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PREPARATION, EVALUATION AND CHARACTERIZATION OF STARCH AND GRAFTED STARCH

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ABSTRACT: The aim of this study was to synthesize the graft copolymer of starch to obtain materials that profit from the particular properties of both natural and synthetic polymeric material. Thus in the present work, a graft copolymer of methyl acrylate and potato starch has been synthesized under microwave irradiation using K2S2O8-TU redox pair, which generates free radical sites on the starch backbone where grafting will occur. MA was chosen as a co-monomer because of its known biocompatibility and non-toxic behavior together with ease of polymerization. Starch was modified through graft copolymerization of poly (methyl acrylate) under microwave irradiation using K2S2O8-TU redox pair. Different parameters were optimized to have a maximum yield of 390%. The effect of PMA grafting onto starch in respect of structural, mechanical, and other properties of grafted starch was investigated by FTIR, TGA, DSC, and SEM analysis. These copolymers could be used as biodegradable fillers and packaging material in the plastic industry. The graft copolymers, therefore, can help increase bioavailability. Due to the biodegradability of starch, St-g-PMA is regarded as eco-friendly material which minimizes environmental crises. Thus its low-cost, safe production in less time, reduced homo-polymerization, and high yield make it a very efficient route for graft copolymerization of natural as well as synthetic polymers.

INTRODUCTION: Polysaccharides cover 75% of all organic materials on the earth [1]. Polysaccharides are naturally occurring, high molecular weight polymers, consisting of hundreds or even thousands of monosaccharide units per molecule where they are linked through oxygen to give complex composition.

Polysaccharides made up of only one kind of monosaccharide unit are called homopoly-saccharide, and those derived from two or more different kinds of monosaccharide units are called heteropolysaccharides.

Polysaccharides are almost of universal occurrence in a living organism where they perform a variety of functions. Because up to three-fourths of the dry weight of plants consists of polysaccharides, it is not surprising that many polysaccharides are readily available at a low cost. Polysaccharides, especially from plant sources, have served various uses in human history, ranging from basic necessities, such as food, clothing, and fuel to

paper and adhesive. Three major carbohydrate polymers, cellulose, starch, and gums, are readily obtained from biomass and are commercially available. Some other naturally occurring polysaccharides such as chitosan, gelatin, and pectin are also used for industrial applications [2-3]. Some of the advantages of polysaccharides are their wide availability, cost-effectiveness, and wide range of structure and properties. Due to many free reactive functional groups, they can be easily modified to obtain some specific properties for special purposes.

Polysaccharides may act as skeletal substances in cell walls of higher plants, Micro-organism, and animals. It also exists as a food reserve in most plants' unfermented seeds, in the form of gum exudates sealing offside of injuries and in micro-organism as encapsulating substances. Another function of polysaccharides is as a thickening agent in the joint fluids of animals.

The biodegradability, biocompatibility, and water solubility, combined with the ability to form hydrogels, make them excellent substances for tissue engineering and drug delivery applications. Cellulose and starches are widely used poly-saccharides and differ in that the former is linear and the latter is a combination of linear and branched polymers.

Starch: Starch is one of the polysaccharides in nature and is made up of the elements carbon, hydrogen, and oxygen. Plant synthesizes and accumulates starch in their structure as an energy reserve. Starch is found in all plant parts, *i.e.,* the leaves, stem, shoots, and storage organs such as tubers (*i.e.* potato, cassava), rhizomes, and seeds (*i.e.* corn, maize, wheat, rice, rice, sorghum, barley, or peas) [4-5]. Most of the starch produced worldwide is derived from corn, but other types of starches such as cassava, sweet potato, potato, and wheat starch are also produced in large amounts [6-8].

Scope of Starch: In the agricultural field, polymers are also widely used for many applications. The starch is processed further to produce raw materials for the paper, chemical, pharmaceutical, and textile industries.

Modification of its structure and physicochemical properties (chemically or physically) can be exploited for beneficial applications. Starches used in the food manufacturing industries are generally modified to enhance pasting properties (such as paste consistency, smoothness, and clarity) and impart freeze-thaw and cold storage stabilities.

Methods of Starch Modification: Starch, a natural biopolymer, is one of the potential candidates that can process into a range of valuable products. However, as starch is highly hydrophilic, it is water sensitive, and the mechanical properties of starch-based films are generally inferior to those derived from synthetic polymers. Therefore, to meet the demanding technological needs of today, the properties of starch are modified by a variety of modification methods which enhances its versatility and satisfies consumer demands. The basis of Starch modification lies in the improvement of its functional properties by changing the physical and chemical properties of such native starch.

The process of starch modification involves the destructerisation of the semi-crystalline starch granules and the effective dispersion of the component polymer. In this way, the reactive sites (hydroxyl groups) of the amylopectin polymers become accessible to electrophilic reactants. The techniques for starch modification have been broadly classified into four categories

1. Physical modification

2. Enzymatic modification

3. Genetic modification

4. Chemical modification with much development already seen in chemical modification.

Graft Copolymerization: Grafting of synthetic polymer onto a natural polymer backbone is a convenient method to add new properties to a natural polymer with minimum loss of the initial properties of the substrate. Due to their structural diversity and water solubility, natural poly-saccharides could be interesting starting materials for synthesizing graft copolymers. Graft copolymers may be produced by adding the vinyl or other monomer onto natural or synthetic polymers using different copolymerization techniques [9-10]. The reason for the growing interest

in graft copolymerization is the intriguing possibility of modifying polymers and obtaining new and interesting properties leading to better performance. The desirable properties of polymers are retained, and additional properties may be acquired by grafting the desired material *in situ* through condensation of reactants or by the decomposition of a preformed polymer. Graft copolymerizations are different from random or block copolymerization in that it leaves the main polymeric substrate backbone essentially intact.

