

Synthesis of New Polymeric Composite Materials and its Application in Sizing of Cotton Textiles

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Abstract: Poly (methacrylamide)- Pregelld starch composite was prepared by polymerizing pregelld starch with methacrylamide (MAAm) using potassium persulphate as initiator. Different factors affecting the composite preparation were studied with respect to concentration of initiator and monomer, polymerization time and temperature as well as rate of stirring. The composites expressed as total conversion of monomer to polymer were applied for sizing of cotton textiles. Results obtained show that, the total conversion of poly (MAAm)-Pregelld starch composite was increased by (a) increasing the persulphate concentrations from 0.1-0.3 based on weight of substrate (ows) then leveled off; (b) increasing the methacrylamide concentration within the range studied; (c) increasing polymerization time up to certain value then leveled off; and (d) increasing polymerization temperature from 55° to 60°C, then decreases by raising the temperature to 65°C. On the other hand, poly (MAAm)- pregelld starch composite serve as a good sizing agent for cotton textiles in comparison with that sized with pregelld starch alone.

Key words: Composite, Methacrylamide (MAAm), $K_2S_2O_8$, Cotton fabric, Sizing, Mechanical properties.

INTRODUCTION

Starch is widely used commercially in different textiles industries such as warp sizing, printing and finishing (1-8). Nevertheless, it suffers from serious drawbacks that not often match with properties required for potential end use, i.e. sizing of cotton textiles as in our case in this work. The most outstanding which are (a) very high molecular size which limit their penetration in the bulk of the textile threads, (b) instability of their viscous solution by fluctuation of temperature during cooking and sizing operation, (c) rigidity of their films particularly in absence of good lubricant, and (d) susceptibility to rot and degradation by microorganisms. To overcome these defects, derivatization of pregelld starch was done via oxidation, hydrolysis, etherification, esterification as well as the most effective mean for improving the pregelld starch properties i.e. grafting (9-21).

This paper presents detailed study on major factors affecting poly (MAAm)-pregelld starch composite synthesis as well as its utilization in sizing of cotton textiles via measuring the mechanical properties of cotton fabric before and after sizing operation.

MATERIALS AND METHODS

Pregelld starch was kindly supplied by Egyptian starch and Glucose Manufacturing Company, Cairo Egypt. Methacrylamide, potassium persulphate sulphuric acid, potassium boromate, potassium bromide, potassium iodide and ethyl alcohol were of laboratory grade chemicals.

Composite synthesis: Pregelld starch was mixed with a calculated amount of water followed by potassium persulphate solution (0.1-0.5 % based on weight of substrate, ows), in a beaker that kept at a temperature (55°-65°C) for 25 min. with continuous stirring to ensure the homogeneity of the sample. At this end, a known concentration of methacrylamide was added to the polymerization medium and a material to liquor ratio of 1:5 was used. The reaction was allowed to proceed under stirring (200-500 r.p.m.) for 1.5 hr at specific temperature. Detailed of the condition used are given in the text. After the desired reaction time, a calculated amount of inhibitor was added to terminate the reaction.

Sizing procedure: It was estimated according to a reported method (22).

Analysis and Testing:

Percentage Total Conversion: It was calculated via quantitative estimation of the double bonds of methacrylamide before and during polymerization according to a reported method (23).

Tensile strength (T.S) and Elongation at break (%): These were measured according to ASTM procedure D-2256-66T.

Abrasion resistance: This was determined using the K-Zweigle abrader.

N.B: Both tensile strength, elongation at break and abrasion resistance were measured three times for each sample as well as their standard deviations.

