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Synthesis of New Thickener Based on Carbohydrate Polymers for Printing Cotton Fabrics with Reactive Dyes

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Abstract: Tailoring of new thickener via graft copolymerization of methacrylonitrile (MAN) onto pregelled starch (PGS) as a carbohydrate polymer was synthesized and the reaction conditions were optimized using potassium monopersulphate (PMPS) in presence of ferrous ion redox pair as initiator. Emphasis was directed towards preparing new thickener for printing cotton fabrics with reactive dyes. The grafting parameter was studied with respect to graft yield (G. Y.) and graft reaction efficiency percent (G.R.E.%). On the other hand, the newly prepared poly (MAN)-pregelled starch graft copolymers were used as a thickener for printing cotton fabrics with reactive dyes, to see their suitability as pastes for printing cotton with the latter dyes. Based on the results obtained, appropriate conditions for grafting methacrylonitrile onto pregelled starch was established and the graft yield is higher under the following conditions: using $0.004 \text{ mmol L}^{-1}$ potassium monopersulphate as initiator, $0.005 \text{ mmol L}^{-1}$ ferrous ion concentration, $0.002 \text{ mmol L}^{-1}$, sulphuric acid; 50% methacrylonitrile concentration (based on weight of substrate), material to liquor ratio, 1:2.5, reaction time, 60 min and polymerization temperature, 40°C . Finally, utilization of poly (MAN)-pregelled starch graft copolymers as a new thickener for printing cotton with reactive dyes proved to be a potential thickener as evidenced by excellent color strength as well as overall fastness properties.

Key words: Reactive printing, grafted pregelled starch, methacrylonitrile, reactive dyes, fastness properties

INTRODUCTION

Starch as a carbohydrate polymer is widely used commercially as a thickener in textile industries particularly in warp sizing and finishing^[1-6]. But, it is well known that starch is not successively used as a thickener for printing cotton fabric with reactive dyes due to its reaction with the dye and the effect of this on the color strength and overall fastness properties of the printed fabric. So, chemical modification of starch via the most important fascinating field of starch modification, i.e. vinyl graft copolymerization was done to synthesize modified starch product with a specific function groups that make it suitable to serve as a new thickener for cotton printing. Among this is the preparation of poly (acrylic acid)-starch graft copolymer^[7]. Beside, using the mixture of carboxymethyl starch with poly acrylic acid and poly acrylic acid with poly methacrylic acid as well as cyanoethylated starches as etherified products as a thickener during printing process^[8-11].

This work is concerned with studying the major factors affecting graft copolymerization of methacrylonitrile onto pregelled starch using potassium

monopersulphate/ Fe^{2+} redox pair as initiator. The products so obtained were used as thickener for printing cotton with reactive dyes to see their suitability as pastes for printing cotton fabric with reactive dyes.

MATERIALS AND METHODS

Pregelld starch: Pregelld starch was kindly supplied by Egyptian starch and Glucose Manufacturing Company, Cairo, Egypt.

Cotton fabric: Mill scoured, bleached and mercerized plain weave fabric (145 cm^{-1}) was used.

Chemicals: Methacrylonitrile stabilized with 0.01% hydroquinone was freshly distilled at 75°C and pressure of 100 mm Hg; it was stored at -10°C until used. Potassium monopersulphate (Aldrich USA), ferrous sulphate (AR, BDH), ethyl alcohol and Dimethylformamide (DMF) were used as supplied.

Reactive dyes: Reactive dyes used were; Procion Blue H based on monochlorotriazine, Procion Blue MX-R based

on dichlorotriazine from Dharma Trading Company (USA), and Sunzol Blue R special based on vinylsulphone from Saraf Chemical Industry, India.

Polymerization procedure: The graft polymerization reaction was carried out in 100 ml flasks containing an aqueous solution of monomer. 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. The pregelled starch and calculated amounts of sulphuric acid and ferrous sulphate were added and the reaction mixture was mixed thoroughly. To initiate the reaction a known amount of potassium monopersulphate solution was added. 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 methacrylonitrile) was removed from the reaction mixture by soxhlet extraction using dimethylformamide for 12 h. It was found experimentally that, 24 h soxhlet extraction using dimethylformamide as an efficient solvent is quite enough to remove poly methacrylonitrile (homopolymer) from its physical mixture via measuring the nitrogen content after each soxhlet extraction. Finally, washed with pure ethanol and air-dried.

