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Grafting onto carbohydrate polymer using novel potassium persulphate/ tetramethylethylene diamine redox system for initiating grafting

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ABSTRACT

Starch as one of the most abundant, renewable, low cost and biodegradable carbohydrate polymers world wide, suffers from some drawbacks, the most outstanding is a lakes of properties of synthetic polymers. So, modification of starch by graft co polymerization will provide a substantial modification route to alter physical and chemical properties of starch thereby enlarges the range of its utilization. by attaching a flexible synthetic polymer onto the rigid natural polysaccharides backbone without greatly changing the latter. In addition to the main disadvantageous of the above technique are the high % of homopolymer and lower % grafting. At this point, our research team directed the work towards how to maximize the graft yields and graft reaction efficiency % and minimize to lower extent the homopolymer % as well as enhancing the water solubility of the prepared copolymers. Based on the results obtained, appropriate conditions for grafting MAA onto pregelled starch were established and the graft yield is higher under the following conditions: using 10 mmol/L potassium persulfate, 8 mmol/L TMEDA, 50% MAA concentration (based on weight of substrate), liquor ratio, 10, reaction time, 60 min; and polymerization temperature, 60°C. On the other hand, grafting enhanced significantly by adding Fe^{3+}, Cu^{2+} and Li^{1+}in the grafting media and follows the order $Fe^{3+} > Cu^{2+} > Li^{1+}$, in addition to the solubility %. Approximately 37.5 % graft yield and 75 % graft reaction efficiency as well as 25 % homopolymerization were obtained when methacrylic acid was graft co polymerized onto pregelled starch as a reactive carbohydrate polymer using a new redox initiation system namely KPS / TMEDA redox pair. Grafting was also enhanced significantly by adding Fe^{3+}, Cu^{2+} and Li^{1+}in the grafting media and follows the order $Fe^{3+} > Cu^{2+} > Li^{1+}$. Furthermore, notable enhancement in solubility % of grafted samples with lower graft yields than that of higher one.

KEYWORDS

Grafting;
Pregelled starch;
MAA;
Cations;
Water solubility.

INTRODUCTION

Today, natural carbohydrate polymers are modified in such away that their inherent characteristics are enhanced and are thus tailored for particular end use requirements. Starch as one of the most abundant, renewable, low cost and biodegradable carbohydrate polymers world wide, suffers from some drawbacks the most outstanding is a lakes of properties of synthetic polymers[1]. For the last few decades, modification of starch by one of the most fascinating, universal, effective and accessible methods i.e. graft co polymerization that provides a substantial modification route to alter physical and chemical properties of starch, thereby enlarging the range of its utilization by attaching a flexible synthetic polymers onto the rigid natural polysaccharides backbone without greatly changing the latter[2-5]. In addition, the properties of the resulting copolymers may be widely controlled by the characteristics of synthetic side chains, including molecular structure, length and number. In the past, starches have been graft co polymerized by different techniques, most of them are based on free radicals tool that are formed along the backbone of the polymer either by chemical initiators[6-10] or by irradiation[11,12]. The main disadvantageous of the above methods especially that based on chemical method are the high % of homopolymer and lower % grafting except in some cases when using ceric ions and MnO_2 as initiation system[13-16]. To our knowledements as well as our recent depth literature survey, there is no report about the graft co polymerization onto pregelled starch via KPS / TMEDA as a redox initiation system.

For simplicity, our present investigation, is aimed at: (1) optimizing the condition of grafting of MAA onto pregelled starch using KPS / TMEDA as a redox initiation system, to establish the optimum conditions for producing grafted starch with higher graft yield and lower homopolymer %, (2) evaluating the addition of different cations on the graft yield % and (3) measuring the solubility % of different grafted samples (having variable amounts of soluble carboxyl groups) to see their effect on the solubility %.

EXPERIMENTAL

Materials

Pregelled starch was kindly supplied by Egyptian starch and Glucose Manufacturing Company, Cairo Egypt. Methacrylic acid stabilized with 0.01% hydroquinone was freshly distilled at 75C and pressure of 100 mmHg; it was stored at –10°C until used. Potassium persulfate (KPS; analytical grade), Tetramethylethylene diamine (TMEDA; biochemical grade) were used without further purification. Ethyl alcohol and sodium hydroxide were used as supplied.

