

Maximizing Graft-ability of Poly Methacrylamide Grafted Pregelled Starch Copolymer via Microwave Initiation Method: Synthesis and Characterization

Kh .M. Mostafa^{1*} and A. A. EL-Sanabary²

- 1- King Abdul Aziz University, Vice President of Development, Center of Teaching and Learning Development, P.O. Box 80200, Jeddah 21589, Saudi Arabia
- 2- King Abdul Aziz University, Girl College, Chemistry Department, Al- Faysalia Distribution, Jeddah 21589, Saudi Arabia.

Corresponding author Email : kh_mostafa@hotmail.com

ABSTRACT: Methacrylamide (MAam) as a reactive monomer was efficiently grafted onto pregelled starch (PSt) as a natural carbohydrate polymer by a microwave initiation technique without using initiator in open vessels reactor. The latter, is fast, highly reliable, reproducible and yields high value grafted product when compared to the conventional method. Radiation time, monomer and pregelled starch concentration as well as microwave power were investigated systematically to examine their effect on maximizing the percent graft yield. The resultant microwave synthesized graft copolymer was characterized using fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) in addition to specific viscosity, swelling behavior, flocculation efficiency and Hg²⁺ ion removal. It is seen from the obtained results that (a) the optimum grafting conditions were found to be as follows: pregelled starch, 2 g; methacrylamide, 4 g; microwave irradiation power, 500 W, reaction time 120 S, (b) FT-IR spectral analysis confirmed amide group grafting onto pregelled starch, (c) SEM studies confirmed the surface morphology change in grafted polymer in comparison with undrafted one, (d) the specific viscosity, swelling behavior, Hg²⁺ ion removal and flocculation efficiency of all different levels of the copolymers used are higher than that of pregelled starch as a starting substrate, and (e) microwave initiation method proved to be a very efficient tool in comparison with other chemical initiator systems especially with respect to graft yield.

Keywords: Grafting, Microwave initiated synthesis, Poly methacrylamide grafted pregelled starch, Flocculent

INTRODUCTION

Grafting technique is one of the most effective fascinating fields for chemical modification of polymers with unlimited possibilities for improving the properties of polymers and increases the range of exploitation. While the major difficulty facing us during synthesizing a graft copolymers reaction, is the lack of commercial methods of synthesis and lower percent graft yield. It is well known that, the most important methods of synthesis engage the employ of chemical free radical initiator i.e. conventional method (Mostafa, Kh M. and El-Sanabary, A. A. 2012 , Mostafa et al 2011 , Mostafa, kh M. 1995 , Khalil et al 1993) , high energy radiations i.e. gamma and X-ray (Clough, R. L. 2001, Huq, T. 2012) , UV- radiation based method (Kiatkamjornwonga, et al 2000 , Mubarak, et al 2006) , and recently the microwave based methods (Zhang X, Liu Z. 2012 , Vandana Singha et al 2006) . The conventional method of grafting uses a chemical free radical initiator to generate steady distribution of the free radical sites on the polymer backbone, where the monomer of the graft gets added up to form the graft chain. This method of synthesis has low reproducibility and is not very fit for commercial scale synthesis. A better method than

the above for the graft copolymerization synthesis is by use of high energy radiation (gamma rays or electron beam) as the free radical generator (Wang, et al 2008 , Vahdat, A. et al 2007). But this method is not suitable for grafting onto carbohydrate polymers due to it can cause damage to the polysaccharide backbone (i.e. radiolysis) at the high energy radiation. While, UV rays in presence of suitable photosensitizer can also be used, but low penetration of UV- rays into the bulk of polymer makes it suitable for surface grafting only. The best method of graft copolymer synthesis is by use of microwave radiation to generate the free radical sites on the natural polymer backbone. Recently, the microwave based methods for the synthesis of graft copolymer has been classified into two main types as shown below (Singha, V. et al 2012).

First: Synthesis using microwave initiated method (i.e.) uses microwave radiation alone to create free radical sites on the carbohydrate polymers backbone, from where the graft chains grow.

Second: Synthesis using microwave assisted method (i.e.) uses a blend of microwave radiation and chemical free radical initiator to produce the free radical sites on the carbohydrate polymers backbone, from where the graft chains grow.

Grafted carbohydrate polymers have different applications in different fields of science and technology i.e. flocculant for wastewater treatment (Sen G., et al 2009), medium for controlled drug release (Sen, G., and Pal, S. 2009) and sizing and finishing agents for cotton textiles (Mostafa, Kh.M. and Samerkandy A. R. 2005 , Mostafa, et al 2009). Worldwide, water is considered as the only most essential resource that decides the future of our life. The present ever increasing population and improving standard of live, simultaneously with consuming water resources have put a strong case on recycling of wastewater. Flocculation is an effective means of wastewater treatment as it not only removes the colloidal particles (as floc) but also the heavy metals and other contaminants that get adsorbed in them. Further, these flocculated colloidal particles include most of the microbes present in the wastewater. Also, removal of colloidal particles makes sterilization of the water easy as the microbes cannot get shelter against the colloidal particles and hence gets full exposure to the sterilizing radiations. Flocculation is a technique where polymers are involved in a solid–liquid separation by an aggregation process of colloidal particles. Both synthetic and natural polymers have been utilized for flocculation. The advantage of flocculation over coagulation is that the former uses only polymeric materials in little quantities. These polymeric materials are mostly physiologically inert and are biodegradable (Mostafa and El-Sanabary, in press).

