SYNTHESIS AND CHARACTERIZATION OF GRAFT COPOLYMERS OF METHACRYLAMIDE ONTO POTATO STARCH USING A REDOX INITIATOR

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Abstract-Graft copolymers of potato starch with methacrylamide were successfully synthesized using a redox initiator. A comprehensive study was conducted to evaluate the effects of various parameters on grafting efficiency, including initiator concentration, monomer concentration, polymerization time, reaction temperature, material-to-liquor ratio, the presence of alcohol in the reaction medium, and stirring speed. Optimal conditions for grafting were established. The formation of graft copolymers was confirmed through detailed characterization techniques like Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), X-ray diffraction (XRD), and thermogravimetric analysis (TGA).

Keywords:
Methacrylamide, Redox Initiator, Grafting, Potato Starch, Grafting Efficiency, Graft Copolymer.

I. INTRODUCTION

Starch is an affordable, renewable, and biodegradable natural polymer. It is widely used in industries like adhesives [1], textiles[2], paper[3], superabsorbents[4], water treatment[4], and bioplastics[5]. But pure starch has limitations, including retrogradation and weak mechanical strength. Many methods are available to overcome on these limitations, one of them is chemical modification. Chemical modification id done via graft copolymerization. Graft copolymerization is a method where vinyl monomers are attached to the starch backbone or combining the traits of both components, starch and monomer[6]. Grafting by redox initiator forms free radicals on the polymer chain. Electrons from hydroxyl group present on starch backbone are accepted by Ce(IV) ions(CAN) and generates free radical sites on polysaccharide chain. Hence CAN has been successfully used to graft different monomers onto starch and other polysaccharides [7].

Present research work emphasise the grafting of methacrylamide (MAM) onto potato starch. MAM was specifically selected because of its amide functional group, which would enhance the hydrophilicity and adhesive properties of the starch backbone[8]. Ceric ammonium nitrate (CAN) as a redox initiator was chosen as it is water-soluble and produces less homopolymer than persulfate systems, as per the literature survey[9].

This study aims to determine optimal grafting parameters, examine structural changes via FTIR, XRD, and SEM, and assess thermal behavior using TGA, DTG, DTA, and DSC.

Previous reports show that CAN-initiated grafting of acrylamide and acrylic acid onto potato starch leads to better water absorbency and thermal stability [1,2]. FTIR shows new amide bonds, XRD indicates reduced crystallinity, SEM displays changes in morphology, and thermal analyses demonstrate higher decomposition temperatures and Tg shifts [4,5]. However, grafting of methylacrylamide onto potato starch is still less explored.

II. MATERIALS AND METHODS

Materials: Analytical-grade potato starch (PS)(Loba Chemie, India) was dried in a hot air oven at 110 °C to remove moisture. Ceric ammonium nitrate (CAN, Loba Chemie, India) was also dried at 110 °C for 6 hours and stored in desiccator. A 0.1 M solution of CAN was prepared in 1 M HNO_3. Methacrylamide (MAM, Otto Chemika) was used as received. Distilled water was used as a solvent.

Synthesis: In a 250 mL beaker, 2.0 g of starch slurry was made by adding 30 mL of distilled water. After stirring the mixture for 10 mins, a specific volume of CAN solution was added. It was stirred at 300 rpm and allowed to react for 10 minutes to create starch radicals. Then, MAM monomer (2.0 gms) except during the study of effect of monomer concentration was added, and the volume was made to 100 mL (material-to-liquor ratio 1:50 by volume) by adding distilled water. This mixture was further stirred at 300 rpm for 90 minutes. After the designated time for polymerization, reaction mixture was filtered. As MAM homopolymer (PMAM) is water-soluble, the filter residue was washed several times with warm water for its complete removal. This ensured only the graft copolymer, which consists of an insoluble starch backbone with grafts, was left. The product was then dried at 70 °C under vacuum for 24 hours and weighed. [10]

Control reactions, where no monomer MAM was added, were run simultaneously to check for any starch loss. A weight loss of about 0.033 g per 2 g of starch was noted and added as a correction factor to the product.

