Carbohydrate Polymers 75 (2009) 71–78

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Graft copolymers of starch and its application in textiles

M.W. Meshram [a], V.V. Patil [a], S.T. Mhaske [b], B.N. Thorat [a,*]

[a] *Department of Chemical Engineering, Institute of Chemical Technology (Formerly UDCT), University of Mumbai, Mumbai 400 019, India*
[b] *Polymer Engineering & Technology Department, Institute of Chemical Technology, University of Mumbai, Mumbai 400019, India*

ARTICLE INFO

Article history:
Received 13 November 2007
Received in revised form 18 June 2008
Accepted 19 June 2008
Available online 25 June 2008

Keywords:
Polymerization
Sizing agent
Percentage grafting
Starch binding
Textile wet processing

ABSTRACT

The graft copolymerization of styrene (ST), methyl methacrylate (MMA)/butyl acrylate (BA) with starch was carried chemically using ferrous ion-peroxide redox system. The grafting was performed at 60 °C and the monomer ratios of ST/MMA and ST/BA was varied with their % composition as 80/20, 50/50 and 20/80 parts by weight. The effect of initiator concentration, starch concentration and the monomer ratio on the grafting efficiency was studied. The grafted starch granules (GSG) were further analyzed for their particle size, bulk density and by sizing on cotton yarn for its physico-mechanical properties such as tensile strength, elongation at break, etc. The rheological properties of the resulting granular product in water as well as the starch graft copolymer emulsion were studied.

1. Introduction

In recent years, modified natural polymers with improved structural, physical and chemical properties have been gaining increasing importance in the industry. The main raw material such as starch is low cost, renewable, biodegradable and available abundantly. The chemical modification of starch via oxidation, hydrolysis, esterification, etherification, grafting and dextrinization has been extensively studied in the past (Whistler, BeMiler, & Paschall, 1984). Such modifications constitute an efficient means for the continued and increased use of starch to provide thickening, gelling, binding, adhesive and film forming properties. Of all these modifications, graft polymerization onto starch appears to be interesting and challenging from the point of imparting incremental properties to the sized cotton fiber. In addition, the starch graft copolymers are increasingly becoming important due to their potential applications in agricultural, medical and food sector (Jianping, Jiugao, Wei, Liming, & Ruchuan, 1998). Starch graft copolymers can be prepared by generating free radicals on the starch backbone and then allowing these macroradicals to react with monomer. Number of initiating methods can be used to prepare the starch graft copolymer and these can be categorized into three groups: (i) initiation by chemical methods (using ceric ammonium nitrate or the ferrous ion-peroxide redox system) (Brockway & Moser, 1963; Mostafa, 1997; Mostafa & Morsy, 2004), (ii) initiation by radiation (using cobalt-60) (Kiatkamjornwong, Mongkolsawat, & Sonsuk, 2002) and (iii) initiation by mastication (Willett & Finkenstadt, 2006).

It is known that starch generates graft copolymers with vinyl monomers such as acrylates, methacrylates and acrylonitriles. The graft polymerization of styrene onto starch, however, has not been extensively studied along with other monomers. Mino and Kaizerman (1958) have reported that cerium (IV) initiation could not give a graft copolymer of granular starch with styrene; however, a graft copolymer with more graft efficiency could be obtained when styrene is mixed with active monomer such as methyl methacrylate or acrylonitrile. There are reports on starch graft copolymers such as starch-g-polystyrene (Cho & Lee, 2002), starch-g-methacrylonitrile (Athawale & Lele, 2000), starch-g-polyvinyl alcohol (Zhai, Yoshii, Kuma, & Hashim, 2002), starch-g-methacrylamide (Meltem, 2006) and starch-g-acrylonitrile (Fanta, Felker, & Shogran, 2004). All these starch graft copolymers have been synthesized by generating free radicals on the backbone of starch granules and the copolymerization of the free radicals with the respective monomers. El-Rafie, Zahran, El Tablawy, and Hebeish (1995) have studied the polymerization of acrylic acid with native as well as hydrolyzed maize starch using a potassium bromate-thiourea dioxide redox initiator system and also, the rheological properties of the products. The study on the major factors affecting the graft copolymerization of acrylamide onto native starch and hydrolyzed starches using a $KMnO_4$/citric acid redox system has been described by Mostafa (2005). The product was then applied for sizing of cotton textiles to see their suitability for improving physico-mechanical properties of cotton textile. There are also reports on the grafting of wool using redox initiation system (Hebeish & Bendak, 1974).

---

* Corresponding author. Tel.: +91 22 2414 5616x289; fax: +91 22 2414 5614.
E-mail address: bnt@udct.org (B.N. Thorat).

0144-8617/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2008.06.012

The choice of grafting method depends in part, on particular monomer (acrylonitrile, acrylic acid, or methyl acrylate) and the purity of the desired product. In case of pharmaceutical application, the quality as well as the purity of the product required is very high. So, for the production of bioadhesive grafted starch copolymers as platform for controlled drug delivery system, the Co-gamma-radiation system is preferred (Geresh et al., 2002). In another method the graft copolymerization of starch was carried by physical mastication to generate free radicals on the starch backbone so that the graft copolymerization of polyacrylamide and co-substrates can be prepared by reactive extrusion method (Willett & Finkenstadt, 2006). Taghizadeh and Khosravy (2003) have studied the kinetics and the mechanism of graft copolymerization by redox initiator system. There are several other reports specific to the synthesis, characterization and stabilization of graft copolymers (Dennenberg & Abbott, 1976; Meltem, 2006; Nguyen, Martin, & Pauley, 1991). Also, the grafted starch emulsion can be used as a binder for making the native starch granules in the final formulation of the product (Fox, 1998).

Thus, from the foregoing discussion and the available literature, it can be said that in most of the cases, the preferred choice has been the redox system for initiation of polymerization. The grafting of starch using single monomer system has been extensively studied; however, the use of combination of two or more monomers for the grafting of starch has received less attention. In the present work, the graft copolymerization initiation was carried by chemical method (ferrous ion-peroxide redox system) using styrene, methyl methacrylate and butyl acrylate. The ratios of the monomers were varied to see the effect on the grafting efficiency, grafting percentage and its physico-chemical properties. The starch graft copolymer emulsion was used as a binder for making native starch free flowing granules. The free flowing granules of starch were dried in a fluidized bed dryer to the desired moisture content. The present study was undertaken with a view to develop improved conditions for graft copolymerization of starch with ST/MMA and ST/BA and to study the graft percentage, tensile strength, rheological properties and its application in the textile industry (Venkatraman, 1999).