Grafting can be expected to add new and additional properties associated with the side chain. A variety of property changes can be imparted to the polymer through grafting without destroying the crystalline or crystallization potential of substrate or reducing its melting point [9]. Some of the most dramatic changes in properties that have been brought about by grafting into polymers are visco-elasticity Stereo-regularity, hygroscopicity, water repellency, improved adhesion to a variety of substances, improved dyeability, stability and soil resistance bactericidal properties, antistatic properties, and thermal stability for its better commercial value [10].

Microwave irradiation is electromagnetic irradiation in the frequency range 0.3 to 300 GHz, corresponding to a wavelength of 1mm to 1m. The microwave region of the electromagnetic spectrum, therefore, lies between infrared and radio frequencies. The major use of MWs is either for transmission of information or for transmission of energy. Most commercial microwave systems, however, utilize irradiation with a frequency of 2450 MHz (wavelength λ =0.122) in order to avoid interference with telecommunication devices.

Two types of MW ovens are available; one is the simple household or multimode ovens, and the other type is single-mode ovens. Multimode ovens provide field patterns with low field areas and high field areas, commonly called hot and cool spots. This non-uniformity of the field leads to the heating efficiency varying drastically between different positions of the sample. Domestic MW ovens lack the ability to monitor and control temperature.

Another type of oven is a single-mode oven, which is used for continuous processing for specific research purposes. A properly designed monomode

reactor can prevent the formation of hot and cool spots. This advantage is very important in organic synthesis since the actual heating patterns can be controlled. Now, much more advanced ovens are available. These reactors allow temperature control *via* changing power and temperature monitoring with preinstalled digital thermometers.

Applications of Grafted Starch in Controlled Release System: Natural polysaccharides have been used as tools to deliver the drug exclusively to a particular site. However, polysaccharides show enormous swelling due to their hydrophilic nature, which results in the premature release of drugs in a specific site. Among the various polysaccharides, starch is cheap, abundantly available natural polymers with good applications perspectives in controlled release devices. The limited use is mainly because of a number of adverse properties of starch, such as low moisture resistance, high brittleness, and incompatibility with hydrophobic polymers.

MATERIALS AND METHODS: Domestic microwave oven (model no LG Intellocook TM MS-1947 C) having 2450 MHz microwave frequency and power output from 0 to 800 W with continuous adjustment was used for all the experiments. All the reagents used were of analytical grade. Distilled water was used throughout the study. A starch sample (Sd Fine Chem Ltd., India) containing 30% amylase and 70% amylopectin was used without further purification. Thiourea and potassium persulfate obtained from Merck, India, was used as procured and methyl acrylate (Sd fine Chem Ltd, India) distilled under reduced pressure before use. FTIR spectra were recorded on a Perkin Elmyer Infrared spectrophotometer using KBr pellets. For SEM LEO 430 series was used. Thermal analysis was carried out on an Exstar TG/DTA 6300 at 25-750 0C at a heating rate of 20 0C under atmospheric conditions.

Preparation of Grafted Starch using Polymethacrylate: In the present chapter, starch was modified through graft copolymerization of poly (methylacrylate) under microwave irradiation using $K_2S_2O_8$-TU redox pair.

Different parameters were optimized to have a maximum yield of 390%. The effect of PMA grafting onto starch in respect of structural, mechanical, and other properties of grafted starch was investigated by FTIR, TGA, DSC, and SEM analysis. These copolymers could be used as biodegradable fillers and packaging material in the plastic industry.

The aim of this study was to synthesize the graft copolymer of starch to obtain materials that profit from the particular properties of both natural and synthetic polymeric material. Thus in the present work, a graft copolymer of methyl acrylate and potato starch has been synthesized under microwave irradiation using K2S2O8-TU redox pair, which generates free radical sites on the starch backbone where grafting will occur. MA was chosen as a co-monomer because of its known biocompatibility and non-toxic behavior together with ease of polymerization.

Graft Copolymerization: To the starch solution (0.1g dissolved in 30 ml of hot distilled water) contained in a 250 ml open-necked flask, TU (0.01M) and K2S2O8 (0.02M) were added, and after vigorous stirring, the MA (0.11M) was added into this reaction mixture.

The flask was kept inside the domestic microwave oven and subjected to controlled irradiation for a definite microwave power and exposure time.

The graft copolymer samples of different % G were obtained by precipitation of the respective reaction mixtures in excess of methanol: water (3:1) mixture in which homopolymer dissolves and crude St-g-PMA was received. Obtained grafted starch was filtered and washed repeatedly with the methanol: water mixture and dried to obtain constant weight under vacuums at 40 ℃.

At optimum microwave power and exposure time, conc. of the MA was varied from 0.0095M to 0.20M to obtain the appropriate monomer conc. for maximum yield, and at this, the conc. of starch was varied from 0.1g to 0.4g/30 ml, TU conc. was varied from 0.0025 M to 0.03M and K2S2O8 conc. was varied from 0.005 M to 0.04M, keeping the other fixed to optimum values. Samples obtained under optimum conditions had 390% grafting and 97.5% efficiency.