Grafting parameters were calculated by weight:

- **Grafting percentage** %G = $100 \times (\omega_2 - \omega_1)/\omega_1$
- **Grafting efficiency** %GE = $100 \times (\omega_2 - \omega_1)/\omega_3$
- **Add-on (%Add)** = $100 \times (\omega_2 - \omega_1)/\omega_2$

where ω_1 is the weight of pure starch, ω_2 the weight of the dried graft copolymer, and ω_3 the weight of monomer charged. An increase in (ω_2–ω_1) (beyond that seen in the control) indicates successful grafting[10].

Parameter Variation: Reaction conditions were systematically varied to optimize grafting. Initiator concentration ([CAN] in mol/L), monomer quantity (MAM in gms), reaction time (min), temperature (°C), material-to-liquor ratio, solvent (water vs. water–alcohol mixtures), and stirring rate (rpm) were individually varied while keeping other parameters same (starch = 2 g, [CAN] = 0.008 M, [MAM] = 2 g, 30 °C, 3 h, 300 rpm, 100 mL total water). After each variation, %G, %GE, and % Add-on were calculated.

Characterization: The characterization of graft copolymers involves use of analytical techniques and procedures to get the necessary information and confirmation of the structure of the graft copolymer. The techniques used FTIR Spectroscopy, X-ray diffraction, SEM, thermal degradation study. These techniques helps in application of grafted copolymer in various fields.

The grafted products were characterized to prove chemical modification.[11]

Infrared spectral analysis (IR)-

IR spectroscopy study involves analysis of an organic compound employing IR spectrometer to obtain a spectrum of the organic compound. The spectrum obtained exhibits peak at the frequency corresponding to certain functional groups present in the compound.[12] Starch graft copolymer shows an additional peak corresponding to the functional group of vinyl monomer as compared to the pure starch. This confirms the formation of the graft copolymer. Thus IR spectroscopy is an important tool for the identification and confirmation of graft copolymers Infrared (IR) spectra of pure potato starch, potato starch graft copolymer(PS-MAM) were recorded on Agilent Cary 630 FTI in the range of 4000-400 cm-1 using ATR method.

Thermogravimetric analysis (TGA)-

Thermogravimetry analysis (TGA) involves stepwise measurement of change in mass of the sample (loss or gain) occurring with small change in temperature over a range of temperature and time. The change in mass in each step is expressed in terms of percentage of the initial sample weight and is used to interpret stepwise degradation process[13]. The thermogram and derivatogram (DTG) of potato starch, grafted starch PS-MAM, was done using Shimadzu Model DTG 60 in the temperature range of 35°C to 495 °C.

Differential thermal analysis (DTA)-

The temperature difference (ΔT) between an inert reference and the sample is measured as a function of temperature in a technique known as differential thermal analysis, or DTA. The ΔT is plotted against either temperature or time and the curve obtained is called as DTA curve.[14] The area covered below the DTA peaks is calculated to determine the change in enthalpy(ΔH). The value of ΔH suggests whether the degradation of the sample takes place endothermically or exothermically. The DTA thermograms of potato starch, grafted starch(PS-MAM) were recorded

in flowing nitrogen atmosphere at a heating rate of 5°C/min using TG-DTA (Shimadzu Model DTG 60) in the temperature range of 35°C to 500 °C.

Differential scanning calorimetry (DSC)-

Differential Scanning Calorimetry (DSC) technique gives the direct measurement (i.e.,shift from the base line) of the glass transition temperature (Tg) of the polymer substance. This, in turn, provides vital information of temperature to calculate specific heat capacity of the polymer sample, hence DSC proves to be an important technique in polymer analysis.[15]

The potato starch and starch graft copolymers PS-MAM were sealed in an aluminium sample pan. An empty aluminium pan of approximately equal weight was used as a reference. The samples were tested through Shimadzu DSC 60 plus analyzer at the heating rate of 10°C/min from ambient temperature to 550°C.