2. Materials and methods

2.1. Starch

Acid modified starch was used as received from M/s. S.A. Pharmachem Pvt. Ltd., Mumbai, India. The starch posses an intrinsic viscosity of 0.46 dl/g measured at 25 °C.

2.2. Monomer

Commercially available methyl methacrylate (MMA), butyl acrylate (BA) and styrene (ST) were used. Before polymerization, the monomers were washed to remove the inhibitors from them. The monomers were first washed with saturated 5% (w/v) $NaHSO_3$ solution and then with 5% (w/v) NaOH solution, while ST monomer of commercial grade was washed with 15% (w/v) KOH solution to remove inhibitors (Forcada & Asua, 1990). Treated monomers were further washed with distilled and deionized water until the washed water becomes neutral.

2.3. Other reagents

Ferrous ammonium sulphate $[Fe(NH_4)_2 \cdot (SO_4)_2 \cdot 6H_2O]$ (FAS), hydrogen peroxide (H_2O_2 30% w/v), sodium hydroxide (NaOH), potassium hydroxide (KOH) were of analytical grade.

2.4. Graft polymerization procedure

In a typical procedure, starch was gelatinized in water (5% w/v) by heating to 75–80 °C in the reactor equipped with thermometer, stirrer and reflux condenser. The gelatinized starch was then cooled down to the reaction temperature of 60 °C. The nitrogen atmosphere was maintained in the reactor by purging the nitrogen gas in the reactor. The ferrous ammonium sulphate was then added to the reactor followed by the addition of monomers. Further, hydrogen peroxide was added to initiate the polymerization reaction. The reaction was carried out at 60 °C in a constant temperature bath for 2 h with a constant stirring at 450 rpm. The monomer to starch ratio of 42 parts monomer to 58 parts starch by weight with the monomers ST/MMA and ST/BA in ratio of 80/20, 50/50 and 20/80 by weight were used. At the end of reaction, the flask contents were added to ethyl alcohol and a precipitate was allowed to form, which consisted of starch graft copolymers and the homopolymers of MMA/BA and ST. This precipitate was then filtered and dried in an oven at 60 °C until constant weight was achieved. The percentage conversion of monomer was calculated from the increase in weight of the starch product. The polyMMA, polyST and polyBA homopolymers in the dried polymer product was separated by Soxhlet extraction using chloroform followed by ethylene dichloride for 12 h each. The percent conversion (PC), graft efficiency (GE), graft yield (GY) and graft percentage (GP) were calculated using following equations:

$$\text{Percentage conversion(PC)} = \frac{w_1}{w_2} \times 100 \tag{1}$$

$$\text{Graft efficiency(GE)} = \frac{w_3}{w_1} \times 100 \tag{2}$$

$$\text{Graft percent(GP)} = \frac{w_3}{w_4} \times 100 \tag{3}$$

$$\text{Graft yield(GY)} = \frac{w_5}{w_4} \times 100 \tag{4}$$

where w_1 is the weight of polymer formed (g), w_2 is the weight of monomer taken (g), w_3 is the weight of grafted polymer (g), w_4 is the weight of starch taken (g), w_5 is the weight of starch grafted polymer (g).

2.5. Apparent viscosity

The apparent viscosities of the samples were measured at 28 °C using Haake Rotovisco RT-10 with cone and plate (35/2° angle) assembly. The grafted starch emulsion was taken as such and for the grafted starch granules (hereafter referred to as, GSG) 5% w/v solution was prepared for viscosity measurement.

2.6. Tensile strength

The tensile strength and elongation at break were measured on Universal Testing Machine (Model: H5KS, Tinius-Olsen, USA) according to ASTM procedure D-2256. Cotton yarns were sized by dipping in the cooked native starch and the modified GSG starch solution (5% w/v) at 90 °C for 5 min and dried in an oven at 100 °C for 3 min.

2.7. Dissolution rate

The dissolution rate was determined by dissolving the known quantity of granules in excess of water using dissolution rate apparatus. The temperature of the solution was maintained at 60 °C with stirring speed of 100 rpm. The samples were collected every 30 s and the turbidity of the samples measured using Turbidimeter (Model: 965-IR, Orbeco-Hellige, USA).

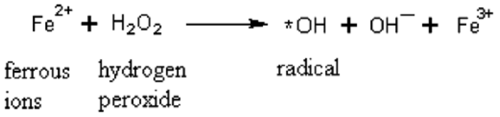
2.8. Fourier transform infrared spectroscopy (FTIR) analysis

Fourier transform infrared spectrum of the starch and the graft copolymer were recorded on FTIR spectrophotometer (Model: Bomem Hartman & Braun MB-series, Germany) using KBr-pellets.

3. Results and discussion

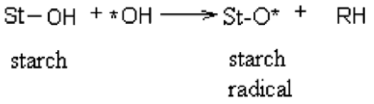
3.1. Mechanism of grafting

The presence of ferrous ions in the polymerization medium produces free radicals according to the reaction mechanism elucidated in reaction (i), given below. The free radical produces pre-gelled starch micro-radicals by direct abstracting hydrogen atoms from the pre-gelled starch molecules, as shown in reaction (ii). In the presence of monomers styrene/methyl methacrylate, the pre-gelled starch radical is added to the double bond of the monomers as shown in reaction (iii), resulting into the covalent bond formation between starch and the monomer with creation of the radical on the monomer i.e. chain initiation. In the present case, the two different monomers are present, which will attach randomly to the growing chain as shown in reaction (iv) and (v). In this way, the propagation of the polymerization reaction will take place. Finally, the termination of the growing grafted chain occurs via reaction with the initiator, coupling or combination, as shown in reactions (vi) and (vii), respectively.