Polymerization procedure

Unless otherwise indicated, the graft polymerization reaction was carried out in 100 ml flasks containing accurate amount of pregelled starch and aqueous solution of monomer. A liquor ratio 10 was used. The flasks were stoppered and placed in a thermostatic water-bath until the required temperature was reached. Nitrogen gas was purged through this solution to remove the dissolved oxygen. To initiate the reaction calculated amounts of KPS solution and TMEDA solution were added by order and the reaction mixture was mixed thoroughly. The contents were shaken occasionally during polymerization. After the desired reaction time, the flask contents were poured over 500 ml of ethyl alcohol where a precipitate was formed that consisted of pregelled starch graft copolymer and the homopolymer. The homopolymer poly (metacrylic acid) was removed from the reaction mixture by washing the precipitate five times with 500 ml of a water/ ethyl alcohol mixture (30:70) for 15 min on the magnetic stirrer at room temperature, filtered and finally dried in an electric oven at 60^{o}C for 3 hr. It was found experimentally that washing five times with the above mixture is quite enough for complete homopolymer removal in physical mixtures of starch/ poly (metacrylic acid) by tracing the carboxyl content of these mixture after each wash until constant value.

Evidence of grafting

This was done via measuring the carboxyl content of grafted samples by a well-known method (17) three times for each samples, as well as their standard deviation. On other words, both the carboxyl content and the standard deviation for each sample were taken as an evidence of grafting onto pregelled starch as a carbohydrate polymer that is free from carboxyl groups when it used as a starting substrate.

Characterization

The graft yield was traced by estimating the carboxyl content and the graft yield was calculated as follows:

$$\text{Graft yield}(\%) = \frac{100(\text{carboxy content } 0.084)}{100 - (\text{carboxy content } 0.084)}$$

where; 0.084 are the molecular weight of MAA/1000. On the other hand, the graft reaction efficiency percent (G.R.E. %) was calculated as follows:

$$\text{G.R.E.}(\%) = \frac{\text{Graft yield}(\%)}{\begin{array}{c}\text{Percent of monomer based}\\ \text{on weight of starch(bows)}\end{array}} \times 100$$

The amount of homopolymer is quantified according to the following relationship:

Homopolymer % = 100 – G.R.E. %

Solubility %

The solubility % of grafted pregelled starch samples was determined at 70°C calorimetrically according to a reported method[18].

RESULTS AND DISCUSSION

Effect of potassium persulfate concentration (KPS)

Figure 1 shows the effect of potassium persulfate concentration on the grafting parameters (i.e. graft yield, graft reaction efficiency % and homopolymerization %) of poly (MAA) - pregelled starch graft copolymers. It was seen from the drown data that the G.Y.% and G.R.E.% increases by increasing KPS concentration up to 10 mmol/L, but beyond this concentration the G.Y.% and G.R.E.% decreased.

The increase in grafting parameter may be duo to the progressive reduction of potassium KPS by TMEDA via charge transfer producing $(CH_3)_2NCH_2$-$CH_2N(CH_3)CH_2^{\cdot}$ and $^{\cdot}OSO_3H$ free radicals that attack pregelled starch molecule (PS) creating more free radical species that participate mainly in graft initiation as shown below in the proposed reaction scheme[19].

While on the other hand, the reduction in grafting parameter after 8 mmol/L KPS may be explained in terms of KPS may decompose to form HSO_4^- and oxygen molecule (O_2) that acts as a free radicals scavenger i.e. termination[20] according to the proposed equations 1-5.

$$S_2O_8^{2-} \rightarrow 2SO4^{-\cdot} \qquad (1)$$

$$SO4^{-\cdot} + H_2O \rightarrow HSO_4^{-\cdot} + HO \qquad (2)$$

$$2HO^{\cdot} \rightarrow H_2O_2 \qquad (3)$$

$$HO. + H_2O_2 \rightarrow H_2O + HO_2^{\cdot} \qquad (4)$$

$$S_2O_8^{2-} + HO^{\cdot}_2 \rightarrow HSO_4^- + SO_4^{-\cdot} + O_2 \qquad (5)$$