X-ray diffraction studies (XRD)-

Starch is a semi-crystalline substance in nature due to the presence of both amylose and amylopectin in varying amounts. Thus, the need to understand the crystallinity of starches obtained from different sources have gained immense importance over last several decades. X-ray diffraction technique is employed by the researchers to determine the type of crystallinity depending upon the X-ray pattern, the degree of crystallinity in terms of percentage of amylopectin present in starch. The effect of grafting of vinyl monomers onto starch on its crystallinity has also been of interest.[16,17]

The X-ray diffraction studies were carried out using an Empyrean X-ray diffractometer by Malvern Panalytical. The graft copolymers and pure potato starch samples were scanned on XRD between 5° and 50°.

Scanning electron microscopy (SEM)-

Morphological changes happen at the surface of Starch when it is grafted by the chemical method. Vinyl monomer is grafted onto the starch surface, these surface changes can be examined in the form of images obtained from Scanning Electron Microscopy technique. It involves the of use instrument with advanced technology, involving interaction of accelerated electrons with the atoms of the substance of very small amounts. The interaction leads to emission of particles such as electrons, X-rays, photons at varied angles of the surface and these signals are collated in the form of an image of very high magnification(x1000).[18,19] The SEM images of the pure and grafted starch are compared for confirmation of grafting. In this study, surface morphology of PS-MAM was studied using a scanning electron microscope (SEM) of Thermofisher Scios 2. The micrographs were taken at a magnification of 1500, and 2500 using 5 KV accelerating voltage.

III. RESULTS

Grafting Observations:

All grafting reactions had produced white powder. Weight change confirmed grafting, as grafted starch always weighed more than pure potato starch, confirming that MAM had attached to the starch backbone rather than simply washing away.[20] In parameter-optimization experiments, the maximum grafting efficiency (around 13%) was achieved with [CAN] = 0.008 M, 2 g MAM, 2 g starch, 90-minute reaction time, 30°C temperature, 1:25 material-to-liquor ratio, and 300 rpm stirring.

Characterization of Sample:

FTIR: FTIR analysis (Figure 1) provided clear evidence of successful grafting. The PS-g-MAM spectrum showed two new absorption bands that were not visible in potato starch FTIR: a sharp C=O stretch at 1633 cm⁻¹ and N-H bending vibration at 1542 cm⁻¹. These peaks are characteristic of amide groups, which can be seen from FTIR spectra of PMAM in figure-1, confirming that MAM units had chemically bonded to the starch. The broad –OH band at nearly 3291 cm⁻¹ (from starch's hydroxyl groups) was still present but noticeably weaker, suggesting that some –OH sites had been converted to ester or ether linkages during grafting[21]. This pattern matches what other researchers have reported for acrylamide-grafted starches