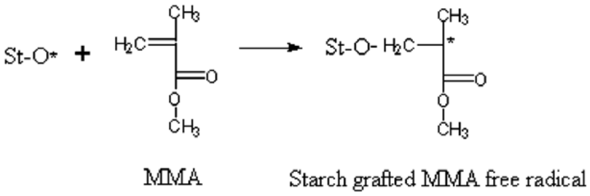
$$Fe^{2+} + H_2O_2 \longrightarrow {*}OH + OH^- + Fe^{3+}$$

(i)

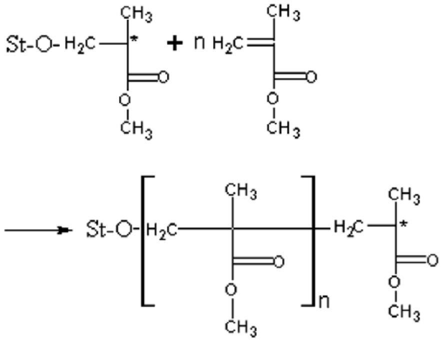


$$St{-}OH + {*}OH \longrightarrow St{-}O{*} + RH$$

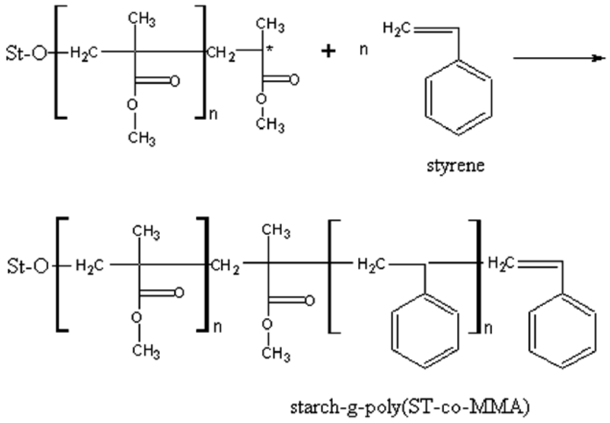
(ii)



(iii)

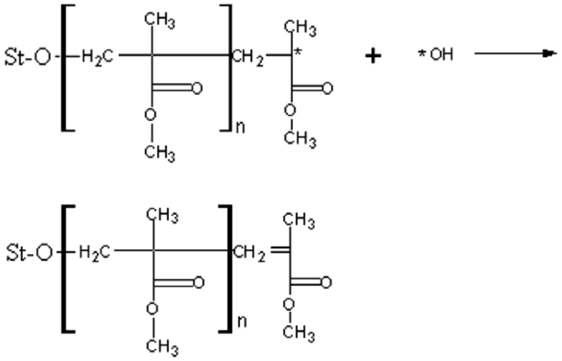


(iv)

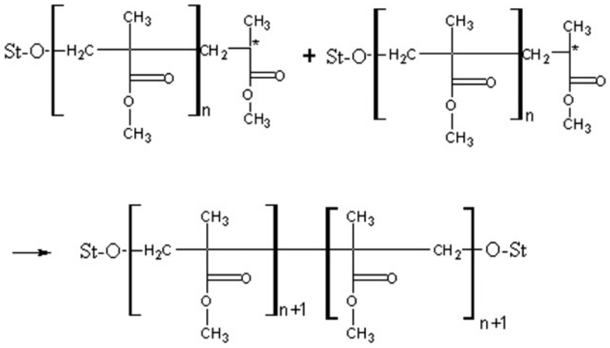


(v)

Graft propagation



Graft termination by initiator radical (vi)



Graft termination by coupling or combination (vii)

3.2. Effect of monomer ratio

The monomer ratio can affect the graft efficiency (GE) as well as the graft percentage (GP). In the following study, the effect of monomer concentration varying in the range of 80/20, 50/50 and 20/80 parts by weight has been discussed. Fig. 1 shows the effect of variation of monomer ratio (ST/MMA) on GE and GP. It can be seen that, in case of ST/MMA system, GE increases with an increase in ST to MMA ratio. However, GP increases initially and thereafter it decreases with further increase in the ST to MMA concentration ratio. Table 1 shows the effect of monomer ratio on monomer con-

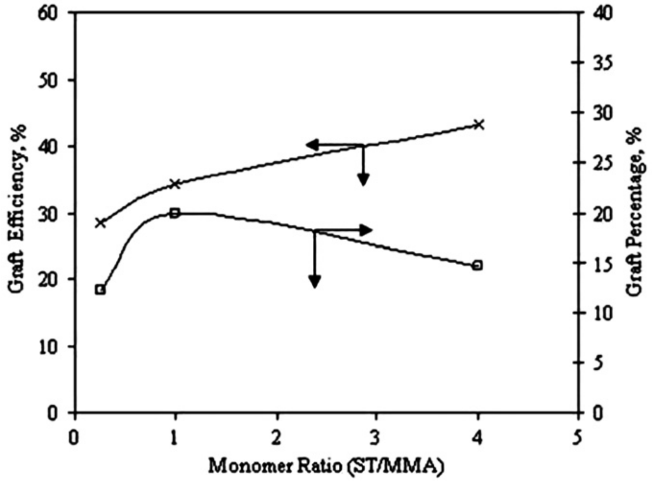


Fig. 1. Effect of monomer concentration on the graft efficiency and graft percentage for ST/MMA system. GP (□), GE (×).

Table 1
Effect of monomer concentration on the PC and GY

Grafted starch granules		Polymer conversion (PC) %	Graft yield (GY) %
ST/MMA ratio	80/20	46.87	114.62
	50/50	80.55	120
	20/80	59.39	112.21
ST/BA ratio	80/20	57.78	120.624
	50/50	89.71	135.94
	20/80	87.36	137.20

version and graft yield. At 80/20 ratio of styrene and MMA or BA, the monomer conversion was found to be least as compared to other ratios of 50/50 or 20/80. Fig. 2 shows the effect of variation of monomer ratio in case of ST/BA system. It shows that as ST/BA ratio increases both the GE and GP decreases, however as compared to ST/MMA system, the ST/BA system shows higher GE and GP.

In case of 50/50 ST/MMA or ST/BA, the polymer conversion was found maximum as shown in Table 1. The ST/BA at the ratio of 20/80 also gave comparable polymer conversion, which was higher than ST/MMA having similar composition. The graft yield was found to vary in the range of 112–137 as shown in Table 1. The higher polymer conversion in case of ST/BA of 50/50 ratio was obtained because of high reactivity ratio. The grafting efficiency of ST/BA system is also higher as compared to ST/MMA system because of the same reason.