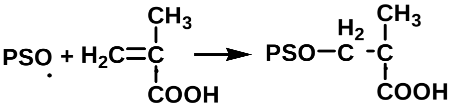
Once the free radical species ($R^{\cdot}$) are formed, they produce pregelled starch macro radical $PS\text{-}O^{\cdot}$ via direct abstracting of hydrogen atoms from pregelled starch molecules. This reaction may be represented as follows:

$$PS\text{-}OH + R^{\cdot} \rightarrow PSO^{\cdot} + RH \qquad (6)$$

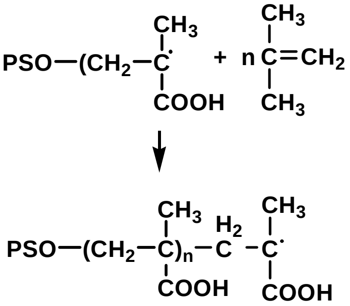
where PS-OH represent the pregelled starch molecule.

In the presence of synthetic vinyl monomer the pregelled starch 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 propogation



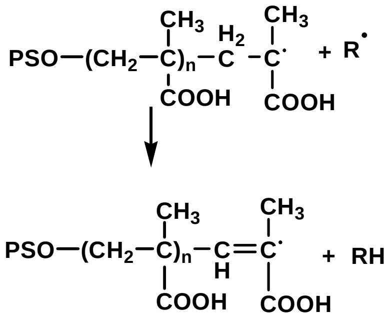
$$PSO^{\cdot} + H_2C{=}C(CH_3)(COOH) \longrightarrow PSO{-}\overset{H_2}{C}{-}C^{\cdot}(CH_3)(COOH) \qquad (7)$$



$$PSO{-}(CH_2{-}C^{\cdot}(CH_3)(COOH) + n\,C(CH_3)(CH_3){=}CH_2 \downarrow PSO{-}(CH_2{-}C(CH_3)(COOH))_n{-}\overset{H_2}{C}{-}C^{\cdot}(CH_3)(COOH) \qquad (8)$$

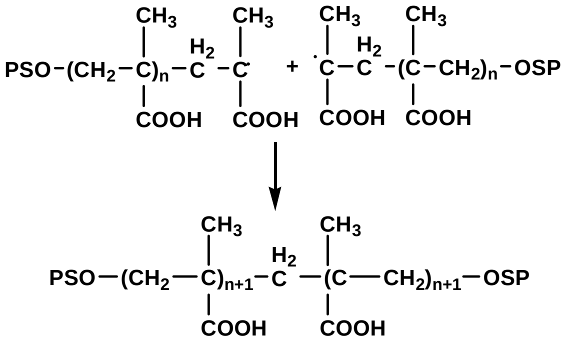
Finally, termination of the growing grafted chain may occur via reaction with the initiator, coupling or combination and disproportionation as follows:

Graft termination by initiator radical



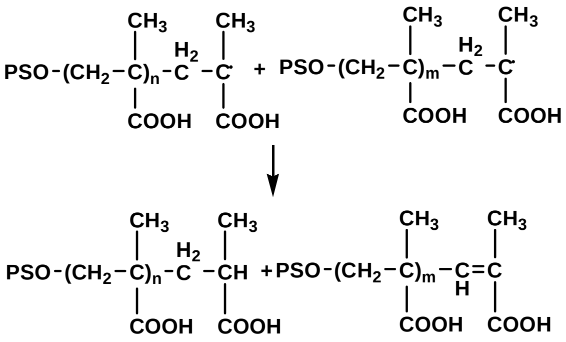
(9)

Graft termination by coupling or combination



(10)

Graft termination by disproportionation



(11)

Effect of TMEDA concentration

Figure 2 declares the effect of TMEDA concentrations on the grafting parameters of poly (MAA)-pregelled starch graft copolymers. Obviously increasing the TMEDA concentrations up to 8 mmol/L is accompanied by an increase in the graft yield but decreases with further increase in the concentration. This can be explained in terms of the increase in the number of free radicals, while the decrease in G.Y. % at higher concentration may be duo to the excess TMEDA further reacts with primary free radical species. The maximum G.R.E. % was observed at 8 mmol/L TMEDA concentration.

