of the gels was determined by following the weight of the hydrogels, which was used in the equation below:

$$\text{\% weght loss} = [(m_i - m_f)/m_i] \text{x100} \quad (4)$$

where m_i and m_f represent the initial and the final weights of the hydrogel samples.

Table 2. Equilibrium swelling percents and the compression strength value against to 60% deformation rate of the hydrogels.

Hydrogel	*Sw%(eq)*	*Compression strength (N)*
A	*2417*	*1.16*
A-0.05C	*2055*	*2.79*
A-0.1C	*1827*	*5.23*
A-1M	*5164*	*2.79*
A-1M-0.05C	*4443*	*3.34*
A-1M-0.1C	*5711*	*1.21*
A-2M	*7712*	*0.93*
A-2M-0.05C	*6680*	*2.90*
A-2M-0.1C	*11465*	*0.92*

Table 3. KNO_3 loading amounts of the hydrogels.

Hydrogel	*KNO3 loading %*
A	*10.66*
A-0.05C	*8.75*
A-0.1C	*6.22*
A-1M	*55.20*
A-1M-0.05C	*50.52*
A-1M-0.1C	*60.71*
A-2M	*63.81*
A-2M-0.05C	*59.40*
A-2M-0.1C	*65.22*

RESULTS AND DISCUSSION

Characterization

Morphological structure:

The SEM images illustrated in Fig. 2 show the inner surface structure of the hydrogels. According to the pictures, it was clearly observed that A has relatively homogenously distributed open pores with an approximate size of 300 micrometer, while A-0.05C and A-0.1C hydrogels obtained by using 0.05 and 0.1 g of chitosan, respectively, was found to have smaller pores than A. Moreover, it was seen that most of the pores in all the nonionic hydrogels were interconnected and homogenously distributed. It was significantly observed from the micrographs that the addition of chitosan into the hydrogel composition caused to decrement in the pore sizes most probably due to the fact that it filled some of the empty space of the pores.

On the other hand, in the case of the ionic hydrogels, the quitely increased pore volumes in both of the A-1M and A-2M are remarkable. In addition to these greater pores, also more foliaceous structure and heterogeneously distributed pores in these gels are noticeable, which may be related to that AAm and MAPTAC units were not well ordered in the hydrogel network. In particular, being have pores with nearly 500 micrometer in size, showed that the hydrogels with MAPTAC created bigger pores compared to the nonionic hydrogels, likely due to the repulsion forces between the quaternize amine groups in MAPTAC units. But, this extent decreased by a quarter with the inserting of 0.05 g chitosan in the hydrogel composition. This fact was ascribed to the similar way with the abovementioned for the A-0.05C and A-0.1C hydrogels. However, in spite of the case in the nonionic hydrogels, further increase in chitosan (0.1 g) resulted in greater pores of which sizes reached to approximately 500 micrometer again. This first decrement and then increment in the pore sizes with the chitosan addition can be suggested that the inserting of chitosan up to a certain amount (0.05 g) increased the bulk density of the gel, filling some of the voids and leading to relatively small pores (first effect), although there is an opposite effect (second effect) which was explained with the repulsion forces between the protonated amine groups in chitosan and the quaternize amine groups in MAPTAC units, contributing to have bigger pores. As seen from the micrographs that the first effect was dominant over the pore size in the case of presence of 0.05 g chitosan. However, when the chitosan content increased to 0.1 g, the number of protonated amine groups originated from chitosan has doubled and much more repulsion between these doubled amine groups and the quaternized amine groups in MAPTAC units occurs and thus the second effect become dominant.

