

Synthesis and Characterization of Starch-g-poly(methyl methacrylate-co-styrene) Copolymer Prepared via Emulsion Polymerization

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ABSTRACT: This investigation reports the synthesis and characterization of a graft copolymer of methyl methacrylate (MMA) and styrene (Sty) onto starch. The copolymers of MMA with Styrene, P(MMA-co-Sty) and the graft copolymer, Starch-g-P(MMA-co-Sty) were prepared via emulsion polymerization using the thermal initiator potassium persulfate (KPS). Sodium Dodecyl Sulfate (SDS) was used as a surfactant in both cases. The polymerizations were carried out at 70°C for 30 minutes for P(MMA-co-Sty) and 3 hours for Starch-g-P(MMA-co-Sty). Attempts had also been made to prepare copolymers with different monomer compositions. The progress of the polymerizations with time was monitored by measuring the conversion of monomers gravimetrically. The grafted Starches were characterized by Nuclear Magnetic Resonance (¹H-NMR) and Fourier Transform InfraRed (FT-IR) spectroscopy analyses. The FT-IR and ¹H NMR analysis of the purified copolymers revealed successful grafting of MMA and Styrene copolymerization onto Starch. The surface morphology was studied by SEM and the thermal study of the graft copolymer was studied by TGA.

KEYWORDS: Starch; Graft copolymer; Methyl Methacrylate; Styrene; Emulsion polymerization.

INTRODUCTION

Starch is an abundant and cheap biopolymer found in nature [1]. It consists of anhydroglucose units linked via α (1-4) and α (1-6) glycosidic bonds and is a mixture of amylose and amylopectin [2,3]. It is biocompatible, non-toxic, and hydrophilic which makes it a great raw material for different applications. However, its poor physical and

mechanical properties restrict its applications. However, chemical or physical modification process, blending may help to improve its properties [2-5]. Different chemical modifications like oxidization, desertification, etherification, graft copolymerization, and cross-linking through hydroxyl groups, are in use for the synthesis of starch graft

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copolymer to synthesize new cost-effective polymers [6-8]. Among them, graft copolymerization has proved to be an efficient one, allowing the modification of starch [7-11]. This modification alters the various properties of starch such as ion exchange capabilities, absorbency, thermal resistance, elasticity, and resistance towards microbiological attack, and also induces biodegradable character in the modified polymer [4, 12-14]. Moreover, starch may be modified with many vinyl monomers *via* graft copolymerization [15, 16].

In this work, graft copolymerization of Styrene and Methyl methacrylate (MMA) onto Starch by free radical emulsion polymerization is reported. Emulsion polymerization is a type of heterogeneous reaction producing numerous polymeric products which are generally referred to as latexes [2, 17, 18]. It provides several advantages over conventional polymerization, like, the yielding of high molecular weight polymer with low polydispersity and other distinct properties [19, 20]. Moreover, the polymerization is carried out in water eliminating the use of volatile organic solvents [1].

The monomer MMA, is one of the most commercially used monomers and its homopolymer has excellent properties such as good processing ability, transparency, and weather ability [10, 20-23]. On the other hand, polystyrene has high abrasion resistance, greater tensile strength, and load-bearing capacity [24, 25, 13]. Thus, the copolymer of styrene and methyl methacrylate grafting onto starch may lead to a significant material. This material may find important applications in paper coating, etc. There have been reports on the preparation of Starch-g-poly(meth) methacrylate, Starch-g-Poly(styrene) copolymers, which are commonly used in different applications such as films, adhesives, etc. [10, 11, 26]. *Qudsieh et al.* reported the synthesis of Starch-g-PMMA using a redox initiator in emulsion [27]. *Li et al.* also reported the synthesis of Starch-g-PMMA using Ceric Ammonium Nitrate (CAN) as an initiator [28]. *Sangramsingh et al.* reported the graft copolymerization of MMA onto starch using Ce (IV)-glucose initiating system [12]. *Pimpan et al.* reported the preparation of Starch-g-PMMA by free radical polymerization in an aqueous medium using benzoyl peroxide (BPO) as an initiator [14]. *Cho et al.* reported the synthesis of Starch-g-PSty copolymer using potassium persulfate as an initiator in emulsion [9]. *Kaewtatip et al.* reported the graft copolymerization of polystyrene onto cassava Starch

(Starch-g-PSty) via free-radical polymerization in suspension [29, 30]. However, the preparation of Starch-g-P(MMA-co-Sty) has not been extensively studied compared to the individual monomer grafted onto starch that is Starch-g-PMMA and Starch-g-PSty.