Liquor ratio

Figure 3 reveals the dependence of the grafting parameters on the liquor ratio of poly (MAA) - pregelled starch graft copolymer. As is evident increasing liquor ratio up to 10 brings about an outstanding enhancement in the grafting parameter, then decrease when the liquor ratio increases up to 20. It is logical that the volume of the reaction medium increases as the liquor increases. Meanwhile, the amount of the reactant relatively decreases and hence their dilution occurs. This dilution decreases, the collision probability of the reaction ingredients thereby decreasing grafting. Thus the enhancement in grafting upon using a liquor ration of up to 10 suggests that this particular ratio offers the most appropriate environment for the collision probability of the reaction ingredients. Higher ratios, on the other hand, decrease this probability and; as a result decreased grafting is observed.

Effect of MAA concentration

Figure 4 shows the dependence of MAA concentration on the grafting parameters of poly (MAA)-pregelled starch graft copolymer. It is clear from the figure that, there is a direct relation between the graft yield and monomer concentration within the range studied. It is certain, however, that increasing MAA concentration up to 50 % based on weight of starch brings about much more significant enhancement in grafting than upon using MAA over a concentration range of 50-200%. Enhancement in grafting by increasing MAA concentration could be associated with greater availability of MAA molecules in the proximity of starch at higher MAA concentration. Needless to say that the starch macroradicales (sites for grafting are immobile and their reaction with MAA molecule would rely on availability of these molecules in the vicinity of pregelled starch.

While on the other hand, with respect to G.R.E., the results reflect that G.R.E. decreases as the MAA concentration increases, unlike the graft yield. This suggests that, beside its favorable effect on grafting reaction, the concentration of MAA seems to have an outstanding effect on the homopolymerization re-

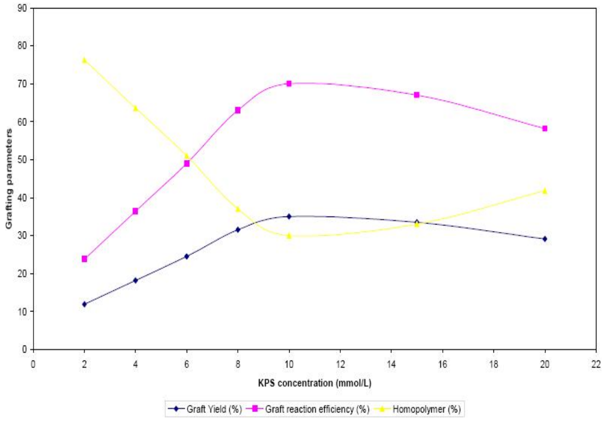


Figure 1 : Effect of potassium persulphate concentrations on the grafting parameters of poly (MAA)-pregelled starch graft copolymers. Reaction conditions: Pregelled starch, 2 g.; [TMEDA], 10 mmol/L; [MAA], (50% based on weight of substrate); liquor ratio, 10; Time, 60 min., and temperature, 60°C

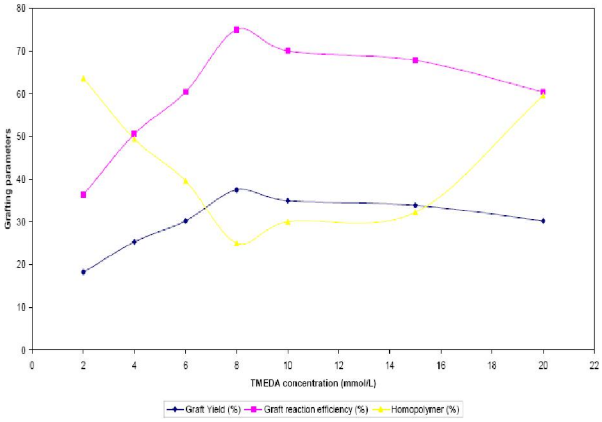


Figure 2 : Effect of TMEDA concentrations on the grafting parameters of poly (MAA) - pregelled starch graft copolymers. Reaction conditions: Pregelled starch, 2 g.; [KPS], 10 mmol/L; [MAA], 50% (based on weight of substrate); liquor ratio, 10; Time, 60 min., and temperature, 60°C