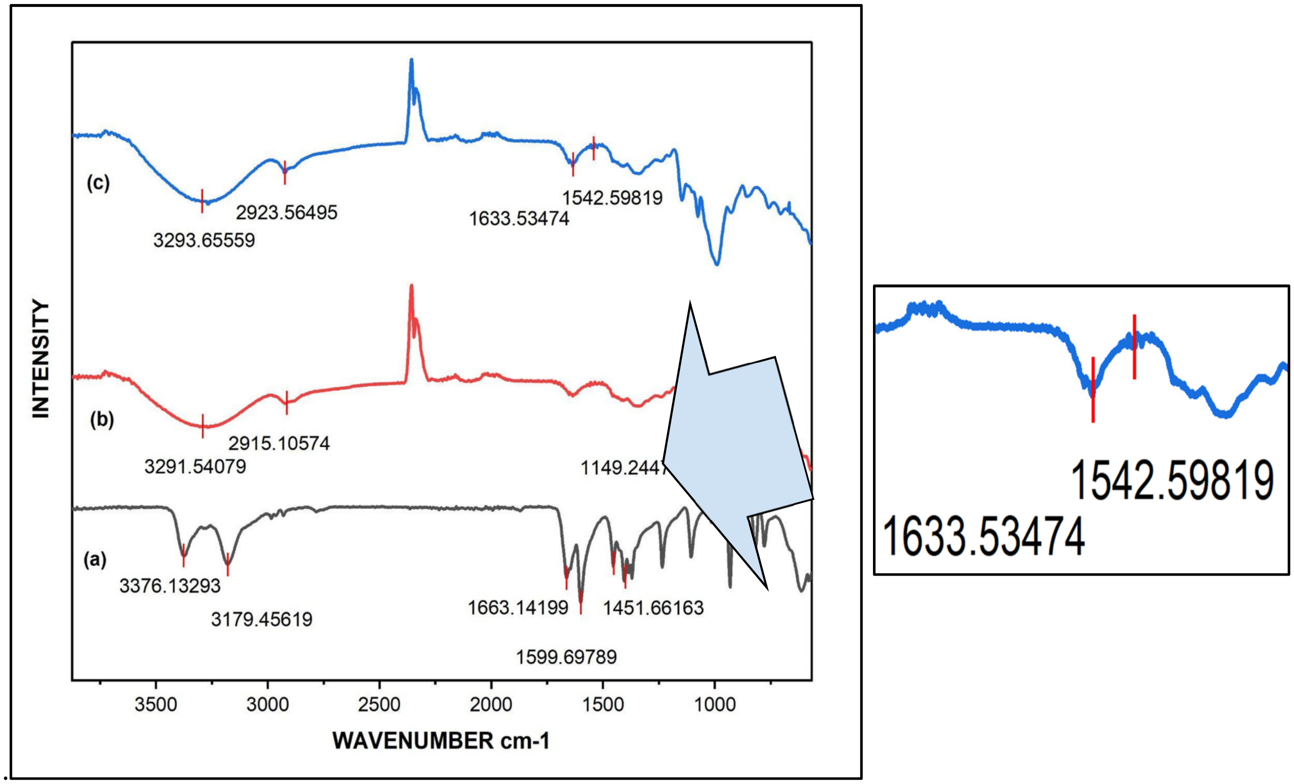


Figure 1: FTIR spectra of (a) PMAM (b) Potato Starch (c) PS-g-MAM

XRD: Comparing XRD patterns of potato starch and grafted starch (PS-g-MAM) from Figure 2 indicates that potato starch displayed characteristic diffraction peaks at 15°, 17°, 18°, and 23 the B-type crystalline pattern[16], however, after grafting, these peaks appeared at the same 2θ positions. This concludes that the basic crystalline structure of starch stayed intact. However, a clear decrease in peak intensity is observed. This suggests that grafting happened predominantly in the amorphous regions of starch granules, where polymer chains are more accessible, and the MAM graft chain did not form a new crystalline domain, they remained as amorphous chains extending from the starch surface. Thus, XRD confirms that PS-g-MAM is semi-crystalline but just slightly less crystalline than the potato starch, indicating successful grafting of MAM.