RESULTS AND DISCUSSION

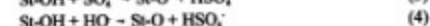
It is well known from the literature that, when persulphate ions heated in aqueous medium, it decomposes to produce sulphate ion radicals as follow:



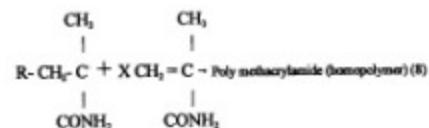
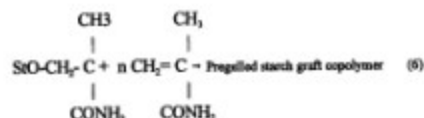
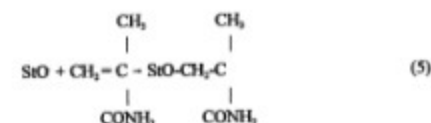
The sulphate radicals may react with water to produce hydroxyl radicals.



The sulphate and the hydroxyl radicals attack the pregelged starch macromolecules via hydrogen abstraction from the hydroxyl groups of pregelged starch molecules. This reaction may be represented as follows:



In presence of methacrylamide monomer, both of poly methacrylamide pregelged starch graft copolymer and poly methacrylamide (homopolymer) are produced as shown below:



The mixture of these products as mention in equations 5 to 8 forms what we called polymethacrylamide pregelged starch composite.

Potassium permanganate concentration: Table 1 shows the effect of $K_2S_2O_8$ concentration on the total conversion (%) of poly (methacrylamide)-pregelged starch composite. It is seen from the tabular data that increasing the persulphate concentration from 0.1 to 0.3 % (ows) brings about a significant increase in the total conversion. Above this value no further increase in the % total conversion is observed. Current data suggest that, the contribution of the primary free radical species participate mainly in the initiation of the polymerization when $K_2S_2O_8$ range from 0.1-0.3 % ows was used, which exhibits higher enhancement in the % total conversion within the range studied. On the other hand, presence of higher $K_2S_2O_8$ concentration leads to a balance between the contribution of the latter in the initiation of polymerization reaction as well as its contribution in the termination of polymerization.

It is further noted that, the % total conversion increases by increasing the duration of polymerization up to certain time then levels off. On other word, % total conversion against 6 min. at 0.1 % $K_2S_2O_8$ concentration to yield 6.2 % total conversion

Table 1: Effect of Potassium persulphate concentration on the % total conversion of poly (methacrylamide)-pregelled starch composite at different polymerization time.

Polymerization time (min.)	% Total conversion, Potassium persulphate concentration (ows)				
	0.1	0.2	0.3	0.4	0.5
2	0.0	6.1	62.5	62.0	60.2
4	0.0	27.5	77.3	75.6	74.3
6	0.9	52.8	90.1	89.9	89.0
8	2.9	54.0	90.1	89.9	89.0
10	4.6	73.5	90.1	89.9	89.0
15	6.0	75.5	90.1	89.9	89.0
30	6.2	78.4	90.1	89.9	89.0
60	6.2	78.7	90.1	89.9	89.0
90	6.2	80.0	90.1	89.9	89.0

Reaction Conditions: Methacrylamide, 50 % (ows); Temperature, 60°C; Material to liquor ratio, 1:5; Rate of stirring, 400 r.p.m. against 6 min. at 0.3 % $K_2S_2O_8$ concentration to yield 90.1 % total conversion. At any event, leveling off of % total conversion could be associated with depletion in monomer and initiator concentration as the reaction proceeds.

Effect of monomer concentration: Figure 1 shows the effect of changing methacrylamide concentration on the

% total conversion of poly (MAAm)- pregelled starch composite. It is clear from the drawn data that, the % total conversion increases significantly by increasing the MAAm concentration from 10-40 % ows. While further increase in MAAm concentration exerts similar effect but to a lower extent. Further more, in the polymerization medium containing MAAm, $K_2S_2O_8$ and pregelled starch, the % total conversion is directly related to MAAm concentration, the higher the MAAm concentration the greater availability of the latter in the vicinity of pregelled