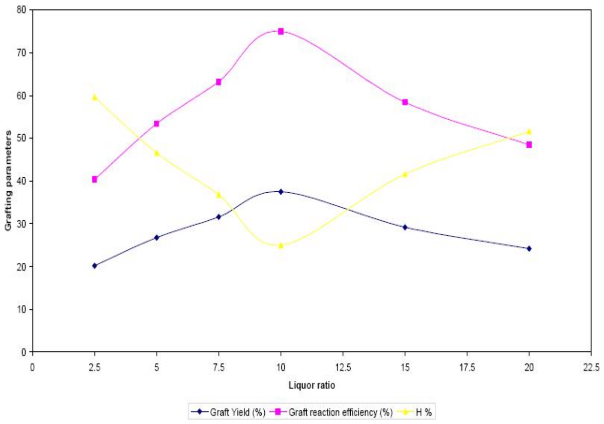


Figure 3 : Effect of liquor ratio on the grafting parameters of poly (MAA) - pregelled starch graft copolymers. Reaction conditions: Pregelled starch, 2 g.; [KPS], 10 mmol/L; [PMPS], 8 mmol/L; [MAN], 50% based on weight of substrate); Time, 60 min., and temperature, 60°C

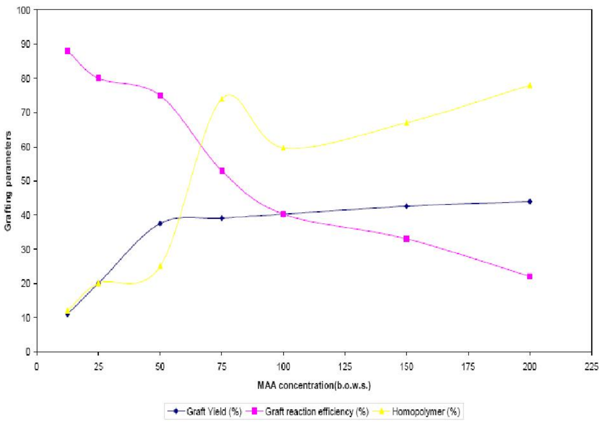


Figure 4 : Effect of methacrylic acid concentrations on the grafting parameters of poly (MAA) - pregelled starch graft copolymers. Reaction conditions: Pregelled starch, 2 g.; [KPS], 10 mmol/L; [PMPS], 8 mmol/L; Liquor ratio, 10; Time, 60 min., and temperature, 60°C

action. Since the grafting reaction competes with the homopolymerization and since the concentration of MAA acts more in favor of the latter and the observed decrement in G.R.E. by increasing MAA concentration can be explained. This is in accordance with the data shown of homopolymerization within the range studied.

Effect of polymerization time

Figure 5 shows the effect of reaction time (period) on the grafting parameters by changing the time of reaction from 15 to 120 min. It is seen figure 5 that, there is an increase in the graft yield and graft reaction efficiency percent as the reaction time increased from 15 to 60 min. then approximately leveled off by increasing the reaction time thereafter. This is seen irrespective of the polymerization temperature used. Increasing the grafting parameter from 15 to 60 min. may be attributed to addition of greater number of MAA molecules to the growing grafted chains. While leveling off grafting parameter after that, could be associated with depletion in monomer and initiator concentration as the reaction proceeds. Beside, it is may also likely that, during the course of grafting, pregelled starch undergoes modification and the modified starch derived thereof is not as amenable to grafting as the unmodified starch, a point which may be taken into consideration when explaining leveling off grafting.

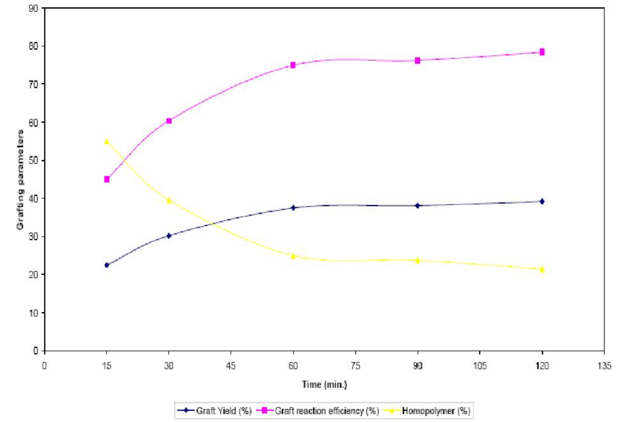


Figure 5 : Effect of reaction time on the grafting parameters of poly (MAA)- pregelled starch graft copolymers. Reaction conditions: Pregelled starch, 2 g.; [KPS], 10 mmol/L; [PMPS], 8 mmol/L; [MAN], 50% based on weight of substrate); Liquor ratio, 10; and temperature, 60°C

