Studying the effect of nitrogen content when Preparation (CMS PAAM –PMBA) graft copolymer using redox system

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Abstract

In order to create grafting polymer, at first, CMS was prepared with starch and chloroacetic acid in an alkali – methanol media, and Carboxymethyl starch (CMS) was prepared by different DS, then AAM was grafted on CMS by redox system using oxidant and reductant.

For investigation of the effect of reaction variables on nitrogen content N%, the synthetic conditions were systematically optimized through studying the influential factors.

Research background

In order to study the nitrogen continent N% for a crosslinking polymer (CMS PAAM –PMBA) prepared by the redoxy system, Kjeldahl method was used

Research objective

Studying the effect of nitrogen content (N%) of (CMS PAAM –PMBA) which prepared by using the redoxy system

Research importance

Studying the nitrogen continent N% by to a Kjeldahl method of a grafting polymer by using

1- Different DS of CMS
2- Using redoxy system on CMS with AAM to make crosslinking substance

Methodology

Experimental analytical approach

Research results

The reactions of grafted copolymer variables that affect the nitrogen continent N% of the grafted polymer were studied. It is seen that with increasing the amount of CMS, the grafting decreasing, and that may have attributed to the increasing of the carboxy groups and hydrophilic group which the residue monomer concentration in the reaction mixture which leads to increasing of radical centers, causing high crosslinking points grafted polymer.

The higher nitrogen content of CMS PAAM –PMBA graft copolymer, APS =0.08g, Sod thiosulfate =0.5g, MBA= 0.8 g, AAm = 5 g, water = 1 ml, H_2SO_4 = 3 ml, temp. (90^oC) and Time = until reaction completes (1.50 min)

Key words: Carboxymethylation, DS, CMS, grafting polymerization, redoxy system and nitrogen continent N%

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1-Introduction

Carboxymethyl starch has become one of the most important modified materials to be widely applied in the textile, food, paper, petroleum, and pharmaceutical industries. (1)

In the textile industry, CMS has been used as a thickening agent in printing pastes using, direct, reactive, disperse, vat and naphthol dyes (2-3) It has been also used as a sizing agent and a finishing agent (4-6)

In this work, the preparation of this superabsorbent is carried out by free radical polymerization of highly concentrated partially neutralized acrylamide in presence of CMS as substrates, using (Al_2S_2O8)/ ($Na_2S_2O_3$) redox system (7) and the nitrogen continent and Degree of Substitution were measured

2- Materials

2-1- Raw material specification

-Native maize starch (NS) was kindly supplied by the Egyptian Company for Starch and Glucose Manufacture, Cairo, Egypt.

2-2-Chemicals

-Carboxymethylation (CMS preparation)

Sodium hydroxide (NaOH), sodium carbonates anhydrous (Na_2Co_3), Monochloroacetic acid ($ClCH_2COOH$) were of laboratory grade, and Ethanol was of commercial grade.

-Grafting (CMS Grafted by Redox system)

-, Acrylamide (AAM) C_3H_5No, Ammonium persulfate APS ($(NH_4)_2S_2O_8$), Sodium thiosulpate ($Na_2S_2O_3$), sulfuric acid (H_2SO_4) and acrylic acid (AA), were of laboratory grade chemicals, supplied by Merck- Schuchardt –German & Fine Chemicals.

-Ethyl alcohol absolute, sodium hydroxide (NaOH), Boric acid 98%.

3- Experimental and Procedures

3-1- Carboxymethylation

A certain amount of native starch (NS) was placed in sealable bottle and mixed together with a known volume of the solvent at room temperature. An aqueous solution of sodium hydroxide was added drop wise to the cellulose-solvent mixture under stirring until the whole amount of sodium hydroxide was added. The sodium salt solution of monochloroacetic acid prepared by the reaction of monochloroacetic acid with sodium carbonate monohydrate was added drop wise to the cellulose -solvent-sodium hydroxide mixture under continuous stirring until complete addition of the sodium monochloroacetate solution.