Evidence of grafting: This was done via measuring the nitrogen % of grafted samples by a well-known Kjeldahl method^[12] two times for each samples, as well as their standard deviation. On other words, both the nitrogen (%) and the standard deviation for each sample were taken as an evidence of grafting onto starch as a carbohydrate polymer that is free from nitrogen groups as a starting substrate.

Characterization: The graft yield was traced by estimating the nitrogen content (%) and the graft yield was calculated as follows:

$$\text{Graft yield (\%)} = \frac{100 (\text{N (\%)} - 4.78)}{100 - (\text{N (\%)} - 4.78)}$$

On the other hand, the graft reaction efficiency percent (G.R.E.%) was calculated as follows:

$$\text{G.R.E. (\%)} = \frac{\text{Graft yield (\%)}}{\text{Percent of monomer based on weight of starch (b.o.w.s.)}} \times 100$$

Cooking method: Poly (MAN)-pregelled starch graft copolymers were mixed with water to obtain 10% solid

content. The latter was then cooked at 90°C for 35 min. with continuous stirring during the cooking process.

Apparent viscosity: It was measured by using co-axial rotary viscometer (Haake RV20), with the rate of shear 516 cm⁻¹ at 90°C.

Preparation of printing pastes: Printing pastes were prepared according to the following recipe:

- Dye (20 g)
- Urea (100 g)
- Sodium bicarbonate (20 g)
- Ludigol (10 g)
- Thickener concentration was (10%)

Then complete the total volume by water to 1000 g (1 Kg)

- 1- The dye was mixed with urea and little amount of water with stirring to insure the homogeneity of the mixture
- 2- The latter mixture was then poured on the thickener suspension and the whole was stirred with the addition of bicarbonate and ludigol
- 3- The total weight of the whole paste was then adjusted to be 1 Kg by addition of water.

N.B.: The thickener was soaked in a little amount of water overnight at room temperature before starting preparation of the corresponding printing pastes.

Printing method: Printing was performed using the flat screen under conditions which were detailed elsewhere^[8].

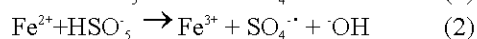
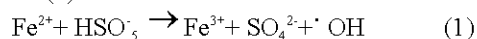
Testing

Color strength: Color strength expressed as (K/S values) was measured according to a reported method^[13].

Over all fastness properties: Fastnesses to washing, rubbing, perspiration (acidic and alkaline) ...etc., were measured according to standard method^[14-16].

RESULTS AND DISCUSSION

Tentative mechanism of grafting: The presence of ferrous ion (Fe²⁺) in the polymerization medium with potassium monopersulphate (KHSO₅) produces sulphate and hydroxyl ions free radicals species, which occur most probably according to the mechanism, suggested by eqs. (1) and (2):

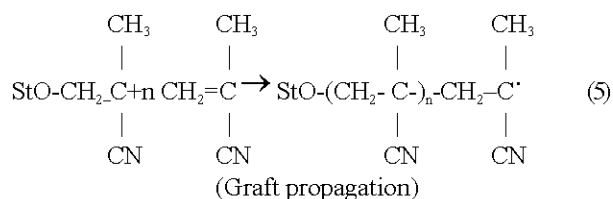
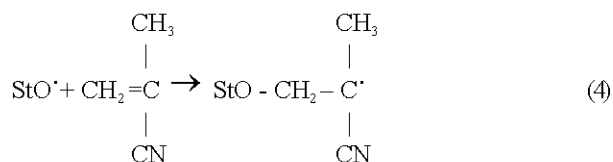


Once the free radical species (R') are formed, they produce pregelled starch macroradical St-O' via direct abstracting of hydrogen atoms from pregelled starch molecules. This reaction may be represented as follows:

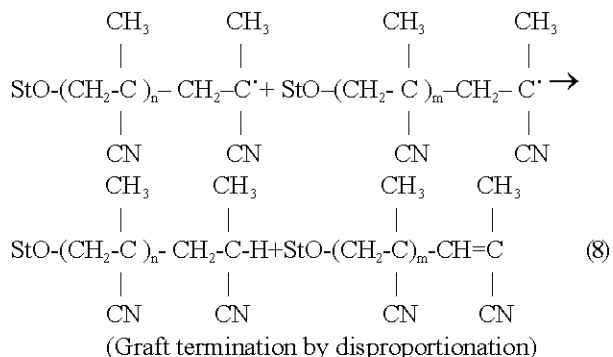
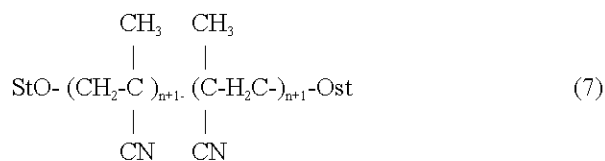
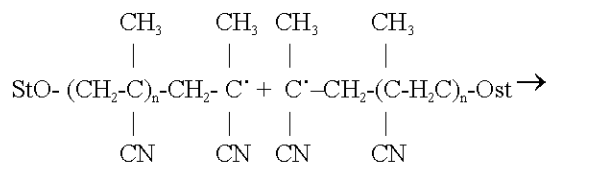
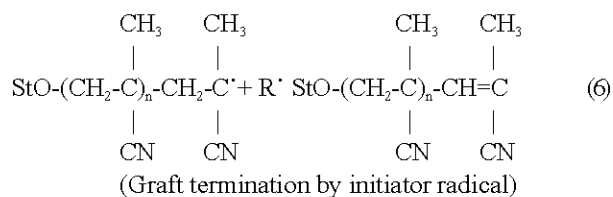


Where St-OH represent the pregelled starch molecule.

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:



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



Potassium monopersulphate concentration (PMPS):

Figure 1 shows the effect of potassium monopersulphate (PMPS) concentration on the grafting parameters (graft yield and graft reaction efficiency%) of poly (MAN)-pregelled starch graft copolymers. It is seen (Fig. 1) that within the range studied, increasing PMPS concentration from 0.002 to 0.004 mol L⁻¹ is accompanied by an increment in the graft yield, but beyond this concentration the graft yields decrease gradually. This is in agreement with the results of the graft reaction efficiency that show a maximum value of about 47% at 0.004 mol L⁻¹ potassium monopersulphate concentrations.

The increase in grafting parameter may be due to the progressive reduction of potassium monopersulphate by ferrous ion producing sulphate ion radicals and hydroxyl free radicals that attack pregelled starch molecule creating more free radical species that participate mainly in graft initiation. On the other hand, the reduction in grafting parameter after 0.004 mol L⁻¹ PMPS may be explained in terms of; (a) self-termination of growing grafted chain via presence of abundance of free radical species and (b) presence of excess of Fe³⁺ ions causes termination of grafted chain due to it has been known as an ideal retarder of free radical polymerization^[17].

Ferrous ion concentration:

Figure 2 shows the effect of Fe²⁺ ion concentrations on the graft yield and graft reaction efficiency percent of poly (MAN)-pregelled starch graft copolymers. Obviously increasing the Fe²⁺ concentrations from 0.001 to 0.005 mol L⁻¹ is accompanied by an increase in the grafting parameters, after that the grafting parameters decrease.

The enhancement in grafting may be due to the increase in KHSO₅/Fe²⁺ concentration adduct which undergoes decomposition at pregelled starch surface resulting in generation of number of free radical species at faster rate at which addition of monomer takes place. On the other hand, the decrease in grafting may be attributed to the excess of Fe³⁺ ion produced during

Table 1: The dependence of controlling factors affecting preparation of poly (MAN)- pregelled starch graft copolymers and their apparent viscosity on the color strength of cotton fabric printed using the above copolymers as a thickener in presence of Sunzol Blue R special as a reactive dye

MAN conc. (b.o.w.s.)	Apparent viscosity (m.pa.s)	K/S	PMPS conc. (mol L ⁻¹)	Apparent viscosity (m.pa.s)	K/S	Polymerization temperature (°C)	Apparent viscosity (m.pa.s)	K/S
25	136	4.08	0.002	157	3.66	20	160	3.80
50	145	4.20	0.004	151	3.69	30	152	4.00
75	156	4.25	0.006	145	4.20	40	145	4.20
100	162	4.25	0.008	141	3.91	50	140	3.70
150	150	4.01	0.010	136	3.71			

Reaction conditions:

- (I) [PMPS], 0.006 mol L⁻¹; [Fe²⁺], 0.005 mol L⁻¹; [H₂SO₄], 0.002 mol L⁻¹; material to liquor ratio, 1:2.5; time, 45 min. and temperature, 40°C.
 (II) [MAN], 50% (b.o.w.s.); [Fe²⁺], 0.005 mol L⁻¹; [H₂SO₄], 0.002 mol L⁻¹; material to liquor ratio, 1:2.5; time, 45 min. and temperature, 40°C.
 (III) [MAN], 50% (b.o.w.s.); [PMPS], 0.006 mol L⁻¹; [Fe²⁺], 0.005 mol L⁻¹; [H₂SO₄], 0.002 mol L⁻¹; material to liquor ratio, 1:2.5 and time, 45 min.
 N.B.: (b.o.w.s.) means based on weight of substrate.