3.3. Effect of initiator concentration

The effect of the initiator concentration on the GP, GE, PC and GY was obtained by changing the concentration of hydrogen peroxide from 50 to 150 mM for a given monomer concentration ratio and the reaction time as shown in Fig. 3 and Table 2. From the graph, the optimum concentration of H_2O_2 for the grafting reaction was found to be 100 mM. The hydroxyl radicals can either recombine among themselves or with some other radicals; they can result in homo-polymerization or can stop propagation of growing chains as shown in reaction mechanism (vi). Further, the higher concentration of initiator produces more free radicals which are likely to participate in the termination of growing chain radicals as well as initiating homo-polymerization.

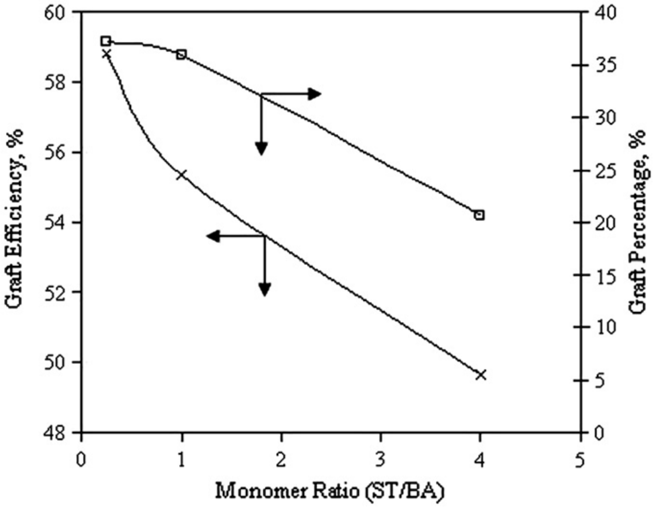


Fig. 2. Effect of monomer concentration on the graft efficiency and graft percentage for ST/BA system. GP (□), GE (×).

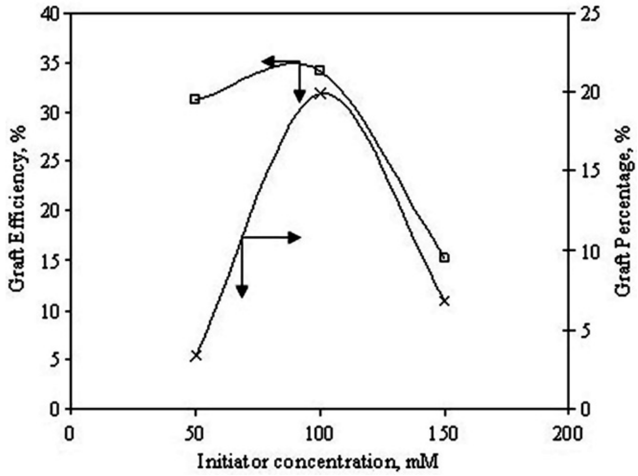


Fig. 3. Effect of hydrogen peroxide concentration on the percentage grafting and graft percentage. GE (□), GP (×) (ST/MMA 50/50 ratio and reaction time 2 h).

Table 2
Effect of hydrogen peroxide concentration on the PC and GY for the ST/MMA (50/50) system

Initiator concentration (mM)	50	100	150
Polymer conversion	14.98	80.55	62.5
Graft yield	103.4	120	106.85

3.4. Effect of starch concentration

The effect of starch concentration on the GP, GE, PC and GY is shown in Fig. 4 and Table 3. The results were obtained by varying the concentration of starch between 3% and 7% w/v for a given monomer concentration (ST/MMA) and time. The graft percentage increases with an increase in starch concentration and approaches asymptotic value of 36% at starch concentration of 7% w/v.

3.5. Granulation of starch and drying

The granulation of the native starch was carried out by adding the grafted starch emulsion onto the native starch. By doing so, it

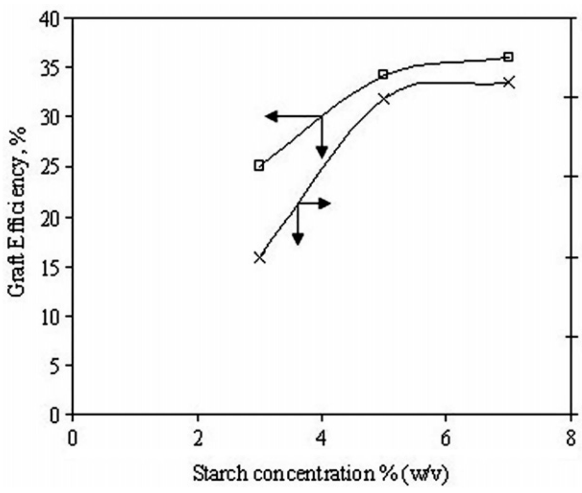


Fig. 4. Effect of starch concentration on the percentage grafting and graft percentage. GE (□), GP (×).

Table 3
Effect of starch concentration on the PC and GY

Starch concentration, % w/v	3	5	7
Polymer conversion	55.24	80.55	95.76
Graft yield	110	120	121

is expected to improve the flowability and the physico-mechanical properties of the native starch. Granulation of starch was carried out in a rapid mixer granulator by spraying varying concentrations of graft emulsion (binder solution) of grafted starch onto the native starch. The grafted starch granules (GSG) were dried in a fluidized bed dryer. The air velocity and temperature for drying were maintained at 1.2 m/s and 60 °C, respectively, in the fluidized bed dryer. A known amount of sample was sieved using gyratory sieve shaker (Secor, India). The weight of residual granules in each sieve was measured for determining particle size distribution and the average mean particle size (D_{50}) (Parrott, 1986). At high binder concentration, the particle size distribution was found to be wider as compared to the lower binder concentration as shown in Fig. 5. The average mean particle size for 10% w/w binder concentration was 290 μm and for both 16.67% and 23.72% w/w binder concentration the average particle size was found to be around 360 μm.