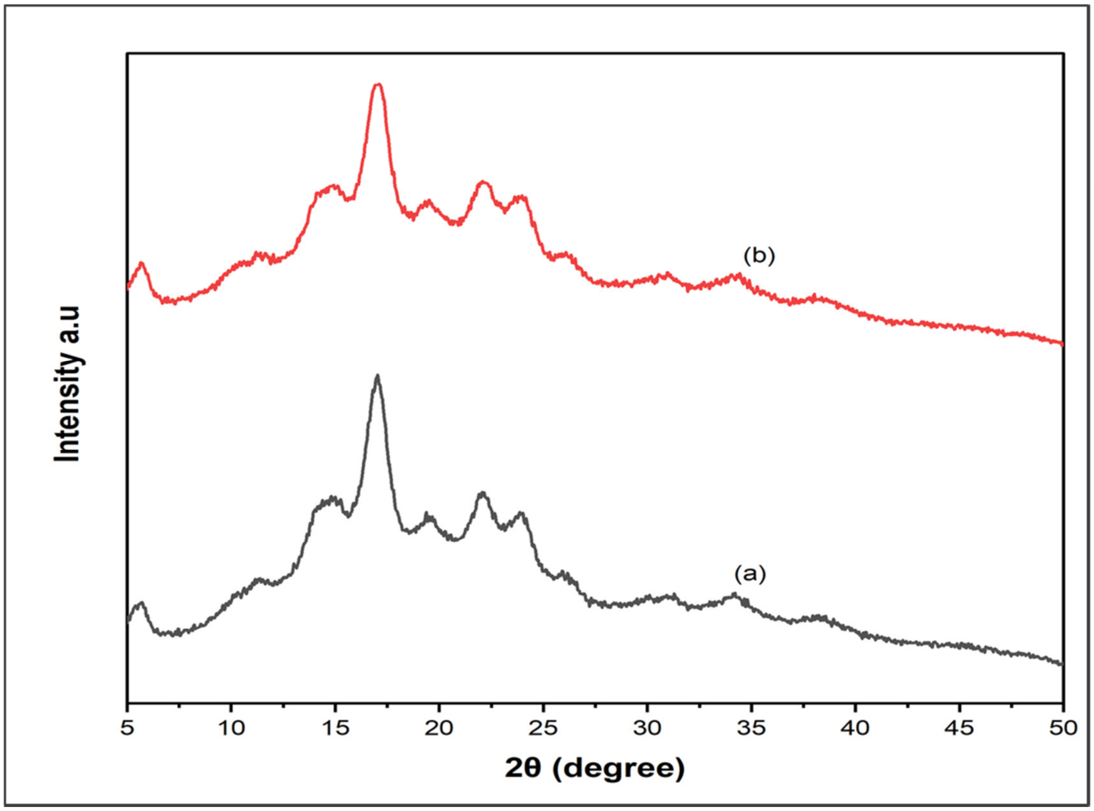
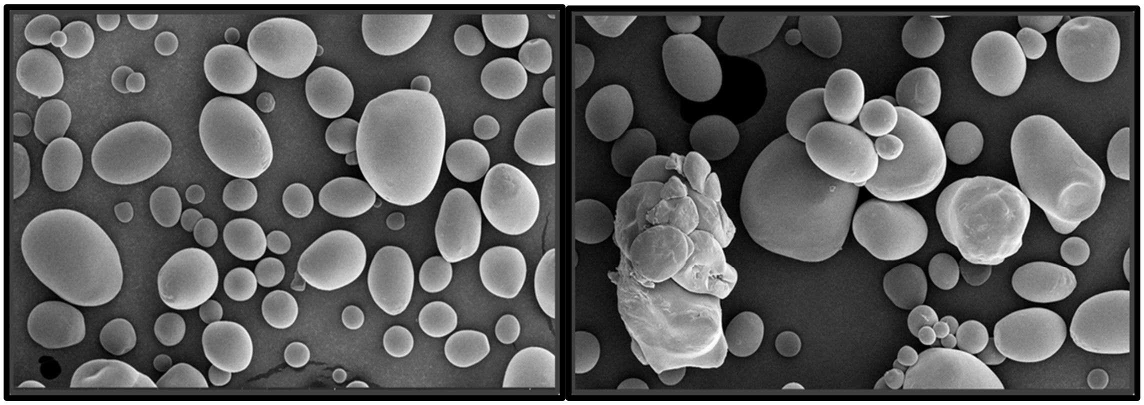


Figure 2: XRD for (a) Potato Starch (b) PS-g-MAM

SEM: SEM micrographs (Figure 3) show visible morphological changes after grafting. Potato starch granules had the expected smooth, oval appearance with a well-defined edge, typical of B-type starch. While grafted starch, PS-g-MAM granules were observed to be noticeably rougher and more irregular, suggesting that MAM polymer chains coated the starch surface. Alfuhaid et al. reported similar changes when grafting other monomers onto starch, the pure starch had oval granules with smooth edges[18,19], while grafted samples showed uneven morphology. The grafting conditions here were mild enough to preserve the starch backbone structure. The SEM images support the interpretation that grafting primarily occurs at or near the granule surface rather than penetrating deep into the crystalline core.