Table 2: The overall fastness properties of printed cotton fabric obtained when poly (MAN)-pregelled starch graft copolymer was used as a thickener for printing reactive dyes

Dyes	Color strength (K/S)	Washing fastness at (90°C)			Rubbing fastness		Acidic perspiration			Alkaline perspiration			Handle
		St ⁺	St ⁺⁺	Alt.	Wet	Dry	St ⁺	St ⁺⁺	Alt.	St ⁺	St ⁺⁺	Alt.	
Procion Blue H	4.25	4	3-4	4-5	3-4	4-5	4	3-4	4-5	3-4	4	4-5	Soft
Procion Blue MX-R	0.41	2-3	3	3	2-3	3-4	3	2-3	3-4	2-3	3	3-4	Soft
Sunzol Blue R special	4.10	4	4-5	4-5	4	4-5	3-4	4	4-5	4	4	4-5	Soft

Where; St. +: Staining on cotton, St. ++: Staining on wool, Alt.: Alteration

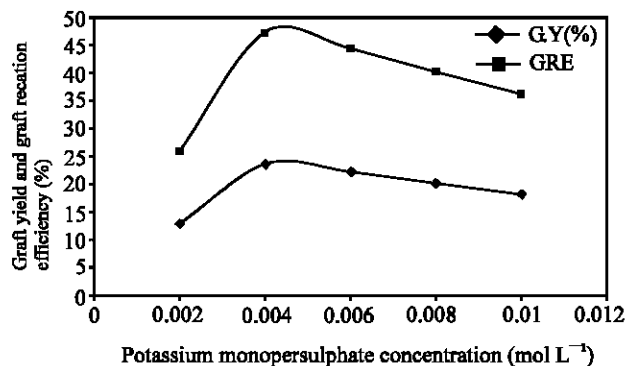


Fig. 1: Effect of potassium monopersulphate concentrations on graft yield (%) and graft reaction efficiency (%) of poly (MAN)-pregelled starch graft copolymers

Reaction conditions: Pregelled starch, 2 g; [Fe²⁺], 0.005 mol L⁻¹; [H₂SO₄], 0.002 mol L⁻¹; [MAN], (50% based on weight of substrate); material to liquor ratio, 1:5; Time, 60 min. and temperature, 40°C.

disproportionation of KHSO₅ / Fe²⁺ couple that retards the radical polymerization reaction^[17].

Effect of sulphuric acid concentration: Figure 3 shows the effect of sulphuric acid concentrations on the grafting parameters. It was found from the above figure that, the grafting parameters increase by increasing the concentration of an acid, reaching a maximum at 0.003 mol L⁻¹, then decreases by raising the acid concentration. Increasing the grafting parameters with increasing the acid concentration may be due to increasing the concentration of the reactive species that

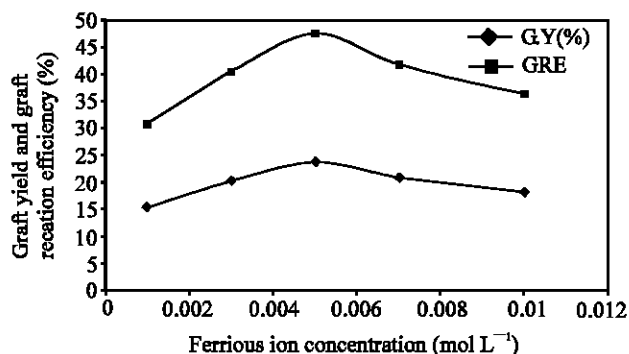
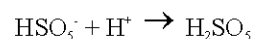


Fig. 2: Effect of ferrous ion concentration on the graft yield (%) and graft reaction efficiency (%) of poly (MAN) - pregelled starch graft copolymers

Reaction conditions: Pregelled starch, 2 g; [PMPS], 0.004 mol L⁻¹; [H₂SO₄], 0.002 mol L⁻¹; [MAN], (0% based on weight of substrate) material to liquor ratio, 1:5; Time, 60 min. and temperature, 40°C.

result in high production of primary free radical species as well as the ability of these radical species to react with other ingredient (s) rather than starch. While, the decrement in grafting parameters above this concentration may be explained on the basis of the fact that, with the increase in the acid concentration, the concentration of the reactive species HSO₅ decreases which results in less production of primary free radical thereby decreasing the grafting parameters.