The grafting parameters such as percentage grafting (%G) and efficiency (%E) were calculated in the following manner.

$$\%G = (\text{Wt of PMA grafted}) \times 100 / (\text{Wt of starch})$$
$$\%E = (\text{Wt of PMA grafted}) \times 100 / (\text{Wt of MA taken})$$

Characterization:

Determination of Particle Size Distribution: St-g-PMA was dispersed in glycerin, and a smear of the dispersion was made and examined under a microscope. The size of 500 particles was measured using a calibrated eyepiece micrometer. The size distribution of St-g-PMA particles was estimated. The results are given in **Table 1**.

TABLE 1: PARTICLE SIZE DISTRIBUTION OF ST-G-PMA POWDER

Size range (µm)	Number of Particles
0-30	20
30-60	40
60-90	230
90-120	180
>120	30

Determination of Bulk density, Bulkiness, Tapped density and Compressibility Index: The bulk density of St-g-PMA was determined by the tapping method. Weighed quantity of St-g-PMA was carefully introduced into a 100 ml graduated cylinder. The cylinder was dropped onto a hardwood surface 3 times from a height of 3 cm at an interval of 2 sec. The bulk density was calculated by dividing the weight of the sample by the volume of the sample contained in the cylinder. Reciprocal of bulk density gives the bulkiness.

The percent compressibility index (I) of St-g-PMA powder was calculated using the following formula, and the results are given in **Table 2**.

$$I = (1 - V_f/V_o) \times 100$$

V_o = Initial volume, V_f = Final volume after tapping

Hausner index was calculated using the formula given below.

$$\text{Hausner index} = (V_o/V_f)$$

V_o = initial volume, V_f = Final volume after tapping

Determination of Flow Properties: Flow properties of powders were determined by the

Angle of repose, Compressibility index, and Hausner index, and the results are given in **Table 2**. The frictional forces in a loose powder can be measured by the Angle of repose (θ). This is the maximum angle possible between the surface of a pile and the horizontal plane. It can be calculated by,

$$Tan\ \theta = h/r$$

h = Height of the pile, r = Radius of the pile

Hausner index was calculated using the formula given below.

$$Hausner\ index = (V_o/V_f)$$

V_o = initial volume, V_f = Final volume after tapping

Determination of Moisture Content: Moisture content was determined by using Karl-Fischer auto titrator M/s. Systronics, Model No.349, and the results are given in **Table 2**.

Determination of pH Value: The pH of 1%w/v aqueous solution of St-g-PMA was determined by using a pH meter (Systronics, Model no.361), and the results are given in **Table 2**.

Determination of Swelling Index: The Swelling index of St-g-PMA was determined by placing one gram of powder in a measuring cylinder. The initial volume of the powder in a measuring cylinder was noted. The volume was made up to 100 ml mark with 0.1N HCl (pH 1.2) at room temperature. The cylinder was stoppered, shaken gently, and set aside for 24 h and the results are given in Table. The volume occupied by the St-g-PMA sediment was noted after 24 h.

The swelling index of the St-g-PMA was calculated by the formula,

$$S.I = \{w_t - w_o / w_o\}$$

Where, S.I. = Swelling index, W_t = Height occupied by swollen gum after 24 h, W_o = Initial height of the powder in a graduated cylinder

Determination of Volatile Acidity: About 1 gm of the St-g-PMA was accurately weighed, transferred to a 700 ml long-necked flask, 100ml of water, and

5 ml of Orthophosphoric acid were added and allowed to stand until the gum was completely swollen (app 24 h). Then, it was boiled for 2hrs under a reflux condenser, steam distilled until 800 ml of the distillate was obtained. The distillate was titrated with 0.1N sodium hydroxide using phenolphthalein as an indicator, and the results are given in Table. The procedure was repeated, omitting the sample. The difference between the two titrations represented the amount of alkali required to neutralize the volatile acid.

$$Each\ ml\ of\ 0.1N\ NaOH = 0.006005\ g\ of\ C_2H_4O_2$$

Determination of Viscosity: The rheological properties of St-g-PMA were evaluated using Brookfield cone and plate viscometer model LV DV-III. St-g-PMA concentrations of 0.5% (w/v) with distilled water were prepared, allowed to swell. 0.5 ml of sample was placed in a plate of viscometer and analyzed for its viscosity, shear stress, rate of shear at 10 rpm.