In this investigation, the synthesis of a graft copolymer of Starch with MMA and Styrene, Starch-g-P(MMA-co-Sty) by emulsion polymerization and their subsequent characterizations via FT-IR, NMR, TGA, and SEM analyses is reported.

EXPERIMENTAL SECTION

Materials

Monomers methyl methacrylate (MMA) (99%, Aldrich, USA) and styrene (98%, Avra, India) were used as received. Initiator potassium persulfate (KPS) (98%, Avra, India) was also used as received. Surfactant, Sodium Lauryl Sulfate (SDS) (99%, SRL, India), and Starch (Starch soluble, Rankem, AR, India) were used as acquired. Distilled water was used for the emulsion polymerization reaction. Other chemicals like Acetone, THF, and glacial Acetic Acid were used as received.

Synthesis of P(MMA-co-Sty) via emulsion polymerization

In a typical emulsion polymerization reaction, distilled water (10 g) and the surfactant SDS (0.1 g, 0.35 mmol) were taken in a dry Schlenk tube equipped with a stirrer, a magnetic bar and a rubber septum. The mixture was stirred for 15 minutes, and then MMA (1 g, 9.98 mmol) and Styrene (1 g, 9.60 mmol) were added to the solution. After 1 hour of stirring, KPS (0.02 g, 0.80 mmol) was added to the system. The Schlenk tube was then sealed and nitrogen gas was passed through the mixture for 15 minutes to remove the dissolved oxygen present in these materials. The polymerization was started by placing the Schlenk tube in a preheated oil bath at 70 °C. The polymerization was carried out for 30 minutes. The aliquot was taken out at the end of the polymerization time to determine the monomer conversion gravimetrically. The same procedure was adopted to carry out emulsion polymerization for different compositions. The nomenclature of the prepared copolymers along with conversion and co-monomer composition are summarized in Table 1.

The synthesis of Starch-g-P(MMA-co-Sty) copolymer was prepared with different weight percentages of Starch (1, 2, 3, 4, and 5 wt%). The starch was dispersed for homogeneous

Table 1: Co-polymerization of MMA with Styrene at 70 °C using KPS as an initiator, copolymerization time = 30 minutes.

Sl. No.	Sample	Monomer feed ratio (in wt %) Styrene : MMA	Monomer Conversion (%)
1	EM-1	1 : 1	98
2	EM-2	1.5 : 0.5	88
3	EM-3	0.5 : 1.5	97

distribution in the solution of MMA (1 g, 9.98 mmol), Styrene (1 g, 9.60 mmol), distilled water (10 g), surfactant SDS (0.1 g, 0.35 mmol) and KPS (0.02 g, 0.80 mmol).

Synthesis of Starch-g-P(MMA-co-Sty) via emulsion polymerization

In a typical emulsion polymerization reaction, distilled water (10 g) and Starch (1% by weight) were taken in a dry Schlenk tube equipped with a stirrer, a magnetic bar, and a rubber septum. The surfactant SDS (0.1 g, 0.35 mmol) was then added to the mixture after 20 minutes. Then MMA (1 g, 9.98 mmol) and Styrene (1 g, 9.60 mmol) were added to the solution. After 1 hour of stirring, KPS (0.02 g, 0.80 mmol) was added to the system. The Schlenk tube was then sealed and nitrogen gas was passed through the mixture for 15 minutes to remove the dissolved oxygen present in the system. The graft copolymerization was started by placing the Schlenk tube in a preheated oil bath at 70 °C. The polymerization was carried out for 30 minutes. Aliquots were taken out at the end of the polymerization to determine the conversion of monomer gravimetrically.