In our recent study reported here, we are trying to tailor what we called poly methacrylamide pregelled starch graft copolymer (PMGPGSC) having different graft yields by microwave initiated method. This was done by measuring the major factors affecting the polymerization reaction with respect to exposure time, monomer and pregelled starch concentration as well as microwave radiation energy (power). Characterization of the prepared copolymer by different physicochemical techniques like FTIR and SEM as well as specific viscosity, swelling behavior and flocculation efficiency in Kaolin suspension in addition to Hg²⁺ ion removal were also studied in details. Furthermore, comparison of the maximum percent of grafting obtained in this study after optimization with the other % of grafting obtained using chemical initiators has been compared. To our best of knowledge, the above method for copolymer synthesis has never been reported before in the literature especially that based on highly swallowed and branched pregelled starch.

MATERIALS AND METHODS

Materials

Pregelged starch having 11.2 % moisture content, 0.07 ash content, 26% amylase and 74 % amylopectin was kindly supplied by Cairo Company for Starch and Glucose, Cairo, Egypt. Methacrylamide was procured from E. Merck, Germany. Analar grade of ethyl and methyl alcohols and hydroquinone were purchased from S.D. Fine Chemicals, Mumbai, India. All the chemicals used were of analytical grade.

Microwave initiated synthesis of poly (MAam)-pregelled starch graft copolymer:

Unless otherwise indicated, pregelled starch (2 gm) was dissolved in 100 ml of double distilled water. Accurate amounts of methacrylamide (0.5 - 5.0 g) were dissolved in 20 ml water and were added to the pregelled starch solution, i.e. the total volume of water was 120 ml. They were mixed well using magnetic stirrer and transferred to the glass conical flask (250 ml). The flask was then placed on the disc spinner of the microwave oven (CE 1111L, Samsung Electronics, India) and microwave irradiated at different values (150 - 600) and various durations (15–180 S) in order to get the optimized irradiation power and duration. At the end of the reaction (i.e. formation of gel

mass), the flasks were placed in ice cooled water. The flasks were kept undistributed for 24 hr to complete the grafting reaction.

Homopolymer removal:

After the desired reaction time, the gel mass poured over 500 ml of ethyl alcohol where a precipitate was formed, which consisted of pregelled starch graft copolymer and the homopolymer. The homopolymer poly (methacrylamide) was removed from the reaction mixture by washing the precipitate five times with 400 ml of water / ethanol mixture (30:70, v/v) for 15 min. at room temperature on magnetic stirrer, filtered and finally dried in an electric oven at 50°C for 3h. It was found experimentally that washing five times with a mixture of water / ethanol mixture (30 / 70, v / v) is quite enough for complete removal of homopolymer in physical mixture of pregelled starch / poly (methacrylamide), by estimating nitrogen content (Vogel, A. I. 1975) of the mixture after each wash until constant value.

N.B. To prepare poly (methacrylamide) - pregelled starch graft copolymers having different graft yields, different amount of methacrylamide ranged from (0.5, 1.0, 1.5, 2.0, 3.0 and 4.0 g) were added to the reaction mixture keeping all other parameters constant.

Estimation of the percent graft yield:

The graft yield was traced by estimating the nitrogen content and was calculated as shown below:

$$\text{Graft yield \%} = \frac{100(N\%).6.07}{100 - (N\%.6.07)}$$

Where;

- N% is the nitrogen percent of the grafted pregelled starch after complete solvent homopolymer removal.
- 6.07 is the molecular weight of MAam / 14.

Proof of grafting:

Based on the well known method and a series of published papers by (Mostafa and El-Sanabary 2012), Mostafa et al 2011), Mostafa and El-Sanabary, in press), proof of grafting was carried out by measuring the nitrogen content with well-known kejeldhal standard method of grafted products three times for each sample, as well as their statistical data (expressed as standard deviation). In other words, both the nitrogen content and standard deviation for each sample were taken as a strong evidence for grafting onto pregelled starch as a carbohydrate polymer that is free from nitrogen groups when used as a starting substrate.

Characterization:

FT-IR Spectroscopy:

The FT-IR spectrums of pregelled starch and poly (methacrylamide)-pregelled starch graft copolymer 51.3 % graft yield were recorded in solid state, by KBr paller method using a FTIR spectrophotometer between 450- 4000 cm^{-1} .

Scanning electron microscopy:

The scanning electron microscopy of pregelled starch and poly (methacrylamide)-pregelled starch graft copolymer has 51.2 % graft yield were analyzed for surface morphology changes via, SEM with a JEOL, JXA-840 A (Tokyo Japan).

Specific viscosity (η_{sp}):

Specific viscosity measurements of poly (MAam) - pregelled starch graft copolymer solutions were carried out with an Ubbelodhe viscometer at room temperature. The viscosities were measured in aqueous solutions. The pH of the solution was neutral. The time of flow for solutions was measured for different poly (MAam) - pregelled starch having different graft yields as well as the pregelled starch as a blank. From the time of flow of polymer solutions (t) and that of the solvent (t₀), for distilled water), relative viscosity (t/t₀) was obtained, and then the specific viscosity was calculated from it as shown below:

Specific viscosity = Relative viscosity – 1.

Swelling behavior in polar and non polar solvents:

The swelling behavior of pregelled starch (blank) and poly (MAam) - pregelled starch graft copolymers having different graft yields was studied in different solvents such as water, ethanol, dimethyl Formamide (DMF), and carbon tetrachloride (CCl₄). Dry samples of pregelled starch and grafted pregelled starch (1.0 g) were suspended in 100 ml of solvents and kept at 30°C for 12 hrs. The samples were then weighted to get the final weight. The percent swelling was calculated as per Mostafa et al. method.