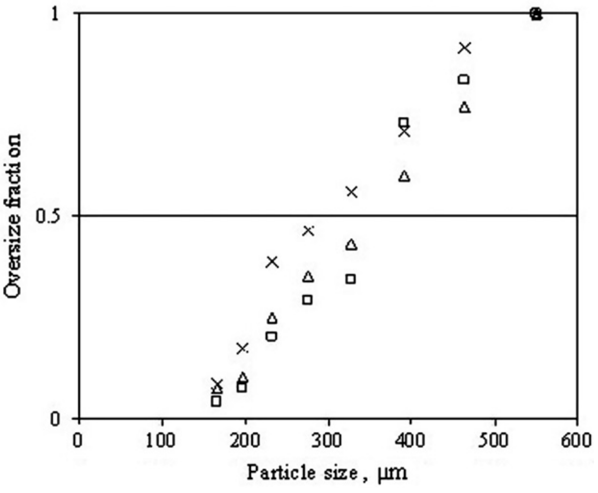


Fig. 5. Particle size distribution of GSG after granulation and fluidized bed drying for binder concentration of 10% (×), 16.67% (□) and 23.72% (Δ) (w/w).

Fig. 6 shows the loss of moisture with time and the dependence of drying rate on the initial binder concentration. The drying kinetics data was fitted by using Page model equation (Hinderson, 1974)

$$\mathrm{MR} = \exp\left[-\left(0.0044 \times C^2 - 0.1846 \times C + 1.9597\right) \times t^{\left(-0.0038 \times C^2 + 0.1739 \times C - 0.8506\right)}\right] \quad (5)$$

where,

$$\mathrm{MR} = \text{moisture ratio} = \frac{X_t - X_e}{X_0 - X_e}$$

C is the concentration of binder (wt%), t is the time (min), X_t *is the moisture content at any time (kg/kg),* X_0 is the initial moisture content (kg/kg), X_e is the equilibrium moisture content (kg/kg). It was found that the Page model fits the drying data very well within ±15%. The time required for the drying of the GSG to the moisture content of 0.04 kg/kg (dry basis) was found to be in the range of 20–25 min.

3.6. Physico-mechanical properties

Table 4 indicates the flowability of GSG in terms of angle of repose and the corresponding bulk density. It can be seen that the granules were of free flowing nature (angle of repose ≈38°) having bulk density in the range of 450–500 kg/m^3 according to the ISO 5311–1992.

3.7. Evidence of grafting

FTIR spectra of pure starch and grafted starch are shown in Figs. 7–9. The spectrum of the grafted starch shows the characteristic absorption of starch at 3000–3800 cm^{-1}due to OH stretching

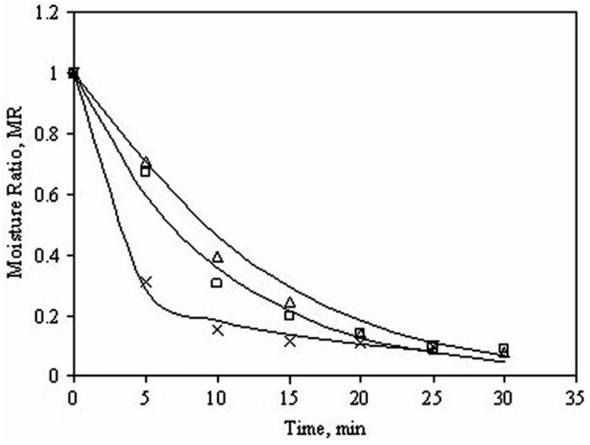


Fig. 6. Moisture content profiles for the GSG of ST/MMA system. Experimental points: 16.67% (□), 23.72% (Δ), 10% (×), from Eq. (5) (–).

Table 4
Angle of repose and bulk density data for the grafted starch granules

System	Ratio by weight	Angle of repose in (°)	Bulk density (kg/m^3)
ST/MMA	80/20		457.35
	50/50	37.65	485.66
	20/80		482.83
ST/BA	80/20		460.53
	50/50	38.65	419.40
	20/80		504.98

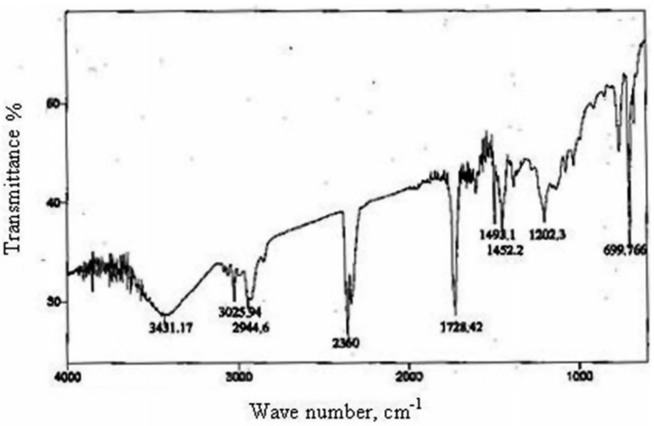


Fig. 7. FTIR spectra of starch grafted with styrene and methyl methacrylate.

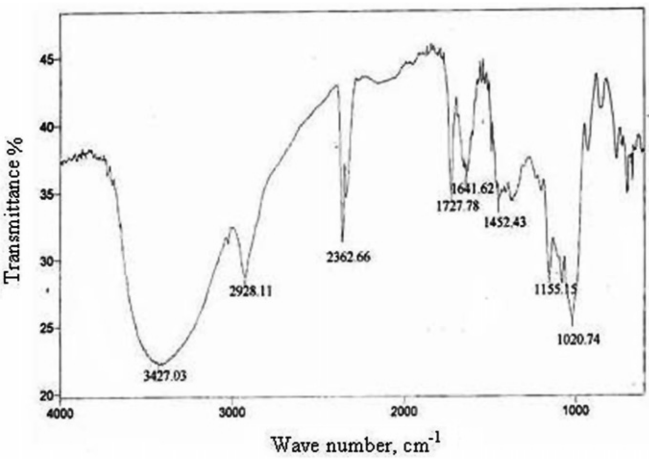


Fig. 8. FTIR spectra of native starch.

