Article

# Graft Copolymerization of Acrylamide onto Corn Starch Using Mohr's Salt/Hydrogen Peroxide Redox System in Aqueous Media under Visible Light

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**Abstract:** The graft copolymerization of Acrylamide (Aam) onto Corn Starch (S) using Mohr's Salt/H<sub>2</sub>O<sub>2</sub> (FAS/H<sub>2</sub>O<sub>2</sub>) redox system in aqueous under visible light was extensively investigated. Many variables affecting the weight conversion (WC %), grafting percentage (GP %) and grafting efficiency (GE %) including time of visible light irradiation and contents of Aam, S, FAS and H<sub>2</sub>O<sub>2</sub> were studied. The UV spectra of FAS and H<sub>2</sub>O<sub>2</sub> were determined. The initial rate of grafting was found to be 0.74% per minute. The rate of graft copolymerization (Rg) was determined. The characterization of the grafted products was done using different techniques such as FTIR, X-ray diffraction, SEM and thermal analysis as TGA and DTA. Water absorption and solvent resistance of S-g-PAam copolymers were examined. The results were discussed and the mechanism of grafting was proposed.

**Keywords:** Starch, Acrylamide, Starch graft polyacrylamide polymers, visible light irradiation.

# **1. Introduction**

Chemical modification of natural polymers through grafting by vinyl monomers has received considerable attention because it adds new properties and alters their physical and chemical properties. Grafting of vinyl monomers onto natural polymers like gum guar (1,2), starch (3,4,5) and cereal flour (6)

with different redox initiators has been studied. Fenton's reagent ( $Fe^{+2}/H_2O_2$ ) is the most suitable initiator giving the highest graft selectivity among other initiators (3). This work aims to study the graft copolymerization of polyacrylamide (PAam) onto corn starch using combined redox initiator such as ferric ammonium sulphate (FAS) and hydrogen peroxide ( $H_2O_2$ ) under visible light irradiation in aqueous medium.

## 2. Experimental and Techniques

## 2.1. Materials

Corn starch (El Gomhouria co.), Acrylamide (RFCL ltd.), Mohr's salt (El Gomhouria co.) and hydrogen peroxide (El Nasr pharmaceutical chemical co.) were used as received. Hydroquinone (BDH), sodium hydroxide, hydrochloric acid and acetic acid were used as received.

#### 2.2. Techniques

The determined quantities of corn starch, Aam, FAS and  $H_2O_2$  were added to distilled water in Pyrex cells. Polymerization experiments were mainly studied under photoactivation with visible light. Fluorescent lamp (160 W, Philips) was used to as a source of visible light irradiation. The Pyrex cells were put around the fluorescent lamp apart by 10 cm in a fixed frame. The polymerization process was finally terminated by pouring the reaction mixture in water/methanol (30/70 V/V) to precipitate the grafted product without homopolymer. The grafted product was dried under 40 °C till constant weight. Grafting percentage (GP %), grafting efficiency (GE %), weight conversion (WC %) and the rate of graft copolymerization (Rg) were calculated according to the following expression:

Grafting percentage (GP %) =  $\frac{A-B}{B} \ge 100$ Grafting efficiency (GE %) =  $\frac{A-B}{C} \ge 100$ Weight conversion (WC %) =  $\frac{A}{B} \ge 100$ 

Rate of graft copolymerization (Rg) =

 $\frac{\text{wt.of grafted polymer}(A - B)}{M_{Aam} \times time \text{ in sec.} \times \text{vol.of reaction mixture in mls.}} \times 1000$ 

where A, B and C are the weights of graft products, starch and monomer respectively and M is the molecular weight of monomer.

The water absorption % (WA %) was calculated according the following relation (7)

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WA % = 
$$\frac{water \ absorbed \ wt}{0.3}$$
 x 100

where the weight of S-g-PAam copolymer taken was 0.3 g.

The resistance of S-g-PAam copolymer toward acids and alkalis was calculated according to the following relation

Sol % = 
$$\frac{wt.of \text{ copolymer after soaking and drying} - 0.09}{0.09}$$
 x 100

where 0.09 is the weight of S-g-PAam copolymer.