Study of Hg 2+ ions removal:

An aqueous solution of Hg²⁺ metal ions (about 200 ppm) was prepared by dissolving an accurately mercuric acetate (Hg (CH₃CO₂)₂, 0.33 g) in distilled water (1 L). Poly (MAam) - pregelled starch graft copolymers (0.5 g and 51.3 % graft yield) were then added to the metal ion solutions (100 ml), and the dispersion was stirred for 20 min at room temperature (26°C ± 0.5) to form a complex with the metal ions. The grafted pregelled starch- heavy metal ions complex was then removed by filtration and the filtrate was used for the residual metal analysis. After the metal ion solution was treated with the grafted cross-linked starch, residual metal ion content in the filtrate was measured by a colorimetric method using Atomic absorption spectrophotometer. Each sample was measured three times each in addition to their standard deviation.

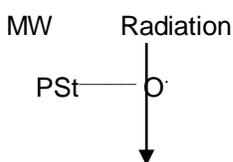
Flocculation studies:

Flocculation efficiencies of poly (MAam) - pregelled starch graft copolymer having different graft yields were studied by standard jar test procedure, in 0.25% kaolin suspension using jar test equipment. The procedure involved taking a calculated amount (800 ml) of the 0.25% suspension in 1000 ml beaker. Calculated amount of the flocculants (Pregelled starch or poly (MAam) - pregelled starch graft copolymers having different graft yield) were added in concentrated solution form (except in case of blank, where no flocculant was added) to get the desired concentrations (ranging from 0 ppm to 0.75 ppm). The solutions were stirred identically (i.e. in ‘jar test’ equipment), at 150 r.p.m for 60 S and another 60 r.p.m for 5 min followed by 30 min of settling time. Afterwards, supernatant liquid was collected and the turbidity was measured in a calibrated nepheloturbidity meter spectronic 20D+ apparatus.

RESULTS AND DISCUSSION

Tentative mechanism of grafting via Microwave Radiation (MWR):

Initiation:

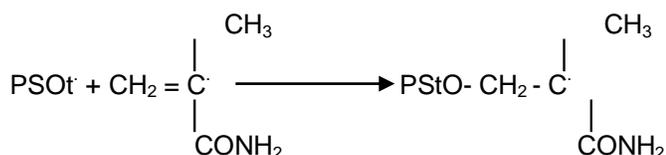


Where,

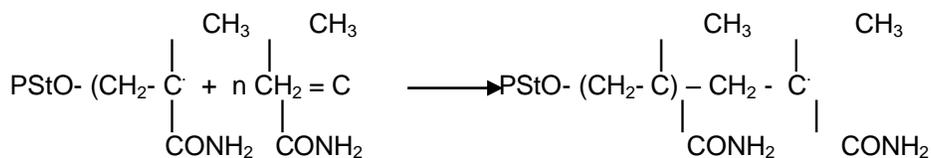
- PSt-OH and PSt-O[•]: Pregelled starch and pregelled starch macro radical.
- MWR: Microwave radiation

Propagation:

In presence of synthetic vinyl monomer, pregelled starch radical is added to the double bond of the vinyl monomer, resulting in a covalent bond between monomer and pregelled starch with creation of a free radical on the monomer, i.e., a chain is initiated. Subsequent addition of monomer molecules to the initiated chain propagates the grafting reaction onto pregelled starch as follows:

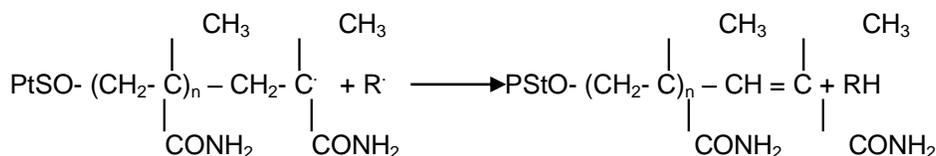


Graft Propagation:

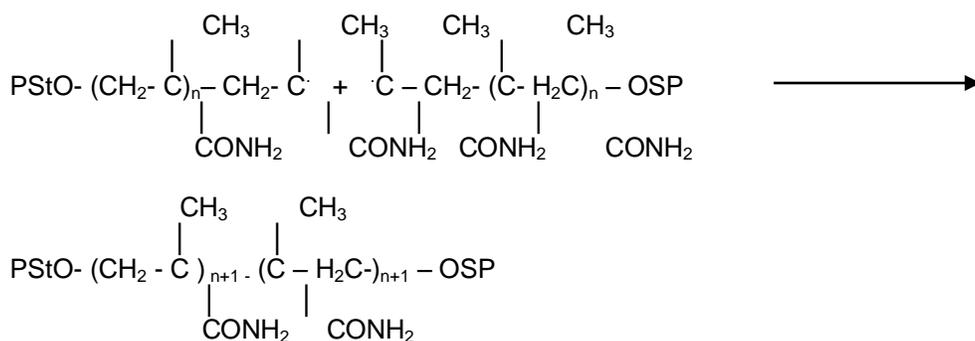


Termination:

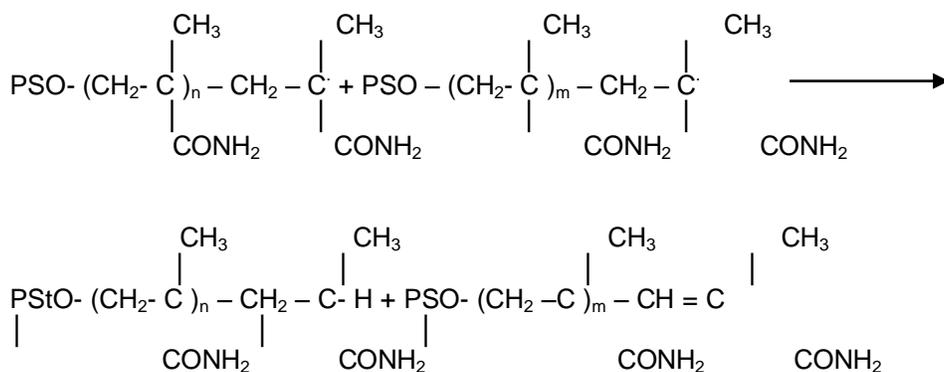
Finally, termination of the growing grafted chain may occur via reaction with the initiator, coupling or combination and disproportionation as follows:



(Graft termination by initiator radical)



(Graft termination by coupling or combination)



(Graft termination by disproportionation)

Optimization of the grafting parameters:

Grafting of methacrylamide as a reactive monomer onto pregelled starch backbone (as a reactive carbohydrate polymer) was achieved by microwave initiation method. The optimum grafting conditions were obtained by applying the grafting reaction protocol as one condition was varied for a set of reaction conditions, keeping other reaction parameters constant. This was done to see the suitability of microwave irradiation method as a green tool for expansively formation of green products through reduction of organic solvents and exposer time in addition to

maximizing the % graft yield as well as exhibiting better properties for commercial utilization than their conventionally synthesized counterparts.

Effect of exposure time:

Figure 1 shows the effect of exposure time on the percent graft yield of poly (MAAm) - pregelled starch graft copolymer. Details of the conditions used are given in the text. It was shown in Figure 1 that, there is an increase in percent graft yield as the exposure reaction time increases from 15 to 120 S and then levels off as the reaction time increases to 180 S. The initial increase in % grafting may be attributed to the addition of greater numbers of MAAm molecules to the growing grafting chains. The latter leveling off could be associated with depletion in monomer and initiator concentrations as the reaction proceeds. Furthermore, during the course of grafting, pregelled starch undergoes modification and becomes may be less amenable to grafting.

Effect of methacrylamide concentration:

Figure 2 declares the effect of changing MAAm concentration on the percent graft yield of poly (MAAm) - pregelled starch graft copolymer using the optimum 120 S exposure time obtained above in section 3.1.1. Details of the conditions used are given in the text. It is clear from the data that there is a direct relation between the percent graft yield and monomer concentration within the experimental range studied, the higher the MAAm concentration the greater availability of the latter in the vicinity of pregelled starch as well as the molecular collision of the reactants. Besides, the microwave radiation rotates the methacrylamide molecules, leading to elongation of its C-C double bond at which the pi bond electron cloud splits up into two localized clouds (i.e. free radical sites on the basic carbon atoms). Both the free radical sites that created on the pregelled starch backbone and that on the methacrylamide by microwave radiation interact through common free radical reaction mechanism, to yield poly (methacrylamide) - pregelled starch graft copolymer.

Effect of microwave irradiation power:

Figure 3 clarifies the effect of microwave irradiation power as one of the powerful controlling factors affect the percent graft yield of poly (MAAm) - pregelled starch graft copolymer using 120 S exposure time and 4 g methacrylamide concentration. To optimize the microwave power, reaction was preceded from 150 to 600 W. It is clear that, the percent graft yield increases initially with increasing microwave power up to 500 W then decreases thereafter. This can be explained in the manner of, when the microwave radiation power increases up to 500 W, the rotation of the methacrylamide molecules increased, which leads to more and more elongation of its bond. As the C-C double bond elongates more, the pi bond electron cloud splits up into two localized clouds (i.e. free radical sites on the constituent carbon atoms). Both the free radical sites thus created on the pregelled starch backbone and that on the methacrylamide by microwave radiation interact rapidly through usual free radical reaction mechanism, to yield higher graft yields of the prepared copolymer. Saying on other word, higher grafting may be account to the more availability of microwave energy at higher microwave power, which causes more and more monomer and macro radical generation. On the other hand, after 500 W microwave power, the decrease in percent graft yield may be attributed to more homopolymer formation at higher microwave powers or to some decomposition of the graft copolymer at higher microwave power.

Pregelld starch dose:

Figure 4 declares the effect of pregelled starch concentration as a starting substrate for grafting MAAm via microwave initiated method using 120 S exposure time and 4 g methacrylamide as well as 500 W microwave powers. This was done by varying the pregelled starch concentration from 0.5 to 3 g. It is seen in Figure 4 that, the percent graft yield of poly (MAAm) - pregelled starch graft copolymer increases by increasing the pregelled starch concentration. This may be attributed to the fact that availability of more and more grafting sites at pregelled starch resulting in enhancement in graft ability.

Optimal Condition for grafting using microwave initiation method:

About 51.3 % graft yield may be obtained by maintaining the following reaction conditions: Pregelled starch, 2.0 gm; [MAAm], 4 gm; exposure time, 120 S; microwave irradiation power, 500 W; material to liquor ratio, 1:60.