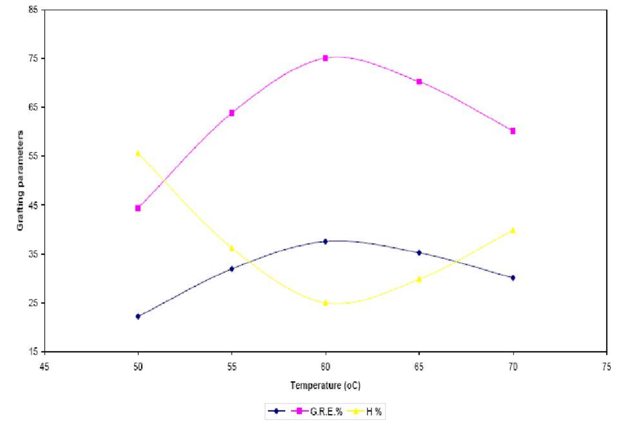


Figure 6 : Effect of polymerization temperature on the grafting parameters of poly (MAA) - pregelled starch graft copolymers. Reaction conditions: Pregelled starch, 2 g.; [KPS], 10 mmol/L; [PMPS], 8 mmol/L; [MAN], 50% based on weight of substrate); Liquor ratio, 10; and time, 60min

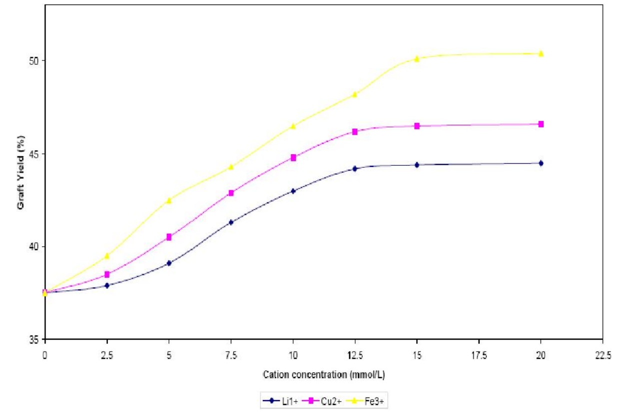


Figure 7 : Effect of different cation concentrations on the graft yield of poly (MAA) - pregelled starch graft copolymers. Reaction conditions: Pregelled starch, 2 g.; [KPS], 10 mmol/L; [PMPS], 8 mmol/L; [MAN], 50% based on weight of substrate); Liquor ratio, 10; time, 60min.; and temperature, 60°C

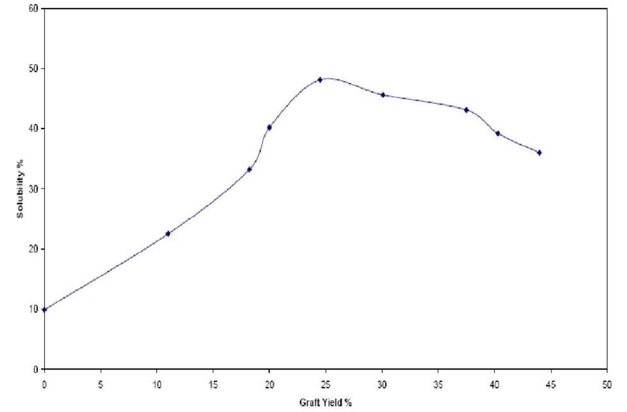


Figure 8 : Solubility % of poly (MAA) - pregelled starch graft copolymers having different graft yields. Reaction conditions: Pregelled starch, 2 g.; [KPS], 10 mmol/L; [PMPS], 8 mmol/L; Liquor ratio, 10; time, 60 min.; and temperature, 60°C

Effect of polymerization temperature

The effect of polymerization temperature on the grafting parameters of poly (MAA)-pregelled starch graft copolymers has been shown in Figure 6. However, the extent of grafting is determined by temperature; the extent of grafting increases by raising the polymerization temperature up to 60°C then decreases by raising the polymerization temperature after that. Results of grafting reaction efficiency are in accordance with those of grafting reaction. This behavior may be explained on the basis of the fact that, the appropriate increase in the temperature favors the activation of pregelled starch backbone and monomer radicals, leading to an increase in graft yields and graft reaction efficiency percent. While on the other hand, the lower grafting observed beyond the optimum temperature above 60°C is, perhaps, duo to faster termination rate. Nevertheless, the possibility of greater amount of homopolymer formation at higher temperature and the adverse effect of this on the graft yield and grafting and graft reaction efficiency % cannot be ruled out.