Stirring was then stopped and the bottle was closed and kept in thermostat shaking water bath at 70^{o}C for certain reaction time. After carboxymethylation, the samples were washed with ethanol: water solution (80:20) while excess alkali was neutralized using acetic acid. After washing, samples were filtered, oven dried at 100^{o}C.

*This method was done by different moles of monochloroacetic acid $ClCH_2COOH$ according to study the effect of degree of substitution (DS)

3-2- (Polymerization reaction)

The decomposition of ($Al_2S_2O_8$)/ ($Na_2S_2O_3$) redox system results in the formation of SO_4-., HO and S_2O_3-. Free radical species (13-14). These radical species (R.) are capable of initiating the following set of reactions:

The grafted polymer obtained of this polymerization reaction is mixture of PAA homopolymer, CMS* PAAM –PMBA, and engrafted CMS, induct and oxidized, All in a state of intimate entanglement with each other.

the results obtained with relevant discussions of studying major factors affecting the preparation of this grafted polymer, this includes the concentrations of MBA, AAM, ammonium persulfate, sodium thiosulpate, also temperature, pH, CMS load, DS, and Using different ratios of acrylic acid with acrylamide were studied

3-2-1- Preparation of (CMS PAAM –PMBA) graft copolymer (polymerization reaction)

An aqueous solution of APS was first added with stirring to the mixer of AAm & MBA. A substrate (CMS) was added to the beaker, then sulfuric acid added, finally an aqueous solution Sodium thiosulpate added with rapid mixing to form a uniform paste.

The beaker was kept in thermostatic water bath. After an induction period, an exothermic reaction commenced with evolution of water vapor, followed by solidification of the paste (8-9)

3-2-1-1-Extraction of grafted copolymer

-The paste poly (CMS PAAM –PMBA) composite was smashed then putted on bags. The insoluble poly (CMS PAAM –PMBA) graft copolymer was removed by centrifugation with 90% commercial ethanol at 25°C. The stirring/centrifugation process was repeated many times for six hours in order to remove any trace quantities of unwanted, attendant homopolymer and residual monomer. The extracted poly (MBA)-CMS* graft copolymer was oven dried at 100 ± 5°C and kept dry for the analyses.

Dried at then kept over P_2O_2 for at least 48h before analysis.

3-3-Analyses and characterizations

3-3-1- Degree of Substitution

The DS of the carboxymethylated cellulose (CMS) samples was determined via determination of the carboxyl content according to a reported method (10)

3-3-2- Nitrogen content percent (N%)

The Nitrogen content percent (N%) was calculated via a quantitative estimation of the grafting of the poly(MBA)-CMS components, before and after the polymerization process, according to a Kjeldahl method (11-12)

4- Results and discussion

4-1- Effect of MBA Concentration on the nitrogen content (N%) of CMS PAAM –PMBA graft copolymer

Table (1) demonstrates the effect of the crosslinker concentration on nitrogen content (N %) of CMS PAAM –PMBA product. According to Figure (1), the nitrogen content (N%) is decreased with increasing the crosslinker concentration. It is a well-known rule in all of hydrogels that a small increase in degree of crosslinking causes an appreciable decrease in swelling capacity.2 In fact, more crosslinking concentration causes a higher crosslinking density and decreases the space between the copolymer chains and consequently, the resulting highly crosslinked rigid structure cannot be expanded and hold a large quantity of water. Such well-known behavior has been reported by pioneering scientists, but by adding more amount of the crosslinker the N% increases again and that may related to that the crosslinking reaction takes place through any site in growing polymer chains and opening the double bonds of groups of the crosslinker, and grafting tend to increase with increasing the percentage of crosslinker since the bifunctionality of the crosslinker could be significantly used for reacting with the polymer radicals of the carboxymethyl substrate. (15)

Table (1): Effect of MBA Concentration on the nitrogen content (N%) of CMS PAAM – PMBA graft copolymer

[MBA]gm	**0**	**0.3**	**0.6**	**0.8**	**1**	**2.5**
N% (before)	10.1	11.46	10.56	10.60	10.81	11.87
N% (after)	9.7	9.85	9.46	9.73	10.04	11.4