TABLE 2: CHARACTERIZATION OF ST-G-PMA

Property	Results Obtained
Tapped density (gm/cc)	0.691±0.33
Bulk density (gm/cc)	0.615±0.22
Bulkiness (cc/gm)	1.60±0.31
Angle of repose(0)	28.23±0.66
Compressibility index (%)	9.33±0.25
Hausner's ratio	1.4±0.98
pH	5.1±0.33
Water retention Capacity(ml)	19±1.67
Swelling index (%)	120±10.00
Volatile acidity (%)	17.2±2.98
Moisture Content	15.33±0.32
Viscosity of 0.5% w/v St-g-PMA at 30 ºC	130.2 cps
Using Speed -10RPM, Shearing stress	25.28
Rate of Shear	-20

Evidence of Grafting: The proof of grafting was obtained from the Fourier transform infrared spectra of pure starch and St-g- PMA. **Fig. 1** shows comparative IR spectra of starch and potato St-g-PMA copolymer. A new strong absorption emerged at 1745 cm^{-1} in the spectra of grafted starch attributed to a carboxylic ester carbonyl group of PMA gives evidence for grafting of PMA, and no such band was observed in spectra of starch. OH bond intensity at 3450.6 cm^{-1} also increased due to the grafting of PMA on the starch backbone (3362.4 cm^{-1}).
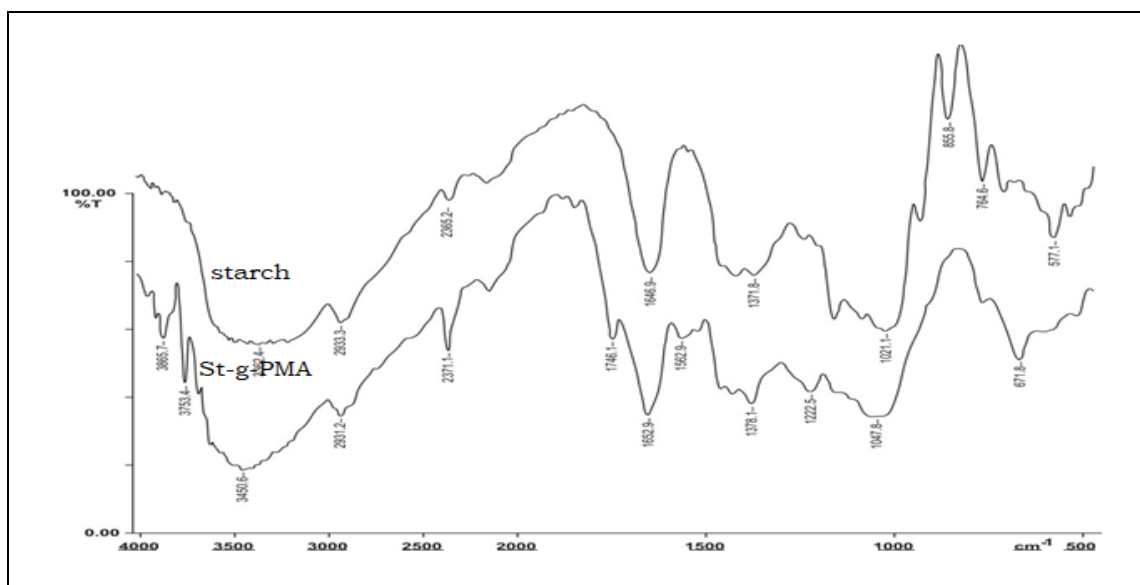
FIG. 1: FTIR OF STARCH AND ST-G-PMA

Surface Morphology: Surface morphology of the starch and grafted starch was evaluated with the help of scanning electron micrographs (SEM). SEM images of starch and grafted starch are shown in **Fig. 2A** & **2B** respectively. The morphology of the starch surface shows granular nature which is quite clear in **Fig 2A**.

Starch granules were partially destroyed during the graft copolymerization and attest to the very good interfacial adhesion between the starch and the poly (methylacrylate) chains **Fig. 2B**. Thus comparison of these figures reveals that grafting has taken place and as a result of grafting morphology of St-g-PMA changes drastically.
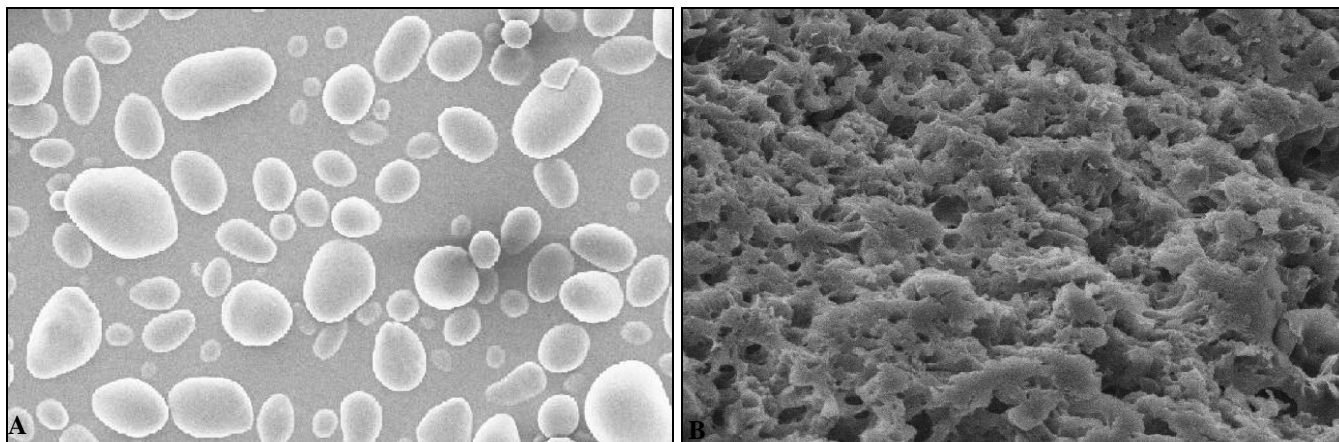
FIG. 2: A: SEM OF STARCH, B: SEM OF ST-G-PMA