Material to liquor ratio: Figure 4 revealed the effect of changing the material to liquor ratio on the graft yield and

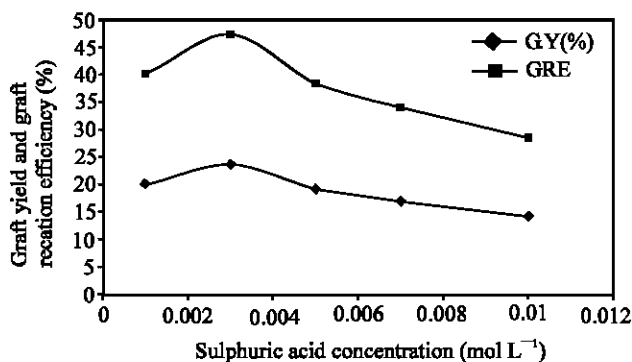


Fig. 3: Effect of sulphuric acid concentration on the graft yield (%) and graft reaction efficiency (%) of poly (MAN) - pregelled starch graft copolymers
 Reaction conditions: Pregelled starch, 2 g; [PMPS], 0.004 mol L⁻¹; [Fe²⁺], 0.005 mol L⁻¹; [MAN], (0% based on weight of substrate); material to liquor ratio, 1:5; Time, 60 min. and temperature, 40°C.

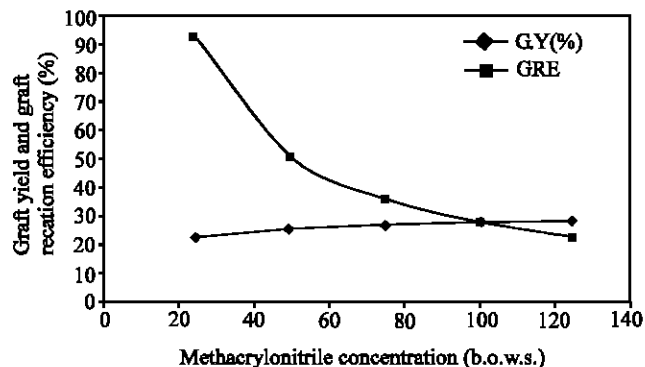


Fig. 5: Effect of methacrylonitrile concentrations on the nitrogen (%), graft yield (%) and graft reaction efficiency (%) of poly (MAN)-pregelled starch graft copolymers
 Reaction conditions: Pregelled starch, 2 g; [PMPS], 0.004 mol L⁻¹; [Fe²⁺], 0.005 mol L⁻¹; [H₂SO₄], 0.003 mol L⁻¹; material to liquor ratio, 1:2.5; Time, 60 min. and temperature, 40°C.

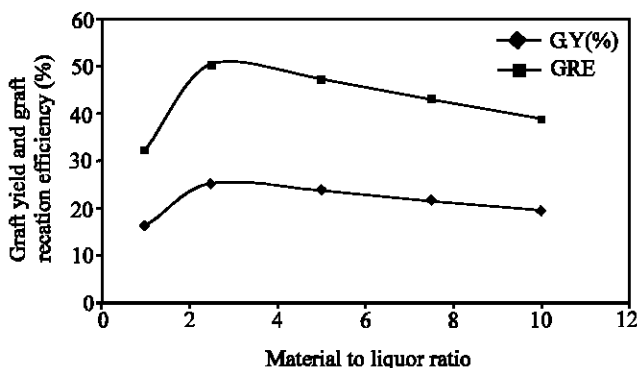


Fig. 4: Effect of material to liquor ratio on the graft yield (%) and graft reaction efficiency (%) of poly (MAN)- pregelled starch graft copolymers
 Reaction conditions: Pregelled starch, 2 g; [PMPS], 0.004 mol L⁻¹; [Fe²⁺], 0.005 mol L⁻¹; [H₂SO₄], 0.003 mol L⁻¹; [MAN], (50% based on weight of substrate); Time, 60 min. and temperature, 40°C.