The latex thus obtained was coagulated by acetic acid, washed thoroughly with distilled water, and filtered. Then it was dried in an oven at 70 °C to remove the unreacted monomers MMA and Styrene. The pure Starch-g-P(MMA-co-Sty) was obtained by removing the ungrafted homo- and co-polymers [PSty, PMMA, or P(MMA-co-Sty)] by selective solubilization technique. The nomenclature of the prepared graft copolymers along with conversion and Starch amount are given in Table 2.

Characterization

FT-IR analysis of the thin film of polymer KBr plate was carried out in Perkin Elmer FT-IR spectrometer for the scanning range from 400 to 4000 cm^{-1} . ^1H NMR spectra were recorded on 400 MHz Bruker NMR spectrometer using CDCl_3 as solvent and TMS as standard. Thermal study of the polymers was done by TGA (STA 6000 model). In Thermogravimetric analysis, 2 mg (approx.)

Table 2: Graft co-polymerization of MMA and Styrene (EM-1) onto Starch at 70 °C using KPS as initiator, copolymerization time = 3 hours.

Sl. No.	Sample	Starch (in wt. %)	Conversion (%)
1	EM-S1	1	95
2	EM-S2	2	90
3	EM-S3	3	91
4	EM-S4	4	98
5	EM-S5	5	86

of the polymer was heated from 30°C to 800°C at 10°C/min heating rate under a nitrogen atmosphere. The surface study of the polymer was performed using ZEISS ULTRA PLUS Scanning electron microscopy (SEM). A dry solid sample of polymer was put on silicon wafer and then it was coated with gold before analysis.

RESULTS AND DISCUSSION

The emulsion polymerizations were carried out at 70°C for 30 minutes for the preparation of P(MMA-co-Sty) and for 3 hours for the preparation of Starch-g-P(MMA-co-Sty). Starch-g-P(MMA-co-Sty) copolymer was prepared using different weight percentages of starch (1, 2, 3, 4, and 5 wt%). The polymerization results are shown in Table 1 and Table 2.

Structural Characterization

In the infrared spectrum of P(MMA-co-Sty), (Fig. 1), the absorption peaks at 1602, 1494, 760, and 700 cm^{-1} obtained for an aromatic ring of styrene and a characteristic C=O stretching band at 1730 cm^{-1} obtained for MMA confirm the copolymerization of MMA with styrene. The infrared spectrum of native Starch (Fig. 1), was characterized as follows: absorption peaks at 1074 and 1144 cm^{-1} for C-O stretching; a broad absorption peak at 3286 cm^{-1} for O-H stretching. Similar characteristic peak for Starch part of Starch-g-P(MMA-co-Sty) was observed at 3449 cm^{-1} . Other peaks for Starch-g-P(MMA-co-Sty) were as follows: peaks at 602, 760 and 700 cm^{-1} for styrene part and peaks at 1730 cm^{-1} for MMA part of the Starch-g-P(MMA-co-Sty). This indicated the successful grafting of P(MMA-co-Sty) onto Starch.

The ^1H NMR spectra of P(MMA-co-Sty) and Starch-g-P(MMA-co-Sty) are shown in Fig. 2. In Fig. 2(a), the chemical shift from $\delta=6.36-7.10$ ppm corresponded to different aromatic protons, the resonance at $\delta=1.62$ ppm was attributed to methylene protons ($-\text{CH}_2$) and the resonance