Thermal Analysis: The thermal characteristic of all samples were investigated over thermal analyzer model Exstar TG/DTA-6300 at 25 -750 ℃ and heating rate of 20 ℃ /min under atmospheric condition using sample size ranging 10.32-12.0 mg with reference to the alumina powder. A comparative thermal data of starch and grafted starch is listed in table 3. The representative TGA curve of starch revealed two steps **Fig. 3**. The first step thermal degradation of starch was started at 250 ℃ with weight loss (% WL) 12.3. Prior to this temperature, a (%WL) 8.5 at 100 0C was reported,

this may be ascribed to the loss of physically bound moisture, it was further evident through DTG curve with a rate of decomposition (0.15 mg/min) peaked at 85 ℃. The second step degradation was reported at 400 ℃ with (% WL) 84.7. Complete thermal degradation of starch was reported at 600 ℃. TG data was further supported by a couple of DTG peak at 289 ℃ (1.36 mg/min) and 520 ℃ (0.32 mg/min). The corresponding DSC curve showed an endotherm at 271 ℃ (3mw) with enthalpy (ΔH) 148 mJ/mg and an exotherm with combined (-ΔH) 2420 mJ/mg at a temperature ranging 389 ℃ (36

mw) to 522 ℃ (50 mw) **Fig. 4**. An early thermal decomposition was reported for starch graft poly(methylacrylate) **Fig. 3**. TGA revealed that the first step thermal decomposition was started at 300 0C (% WL; 41.8). The thermal degradation of samples were terminated at 789 ℃ leaving char residue (% Wr) 11.3. TGA data also provided 3.7% moisture content at 100 ℃. TGA data was further supported by two derivative curve peaks at 290 ℃ with a rate of decomposition (1.60 mg/min) and 437 ℃ with rate of decomposition (0.77 mg/min).

TABLE 3: COMPARATIVE THERMAL DATA OF STARCH AND GRAFTED STARCH

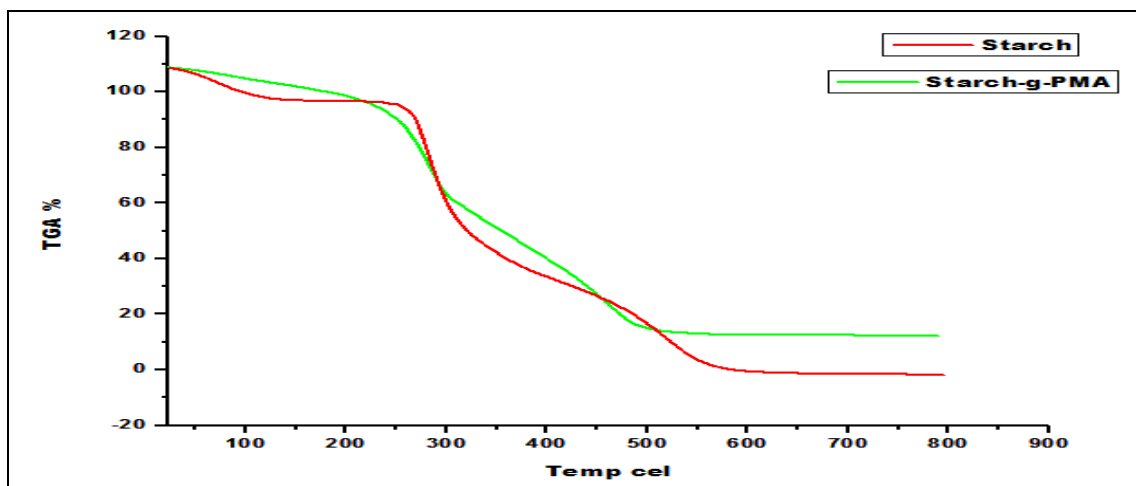| Samples	TGA % (^{0}C)				DTG		DSC		
	I	II	Moisture content (%)	%Wr(^{0}c)	Peak Temp (^{0}C)	Rate (mg/min)	T(^{0}C)	Signal (mw)	ΔH(mJ/mg)
Starch	12.3(250)	84.7(500)	8.5	0.0(795)	83	0.15	271	3	148
					289	1.36	389	36	-2420
					520	0.32	522	50	-2420
St-g-PMA	9.4 (200)	41.8(300)	3.7	11.3(789)	290	1.60	358	71	-4390
					437	0.77	448	153	-4390
					465	0.73	469	158	-4390