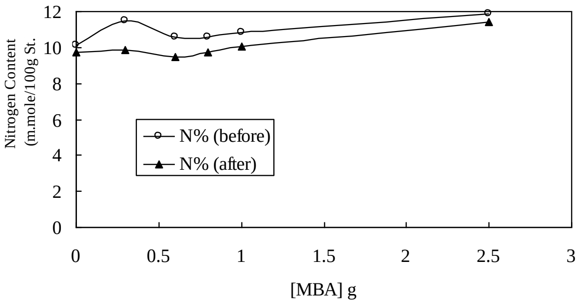

Fig. (1): Effect of MBA Concentration on the nitrogen content (N%) of CMS PAAM –PMBA graft copolymer

4-2- Effect of (AAm) concentration on Nitrogen content of CMS PAAM –PMBA graft copolymer

Next table & figure (2,2) show that the nitrogen content (N %) increases with an increase in the concentration of AAM and the highest result is at 5g of AAm then the nitrogen content decrease at higher concentrations of AAM and that may due to the grafting efficiency decreases when the percentages of the homopolymer and free polymer increase. The increasing homopolymer content may be caused by the formation of polyacrylamide or the random copolymerization of AAm radicals with the monomers, leading to the formation of the ungrafted, free copolymer of AAm. The percentage of grafting efficiency thus decrease which could be caused by an increase in the non-grafted polymers in the solution phase, compared with a heterogeneous phase grafting between the two monomers with the gelatinized starch. (16)

Table (2): Effect of (AAm) concentration on Nitrogen content of CMS PAAM –PMBA graft copolymer

[AAM]gm	0	1	3	5	7
N% (before)	2.2	4.62	7.43	10.5	10.46
N% (after)	1.52	4.51	7.06	10.19	9.89

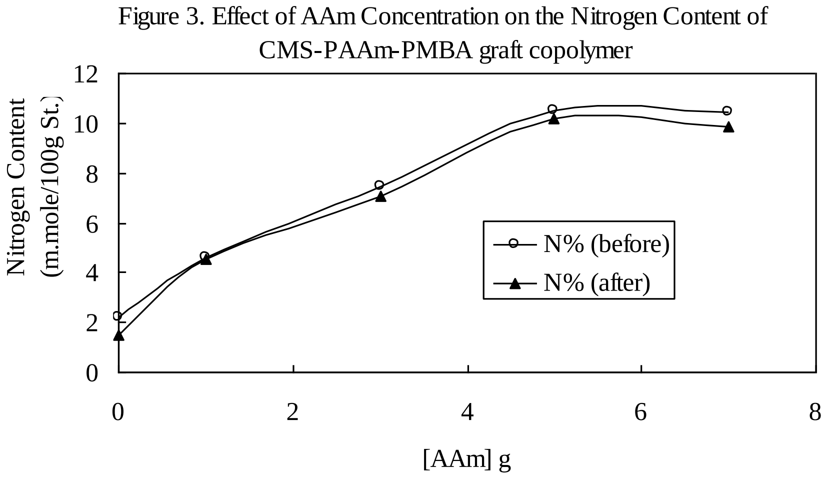

Fig. (2): Effect of (AAm) concentration on nitrogen content (N %) of CMS PAAM –PMBA graft copolymer

4-3-Effect of (APS) concentration of on Nitrogen content (N %) of CMS PAAM –PMBA graft copolymer

Ammonium persulfate (APS) and sodium thiosulfate (STS) were used as the redox initiating system. The reaction between APS and (STS) produces $SO^{-\cdot}$, HO and $S_2O_3^{-\cdot}$ free radical. The kinetic chain length decreases with increasing initiator concentration, which directly affects the molecular weight of the polymer. The mechanisms of the graft copolymerization via the redox system involved the chain transfer reaction. Since free radicals on the CMS are not formed initially, but they are produced through the chain transfer reaction with an existing free radical, significant amounts of homopolymer or free copolymer are often formed by the reaction of initially formed radicals with monomer(s) before chain transfer to CMS can occur. Therefore, the percentage of free polymers increases with increasing concentration of the redox initiator.