Swelling properties of the hydrogels

The swelling percentages seen both in Fig. 3 and Table.2 showed that presence and increase of ionic comonomer (MAPTAC) enhanced the water absorption of the hydrogels. It resulted as (Sw(A)< Sw(A-1M) < Sw(A-2M)) as expected. The maximum swelling degree was achieved with A-2M hydrogel had a value of 7712% wt. On the other hand, including 0.05 g of chitosan into the composition was found to reduce their swelling capacities. This fact can be explained in the following way: Addition of chitosan into monomer feed resulted in lower swelling extents, decreasing the pore size by filling the some spaces of the pores for all the hydrogels, as seen in the their micrographs, although it has many ionic and hydrophilic groups. However,in spite of the abovementioned case, further increment in chitosan improved the water absorption of the ionic hydrogels, while the nonionic ones remained their water uptake decrement. For example, the swelling degree of A-1M-0.05C was found to be 4413%, whereas it was calculated to be 6680% at 0.1g chitosan content. Similarly, A-2M-0.05C was found to have a swelling value of 5711% , while A-2M-0.1C exhibited a swelling degree of 11465% .This first increase and then decrease pattern of the ionic hydrogels can be assessed with two opposite effects which created most probably by addition of chitosan and explained above for their morphological structure. One of these effects may be suggested that pore sizes declined with chitosan addition due to its filling some spaces of the pores, leading to lower swelling degrees, the second one may be explained with the repulsion forces between the cationic groups in chitosan and MAPTAC, which accounts for having more extended structure of the networks, resulting in more water absorption. These swelling behavior of the ionic hydrogels can be also supported by their SEM images. According to the results, it is obvious that the hydrogels having 0.05 g chitosan exhibited lower swelling degrees due to the fact that the first effect is dominant, while those containing 0.1 g chitosan was found to have higher water absorption capacities as a consequence of the second effect, which become dominant in this composition because of the fact that cationic groups in chitosan has doubled with the 0.1 g of chitosan addition. In addition to having extended structure and greater pore size, the ionic species in the gel play an important role in the water absorption, creating ion-dipol and dipol-dipol interactions between the ionic groups and water molecules, which enable the more water molecules to enter into the network.

On the other hand the gradually decrement in water uptake capacities of the nonionic hydrogels (A, A-0.05C and A-0.1C) with increased chitosan is proved to the abovementioned suggestion, which was done with the repultion forces between the ionic groups, for the hydrogels with MAPTAC.

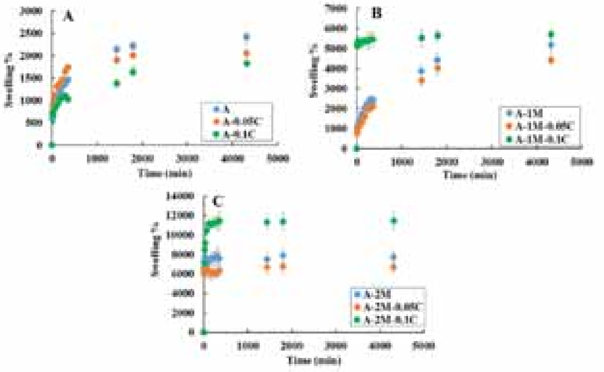

Figure 3. Swelling curves of the poly(AAm-co-MAPTAC)-chitosan semi-IPN hydrogels in deionized water (A): Acrylamide hydrogels ; neat and including 0.5 and 1 % wt. chitosan, (B): Acrylamide hydrogels having 1% mol ratio of MAPTAC; neat and 1 % wt. chitosan, (C): Acrylamide hydrogels having 2% mol ratio of MAPTAC; neat and 1 % wt. chitosan

Mechanical properties of the hydrogels:

The mechanical strengths of the swollen hydrogels were identified by utilizing an uniaxial compression tests. The results were presented as stress-strain curves in Fig.4 and the maximum compression force values against to 60% deformation were given in Table.2. The mechanical measurements showed that incorporation of chitosan into the nonionic poly(acrylamide) hydrogels increases the maximum compression force from 0.81 N up to 5.23 N, as expected. This improvement in the mechanical performance can be ascribed to formation of smaller pores with addition of chitosan, leading to higher resistance to deformation and also homogenously distribution of the stress in the hydrogel matrix. This enhanced mechanical stability was also observed for the ionic hydrogels having 0.05 g of chitosan, most probably due to the same reason with the nonionic ones. However at higher chitosan content, this gradually increment obtained from nonionic hydrogels was not observed for the ionic ones. For instance, the maximum force applied to A-1M-0.05C at 60% deformation rate was calculated to be 3.34 N, whereas that performed to A-1M-0.1C was found to decrease to 1.21 N. Like to the hydrogels containing 1% wt. MAPTAC, also the A-2M-0.05C and A-2M-0.1C hydrogels displayed the similar mechanical behavior in response to further chitosan addition. These variation in the gel strength can be attributed to the both of the morphological structures and swelling values of the ionic hydrogels. Since the mechanical tests were performed with the samples in wet form, the hydrogels having high absorption capacities exhibited poor mechanical stability.

On the other hand, it was interestingly found that the A-1M hydrogel displayed greater mechanical performance in comparison to A, in spite of the expectations. It is thougt that this increment was related to the difference in the sizes of the pendant groups of AAm and MAPTAC units. Having larger pendant group made A-1M hydrogels exhibited better mechanical performance with respect to A gels, due to the resistance of larger side groups to deformation. However, for A-2M hydrogel, the gel strength was found to be close to that of A, most probably due to its high swelling capacity which influence the mechanical stability alhough it has also the large side groups originated from MAPTAC. According to the results it can be inferred that the high swelling property of A-2M determines the mechanical performance of the gel compared to the large side group effect.

KNO_3 loading and release behavior of the hydrogels

The nitrate loading % values of the hydrogels immersed in 1% (wt.) KNO_3 solution for 48 h were obtained from the conductimetric measurements by using the calibration curve and given in Table.3. The results showed that ionic hydrogels absorbed more NO_3^- ions than nonionic ones most probably due to the both reason of their high number of cationic groups which act as a receptor for negative charges like nitrate and great swelling capacities which increase nitrate penetration. On the other hand, it is seen that the hydrogels having 0.1 g of chitosan displayed a slightly increased loading capacities. This fact can be ascribed to the extra cationic groups presented by increased amount of chitosan. The nitrate release % values of the hydrogels were illustrated in Fig.5. Among the hydrogels, the lowest release percents ranged between 31 and 35% were obtained for the nonionic hydrogels.

This fact can be attributed to the lower swelling capacities of A, A-0.05C and A-0.1C hydrogels, which govern release process of the entrapped ions. Additionally, the maximum release ratio was achieved by A-2M hydrogel with a release percent of 82%. On the other hand, the nitrate release ratios of all the ionic hydrogels were found to be close to eachother and varried between 71 and 82. However in the agricultural applications, it is desired the superabsorbents to have slow release rates in order to be efficient. When this factor is taken into account, A-1M-0.05 hydrogel seem to have optimized composition with its especially slower release rate, moderate good swelling capacity and also good mechanical stability which is also very important in these application, because of the fact that if the material has not adequate strength, it loss its physical integrity and some cracks occur on its surface leading to burst release.

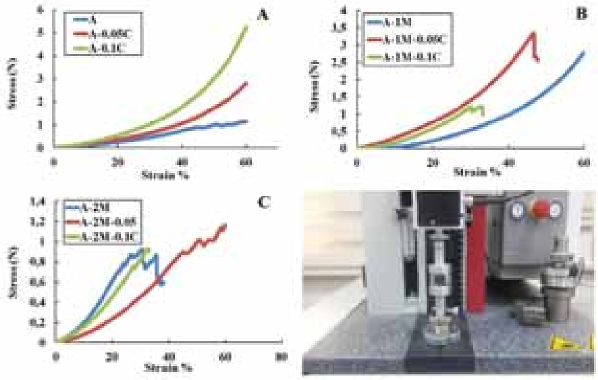

Figure 4. Stress-strain curves of the poly(AAm-co-MAPTAC)-chitosan semi-IPN hydrogels (A): Acrylamide hydrogels ; neat and including 0.5 and 1 % wt. chitosan, (B): Acrylamide hydrogels having 1% mol ratio of MAPTAC; neat and 1 % wt. chitosan, (C): Acrylamide hydrogels having 2% mol ratio of MAPTAC; neat and 1 % wt. chitosan