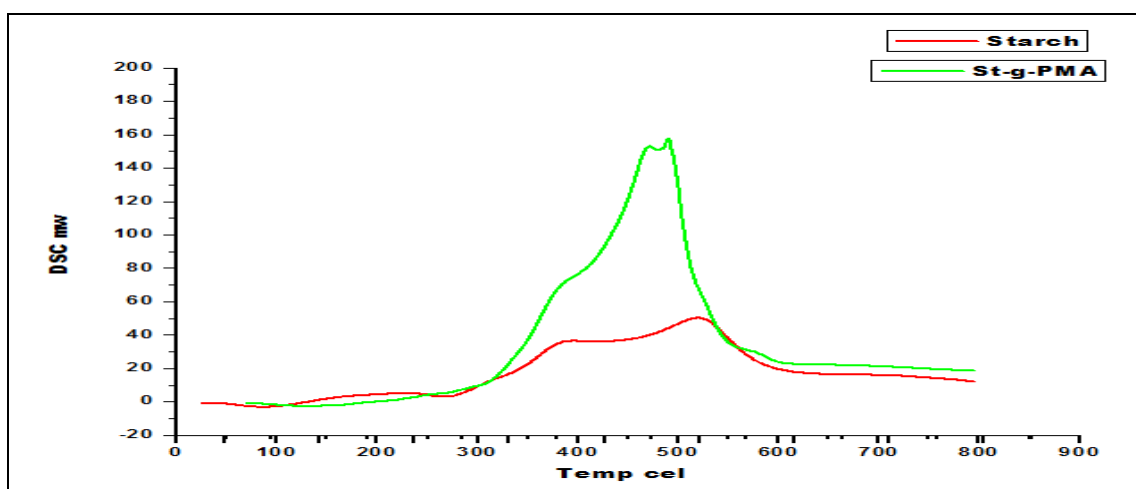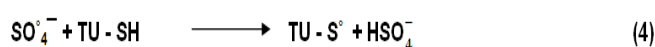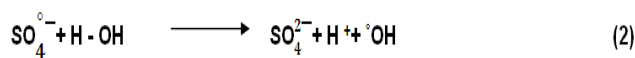**FIG. 3: TGA CURVE OF STARCH AND GRAFTED STARCH**

FIG. 4: DSC CURVE OF STARCH, ST-G-PMA

The corresponding DSC exotherm **Fig. 4** with (-ΔH) 4390 mJ/mg was reported at a temperature ranging 358 ℃ (71 mw) to 469 ℃ (158 mw). Comparative thermal study of pu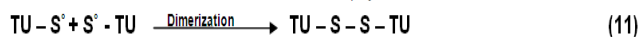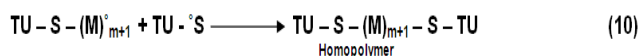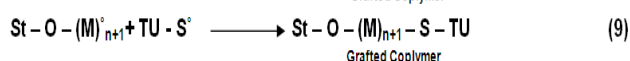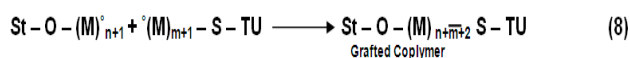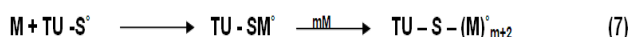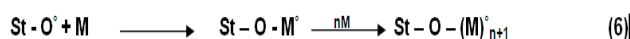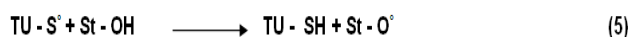re starch and grafted starch reveals that grafting of methyl acrylate onto potato starch improves the thermal stability of starch up to 800 ℃; however, it showed flame retardancy beyond 600 ℃ while pure starch degraded completely below 600 ℃.

Results and discussion: The following tentative mechanism has been proposed for the graft copolymerization of methyl acrylate onto potato starch by $K_2S_2O_8$-TU redox pair, on the basis of the mechanism.
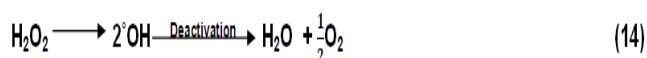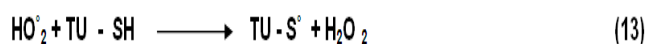
Starch is represented by St-OH, thiourea as TU-SH and monomer MA as M.

$$S_2O_8^{2-} \longrightarrow 2SO_4^{\circ-} \qquad (1)$$

$$SO_4^{\circ-} + H \cdot OH \longrightarrow SO_4^{2-} + H^+ + {}^\circ OH \qquad (2)$$

$$TU + H^+ \longrightarrow TU \cdot SH \qquad (3)$$

$$SO_4^{\circ-} + TU \cdot SH \longrightarrow TU \cdot S^\circ + HSO_4^- \qquad (4)$$

The thio free radicals TU-S° this produced abstracts hydrogen from the reactive functional group of starch and produces starch macroradicals. This substrate macroradical interacts with the monomer and thus gives rise to the graft copolymer.

$$TU \cdot S^\circ + St \cdot OH \longrightarrow TU \cdot SH + St \cdot O^\circ \qquad (5)$$

$$St \cdot O^\circ + M \longrightarrow St - O \cdot M^\circ \xrightarrow{nM} St - O - (M)^\circ_{n+1} \qquad (6)$$

$$M + TU \cdot S^\circ \longrightarrow TU \cdot SM^\circ \xrightarrow{mM} TU - S - (M)^\circ_{m+2} \qquad (7)$$

$$St - O - (M)^\circ_{n+1} + {}^\circ(M)_{m+1} - S - TU \longrightarrow St - O - (M)_{n+\overline{m}+2} S - TU \qquad (8)$$
Grafted Coplymer

$$St - O - (M)^\circ_{n+1} + TU \cdot S^\circ \longrightarrow St - O - (M)_{n+1} - S - TU \qquad (9)$$
Grafted Coplymer

$$TU - S - (M)^\circ_{m+1} + TU \cdot {}^\circ S \longrightarrow TU - S - (M)_{m+1} - S - TU \qquad (10)$$
Homopolymer

$$TU - S^\circ + S^\circ \cdot TU \xrightarrow{Dimerization} TU - S - S - TU \qquad (11)$$