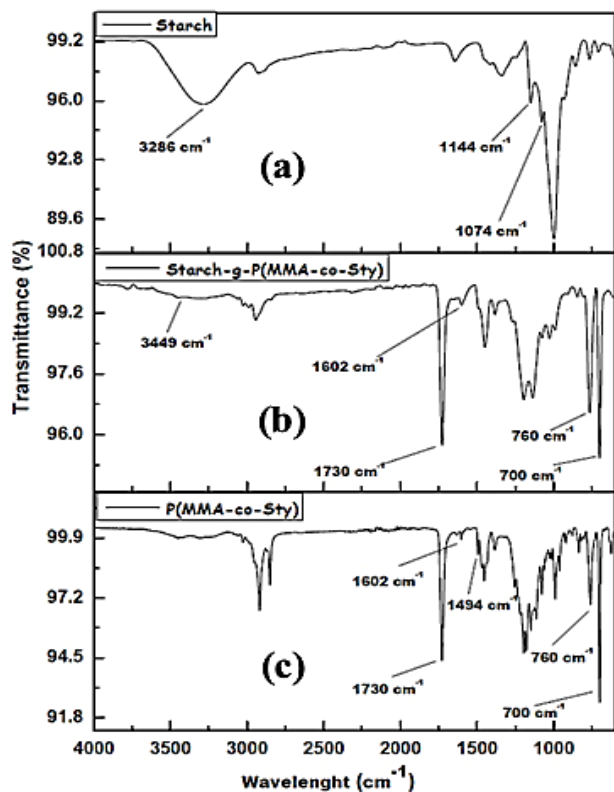


Fig. 1: FT-IR spectra of (a) Starch (b) Starch-g-P(MMA-co-Sty) and (c) P(MMA-co-Sty)

at $\delta=2.75$ ppm was assigned to the methine proton of styrene. While the chemical shift at $\delta=1.85$ ppm was assigned to methylene protons ($-\text{CH}_2$), $\delta=1.29$ ppm was assigned to methyl protons ($-\text{CH}_3$), and $\delta=3.66$ ppm was assigned to methoxy protons ($-\text{OCH}_3$) of MMA in copolymer. In Fig. 2(b) the signals between 3.72–6.15 ppm were assigned to the protons of the anhydroglucose units of starch. When comparing the spectra, P(MMA-co-Sty) Fig. 2(a) and Starch-g-P(MMA-co-Sty) Fig. 2(b) shows the appearance of the individual monomer characteristics peak, confirming the successful grafting of MMA and Sty onto starch.

Thermal Property

The thermal stability of the Starch-g-P(MMA-co-Sty) copolymer was evaluated by using ThermoGravimetric Analysis (TGA). The TGA and DTG curves for native Starch, purified P(MMA-co-Sty), and Starch-g-P(MMA-co-Sty) with different percentages of Starch (1 to 5 wt%) are shown in Fig. 3. All the TGA curves show a single-stage degradation. From the TGA curves, this is observed that the thermal stability of Starch grafted with MMA and Sty is higher than the native Starch and the copolymer,

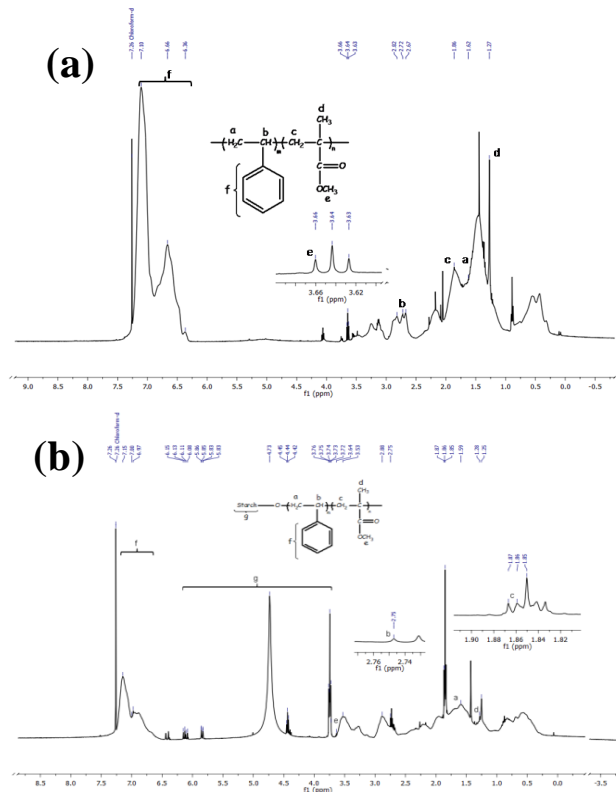


Fig. 2: (a) ^1H NMR spectrum of P(MMA-co-Sty), (b): ^1H NMR spectrum of Starch-g-P(MMA-co-Sty).