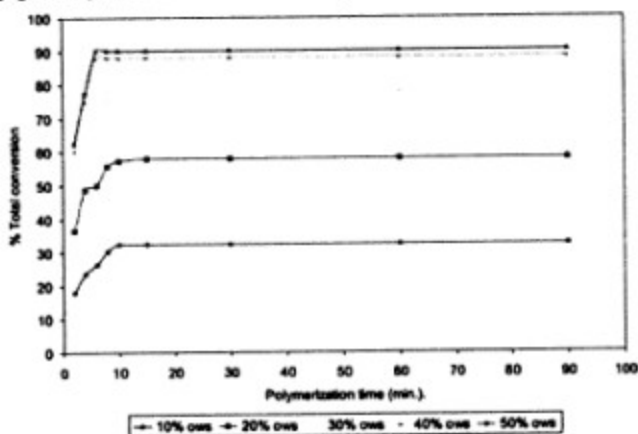


Fig. 1: Effect of methacrylamide concentration on the % total conversion of poly (methacrylamide)-pregelled starch composite at different polymerization time. N.B. Methacrylamide concentration ranged from 10-50 % ows (based on weight of substrate as shown in the above legends).

Reaction Conditions: $K_2S_2O_8$, 0.3 % (ows); Temperature, 60°C; Material to liquor ratio, 1:5; Rate of stirring, 400 r.p.m.

starch as well as the molecular collision of the reactants. Greater collision of initiated MAAm molecule with its own molecules would also enhance what we called homopolymerization. It is needless to say that, increasing in MAAm concentration is to

bring about enhancement in both grafting and homopolymerization (% total conversion) as a result of the greater availability of MAAm molecules and the subsequent onset of this on the course of the polymerization reaction.

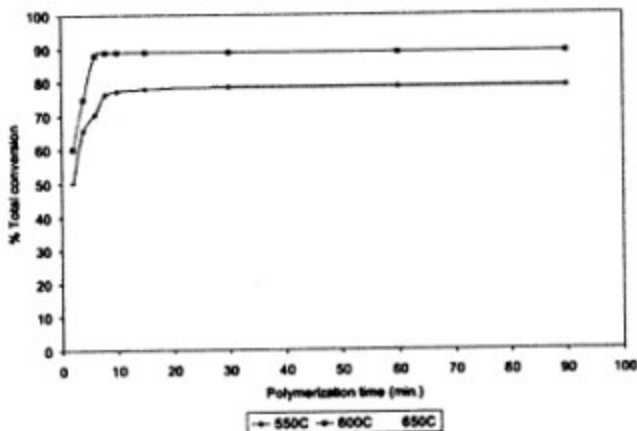


Fig. 2: Effect of polymerization time and temperature on the total conversion of poly (MAAm)-pregelled starch composite. N.B. The Temperatures used are 55°C, 60°C and 65°C as in the legends shown above.

Reaction Conditions: $K_2S_2O_8$, 0.3 % (ows); methacrylamide concentration, 40 % (ows); Material to liquor ratio, 1:5; Rate of stirring, 400 r.p.m.

Temperature of Polymerization: Figure 2 shows the effect of temperature of polymerization on the % total conversion of MAAm monomer to poly (MAAm) in the poly (methacrylamide)-pregelled starch composite. It is clear from the drawn data that, the % total conversion increases substantially by raising the polymerization temperature from 55° to 60°C on using a polymerization time from 2 to 10 min. Further more, allowing the polymerization to proceed for more than 10 min. offsets the significant effect of the temperature and the value of the % total conversion obtained at 55°, 60° and 65° C are comparable. However, the % total conversion values at 65°C are lower than that at 55°C and 60°C regardless of the time of polymerization, that reflects the faster termination rate at 65°C. The comparison of the three temperature in questions follows the following order:

$$60^{\circ}\text{C} > 55^{\circ}\text{C} > 65^{\circ}\text{C}.$$

The favorable effect of temperature (up to 60°C) on the % total conversion could be ascribed to: (a) Swell ability of pregelled starch, (b) diffusion of MAAm onto the pregelled starch structure, (c) formation of primary free radical species and their subsequent reaction with pregelled starch to form pregelled starch macroradicals, (d) mobility of MAAm molecules and their collision with

pregelled starch macroradicals for initiation of grafting, and (e) propagation of the graft.