Grafted copolymer is formed in steps (8) and (9), while homopolymer precedes through step no (10). In addition to the above mechanism in the presence of air TU-S radicals may also be produced as below

$$TU \cdot SH \xrightarrow{Air} TU \cdot S^\circ + HO_2^\circ \qquad (12)$$

$$HO_2^\circ + TU \cdot SH \longrightarrow TU \cdot S^\circ + H_2O_2 \qquad (13)$$

$$H_2O_2 \longrightarrow 2{}^\circ OH \xrightarrow{Deactivation} H_2O + \frac{1}{2}O_2 \qquad (14)$$

Effect of monomer Concentration: The grafting percentage and efficiency both increased on increasing the monomer concentration from

0.095M to 0.11M under fix variables; 0.01M TU, 0.02M $K_2S_2O_8$, 0.1 g/30 ml starch at 320W MW power for 3min. Then it starts declining, giving lower %G and %E **Fig. 5**.

The increase is expected due to the greater accumulation of MA monomer with respect to starch macro radicals, which can lead to a larger possibility of grafting.

Beyond 0.11M decrease is merely due to more homopolymerization, which hinders the role of penetration of MA monomer molecules to starch macro radicals.
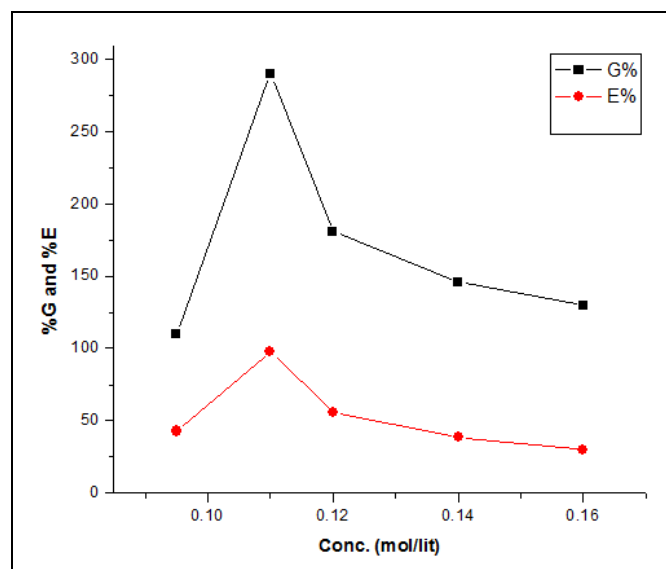

FIG. 5: EFFECT OF MONOMER CONCENTRATION AT TU=0.01M, $K_2S_2O_8$=0.02M, STARCH=0.1G/30 ML, EXPOSURE TIME = 3MIN AT 320W MW POWER
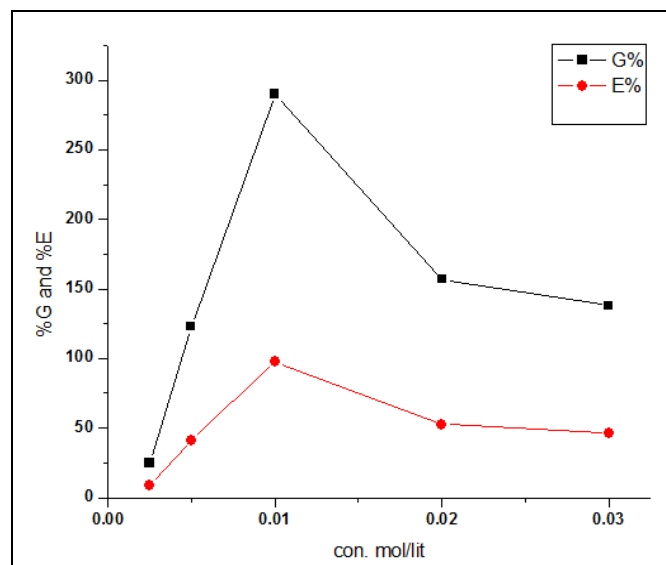

FIG. 6: EFFECT OF THIOUREA CONCENTRATION AT MA=0.11M, $K_2S_2O_8$=0.02M, STARCH=0.1G/30 ML, EXPOSURE TIME=3MIN AT 320W MW POWER

On increasing concentration of thiourea from 0.0025M to 0.01M keeping other variables constant %G and %E initially increased than declined as depicted in **Fig. 6**. The enhancement is due to more primary free radicals producing macro radicals with thiourea and this macro radical's abstract hydrogen radical from starch and creating active sites where methyl acrylate is added. Beyond this TU concentration %G and %E decrease due to the fact that an increase in hydrogen radicals increases recombination and disproportion of macro graft radicals is less possible.