Effect of adding cations

Figure 8 shows the effect of concentration of Li^{1+}, Cu^{2+} or Fe^{3+} ion in the polymerization medium on the graft yield % of poly (MAA)-pregelled starch graft copolymer. It is clear that; graft yield increases significantly by incorporation of any of these cations in the polymerization system. Moreover, the extent of grafting increases by increasing the cation concentration irrespective of the valancy of the cation used. Nevertheless, trivalent cations, namely Fe^{3+}, bring about the highest grafting while the monovalent cation, namely, Li^{1+} produce the least. Divalent cation, i.e., Cu^{2+}, stand in mid-way position.

That significant enhancement in grafting could be achieved by mere incorporation of the said cations and that the magnitude of this enhancement relies on the valiancy of cation are rather interesting. It is logical to assume that the cation participation in initiation of grafting via accelerating formation of the primary free radical species. The cation may also form a redox system with the monomer. As a result it is converted to the reduced form, which would be oxidized back by atmospheric oxygen, and this conversion presumably involves radical intermediate capable of initiating grafting. By way of example mention is made of the following:

MAA and Cu^{2+} ion form perhaps a redox system. Once this is the case, Cu^{2+} is converted to Cu^{1+} ion. The latter would be oxidized back to the cupric state by atmospheric oxygen, and this conversion must presumably entail radical intermediate as suggested by equations 12-14[21,22].

$$O_2\ (gas) \rightarrow O_2\ (liquid) \qquad (12)$$

$$O_2 + Cu^{2+} \rightarrow CuO_2^{+} \qquad (13)$$

$$CuO_2^{+} + H^{+} \rightarrow Cu^{2+} + HO_2^{\cdot} \qquad (14)$$

The $HO_2^{\cdot}$ radical may be involved presumably in the initiation of grafting or can undergo a reaction leading to formation of hydrogen peroxide as well hydroxyl radicals ($HO^{\cdot}$). Moreover, the formation of both $HO^{\cdot}$ and $HO_2^{\cdot}$ radicals in the decomposition of hydrogen peroxide by metallic ion have been reported[23,24]. The grafting order: $Fe^{3+} > Cu^{2+} > Li^{1+}$ could be associated with difference in mode of adsorption on the pregelled starch. Most probably the cation is attached to the starch molecules via ionic and chelate bonding. Cations, which are strongly associated with pregelled starch, would play relatively smaller role in the grafting reaction. The opposite is the case with those cations, which are not strongly bonded to pregelled starch. Current data suggest that the strength of the bonds holding the cation with pregelled starch is least with Fe^{3+} and highest with Li^{1+} and moderate with Cu^{2+}. Nevertheless, differences among these cations with respect to ease of conversion of the cation to the reduced form and the subsequent back oxidation with formation of free radical intermediate capable of grafting cannot be ruled out.

Solubility %

Figure 8 shows the solubility % of poly (MAA)-pregelled starch graft copolymer vis-à-vis their graft yields. It is obvious that, the solubility % increases by increasing the graft yield up to a certain value and then decreases. For example, the solubility % increases from 9.9 % to 50.6 % when the graft yield increases from 0 to 24.5 %. On the other hand, lower solubility % is observed with the grafted samples having graft yield higher than 24.5 %. This can be explained as follows:

Introduction of graft yield i.e. (soluble carboxyl groups) into the molecular structure of pregelled starch at relatively low degree of substitution up to 24.5 % leads to a decrease in hydrogen bonding between pregelled starch molecules which increases solubility %, and (b) Further Increase in the degree of grafting of poly (MAA)-pregelled starch graft copolymer leads to increasing the molecular weight of the starch which adversely affect the solubility % of the grafted pregelled starch.