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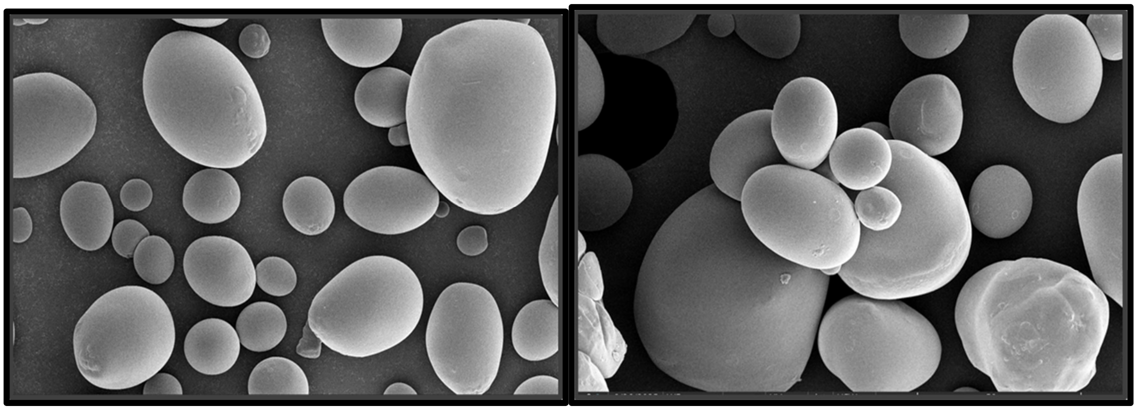


Magnification 2500x Magnification 2500x

(a) (b)

Figure 3:. SEM of (a) potato starch and (b) PS-g-MAM graft copolymer (magnification 1500x and 2500x)

Thermal analysis:

Grafting potato starch with methylacrylamide modifies its thermal profile. DSC thermograms (Figure 4) showed that grafting had a very small impact on the starch gelatinization endotherm, which correlates with the XRD data, which indicated only minor changes to crystallinity. As seen in Table-1 and Figure-4, Potato starch shows its main degradation around 327°C, while grafted starch (PS-MAM) decomposes slightly later (339°C), indicating improved thermal stability. The delayed and broadened endotherm in grafted starch (PS-MAM) suggests enhanced crosslinking and restricted mobility of starch chains. The enthalpy decreases slightly after grafting (from –408 to –375 J/g), showing reduced water retention and increased hydrophobicity due to grafted acrylamide chains.[22-24]. DSC analysis reveals reduced enthalpy of gelatinization and higher decomposition onset, confirming successful copolymerization and restricted molecular mobility.

However, TGA revealed that thermal stability is improved after grafting. The TGA curve of potato starch in figure -5 shows three main mass-loss stages, an initial low-temperature loss (moisture), a major decomposition step, and a slow high-temperature carbonization. As seen in data from Table-2, the instrument analysis reports total weight loss of 87.37% , leaving 12.6 % residue. This is typical for starches, which usually yield approximately 10–20% char after full pyrolysis. The grafted starch (PS-g-MAM) also shows three-stage decomposition pattern, initial moisture loss, main exothermic degradation, formation of carbonaceous residue, with weight loss of 85.33% and reside 14.66%. Thus, grafting shows slightly higher thermal stability and residue compared to potato starch (PS).

Alfuhaid and colleagues found similar results in their work, their starch-g-MAM decomposed around 314°C compared to just 249°C for pure starch[18]. They suggested that the amide and carboxyl groups in the grafted chains create stronger hydrogen bonding networks. Current data also support this interpretation[24]. The –CONH– groups from MAM side chains can form multiple hydrogen bonds with each other and with remaining starch hydroxyl groups, essentially creating a more thermally robust polymer network[25]. This stability could be useful for applications requiring heat processing.