Effect of Potassium Persulfate Concentration: The increase in $K_2S_2O_8$ concentration from 0.005M to 0.02M corresponds to an increase in graft yield and efficiency but beyond this conc. both decreased. The results are demonstrated in **Fig. 7**. Enhancement is associated with the rapid activation of starch backbone for grafting. Further decrease is attributed to an increase in the number of backbone radicals terminated prior to MA addition. Furthermore, low yield is associated with more homopolymer formation, which competes with the grafting reaction for monomer availability.
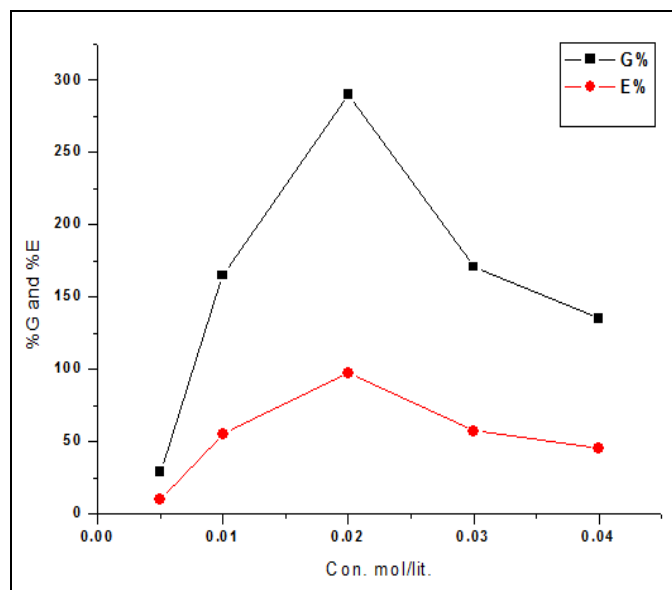

FIG. 7: EFFECT OF POTASSIUM PERSULFATE CONCEN-TRATION AT TU=0.01M, MA=0.11M, STARCH=0.1G/30 ML, EXPOSURE TIME=3MIN AT 320W MW POWER

Effect of Microwave Power Variation: On increasing microwave power, Percentage grafting and efficiency increased up to 320W at fix variables **Table 4**. The increment is associated with formation of more macro radicals which produces starch macro radicals for graft copolymerization.

Beyond this power, the decrease is assumed due to the disproportion of free radicals, which terminate the grafting reaction.

At the same time the chance of transfer reaction to monomer increase and the homopolymerization of PMA rise.

TABLE 4: EFFECT OF MW POWER VARIATION AT $K_2S_2O_8$ = 0.02M TU=0.01M, MA=0.11M, STARCH = 0.1G/30 ML, EXPOSURE TIME=3MIN

MW power (W)	Yield %	Grafting %	Efficiency%
160	110	10	3.36
320	390	290	97.48
480	330	230	77.32
640	290	190	63.87
800	125	25	8.40

Effect of Exposure Time Variation: As the reaction time increased, more energy provided to the reactants; thus, % G and % E increased up to 3 min at fixed variables, but after 3 min decrease indicated that higher microwave radiation accelerated the reaction, which terminates the chain propagation reaction with more homopolymer formation thus yield of grafted starch is lowered **Table 5**.

TABLE 5: EXPOSURE TIME AT K2S2O8=0.02M, TU=0.01M, MA=0.11M, STARCH=0.1G/30 ML, MW POWER=320 W

Exposure time (min.)	Yield %	Grafting %	Efficiency%
1	120	20	6.72
2	210	110	36.98
3	390	290	97.48
4	350	250	84.04
5	314	214	71.94

Effect of Starch Concentration: The grafting was carried out with different starch concentrations from 0.1 to 0.4, keeping the other variables constant. Results are shown in **Fig. 8**. It is obvious that %G and %E decreased on increasing starch concentration.

This may be due to the fact that as the total volume was fixed with an increasing amount of starch, the initiator reacts with reactant to produce radicals and further to initiate polymerization of MA onto starch; thus, total wt of starch increased but %G and %E decreased which may be due to insufficient amount of initiator and monomer to produce reaction sites for grafting.
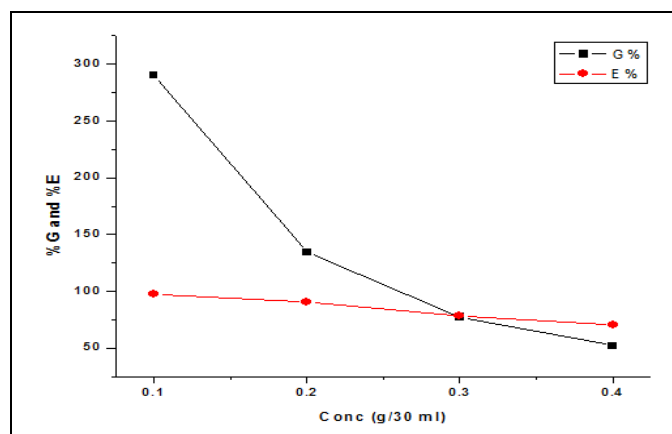
FIG. 8: EFFECT OF STARCH CONCENTRATION AT TU=0.01M, K2S2O8=0.02M, MA=0.11M, EXPOSURE TIME=3MIN AT 320W MW POWER

CONCLUSION: Starch-g-PMA was grafted successfully by using K2S2O8, -TU redox pair under MW irradiation, it was observed that reaction parameters significantly affect grafting characteristics of the resulting copolymer, and the maximum yield of St-g-PMA was obtained at 0.01M TU, 0.02M K2S2O8, 3 min at 320W MW power. The graft copolymers, therefore, can be helpful in increasing bioavailability. Due to the biodegradability of starch, St-g-PMA is regarded as eco-friendly material which minimizes environ-mental crises. Thus its low-cost, safe production in less time, reduced homopolymerization, and high yield make it a very efficient route for graft copolymerization of natural as well as synthetic polymers.

CONFLICTS OF INTEREST: The authors declare that they have no conflict of interest for this study.

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