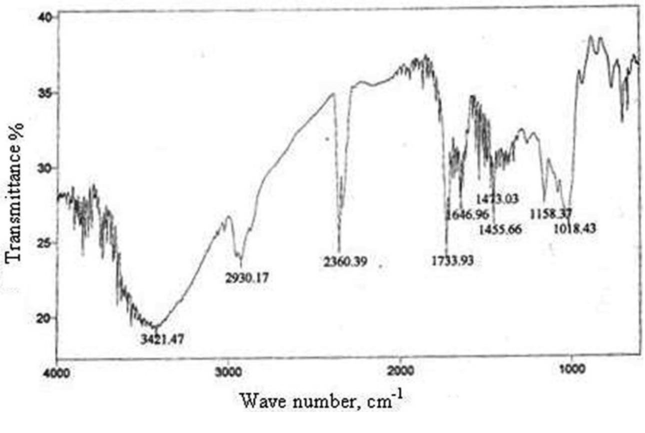


Fig. 9. FTIR spectra of starch grafted with styrene and butyl acrylate system.

band, the aromatic CH bonding at 3100–3000 cm^{-1}, aliphatic CH stretching at 2944 cm^{-1}and ester C=O stretching at 1630–1860 cm^{-1}, coming from the grafted starch. These characteristic peaks indicate the presence of polystyrene and polymethyl methacrylate molecules. Thus, the FTIR spectra of ST/MMA-grafted starch and ST/BA-grafted starch gives supporting evidence that both the polymers were successfully grafted on to the starch molecules.

3.8. Dissolution rate study

The dissolution rate study of the GSG was carried at 60 °C in distilled water as a medium. Five hundred milligrams of GSG was taken directly in 100 ml of distilled water. Uniform temperature was maintained using water bath and the samples were collected every 30 s. The concentration of dissolved solids was measured using Turbidimeter. The dissolution data is as shown in Fig. 10. The dissolution rate of the GSG decreases with an increase in the styrene concentration in both the cases. The asymptotic concentration of GSG increases with the decrease in styrene composition, thereby limiting the styrene contribution. It is therefore desired to keep the styrene content to minimum and increase the concentration of either methyl methacrylate (MMA) or butyl acrylate (BA).

3.9. Viscosity

The rheological properties of aqueous solution of GSG (5% w/v), polymerization product of starch–ST–MMA/BA and the emulsion of ST–MMA were studied. Figs. 11–13 show the plot of the viscosity of the above solutions versus the shear rate. As shown in the fig-

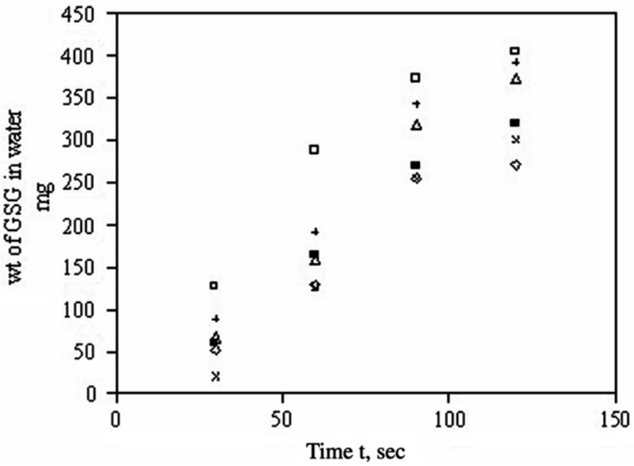


Fig. 10. Plot of time versus dissolved solids for the starch grafted with different monomer ratios: ST/MMA: 80/20 (×), 50/50 (+), 20/80 (■) and ST/BA: 80/20 (◇), 50/50 (Δ), 20/80 (□).

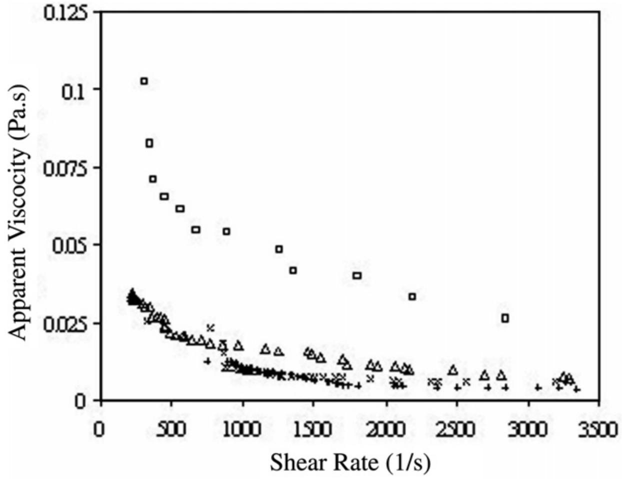


Fig. 11. Plot of shear rate versus viscosity for the GSG of ST/MMA system. Starch (×), 80/20 (□), 50/50 (Δ), 20/80 (+).

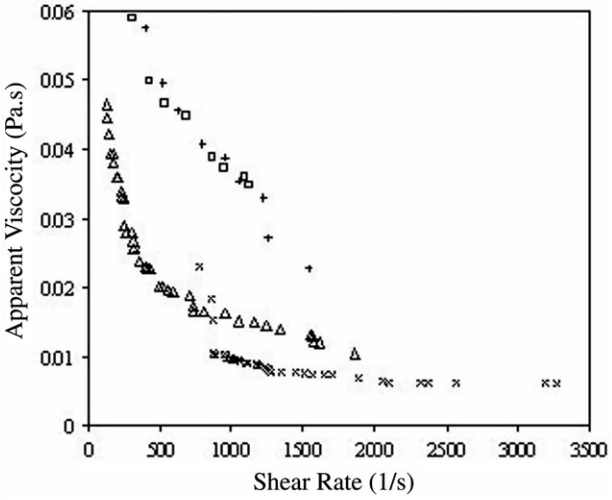


Fig. 12. Plot of shear rate versus viscosity for the GSG of ST/BA system. Starch (×), 80/20 (□), 50/50 (Δ), 20/80 (+).