CONCLUSIONS

Approximately 37.5 % graft yield and 75 % graft reaction efficiency as well as 25 % homopolymerization were obtained when methacrylic acid was graft co polymerized onto pregelled starch as a reactive carbohydrate polymer using a new redox initiation system namely KPS / TMEDA redox pair. This was obtained by applying the following optimum grafting conditions: using 10 mmol/L potassium persulfate, 8 mmol/L TMEDA, 50% MAA concentration (based on weight of substrate), liquor ratio, 10, reaction time, 60 min; and polymerization temperature, 60°C. Grafting was also enhanced significantly by adding Fe^{3+}, Cu^{2+} and L^{i1+}in the grafting media and follows the order Fe^{3+}> Cu^{2+}> L^{i1+}. Furthermore, notable enhancement in solubility % of grafted samples with lower graft yields than that of higher one.

REFERENCES

[1] B.S.Chiou, Y.Emma, M.G.Greg, J.William Orts; Carbohydrate Polymer, **59**, 467-475 **(2005)**.

[2] M.Fang, P.A.Fowler, C.A.S.Hill; Journal of Applied Polymer Sci., **96**, 452-459 **(2005)**.

[3] M.K.Beliakova, A.A.Aly, F.A.Abdel-Mohdy; Starch/ starke, **56**, 407-412 **(2004)**.

[4] L.Chen, S.H.Gordon, S.H.Imam; Biomacromolecules, **5**, 238-244 **(2004)**.

[5] W.M.Choi, I.D.Jung, S.K.Kwon, C.S.Ha, W.J.Cho; Polymer Degradation and Stability, **61**, 15-20 **(1999)**.

[6] Kh.M.Mostafa; Polymer Degradation and Stability, **55(2)**, 125 **(1997)**.

[7] Kh.M.Mostafa, A.A.El-Sanabary; Polymer Degradation and Stability, **55(2)**, 181-184 **(1997)**.

[8] Kh.M.Mostafa; Carbohydrate Polymers, **51**, 63-68 **(2003)**.

[9] Kh.M.Mostafa, A.A.El-Sanabary; Journal of Applied Polymer Science, **88**, 959-965 **(2003)**.

[10] G.Lee, Stanek, M.Steven, Helimann, B.William, Gleason; Carbohydrate Polymer, **65**, 552-556 **(2006)**.

[11] S.Kiatkamjornwong, K.Mongkolsawat, M.Sonsuk; Polymer, **43**, 3915-3924 **(2002)**.

[12] V.Singh, A.Tiwari, D.N.Tripathi, R.Sanghi; Carbohydrate Polymers, **58**, 1-6 **(2004)**.

[13] V.D.Athawale, V.Lele; Carbohydrate Polymers, **41**, 407-416 **(2000)**.

[14] V.D.Athawale, V.Lele; Carbohydrate Polymers, **35**, 21-27 **(1998)**.

[15] Kh.M.Mostafa; J.Applied Polymer.Sci., **56**, 263 **(1995)**.

[16] Kh.M.Mostafa; Polymer Degradation and Stability, **50**, 189-194 **(1995)**.

[17] D.Daul, R.M.Reinhardt, J.D.Reid; Textile Research Journal, **23**, 719 **(1953)**.

[18] P.G.Seydel; 'Textile warp Sizing', Long and Clopton, Inc., Atlanta, Georgia, Chapter, 4, **(1972)**.

[19] Y.B.Tan, L.M.Zhang, Z.M.Li; Journal of Applied Polymer Sci., **69**, 879-885 **(1998)**.

[20] I.Y.M.Qudsieh, Fakhru, A.l-Razi, S.A.Muyibi, M.B.Ahamed, M.Z.A.Rahman, W.M.Z.Yunus; Journal of Applied Polymer Sci., **94**, 1891-1897 **(2004)**.

[21] M.H.El-Rafie, M.I.Khalil, A.Hebeish; Journal of Applied Polymer Sci., **19**, 1677 **(1975)**.

[22] M.H.El-Rafie, A.Hebeish; Journal of Applied Polymer Sci., **15**, 131 **(1975)**.

[23] C.Coppinger; J.Am.Chem.Soc., **79**, 2758 **(1957)**.

[24] W.G.Bard, Baxendale, R.George, K.R.Hargrave; Trans Faraday Soc., **52**, 591 **(1951)**.