Characterization:

Specific viscosity (η_{sp}):

Pregelld starch as a starting substrate and six levels of poly (MAAm) - pregelled starch graft copolymers having different graft yields with increasing order i.e. 12.5-51.3 and designated as PMPSGC-1 to PMPSGC-6 were

monitored for specific viscosity as mentioned in Figure 5. Details of the conditions used are given in the text. It is well known that, the specific viscosity is taken as a strong evidence for the molecular size (weight) of polymer. Hence higher specific viscosity (i.e. higher hydrodynamic volume) would imply higher molecular size i.e. higher graft yield. It is obvious that the specific viscosities of all different levels of the aforementioned copolymers are greater than that of pregelled starch as a starting substrate. This can be explained by the higher molecular weight of the copolymers than pregelled starch, due to the grafting of the poly methacrylamide branches on the main polymer backbone.

Swelling behavior:

Percent swelling (PS) of pregelled starch and poly (MAam)- pregelled starch graft copolymers having different graft yields in different polar and non polar solvents namely water, methanol, DMF and CCl_4 is shown in Figure 6. It is well known that, pregelled starch possesses only hydrophilic $-\text{OH}$ groups, which have certain affinity to water. Consequently pregelled starch showed maximum swelling with polar solvents like water and to lesser extent with methanol and the least swelling with non polar solvents like DMF and CCl_4 . It can also be observed from the Figure that percent swelling of poly (MAam) - pregelled starch graft copolymers increased by increasing the degree of grafting and was found to be about 22 % higher than pregelled starch in distilled water at higher grafting level (i.e. PMPSSGC-6).

While, the percent swelling in ethanol and DMF at higher grafting level i.e. PMPSSGC-6 was also higher, while the percent swelling in CCl_4 was less than of the pregelled starch. The lower percent swelling of poly (MAam) - pregelled starch graft copolymers in CCl_4 was due to the less interaction of CCl_4 with the introduced grafted functional CO-NH_2 groups in comparison to the hydroxyl groups that already present in pregelled starch.

Flocculation studies:

The flocculation study in 0.25% kaolin suspension in 'jar test' apparatus has been graphically represented in Figure 7. The entire poly (MAam) - pregelled starch graft copolymers (PMPSSGC-1 to PMPSSGC-6) has shown better flocculation efficiency than pregelled starch. This is due to the higher hydrodynamic volume (i.e. specific viscosity) of the former, as we explained before in Figure 5. The higher hydrodynamic volume of the graft copolymer macromolecule leads to its higher flocculation efficiency. Furthermore, among the different levels of aforementioned copolymers, the higher grafting grade (PMPSSGC 6) showed maximum flocculation efficiency due to its highest hydrodynamic volume. A strong correlation is evident between percent grafting, specific viscosity and flocculation efficiency, as already stated before. For all the polymers, there is an optimal concentration at which the flocculation caused by it is maximum (i.e. the turbidity of the supernatant collected is minimum). Beyond this dosage, the flocculation decreases (i.e. turbidity of the collected supernatant increases) due to destabilization of the flocs formed by the excess polymers (Mostafa and El-Sanabary, in press).

On the other hand, the flocculation curve confirms the bridging mechanism (Amal A. A. 2006), Khalil M. I. and Amal, A. A. 2001), Karmakar, G. P., Singh, R. P. 1998) involved behind the phenomenon. According to bridging mechanism, when long chain polymers in small dosage are added to a colloidal suspension, they get adsorbed onto two or more particle surfaces and thus form a bridge between them. There should be enough unoccupied space on the particle surface so as to form the polymer bridging. This phenomenon is observed up to a particular dosage of polymer beyond which flocculation diminishes, the process being known as steric stabilization. As a result, at lower dosages of polymer, no major bridging occurs between and hence flocculation remains low. Similarly at higher dosages of polymer, there is insufficient particle surface for attachment of the polymer segments leading to destabilization of flocs. The optimal dosage of PMPSSGC-6 as flocculant, in 0.25% kaolin suspension is at 0.75 ppm.

Hg²⁺ ions removal:

Five levels of poly (MAam) - pregelled starch graft copolymers prepared by microwave irradiation technique their graft yields ranged from (12.5 – 51.3 %) were used for removing Hg^{+2} metal ions from its solutions at a concentration (about 200 ppm). Details of the conditions used are set out elsewhere. The obtained results are set out in Figure. 8. It is seen from Figure 8 that, the residual amount of Hg^{+2} metal ions removed is governed by the percent graft yield. So, when the graft yield increased from 16.5 – 51.3 % the residual removal of Hg^{+2} heavy metal increased. This may be due to higher graft-ability, would offer more additional metal binding sites i.e. CONH_2 groups.

FT-IR Spectroscopy:

From the FTIR spectrum of pregelged starch (Figure. 9 [1]), it is being observed that a broad peak at 3603.03 cm-1 is due to the stretching vibration of O-H groups. A smaller peak at 2887.44 cm-1 attributed to the C-H stretching vibrations. The bands at 985.62 cm-1 and 929.69 cm -1 are assigned to C-O-C stretching vibrations. In case of Poly (methacrylamide)-pregelged starch graft copolymer has 51.3 % graft yield (Figure. 9 [2]), O-H stretching band of hydroxyl group of pregelged starch and N-H stretching band of amide group of poly methacrylamide overlap with each other and lead to a peak at 3728.40 cm-1 and a shouldered peak at 3628 cm-1. A small peak at 3030 cm-1 is attributed to the C-H stretching vibration. The bands at 881.47 cm-1 and 829.29 cm-1 are assigned to C-O-C stretching vibrations. The appearance of a sharp peak at 1791.87 cm-1 and at 1504.48 cm-1 for Poly (methacrylamide)-pregelged starch graft copolymer has 51.2 % graft yield are attributed to C=O and N-H stretching (i.e. Amide I and amide II stretching) respectively. Further, there is one more additional peak present in grafted product i.e. at 1334.74 cm-1, which is assigned to the C-N stretching. Thus, the presence of these additional peaks in case of grafted starch compared to that of starch confirms the successful grafted of MAam chains onto the backbone of pregelged starch.