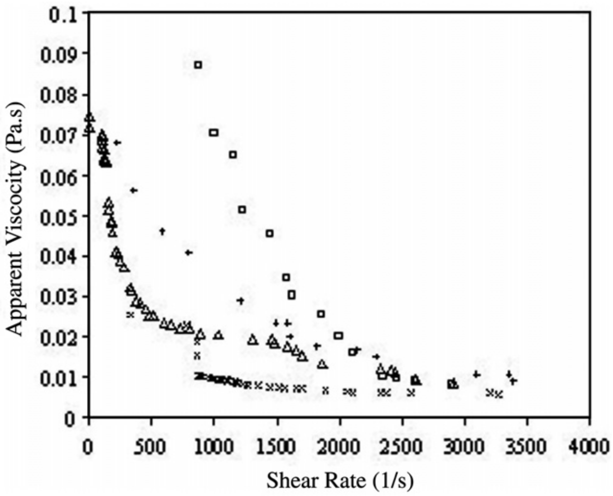


Fig. 13. Plot of shear rate versus viscosity for the emulsion of ST/MMA system. Starch (×), 80/20 (□), 50/50 (Δ), 20/80 (+).

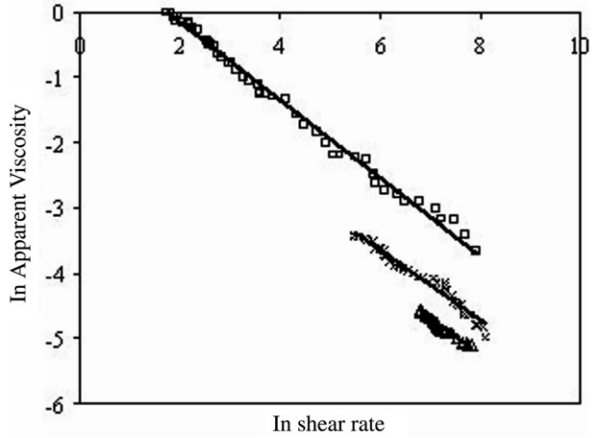


Fig. 14. Log–log plot of shear rate versus apparent viscosity for the GSG of ST/MMA system. 80/20 (□), 50/50 (×), starch (Δ).

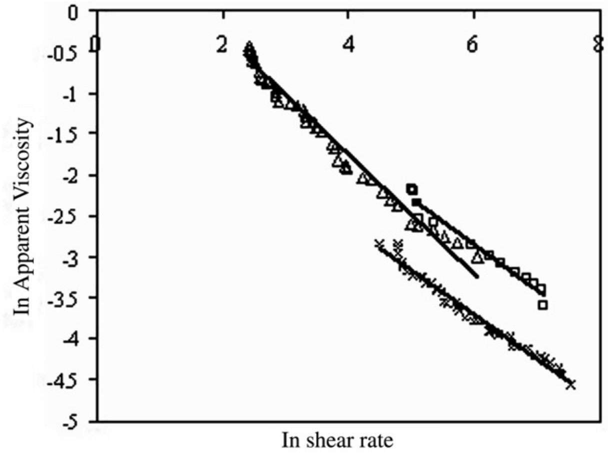


Fig. 15. Log–log plot of shear rate versus apparent viscosity for the GSG of ST/BA system. 80/20 (Δ), 20/80 (□), 50/50 (×).

Table 5
Percentage grafting and power index data for the grafted starch granules of ST/MMA and ST/BA system

Grafted starch granules		Grafting efficiency	Power index
Starch		–	0.461
ST/MMA ratio	80/20	43.80	0.411
	50/50	34.12	0.459
	20/80	28.39	–
ST/BA ratio	80/20	49.65	0.377
	50/50	55.34	0.446
	20/80	58.82	0.461

ure, the viscosity of the solutions decreases with an increase in the shear rate showing shear-thinning property.

The power low model for the aqueous solution of GSG given in the below equation was used to fit the experimental data

$$\mu_a = k\dot{\gamma}^{(n-1)} \tag{6}$$

where μ_a is the apparent viscosity (Pas), k is the consistency coefficient (N s^n/m^2), $\dot{\gamma}$ is the shear rate (1/s), n is the power law index.

As shown in Figs. 14 and 15, the shear-thinning behavior is observed for all the solutions. The power law index varies in between 0.5 and 0.33. In case of ST/BA system the value of the n decreases with an increase in the ST concentration as shown in Fig. 15. This is due to the increased viscosity with an increase in grafting efficiency.

Table 5 shows the grafting efficiency and power index for aqueous solution (5% w/v) of GSG obtained by varying the ratios of monomers. The native starch solution was used to compare these properties. It can be seen that the power law index for the native starch is higher as compared to GSG of ST/MMA system and nearly the same as compared to ST/BA (20/80) system. The initiator present in the reaction system causes the break down of the starch molecules during the reaction and so the power law index decreases to some extent after grafting reaction. Also, the viscosity of the final emulsion depends on the grafting efficiency and in case of ST/BA system the power law index remains the same as that of native starch.

3.10. Sizing of cotton textiles

The work presented in this section aims at applying the newly synthesized sized products in sizing of cotton textiles to see its suitability for the temporary improvement of the physico-mechanical properties. Starch has been widely used commercially in tex-

Table 6
Physico-mechanical properties of cotton fabric sized with GSG

Fabric sample	Tensile strength (kgf)	Elongation at break %
Unsized	1.139	8.45
Sized with native starch	1.266	7.65
Sized with ST/BA grafted starch granules		
80/20	1.36	7.23
50/50	1.39	6.92
20/80	1.47	6.18
Sized with STMMA grafted starch granules		
80/20	1.392	7.78
50/50	1.456	6.76
20/80	1.454	7.76

tile warp sizing, particularly in cotton textiles. Nevertheless, it suffers from serious defects, the most outstanding of which are (a) very high molecular size which limits their penetration into the bulk of the textile threads; (b) instability of the viscous solution due to fluctuation of temperature during cooking and sizing operations; (c) rigidity of the film, particularly in the absence of a good lubricant; and (d) susceptibility to rot and degradation by microorganism. To overcome or at least to minimize these defects chemical modification via hydrolysis and grafting as in our case, have been emphasized. Table 6 shows the physico-mechanical properties such as tensile strength and elongation at break point of the cotton yarn sized with the plain starch and the grafted starch.

The results in Table 6 reveal a number of interesting features:

1. Cotton yarn samples sized with native starch shows an increase in tensile strength, while elongation at break decreases with respect to the unsized one.
2. Cotton yarn samples sized with ST/BA and ST/MMA-grafted starch granules exhibit higher tensile strength and further lower elongation at break as compared to the sizing with native starch.
3. Cotton yarn samples sized with ST/BA (20/80) grafted starch granules shows the highest tensile strength and even further lower elongation at break as compared to the earlier case.