#### 2.3. Instrumental Analysis

The UV spectrum of Mohr's salt and  $H_2O_2$  was measured by UV Spectrophotometer (Perkin Elmer Lambda 3B) and their  $\lambda_{max}$  in the visible region were determined.

The chemical structures of the grafted products were examined by IR spectrophotometer (Perkin Elmer 1430) using KBr to prepare its disks.

The thermal analysis of Starch and S-g-PAam copolymers was determined using thermal analyzers (Shimadzu DTA-50 and Shimadzu TGA-50 H) under nitrogen atmosphere.

Powder samples of polymers were subjected to X-ray Diffraction (D8 Advance X-Ray diffractometer; Bruker AXS) which was used in this study using Co K<sub> $\alpha$ </sub> radiation. The scattering angle 2 $\theta$  was varied from 5<sup>o</sup> to 70<sup>o</sup>.

Scanning electron microscope (SEM) examinations were performed using (JEOLJSM-5500LV SEM, JEOL Ltd, Japan) fitted with 20 kV.

# 3. Results and Discussion

Primary experiments of grafting were carried out in dark and in presence of visible light and results are shown in **Table 1**.

Table 1: Graft copolymerization of acrylamide onto starch in aqueous medium, starch 35 g/l,

Initiator system	Polymn. conditions	GP%
Mohr's salt /H <sub>2</sub> O <sub>2</sub>	Photo (30 min.)	76.43
$H_2O_2$	Photo (30 min.)	30
Mohr's salt	Photo (30 min.)	a
Mohr's salt /H <sub>2</sub> O <sub>2</sub>	Dark (24 hrs.)	81.29
$H_2O_2$	Dark (24 hrs.)	a
Mohr's salt	Dark (24 hrs.)	a

Aam, 0.985 mol/l, initiator system: H<sub>2</sub>O<sub>2</sub>, 0.44 mol/l, FAS 0.0221 mol/l.

a: Indicates no grafting

The results showed that the presence of the combined initiator of Mohr's salt /  $H_2O_2$  in the presence of visible light irradiation gave highest value of GP % which was 76.43 % after only 30 minutes, but in case of dark and after 24 hrs., GP % was found 81.29 %. This explains that the energy absorbed by the combined initiator enhances the rate of cleavage of O-O bond in the structure of  $H_2O_2$  yielding 'OH free radicals as found in the following reaction (equation 1):

$$H_2O_2 + hv \rightarrow 2 \text{ OH}$$
(1)

The bond O-O in  $H_2O_2$  has been estimated to be 51 k. cal. / mol. Another research has reported the distance of the O-O bond in solid  $H_2O_2$  was 1.453 A<sup>o</sup> (8).

The UV spectrum of  $H_2O_2$  shows slight absorption at 379 nm and 400 nm and the extinction coefficient values corresponding to them are  $342 \times 10^{-3}$  and  $321 \times 10^{-3}$  l. mol.<sup>-1</sup> cm.<sup>-1</sup> respectively. Whereas Mohr's salt did not absorb in the visible region of UV spectrum (**Table 2**).

Table 2: Characteristics of H<sub>2</sub>O<sub>2</sub> and Mohr's salt in the visible light region

Name	Structure	$\lambda$ (max) (nm)	ε coeff. In l mol <sup>-1</sup> cm <sup>-1</sup>
Hydrogen peroxide	$H_2O_2$	379 nm	342x10 <sup>-3</sup>
		400 nm	321x10 <sup>-3</sup>
Mohr's salt	FeSO <sub>4</sub> (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> .6H <sub>2</sub> O		

This finding shows the activity of  $H_2O_2$  as a good initiator when used alone (GP 30%) and when coupled with Mohr's salt in presence of visible light (GP 76%) (**Table 1**). This indicates that the irradiation of starch in the presence of air produces hydroperoxides that are decomposed by the following reaction:

$$ROOH + Fe^{+2} \rightarrow RO^{\bullet} + {}^{-}OH + Fe^{+3}$$
(2)

To produce radicals capable of initiating graft copolymerization (9). In addition to this, FAS do not absorb in the visible region as shown in **Table 2**. This supports the reaction presented in equation 2.