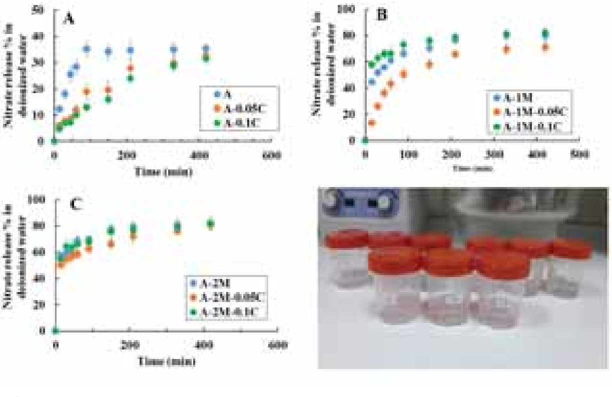

Figure 5. KNO3 release pattern of the hydrogels in deionized water. hydrogels (A): Acrylamide hydrogels ; neat and including 0.5 and 1 % wt. chitosan, (B): Acrylamide hydrogels having 1% mol ratio of MAPTAC; neat and 1 % wt. chitosan, (C): Acrylamide hydrogels having 2% mol ratio of MAPTAC; neat and 1 % wt. chitosan.

KNO_3 release behavior of the hydrogels in soil

Since the most efficient composition was determined to be A-1M-0.05C, the experiment in soil was conducted with the only these hydrogel samples. The release behavior in soil was depicted in Fig.6. According to the results it was revealed that at the beginnig of the process, the burst release was observed, after that the release rates become slower. The final release value of A-1M-0.05C in soil, attained by approximately 18th day, was found to be 67%, which is said to be close to that of in deionized water.

Biodegradability

Like to the release experiments carried out in soil media, the biodegradability test was performed with the only A-1M-0.05C hydrogel samples. The results obtained from the soil burial test were illustrated in Fig.7. According to the weight loss ratios, it was found that the hydrogel with 1% MAPTAC prepared by using 0.05 g of chitosan, exhibited relatively poor biodegradability. The maximum biodegradation ratio (12.3 %) was achieved after 35 days. In fact, this low biodegradability was estimated before the test due to the synthetic structure and relatively high crosslink density of the hydrogel, which increase the resistance to biodegradation. However although its degradation ratio was found to be low, it can be interpreted that the high pore size and also the natural biodegradable chitosan content of the hydrogel slightly increased to its biodegradability, when compared to corresponding conventional materials in the literature, which states that less than 10% of polyacrylamide hydrogels degrade after 28 days [28].

CONCLUSION

In present study, new poly(AAm-co-MAPTAC)-chitosan semi-IPN hydrogels were succesfully prepared to improve the properties of the poly(AAm-co-MAPTAC) hydrogels. The mophological analyses showed that chitosan addition caused to reduce the pore sizes of nonionic hydrogels. However, this case was found to be different for the hydrogels with MAPTAC. It was observed that the ionic hydrogels had smaller pores when 0.05 g of chitosan was incorporated into the composition, but with the further amount resulted in greater pore sizes, most probably due to the extended hydrogel structures arising from repulsion forces between the positive charges in chitosan and MAPTAC units. On the other hand, it was found that introducing chitosan at a 0.05 g dosage decreased to the swelling extents, while addition of 0.1 g of chitosan resulted in increment in the water uptake values except for the nonionic hydrogel. It was suggested that existence of a certain amount of chitosan, which seems to be 0.1 g, provided the ionic gels to have higher swelling values as a consequence of formation and become noticeable of the repultion forces between the positive charged amine and quaternize ammmonium groups, which belong to chitosan and MAPTAC units, respectively and also it may be related to extra hydrogen bonds, ion-dipol and dipol-dipol interactions occured between the high number of ionic groups and water molecules which enhance the swelling capacities, by facilitating diffusion of water molecules into the hydrogels. These swelling results showed that chitosan addition beyond a certain amount improved the water absorption behavior of the ionic hydrogels. Additionally, these swelling results are also good agrement with their pore sizes and can be explained with the morphological structures.