Scanning electron microscopy (SEM) analysis:

It is obvious from the SEM micrographs of pregelged starch (Figure. 10 [1]), and that of the higher grade of Poly (methacrylamide)-pregelged starch graft copolymer has 51.3 % graft yield (Figure. 10 [2]), that intense morphological change, in form of transition from granular to tie or lace like structure, have taken place because of grafting of MAam chains onto pregelged starch. Thus, it is evident that the grafting morphology of pregelged starch is missing after grafting and transformed into lacy morphology.

Comparison with other chemical initiators:

In order to justify the efficiency of initiation process using the microwave tool as in our case and other chemical initiators process with respect to % graft yield. We introduced the maximum graft yield % obtained in the literature using various chemical initiators under the most appropriate grafting conditions established. Table I shows the higher % graft yield values obtained using various type of chemical initiator used under the optimum condition of grafting. It is shown from the cited data in table I that, % graft yield using microwave initiation technique showing higher value than that other chemical initiators used, which reflects the privilege of using microwave initiation technique for grafting process over the other chemical initiation systems. Indeed, microwave irradiation comprehensively form green products via reduction of the organic solvents and exposer time used in addition to maximizing the % graft yield as well as exhibiting better properties for commercial utilization than their conventionally synthesized counterparts.

Table 1. Comparison between initiation method using microwave alone and cited chemical initiation tools with respect to % graft yield

Types of chemical initiator	Graft Yield %	References
Vanadium-mercaptoposuccinic acid redox pair	26.5	23
Potassium permanganate/ nitric acid system	38.6	24
Potassium persulphate	22.94	25
Bormate/ cyclohexanone redox system	40.9	26
Potassium monopersulphate/ Fe2+ redox pair	24	27
Potassium persulphate/ tetramethylene Diamine redox system	37.5	28
Ceric ammonium nitrate	47	29
Microwave initiation method	51.3	Our work

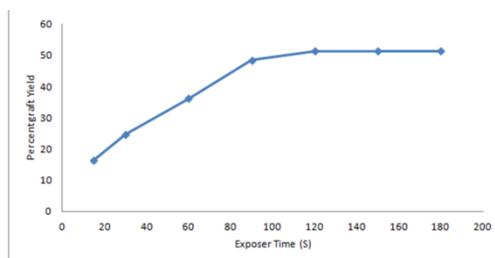


Figure. 1. Effect of exposer time on percent graft yield of poly (methacrylamide)-pregelged starch graft copolymer

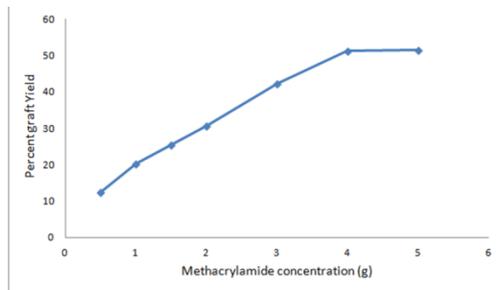


Figure. 2. Effect of methacrylamide concentration on percent grafting of poly (methacrylamide)-pregelled starch graft copolymer

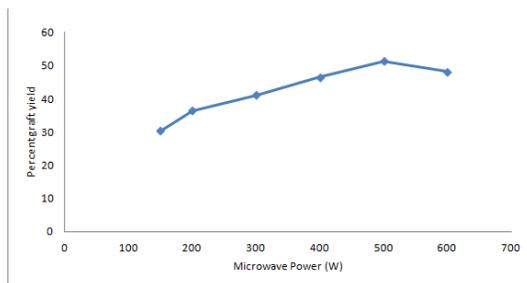


Figure. 3. Effect of microwave power on percent grafting of poly (methacrylamide)-pregelled starch graft copolymer

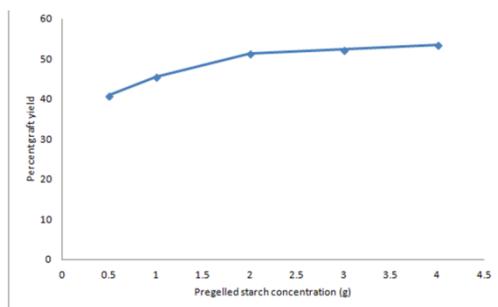


Figure. 4. Effect of pregelled starch concentration on percent grafting of poly (methacrylamide)-pregelled starch graft copolymer

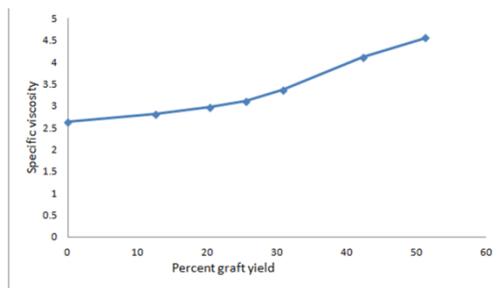


Figure. 5. Relation between percent graft yield of poly (methacrylamide)-pregelled starch graft copolymer and the specific viscosity