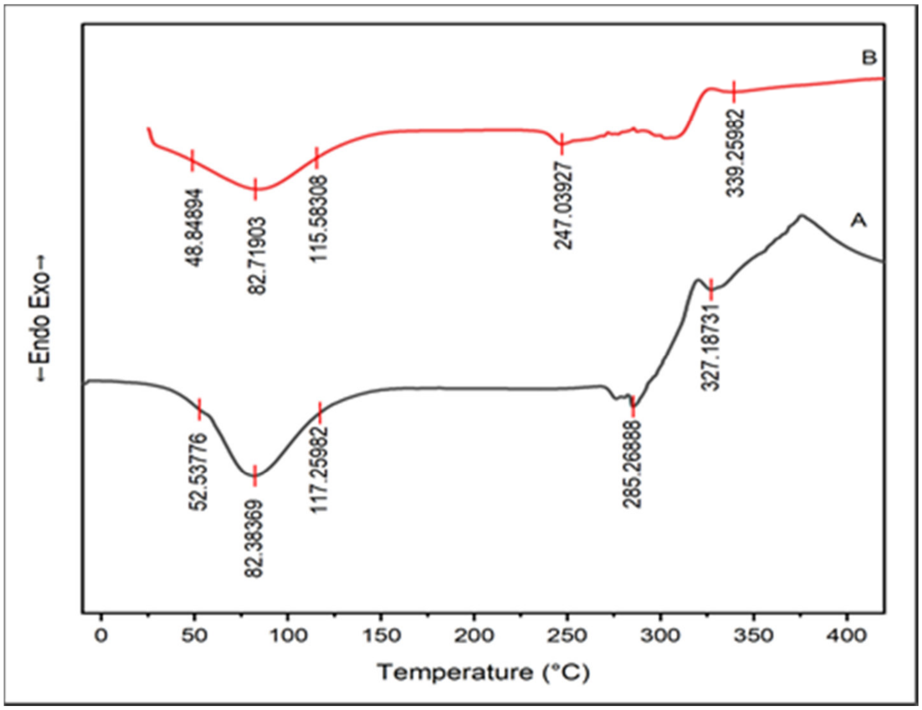
Table 1 DSC data for Potato Starch and PS-g-MAM

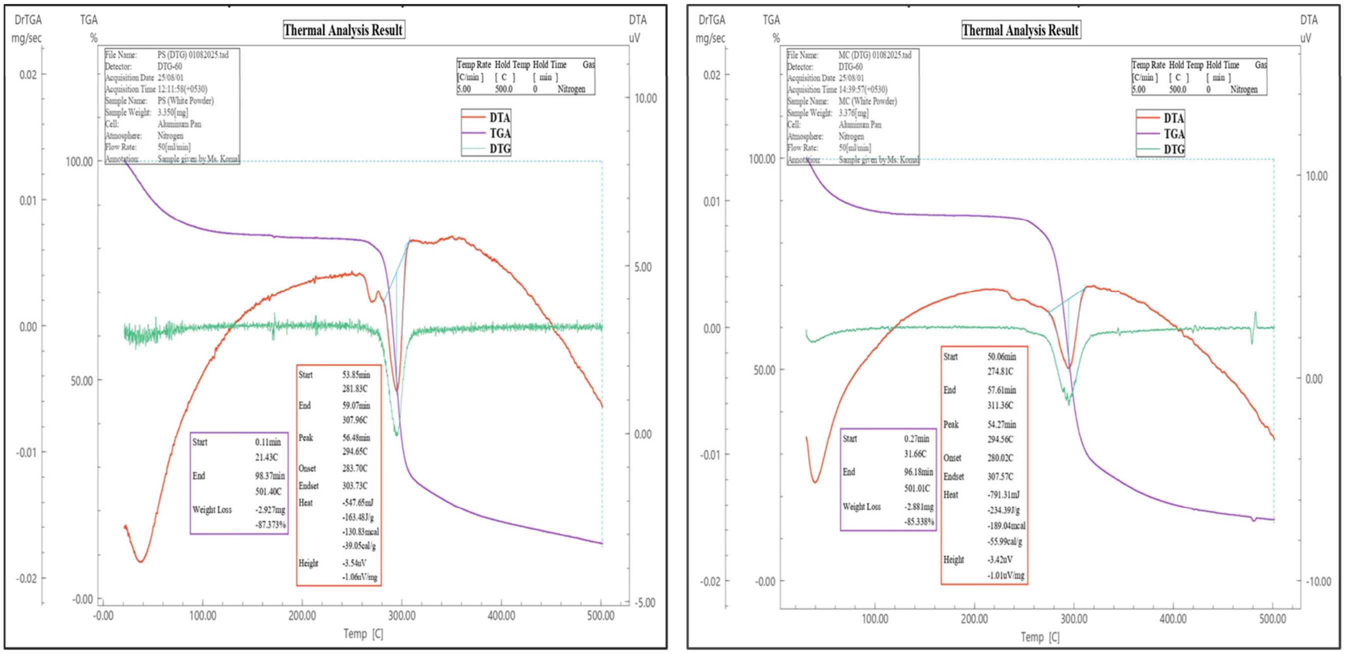
Polymer	**Onset (°C)**	**Midpoint (°C)**	**Peak 1 (°C)**	**Peak 2 (°C)**	**ΔH ($J \cdot g^{-1}$)**
PS (Potato Starch)	52	82	285	327	–408
(PS-g-MAM)	49	84	247	339	–375