#### 3.1. Influence of Time of Irradiation

The effect of reaction time on graft copolymerization of acrylamide onto starch is shown in **Figure 1**. The results showed that WC%, GP% and GE% increased by increasing time of irradiation till reach an optimum condition at time 150 min. then slightly decreased or leveled off by increase in time. Moreover, graft copolymerization rate (Rg) is shown in **Figure 2**, which indicates that the Rg values decreased by time increase. Moreover, it was observed that the highest value of Rg was found at the beginning of graft reaction after only 30 min. Similar results were reported (10,11).



**Fig. 1:** Influence of time on the photo-induced grafting of Aam onto Starch in presence of FAS/H<sub>2</sub>O<sub>2</sub> as initiator in aqueous medium: Starch 35 g/l, Aam 0.985 mole/l, initiator system FAS 0.0255 mole/l, H<sub>2</sub>O<sub>2</sub> 0.44 mole/l.



Fig. 2: the rate of graft copolymerization (Rg) of Aam onto starch in different periods of time.

## 3.2. Influence of Starch Concentration

It was reported that GP% decreases with increasing polymer content. The dependence of grafting on the amount of starch was studied (**Fig.3**). All the other variables were kept constant. The grafting parameters as WC% and GP% were decreased by starch content increasing, whereas GE% slightly increased then decreased. The increase in starch content would facilitate the formation of starch macroradicals because of an increase in the relative ratio of starch to primary radicals, leading to an increase that observed in GE% values. So by continues increase in starch content, the viscosity of the medium was increased and this in consequence restricts the mobility of macrofree radicals and this also decrease the GE%. In addition to this, the decrease observed in GP% may be due to the decrease in the monomer to starch ratio, with increasing the amount of starch (11,12,13). On the other hand, graft

copolymerization rate (Rg) is shown in **Figure 4**, which explains that the Rg slightly increased during the grafting reaction and then finally decreased (11).



**Fig. 3:** Influence of starch content on the photo-induced grafting of Aam onto Starch in presence of FAS/H2O2 as initiator in aqueous medium: Aam 0.985 mole/l, initiator system FAS 0.0255 mole/l,  $H_2O_2 0.44$  mole/l for 90 min.



Fig. 4: the rate of graft copolymerization (Rg) of Aam onto starch in different amounts of starch.

## 3.3. Influence of Monomer Concentration

The effect of monomer content on WC%, GP% and GE% was studied (**Fig.5**). The results showed that WC%, GP% and GE% increase with monomer content increase in the range of monomer concentration used. It is accepted that the grafting reaction mainly depends on the ratio between the monomer and initiator content (14,15,16). Moreover, graft copolymerization rate Rg is shown in **Figure 6** which indicates that it is rapidly increased by increasing acrylamide content in the range used as was previously reported (17,18).



**Fig. 5:** Influence of Aam content on the photo-induced grafting of Aam onto Starch in presence of FAS/H<sub>2</sub>O<sub>2</sub> as initiator in aqueous medium: Starch 35 g/l, initiator system FAS 0.0255 mole/l, H<sub>2</sub>O<sub>2</sub> 0.44 mole/l for 90 min.



Fig. 6: the rate of graft copolymerization (Rg) of Aam onto starch in different concentrations of monomer.

#### 3.4. Influence of Hydrogen Peroxide Concentration

The data showing the variation of  $H_2O_2$  content (**Fig.7**) indicates that the WC%, GP% and GE% increase rapidly at the beginning of grafting reaction with increasing  $H_2O_2$  content till reaching an optimum at concentration of 0.66 mol/l and then slightly decreased. The increasing trend may be due to the formation of more grafting sites on starch backbone with increasing the amount of  $H_2O_2$  while the content of Mohr's salt was kept at 0.0221 mol/l and under visible light irradiation. The formation of different free radicals as a result of increasing  $H_2O_2$  content can be explained by the extended scheme of Fenton's reactions (19,20).