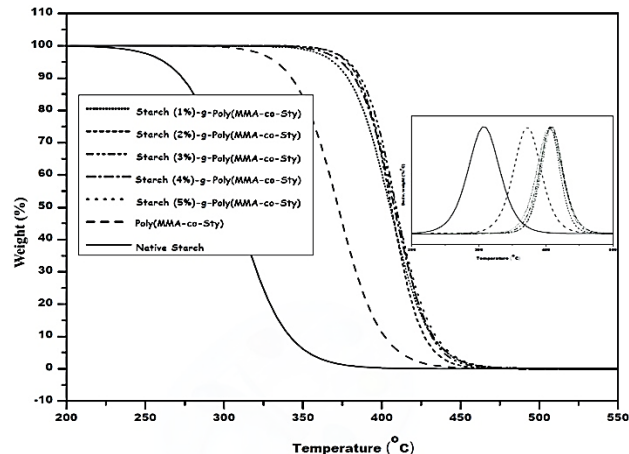


Fig. 3: TGA and DTG curves of native Starch, P(MMA-co-Sty) and Starch-g-P(MMA-co-Sty)

P(MMA-co-Sty). Chen et.al. also reported a similar kind of result that the thermal stability of oxidized Starch-g-P(St-co-BA) is higher than that of P(St-co-BA).[20] This also confirms the grafting of MMA and Styrene onto starch. Further, the effect of different amounts of Starch (1 to 5wt%) on the thermal stability of the grafted polymer was also studied. It was obtained that with an increase

Table 3: Thermal properties of Starch, P(MMA-co-Sty) and Starch-g-P(MMA-co-Sty) (1-5wt%)

Sl. No.	Sample	T _{onset} (in °C)	T _{max} (in °C)
1	Starch	261	305
2	P(MMA-co-Sty)	333	372
3	Starch(1%)-g-P(MMA-co-Sty)	366	405
4	Starch(2%)-g-P(MMA-co-Sty)	377	405
5	Starch(3%)-g-P(MMA-co-Sty)	377	405
6	Starch(4%)-g-P(MMA-co-Sty)	372	405
7	Starch(5%)-g-P(MMA-co-Sty)	372	411

in the amount of Starch in the graft copolymer, the stability initially remained the same from 1% to 4% but increased by 6 °C for 5% Starch in the graft copolymer. Table 3 shows the decomposition temperatures of native Starch, purified P(MMA-co-Sty), and Starch-g-P(MMA-co-Sty) with different amounts of Starch (1 to 5 wt%). It is also observed that the T_{onset} (calculated from the 5% weight loss in the TGA curves) and the T_{max} for Starch-g-P(MMA-co-Sty) are much higher than P(MMA-co-Sty) and native Starch.

CONCLUSIONS

Synthesis of copolymer of styrene (Sty) with methyl methacrylate (MMA) and the graft copolymer of styrene (Sty) and methyl methacrylate (MMA) onto starch were prepared successfully using free radical emulsion polymerization. FT-IR and ¹H NMR spectra of copolymer and graft copolymer indicated that MMA and Styrene had been successfully grafted onto starch. The effect of MMA and Styrene grafting upon the surface morphology of Starch was investigated by SEM. The SEM photos of pure Starch and Starch-g-P(MMA-co-Sty) (1- 5% Starch by mass) are shown in Fig. S1. The photos explained that the granular structure of starch was not maintained after graft copolymerization. Finally, the thermal stability of native starch was found to increase after being grafted with MMA and Sty.

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