4. Conclusions

The grafted starch was synthesized by graft copolymerization of starch with ST and MMA/BA. The optimum monomer concentration ratio and the initiator concentration were determined. The percentage grafting of the starch-g-polyST/polyMMA of 50/50 and starch-g-polyST/polyBA of 20/80 were found to be higher as compared to other ratios. The optimum concentration of the hydrogen peroxide initiator was found to be 100 mM. The maximum percentage grafting was found in case of starch-g-polyST/polyBA system. The grafting of starch was confirmed by FTIR analysis. The cotton yarn sized with GSG of ST/BA system gives higher tensile strength and lower elongation at break. The time required for the dissolution of the grafted starch granules was high when the percentage grafting is high. In addition, the viscosity of the grafted starch granules can be increased by increasing the percentage graft. The monomer ratio of 20/80 in case of ST/BA was found to give the highest tensile strength with the corresponding lowest elongation at break.

References

Athawale, V. D., & Lele, V. (2000). Synthesis and characterization of graft copolymers of maize starch and methacrylonitrile. *Carbohydrate Polymers, 41*(4), 407–416.

Brockway, C. E., & Moser, K. B. (1963). Grafting of poly (methyl methacrylate) to granular corn starch. *Journal of Polymer Science: Part A, 1*, 1025–1039.

Cho, C. G., & Lee, K. (2002). Preparation of starch-g-polystyrene copolymer by emulsion polymerization. *Carbohydrate Polymers, 48*(2), 125–130.

Dennenberg, R. J., & Abbott, T. P. (1976). Rapid analysis of starch graft copolymers. *Polymer Letter Edition, 14*, 693–696.

El-Rafie, M. H., Zahran, M. K., El Tablawy, Kh. F., & Hebeish, A. (1995). A comparative study of the polymerization of acrylic acid with native and hydrolyzed maize starches using a potassium bromate-thiourea dioxide redox initiation system. *Polymer Degradation and Stability, 41*, 73–85.

Fanta, G. F., Felker, F. C., & Shogran, R. L. (2004). Graft copolymerization of acrylonitrile onto spherocrystals formed from jet cooked corn starch. *Carbohydrate Polymers, 56*(1), 77–84.

Forcada, J. F., & Asua, J. M. (1990). Modelling of unseed emulsion copolymerazation of styrene and metha methylacrylate. *Journal of Applied Polymer Science, 28*, 987–1009.

Fox, C. J. (1998). Methods and materials for coating textile compositions. *United States Patent No. 5707720*.

Geresh, S., Gilboa, Y., Peisahov-Korol, J., Gdalevsky, G., Voorspoels, J., Remon, J. P., et al. (2002). Preparation and characterization of bioadhesive grafted starch copolymers as platforms for controlled drug delivery. *Journal of Applied Polymer Science, 86*(5), 1157–1162.

Hebeish, A., & Bendak, A. (1974). Redox-initiated vinyl graft polymerization onto wool with thiourea as the reductant I. Grafting of methyl methacrylate with hydrogen peroxide-thiourea catalyst system. *Journal of Applied Polymer Science, 18*, 1305–1317.

Hinderson, S. M. (1974). Progress in developing the thin layer drying equation. *Transactions of ASAE, 17*, 1167–1172.

Jianping, G., Jiugao, Y., Wei, W., Liming, C., & Ruchuan, T. (1998). Graft copolymerization of starch-AN initiated by potassium permanganate. *Journal of Applied Polymer Science, 68*(12), 1965–1972.

Kiatkamjornwong, S., Mongkolsawat, K., & Sonsuk, M. (2002). Synthesis and property characterization of cassava starch grafted poly[acrylamide-co-(maleic acid)] superabsorbent via γ-irradiation. *Polymer, 43*, 3915–3924.

Meltem, C. (2006). Preparation and characterization of starch-g-polymethacrylamide copolymers. *Journal of Polymer Research, 13*, 427–432.

Mino, G., & Kaizerman, S. (1958). A new method for the preparation of graft copolymers. Polymerization initiated by ceric ion redox system. *Journal of Polymer Science, 31*, 242–243.

Mostafa, Kh. M. (1997). Synthesis of poly(acryl amide)-starch and hydrolyzed starch graft copolymers as a size base material for cotton textiles. *Polymer Degradation and Solubility, 55*, 125–130.

Mostafa, Kh. M. (2005). Grafting of methacrylamide onto cotton yarn part I: Tensile strength. *Journal of Applied Sciences, 5*(2), 341–346.

Mostafa, Kh. M., & Morsy, M. S. (2004). Modification of carbohydrate polymer via grafting of methacrylonitrile onto pregelled starch using potassium monopersulphate/Fe2+ redox pair. *Polymer International, 53*, 885–890.

Nguyen, C. C., Martin, V. J., & Pauley E. P. (1991). Starch graft copolymer. *United States Patent No. 5003022*.

Parrott, E. L. (1986). Milling. In L. Lachman, H. A. Lieberman, & J. L. Kanig (Eds.), *The theory and practice of industrial pharmacy* (3rd ed., pp. 21–47). Philadelphia: Lea & Febiger.

Taghizadeh, M., & Khosravy, M. (2003). Kinetics and mechanism of graft copolymerization of vinyl monomers (acrylamide, acrylic acid, and methacrylate) onto starch by potassium dichromate as redox initiator. *Iranian Polymer Journal, 12*(6), 497–505.

Venkatraman, V. A. (1999). Important factors in sizing of textiles. *New Cloth Market, 13*(12), 19–28.

Whistler, R. L., BeMiler, J. N., & Paschall, E. F. (1984). *Starch chemistry and technology* (2nd ed.). Orlando, FL: Academic Press Inc..

Willett, J. L., & Finkenstadt, V. L. (2006). Reactive extrusion of starch–polyacrylamide graft copolymers using various starches. *Journal of Polymers and the Environment, 14*, 125–129.

Zhai, M., Yoshii, F., Kuma, T., & Hashim, K. (2002). Synthesis of PVA/starch grafted hydrogels by irradiation. *Carbohydrate Polymers, 50*(3), 295–303.