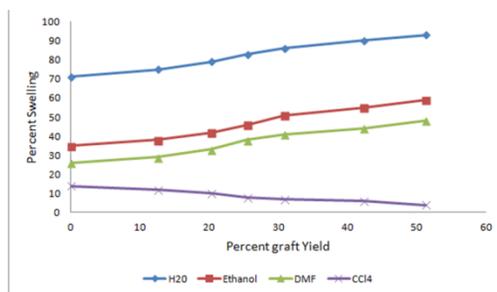


Figure 6. Effect of percent grafting of poly (methacrylamide)-pregelled starch graft copolymer on swelling behavior using different solvent

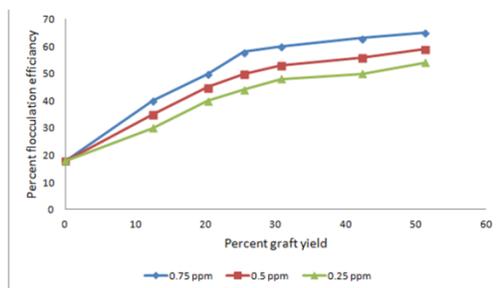


Figure 7. Flocculation efficiency percent of pregelled starch and poly(MAam)-pregelled starch graft copolymers at different doses

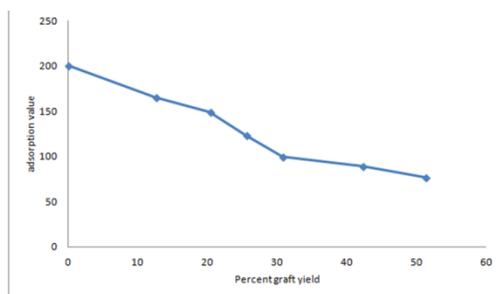


Figure 8. The adsorption value of Hg²⁺ on poly (MAam)-pregelled starch graft copolymers having different graft yields.

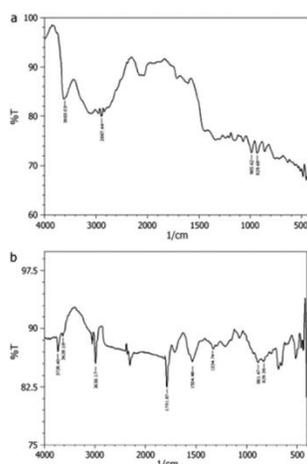


Figure 9. FTIR spectrum of (a) pregelled starch and (b) Poly (methacrylamide)-pregelled starch graft copolymer having 51.3 % graft yield.

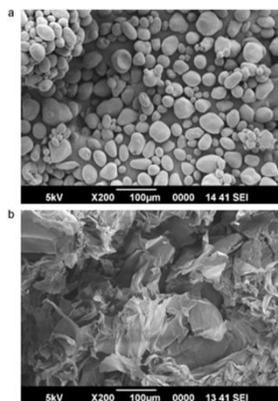


Figure 10. SEM micrograph of (a) pregelged starch and (b) Poly (methacrylamide)-pregelged starch graft copolymer having 51.3 % graft yield.

CONCLUSION

Poly methacrylamide pregelged starch graft copolymer has been synthesized by microwave initiation method which involves microwave radiation alone to initiate grafting without using of chemical initiator. The synthesized grades of the graft copolymer were characterized through various physicochemical techniques. The % graft yield was found to be the highest value when using 120 S as exposure time and 500 W microwave power in addition to 4 and 2 gram methacrylamide and pregelged starch respectively. Furthermore, the resultant copolymers were found to be of higher specific viscosities, swelling behavior, and Hg²⁺ ion removal as well as flocculation efficiency in kaolin suspension than pregelged starch as a starting substrate. Beside, FT-IR spectral analysis and SEM confirmed the grafting of methacrylamide onto pregelged starch backbone and surface morphology change in the resultant copolymer in comparison with pregelged starch as a parent substrate. Finally, microwave initiation technique showed the privilege in obtaining higher graft yield % with respect to other chemical initiation systems.

REFERENCES

- Mostafa, Kh. M. and El-Sanabary, A. A. 2012. Harnessing of Novel Tailored Modified Pregelged Starch Derived Products in Sizing of Cotton Textiles, *Advances in Polymer Technology*, Vol. 31, No. 1, 52–62.
- Mostafa, Kh. M., Samarkandy, A. R. and El-Sanabary, A. A. 2011. Grafting onto Carbohydrate Polymer Using Novel Potassium Persulphate/Tetramethylethylene Diamine Redox System for Initiating Grafting, *Advances in Polymer Technology*, Vol. 30, No. 2, 138 –149.
- Mostafa, Kh. M. 1995. Graft polymerization of acrylic acid onto starch using potassium permanganate acid (redox system), *Journal of Appl. Polymer Sci.*, 56, 263-269.
- Khalil, M. I., Mostafa, Kh. M. and Hebeish, A. 1993. Graft polymerization of acrylamide onto maize starch using potassium persulfate as initiator, *Die Angewandte Macromoleculare Chemie*; 213, 14.
- Clough, R. L. 2001. High-energy radiation and polymers: A review of commercial processes and emerging applications, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 185, (1–4), 8–33.
- Huq, T., Khan, A. , Dussault, D. , Salmieri, St. , Khan, R. A. , Lacroix, M. 2012. Effect of gamma radiation on the physico-chemical properties of alginate-based films and beads, *Radiation Physics and Chemistry*, 81, 8, 945–948.
- Kiatkamjornwonga, S., Chomsaksakulb W., Sonsukc, M. 2000. Radiation modification of water absorption of cassava starch by acrylic acid/acrylamide, *Radiation Physics and Chemistry*, 59, 4, 413–427.
- Mubarak, A. K., Bhattachariaa, S. K., Kaderb M. A., Baharic, K. 2006. Preparation and characterization of ultra violet (UV) radiation cured bio-degradable films of sago starch/PVA blend, *Carbohydrate Polymers*, 63, 4, 18, 500–506.
- Zhang X, Liu Z. 2012. Recent advances in microwave initiated synthesis of nanocarbon materials, *Nanoscale*, 4 (3) 707-714.
- Vandana Singha, Devendra Narayan Tripathia, Ashutosh Tiwaria, Rashmi Sanghib (2006). Microwave synthesized chitosan-graft-poly(methylmethacrylate): An efficient Zn²⁺ ion binder, *Carbohydrate Polymers*, 65, 1, 10, 35–41.
- Wang, J. P., Chen, Y. Z., Zhang, S. J., Yu, H. Q. 2008. A chitosan - based flocculant prepared with gamma-irradiation-induced grafting, *Bioresour. Technol.* 99, 3397–3402.