The grafting tended to increase with increasing the concentration of initiator, reached an optimum value and then decreased. Free radicals were generated as a result of decomposition of APS in various reactions in the polymerization media to initiate, propagate, and terminate the growing polymer chains. An increase in the concentration of the initiator increases the chance of hydrogen abstraction from the CMS backbone, and chain transfer reaction of the copolymer chain with CMS rendered the grafting to increase. However, the excessive increase in the concentration of APS produced free radical species from the decomposition of APS and (STS) to give the termination reaction with CMS macroradicals or the growing polymer chain or a combination reaction between them. Consequently, the grafting decreased. (15) Figure (3) shows the effect of Ammonium persulfate (oxidant) concentration on the Nitrogen content (N%).

Table (3): Effect of (APS) concentration of on Nitrogen content (N %) of CMS PAAM –PMBA graft copolymer

[APS]gm	**0**	**0.06**	**0.08**	**0.3**	**0.5**
N% (before)	8.59	8.7	8.9	8.53	8.32
N% (after)	7.38	8.6	8.71	8.49	8.38

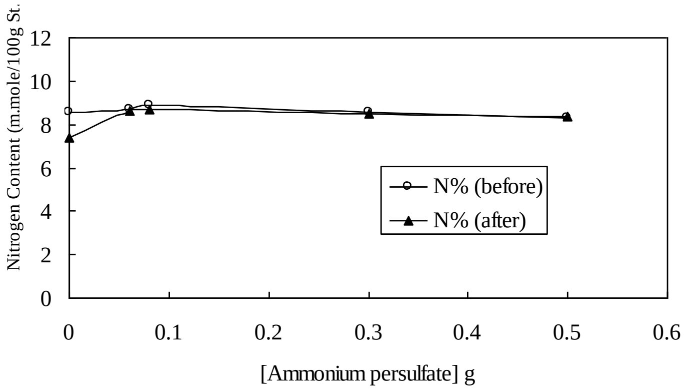

Fig. (3): Effect of APS Concentration on the Nitrogen Content of CMS PAAM –PMBA graft copolymer.

4-4- Effect of (STS) concentration of on Nitrogen content (N %) of CMS PAAM –PMBA graft copolymer

In a simultaneous redox-polymerization and crosslinking process the oxidant and reductant influences to a great extent and also contributes to the degree and molecular weight between the two crosslinking points. In the present investigation, CMS PAAM –PMBA was prepared by employing APS and STS as oxidant and reductant, respectively. As a part of this investigation, the influence of STS concentration on the nitrogen content (N %) of CMS PAAM –PMBA was studied. Reductant (STS) concentration was varied from 0 to 0.5 gm. The results are shown in Figure (4) and table (4) and suggest that the nitrogen content (N %), gradually increases with increase of STS concentration from 0.08 to 0.1 gm. and It is observed that it decreased by increasing the concentration of STS from 0.3 to 0.5 gm, (17)

The redox reaction produces hydrogen sulfate free radical, which directly affects the molecular weight of the polymer. The mechanisms of the graft copolymerization via the redox system involved the chain transfer reaction. Since free radicals are not formed initially, but they are produced through the chain transfer reaction with an existing free radical, significant amounts of homopolymer or free copolymer are often formed by the reaction of initially formed radicals with monomer(s) before chain transfer can occur. Therefore, the percentage of free polymers increases with increasing concentration of the redox initiator and activator (oxidant and reductant).

With increasing the concentration of reductant, reached an optimum value and then decreased. Free radicals were generated as a result of decomposition of APS and STS in various reactions in the polymerization media to initiate, an increase in the concentration of the reductant increases the chance of hydrogen abstraction from the grafted polymer, and chain transfer reaction of the copolymer chain with starch rendered the graft yield to increase, and that may decrease the (N %) of the grafted polymer. (15)

Table (4): Effect of (STS) concentration of on Nitrogen content (N %) of CMS PAAM – PMBA graft copolymer

[STS]gm	**0**	**0.08**	**0.1**	**0.3**	**0.5**
N% (before)	9. 44	8.8	10.64	8.83	8.65
N% (after)	9.2	8.66	10.52	8.66	8.56