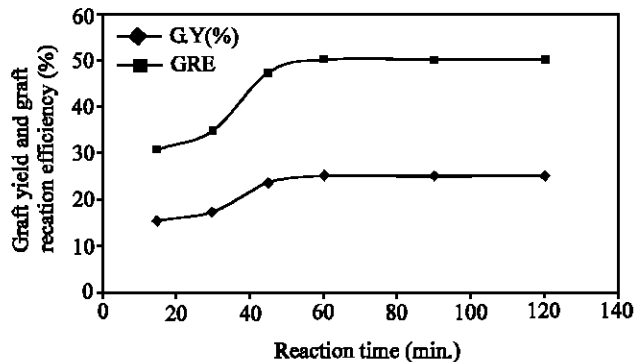


Fig. 6: Effect of reaction time on the graft yield (%) and graft reaction efficiency (%) of poly (MAN)-pregelled starch graft copolymers
 Reaction conditions: Pregelled starch, 2 g; [PMPS], 0.004 mol L⁻¹; [Fe²⁺], 0.005 mol L⁻¹; [H₂SO₄], 0.003 mol L⁻¹; [MAN], 50% (based on weight of substrate); material to liquor ratio, 1:2.5 and temperature, 40°C.

graft reaction efficiency of poly (methacrylonitrile)-pregelled starch graft copolymer. Increasing the material to liquor ratio up to 1:2.5 is accompanied by an increase in the grafting parameter, then decrease when the liquor ratio increases up to 1:10. So, it is logically to say that, of all liquor ratio studied, a material to liquor ratio 1:2.5 constitute the best. It is likely that at this particular liquor ratio a good grafting environment is created through intimate association of the monomer and initiator with the pregelled starch macromolecules. Once this is the case, greater availability of the monomer and initiator in the vicinity of the pregelled starch macromolecules occurs,

thereby leading to higher grafting. Opposite situation is encountered at higher material to liquor ratio.

Effect of MAN concentration: Figure 5 shows the dependence of methacrylonitrile concentration on the graft yield and graft reaction efficiency (%) of poly (methacrylonitrile)-pregelled starch graft copolymer. It is clear that, there is a direct relation between the graft yield and monomer concentration within the range studied. This is truly due to greater availability of the monomer molecules at higher methacrylonitrile concentration in the proximity of pregelled starch.

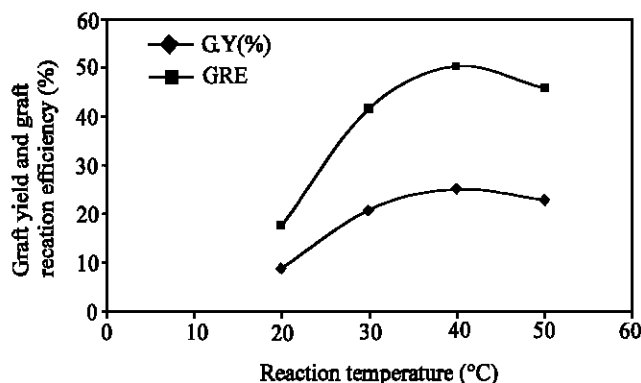


Fig. 7: Effect of polymerization temperature on the graft yield (%) and graft reaction efficiency (%) of poly (MAN)-pregelled starch graft copolymers

Reaction conditions: Pregelled starch, 2 g; [PMPS], 0.004 mol L⁻¹; [Fe⁺²], 0.005 mol L⁻¹; [H₂SO₄], 0.003 mol L⁻¹; [MAN], (50% based on weight of substrate); material to liquor ratio, 1:2.5 and reaction time 60 min.

On the other hand, with respect to G.R.E., the results reflect that G.R.E. decreases as the methacrylonitrile concentration increases, unlike the graft yield. This suggests that, beside its favorable effect on grafting reaction, the concentration of methacrylonitrile seems to have an outstanding effect on the homopolymerization reaction. Since the grafting reaction competes with the homopolymerization and since the concentration of methacrylonitrile acts more in favor of the latter, and the observed decrement in G.R.E. by increasing methacrylonitrile concentration can be explained.

Effect of polymerization time: Figure 6 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 from 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 leveled off by increasing the reaction time to 120 min. 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 methacrylonitrile 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. Furthermore, 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.