Table -2 Thermal decomposition data Potato Starch and PS-g-MAM

Sample	**Number of Stages**	**Temperature Range (°C)**	**Tmax (°C)**	**% Weight Loss**	**Residue at 495 °C (%)**
PS (Potato Starch)	1	25 – 100	80	15 – 16	
	2	250 – 310	295	60 – 62	
	3	310 – 500		10 – 12	**12.6**
PS-g-MAM	1	25 – 100	90	10 – 12	
	2	250 – 310	295	60 – 65	
	3	310 – 500		13 – 15	**14.66**

Figure 4: DSC curve for (a) Potato Starch (b) PS-g-MAM





(a) (b)

Figure 5: TGA,DTAand DTG curve for (a) Potato Starch (b) PS-g-MAM

IV. DISCUSSION

The results show that grafting of MAM onto starch is successful using CAN initiation, with an optimum reaction conditions. Optimized concentrations for initiator and monomer are consistent with usual grafting behavior: insufficient initiator gives low radicals and poor grafting, whereas an excess produces homopolymer and decreases %G. In like manner, moderate monomer concentrations favor successful grafting, while excess monomer drives the reaction toward free radical polymerization of MAM. Such trends are in line with earlier work on ceric-starch systems[26-28]. From experimental data, it was observed that 90 mins is the maximum time to get optimum grafting efficiency.[28-30]. The about 13% grafting in terms of mass obtained here is acceptable for starch, which contains a hydrophilic backbone, and amide monomers.

Characterization validates the copolymer structure. FTIR detects amide bonds, XRD only detects slight loss of order, SEM detects a surface coating, and TGA/DSC detect changed thermal properties. These alterations are consistent with results on starch grafting, where grafting tends to result in a slight decrease in starch crystallinity and more rugged granule surfaces due to the fact that graft chains remain close to the surface. The enhanced thermal stability is consistent with predictions because the addition of amide and carboxyl groups leads to more intense interactions and a more rigid network[31]. Overall, the CAN-induced grafting resulted in a PS-g-MAM copolymer with reaction variable-dependent behavior.

V. CONCLUSION

Grafting of methacrylamide onto potato starch using CAN as a redox initiator was successful with optimal conditions yielding around 13% grafting efficiency. Characterization analysis verified the grafted polymer structure through multiple techniques, like FTIR detected new amide bonds, XRD showed the crystalline starch structure remained largely intact with slightly reduced order, SEM revealed surface roughening from polymer chain coating and thermal analysis demonstrated improvement in decomposition temperature. The enhanced thermal stability most likely comes from additional hydrogen bonding between amide groups in the grafted chains.

Future aspect :

PS-g-MAM copolymers combine starch's renewability and biodegradability with improved functionality from the MAM grafting. Hydrophilicity, thermal resistance, and surface properties are improved. This grafted copolymer are suitable for applications like superabsorbents, biodegradable plastics, water treatment materials, and controlled-release pharmaceutical carriers[32]. We are planning to prepare superabsorbents through hydrogels.

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Conflicts of Interest: The authors declare that they do not have any conflicts of interest for this study.

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