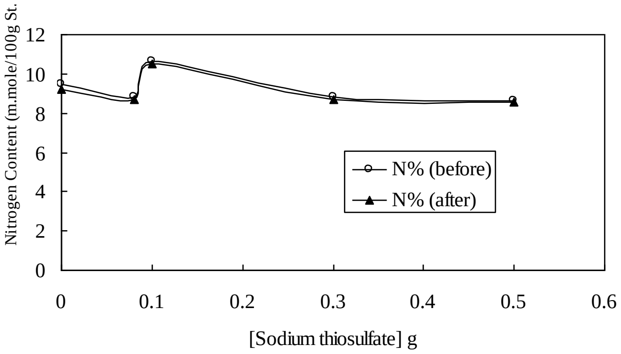

Fig. (4): Effect of STS Concentration on the nitrogen content (N %) of CMS PAAM –PMBA graft copolymer.

4-5- Effect of pH concentration of on Nitrogen content of CMS PAAM –PMBA graft copolymer

The influence of pH (2–4.5) of the redox system on nitrogen content of graft copolymer is shown in Table (5) and figure (5).

The CMS PAAM –PMBA graft copolymer contains carboxylate and carboxamide groups which are the majority of anionic-type superabsorbent polymer.

At a low pH the grafting reaction gives high N%, and then the grafting was found to decrease with pH increases, this decrease in N% may due to that the reaction is begin to go to alkalify and that is effect the efficiency of the reaction.

Table (5): Effect of pH concentration of on Nitrogen content of CMS PAAM –PMBA graft copolymer

pH	**2**	**3.5**	**4**	**4.5**
N% (before)	6. 63	6. 61	6.59	6.17
N% (after)	6.57	6.49	6.25	6. 16

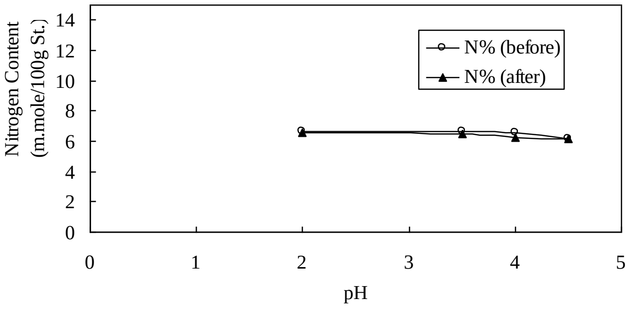

Fig. (5): Effect of pH concentration of on nitrogen content of CMS PAAM –PMBA graft copolymer.

4-6-Effect of reaction temperature on the Nitrogen content of CMS PAAM –PMBA graft copolymer

Fig (6) shows the effect of temperature on the (N %).it is clear that, the raising the temperature from 30 to 90 0C is accompanied by noticeable enhancement in the N%. this can be ascribed (18) to the favorable effect of temperature on: (a) faster decomposition of the initiating system, giving rise to higher density of free radicals, (b) promoting the mobility of free radicals, thereby enhancing the probability of their collision, (c) supplying the system with enough energy to overcome the activation energy barrier of homopolymerization and graft copolymerization reaction. (19)

By increase in the temperature favors the increasing of radical centers, causing high crosslinking points in the hydrogel. So, the swelling capacity of the hydrogel is decreased

Table (6): Effect of temperature on the Nitrogen content of CMS PAAM –PMBA graft copolymer

Temp.	**30**	**50**	**70**	**90**
N% (before)	8. 43	8.71	8.82	8.32
N% (after)	8.26	8.38	8. 39	8.15

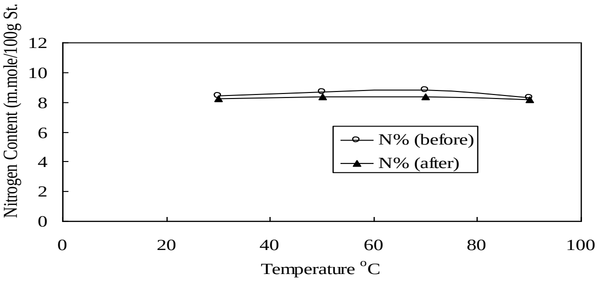

Fig. (6): Effect of reaction temperature of on nitrogen content of CMS PAAM –PMBA graft copolymer.