- Vahdat, A., Bahrami, H., Ansari, N., Ziai, F. 2007. Radiation grafting of styrene onto polypropylene fibres by a 10 MeV electron beam, *Phys. Chem.* 76, 787–793.
- Singha, V., Kumara, P. Sanghib, R. 2012. Use of microwave irradiation in the grafting modification of the polysaccharides – A review, *Progress in Polymer Science*, 37, 2, 340–364.
- Sen G., Kumar, R., Kumar, S., Pal, S. 2009. A novel polymeric flocculants based on polyacrylamide grafted carboxymethylstarch, *Carbohydrate Polymer*, 77, 822–831.
- Sen, G., Pal, S. 2009. Microwave initiated synthesis of polyacrylamide grafted carboxymethylstarch (CMS-g-PAM): Application as a novel matrix for sustained drug release, *International journal of biological macromolecules*, 45, 48–55.
- Mostafa, Kh.M. and Samerkandy A. R. 2005. Synthesis of New Polymeric Composite Materials and its Application in sizing of Cotton Textiles, *Research Journal of applied Sciences*, 1 (5), 353-340.
- Mostafa, Kh.M. and Samerkandy A. R. and El- Sanabary, A. A. 2009. Using Persulfate Oxidized Chitosan as a Novel Additives in Easy-Care Finishing for Cotton Textiles, *Polymer Plastic Technology & Engineering*, 48, 2, 130-135.
- Mostafa, Kh. M. and El- Sanabary, A. A. Synthesis and Characterization of Novel Smart Flocculant Based on Poly (MAam) – Pregelled Starch Graft Copolymers and Their Degraded Products. *Advances in Polymer Technology*, accepted for publication.
- Vogel, A. I. 1975. *Elementary Practical Organic Chemistry*, 2nd ed.; Longman: London, Part 3, p 652).
- Amal A. A. 2006. Preparation, Characterization and Evaluation of Anionic Starch Derivatives as Flocculants and for Metal Removal, *Starch/ Stärke*, 58, 391–400.
- Khalil, M. I., Amal A. A. 2001. Preparation and Evaluation of Some Cationic Starch Derivatives as Flocculants, *Starch/ Stärke*, 53, 84–89.
- Karmakar, G. P., Singh, R. P. 1998. Flocculation studies using amylase - grafted polyacrylamide, *Colloids Surf. A*, 733, 119-124.
- Mostafa, Kh.M. El- Sanabary, A. A. and Samerkandy A. R. 2007. Modification of carbohydrate polymers: Part2: Grafting of Methacrylamide onto Pregelled Starch Using Vanadium-mercaptopsuccinic acid redox pair, *Journal of Applied Science Research*, 3 (8), 641- 647 2007.
- Mostafa, Kh. M. 2005. Grafting of Methacrylamide onto Cotton Yarn” Part 1: Tensile Strength, *Journal of applied science*, 5 (2), 341-346 2005.
- Nikolic, V., Velickovic, S., Popovic, A. 2012. Amine activators influence on grafting reaction between methacrylic acid and starch, *Carbohydrate Polymers*, 88, 4, 1407–1413.
- Mostafa, Kh.M. and Samerkandy A. R. and El- Sanabary, A. A. 2010. Synthesis and characterization of (poly (N-vinyl Formamide) - Pregelled Starch-graft copolymer. Kh. M. Mostafa, Abdul Rahim Samarkandy and A.A.El-Sanabary, *Journal of Polymer research*, 17, 789 - 800.
- Mostafa, Kh. M. and Morsy, M.S. 2004. Modification of Carbohydrate Polymers via Grafting of Methacrylonitrile onto Pregelled Starch using Potassium Monopersulphate /Fe²⁺ Redox Pair, *Polymer International*, 53, 7, 885-890.
- Mostafa, Kh.M. and Samerkandy A. R. and El- Sanabary, A. A. 2011. Grafting onto Carbohydrate Polymer Using Novel Potassium Persulphate/Tetramethylethylene Diamine Redox System for Initiating Grafting, *Advances in Polymer Technology*, 30, 2, 138–149.
- Sen, G., Kumar, R., Ghosh, S., Pal, S. 2009. A novel polymeric flocculant based on polyacrylamide grafted carboxymethylstarch, *Carbohydrate Polymers*, 77, 4, 19, 822–831.