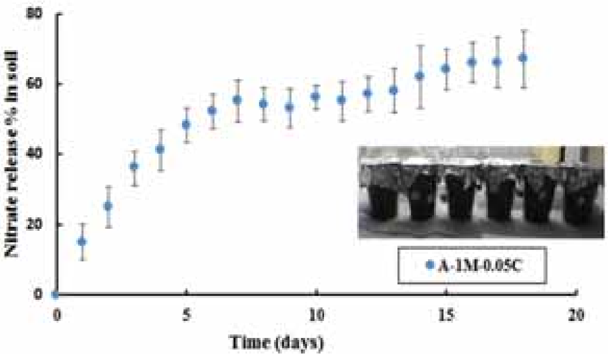

Figure 6. KNO3 release pattern of the hydrogels in soil.

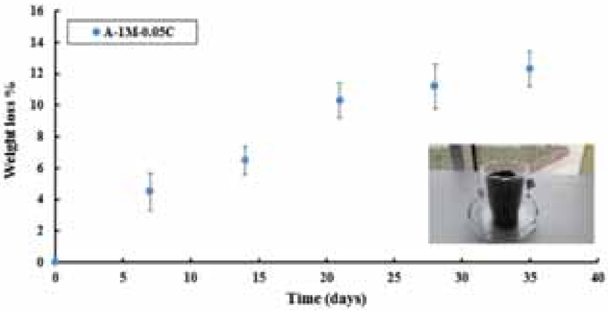

Figure 7. Weight loss % of the hydrogels versus time

The obtained mechanical results revealed that the gel strengths were strongly correlated with their swelling ratios, since as it is well known that high swelling capacities make the gels more fragile and easy breakable. However it should be noticed in some comparisons in the modul values of the hydrogels that the MAPTAC units can influence the mechanical performance by offering relatively larger pendant groups with respect to AAm units to the structure as well as the swelling ratio. Therefore the mechanical results showed that A-2M had higher compression strength than the nonionic hydrogel (A), although it had quite high swelling degree.

As to the fertilizer loading and release behavior, the positive charges in the hydrogels played an important role in both of the loading and release experiments. Negative charged nitrate ions were more absorbed by A-2M-0.1C, and also among the semi-IPN hydrogels, the maximum release amount and percentages were obtained with the same hydrogel composition, as expected from its high water uptake capacity, which drive the loading and release process of solute molecules by hydrogels. According to the results it was seen that the second place was taken by A-1M -0.1C. The further experiments, which were carried out in soil media and performed with the only the ionic hydrogel having 1% MAPTAC and 0.05 g of chitosan (A-1M-0.05C), regarding the potential efficiency of this hydrogel after the evaluation of all the results obtained from swelling, mechanical tests and also its slower release rates found from release experiments in water, showed that nitrate release continued upto almost 20 th day in soil media, by release 69% of pre-loaded nitrate , which can be considered as a slow fertilizer release. On the other hand biodegradability results demonstrated that the maximum biodegradation ratio (12.3 %) was achieved after 30 days for this hydrogel. Here although this low biodegradability seems to be negative side of this hydrogel for agricultural applications, one can evaluated that this disadvantageous can be reverse, when its efficieny in both of loading and release is taken into account, due to the fact that smaller quantity of the hydrogel would be sufficient as controlled fertilizer release material as compared to easily degraded ones.

It can be concluded that the new hydrogels in which semi-IPN structure obtained by combination of poly(AA-co-MAPTAC) and chitosan have a potential to use them as a nitrate fertilizer carrier. Especially the further investigations performed with A-1M-0.05C hydrogel in soil media revealed that the hydrogel at this combination can be evaluated as one of the promising materials which can be safely used as controlled fertilizer release system.

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