4-7- Effect of DS on the Nitrogen content of CMS PAAM –PMBA graft copolymer Nitrogen content

The influences of the Degree of Substitution on the grafting reactions are presented in Figure (7). At DS 0.26, the grafting representing in (N %) is rather low. Thereafter, the graft gradually increases. Increasing the DS significantly increases the grafting polymerization that may due to the amount of carboxymethyl groups affect the grafting. (20)

Table (7): Effect of DS on the Nitrogen content of CMS PAAM –PMBA graft copolymer Nitrogen content

DS	**0.26**	**0.29**	**0.35**
N% (before)	6. 62	6.76	9.7
N% (after)	6.49	6. 53	9.3

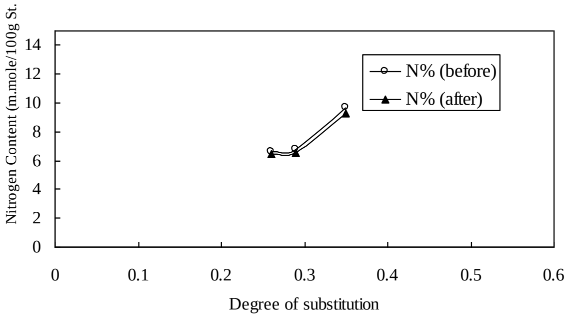

Fig. (7): Effect of DS of on nitrogen content of CMS PAAM –PMBA graft copolymer.

4-8- Effect of CMS load on the Nitrogen content of CMC-PMBA graft copolymer

The Effect of CMS load on the Nitrogen content of CMC-PMBA graft copolymer is presented in Table (8). It is seen that with increasing the amount of CMS, the grafting decreasing, and that may have attributed to the increasing of the carboxy groups and hydrophilic group which the residue monomer concentration in the reaction mixture which leads to increasing of radical centers, causing high crosslinking points in the hydrogel. So, the swelling capacity of the hydrogel is decreased

Table (8): Effect of CMS load on the Nitrogen content of CMS PAAM –PMBA graft copolymer

CMS Load	**1**	**3**	**5**	**7**	**9**
N% (before)	12.51	10.54	8.32	7.35	6.61
N% (after)	11.6	9.84	8.15	7.21	6.49

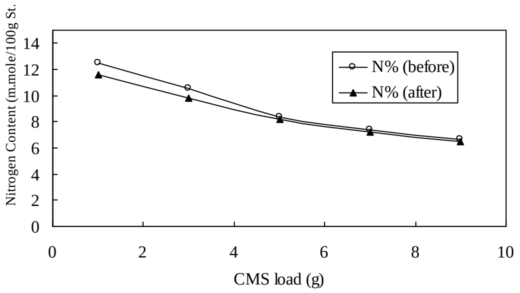

Fig. (8): Effect of CMS load on nitrogen content of CMS PAAM –PMBA graft copolymer

Conclusion

The maximum nitrogen content (N %) was achieved under the optimum conditions of poly CMS that found to be CMS (DS 0.26) 1gm, APS =0.08g, Sod thiosulfate =0.5g, MBA= 0.8 g, AAm = 5 g, water = 1 ml, H_2SO_4 = 3 ml, temp. (90°C) and Time = until reaction completes (1.50 min) that may related to the increasing of the carboxy groups and also hydrophilic group which the residue monomer concentration in the reaction mixture which leads to increasing of radical centers, causing high crosslinking points in the grafted polymer.