Rate of stirring: Figure 3 shows the effect of stirring on the % total conversion of MAAm monomer into poly (MAAm) in the poly (MAAm)-Pregelled starch composite. The drawn data reflects the following findings: (a) lower % total conversion is observed when faster stirring rate (500 r.p.m) was used when the polymerization was done for 2-10 min., while maximum total conversion is observed under stirring of 400 r.p.m irrespective of the polymerization time used., (c) lower stirring rate (200 r.p.m) brings about higher % total conversion than that of faster one (500 r.p.m) within the range studied.

It is needless to say that, the above findings reflect the role of stirring, with respect to compatibility of the ingredients of polymerization as well as the degree of their association. The disaggregating of the polymerization ingredients under the effect of faster rate of stirring was observed in the current drawn data in figure 3. Pre-requisites such as intimate association of pregelled starch, MAAm and the $K_2S_2O_8$ are perturbed by faster stirring rate. It is well known that, such pre-requisites govern the % total conversion since they control the magnitude of both grafting of MAAm onto Pregelled starch and its homopolymerization in the reaction medium, and, hence the % total conversion.

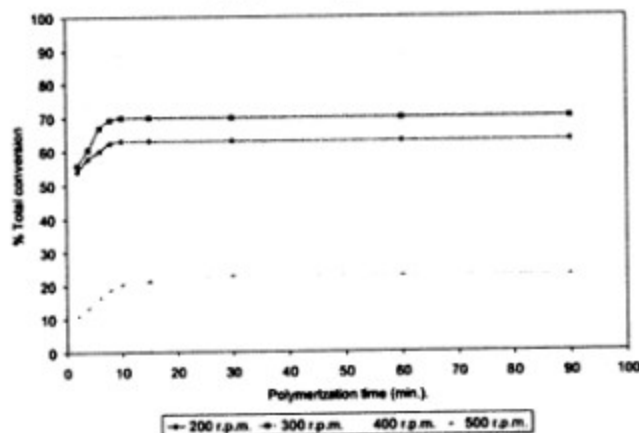


Fig. 3: Effect of rate of stirring on the % total conversion of methacrylamide monomer to poly (MAAm)-pregelled starch composite at different polymerization time. N.B. The rates of stirring are ranged from 200 r.p.m. to 500 r.p.m. as shown in the legends above.

Reaction Conditions: $K_2S_2O_8$, 0.3 % (ows); methacrylamide concentration, 40 % (ows); Material to liquor ratio, 1:5; Rate of stirring, 400 r.p.m.

Table 2: Tensile strength, elongation at break and abrasion resistance of light cotton fabrics sized with original pregelled starch and poly (MAAm)-pregelled starch composite having different % total conversion.

% Total Conversion of poly (MAAm)-pregelled starch composite	Tensile strength (Kg)	Elongation at break (%)	Abrasion resistance (Cycle)
32.5	48.0	10.0	897
58.0	49.5	99.1	912
77.0	51.0	99.5	924
88.9	52.5	99.6	934
90.1	53.5	99.7	948
Untreated fabric	48.0	10.0	880
Sized with pregelled starch	49.9	99.1	899

Sizing of cotton textiles: Table II shows the mechanical properties namely tensile strength, elongation at break and abrasion resistance (as a measuring factors of sizing efficiency) of cotton fabric sized with pregelled starch (control) and poly (MAAm)-pregelled starch composite having different total conversion. It is seen that, cotton fabrics sized with pregelled starch exhibits somewhat higher tensile strength and abrasion resistance than unsized fabric. While the elongation at break exhibits lower values than untreated cotton. On the other hand, cotton fabrics sized with poly (MAAm)-pregelled starch composite exhibits tensile strength, elongation at break and abrasion resistance values higher than that sized with pregelled starch. This reflects the advantages of the prepared composite with respect to: (a) better film forming properties, (b) strong adhesion, and (c) more uniform coverage with elastic films in comparison with original pregelled starch. It is needless to say that the poly

(MAAm)-pregelled starch composite is measured for the latter mechanical properties to see their suitability as sizing agent for cotton textiles

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