Effect of polymerization temperature: The effect of polymerization temperature on the graft yield and graft reaction efficiency percent of poly (MAN)-pregelled starch graft copolymers has been shown in Fig. 7. However, the extent of grafting is determined by temperature; the extent of grafting increases by raising the polymerization temperature from 20 to 40°C then decreases by raising the polymerization temperature to 50°C. 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 with increase in temperature, rate of production of primary free radicals species increase which generate the grafting sites at greater rate thereby increasing grafting. Beside the favorable effect of temperature (up to 40°C) on grafting could be ascribed to:

- 1- Better decomposition of the redox system, giving rise to more free radicals,
- 2- Increased mobility of methacrylonitrile molecules;
- 3- Greater swellability of the pregelled starch;
- 4- Higher diffusion of MAN onto the pregelled starch structure and
- 5- Higher rate of initiation and propagation of the grafted chain.

However, the lower grafting observed at 50°C is, perhaps, due 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 graft reaction efficiency (%) cannot be ruled out.

Characterization: For simplicity the following section was discussed as follows:

- 1- The dependence of changing major factors affecting preparation of the newly prepared thickener in question as well as their rheological properties (i.e. apparent viscosity) on the color strength of cotton fabric printed with the above thickener in presence of Sunzol Blue R special based on vinylsulphone as a reactive dye.
- 2- Evaluation of the newly prepared thickener for over all fastness properties with the three reactive dyes in question.

Color strength: Table 1 shows the dependence of major factors affecting preparation of poly (MAN)-pregelled starch graft copolymers as a new thickener on the color strength of cotton fabric printed in presence of Sunzol

Blue R special based on vinylsulphone as a reactive dye. The apparent viscosity is also given in Table 1 as a rheology characterization that greatly affects the flows of the paste on fabric as well as to evaluate the printing quality. The color strength (expressed as K/S) was measured for prints obtained as a freshly prepared paste. It is seen from the above table that, the highest K/S value was 4.25 and the lowest was 3.50. This can be explained in the manner of the structural differences of the newly prepared poly (MAN)-pregelled starch graft copolymers used, which occur as the result of changing the major factors that affects the preparation of the copolymers. On the other hand, the given values of the apparent viscosity reflect the main role that plays on the quality of the print as evidenced by the K/S values.

Over all fastness properties: Based on the results obtained, appropriate conditions for grafting methacrylonitrile onto pregelled starch using potassium monopersulphate /Fe⁺² redox pair as initiation system was established. These conditions involve using potassium monopersulphate concentration of 0.004 mol L⁻¹, ferrous ion concentration of 0.005 mol L⁻¹, sulphuric acid concentration of 0.003 mol L⁻¹, methacrylonitrile concentration of 50% (b.o.w.s), and the polymerization was allowed to proceed for 60 min at 40°C. The poly (MAN)-pregelled starch graft copolymers so obtained were then applied as a new thickener in printing of cotton fabric with different reactive dyes, namely, Procion Blue H based on monochlorotriazine, Procion Blue MX-R based on dichlorotriazine and *Sunzol Blue R Special* based on vinylsulphone.

The poly (MAN)-pregelled starch graft copolymers were used immediately after preparation of the printing pastes. After drying, the printed samples were fixed by steaming, washed thoroughly, dried and finally air condition at 65°C and relative humidity 25°C. The samples were then measured for color strength as well as over all fastness properties. It is clear from (Table 2) that the color strength for procion Blue H (based on monochlorotriazine) and Sunzol Blue R Special (based on vinylsulphone) is higher than that of Procion Blue M-3G that (based on dichlorotriazine). This reflects the effect of the nature of dye as well as the difference between them with respect to substituents presents thereon, molecular weight, reactive groups and configuration. The latter differences play a dominant role on the susceptibility of dye towards cotton fabric and thickener.

It is seen from the Table 2 that, all printed samples show soft handle independent of the conditions and dye used. At the same time, the dry rubbing fastness was higher than that the wet rubbing fastness. The magnitude

of both the wet and dry rubbing fastness was mainly dependent on the nature of dye. For example, a highly reactive dye (Procion Blue MX-R), which is based on dichlorotriazine, acquires lower fastness properties to washing and to wet and dry rubbing as well as alkaline and basic perspiration than that based on monochlorotriazine (Procion Blue H) and that based on vinylsulphone (Sunzol Blue R special).

It was concluded that, poly (MAN)- grafted pregelled starch copolymers serve as a potential thickener for printing cotton fabric with reactive dyes as evidenced by color strength and over all fastness properties as well as soft handle.

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