Referances

1 Zhang , Jingw , Wu , Dahua, " *Characteristics of the aqueous solution of Carboxymethyl cellulose starch ether* " , Journal of Applied polymer , 46 ,1992, 369-374

2 Ragheb, Amira A. , El-Sayiad , Hassan S., and Hebeish ,A. "*Preparation, characterization and technological evaluation of CMC derived from rice-straw as thickening agents in discharge, discharge–resist and burn-out printing*" , 49 , 1997 , 238-245

3 Kumbasar , E. Perrin Akcakoca ,Bide , Martin , " Reactive dye printing with mixed thickeners on viscose " , Dyes and pigments , 47 , 2000 , 189-199

4 Hebeish ,A., Khalil , M. I., and Hashem , A., *":Carboxymethylation of Maize Starch*" , Starch, 42 , 1990 , 60-63

5 Mostafa , Kh . M., "*Synthesis of poly(acrylamide)-starch and hydrolyzed starch graft copolymers as a size base material for cotton textiles*" , Polymer Degradation and Stability , 55, 1997 , 125-130

6 Mostafa Kh. M., Morsy , M. S., "*Utilization of newly tailored modified starch products in easy-care finishing*" , Carbohydrate Polymers, 55, 2004 , 323-331

7 Al-Karaw ,Ahmed Jasim M. , Al-Daraji , Ali Hussein R._ "*Preparation and using of acrylamide grafted starch as polymer drug carrie*r " ,Carbohydrate Polymers ,79 , 2010 , 769-774

8 1. H. Yangcheng, H. Jiang, M. Blanco, and J. L. Jane, "*Characterization of normal and waxy corn starch for bioethanol production*," Journal of Agricultural and Food Chemistry, 61, 2013 , 379–386 .

9 T. V. Shevchenko, E. A. Kondratov, E. V. Ul'rich, A. M. Popov, V. S. Lobanova, and I. O. Tokmakova, "*On the variation of physicochemical properties of starch samples treated by microwave radiation*," Russian Journal of Applied Chemistry, 86, 2013, 127–131.

10 El-Sheikh , Manal A. , *"A novel photo-grafting of acrylamide onto carboxymethyl starch. 1. Utilization of CMS-g-PAAm in easy care finishing of cotton fabrics"* , Carbohydrate Polymers , 152 , 2016 , 105-118

11 ASTM standard test method E,258-67 ,1987.

12 Vogel , A.I. , "*Elementary Particle Organic Chemistry*" , Part 3, "Quantitive Organic analysis", 2 nd Ed.; Longman Group Ltd, London, 1957

13 Maji ,Tarun Kumar , Banerjee, Amar Nath, "*Photograft copolymerization of methyl methacrylate on silk fiber using titanium(III) chloride–potassium persulphate redox initiator in a limited aqueous system* " I, Journal of Applied Polymer Science, 73, 1999, (2187-2193),

14 C.H Sorum, and J.O. Edwars, J.Amer. Chem.Soc.,74 ,1952

15 Kiatkamjornwongc , S., Lanthong , P. , Nuisin , R. , " *Graft copolymerization, characterization, and degradation of cassava starch-g-acrylamide/itaconic acid superabsorbent",* Carbohydrate Polymers , 2006, 229-245

16 Kiatkamjornwonga , Suda , Chomsaksakul , Wararuk , Sonsukc , Manit , “*Radiation modification of water absorption of cassava starch by acrylic acid/acrylamide“* , Radiation Physics and Chemistry , 59 , 2000 , 413-427

17 P.S. Murthy, Y. Mohan , J. Sreeramulu , K. Mohana ,” Semi-IPNs of starch and poly(acrylamide-co-sodium methacrylate): Preparation, swelling and diffusion characteristics evaluation” , Reactive & Functional Polymers, 66 ,2006 , 1482- 1493

18 .El-Sayed , Z., Fahmy , M.H., Ibrahim , N.A. and Abo Shosa , M.H., "*preparation of polycarboxylic acid/pyrodextrin adducts and Utilization in cotton sizing*", Egyptian Journal of Chemistry , 47 , 2002 , 641-655 .

19 Elzairy , E.m., M.Sc. Thesis "Synthesis, “*Characterization and Utilization of new thickners based on modification of polylol compounds with vinyl monomers in Reactive Printing”* , Helwan University , faculty of Applied Arts , 2003.

20 Bokias , Georges, Durand, Alain and Hourdet , Dominique, *“ Molar mass control of poly(N- isopropylacrylamide) and poly(acrylic acid) in aqueous polymerizations initiated by redox initiators based on persulfates* “ , Macromolecular Chemistry and Physics, 199, 1998, 1387-1392 .