On the other hand the graft copolymerization rate Rg is shown in **Figure 8** which prevails that it firstly increases rapidly then no obvious increase was observed by increase in  $H_2O_2$  content. This finding was in correspondence with the change observed in grafting parameters values (**Fig.7**).



**Fig. 7:** Influence of  $H_2O_2$  content on the photo-induced grafting of Aam onto Starch in presence of FAS/ $H_2O_2$  as initiator in aqueous medium: Starch 35 g/l, Aam 0.985 mole/l, FAS 0.0255 mole/l for 90 min.



Fig. 8: the rate of graft copolymerization (Rg) of Aam onto starch in different concentrations of H<sub>2</sub>O<sub>2</sub>.

#### 3.5. Influence of Mohr's Salt Concentration

The variation of FAS concentration and keeping the  $H_2O_2$  concentration constant at 0.44 mole/l on the photo-induced graft copolymerization of Aam onto starch was examined (**Fig. 9**). It was found that the GP%, GE% and WC% values decrease by increasing the FAS concentration. This behavior may be

attributed to the consumption of the sulphate ion radical (SO4<sup>-</sup>) by Fe<sup>+2</sup> ions present in the system (22) as in the following equation:

 $Fe^{+2} + SO4^{-2} \rightarrow Fe^{+3} + SO4^{-2}$ 

Similar observations were also reported (23,24).



**Fig. 9:** Influence of FAS content on the photo-induced grafting of Aam onto Starch in presence of FAS/H<sub>2</sub>O<sub>2</sub> as initiator in aqueous medium: Starch 35 g/l, Aam 0.985 mole/l, H<sub>2</sub>O<sub>2</sub> 0.44 mole/l for 90 min.

Also the graft copolymerization rate Rg is shown in **Figure 10** indicating the decrease in its values as the FAS content increases and then it is levels off. This observation was correspondence with the change observed in grafting parameters values (**Fig. 9**)



**Fig. 10:** the rate of graft copolymerization (Rg) of Aam onto starch in different concentrations of FAS.

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#### 3.5.1. Water and saline absorption measurements

Starch is considered a hydrophilic compound because it contains many hydroxyl groups in its structure. In a trial to increase the hydrophilic nature of starch it was copolymerized by acrylamide under the conditions used previously in **Fig.5**. The data obtained in **Table 3** showed that the increase in nitrogen content and GP% increases the water uptake % and saline uptake % values. This means that the S-g-PAam copolymers appeared the hydrophilic character higher than starch itself.

## 3.5.2. Chemical resistant measurements

The data observed in **Table 4** show that the resistance character of starch and S-g-PAam copolymer in some selected solvents was found to be decreased in the following order: 1N NaOH < 1N acetic acid < 0.5N HCl < 6N HCl.

Table 3: Water and saline absorption measurements: 0.3 g of the graft copolymer was	soaked	in 15 ml
distilled water for 24 hrs, then weighing the wet copolymer after filtration.		

GP%	Wt. of wet copolymer in water (g)	Water uptake%	Wt. of wet copolymer in saline (g)	Saline uptake%	N%
70.29	1.99	663.33	2.48	826.67	7.96
193.43	2.19	730	2.305	768.33	11.63
300.34	2.885	961.67	3.425	1141.67	13.77
388.29	2.91	970	3.58	1193.33	13.59
541.71	4.125	1375	4.92	1640	14.77

**Table 4:** Chemical resistance measurements: Soaking 0.09 g of s-g-PAam (GP%=388.29%) in 10 ml solvent for 24 hrs, drying till constant weight, then weighing.

	Wt. of pure		Wt. of S-g-PAam	
Solvent	starch after	Sol. %	(GP%=388.29%) after drying	Sol. %
	drying (g)		(g)	
1N NaOH	1.435	1494.44 (swollen)	3.44	3722.22
1N acetic	0.045	50% dissolved	0.83	822.22
acid				
0.5N HCl	0.02	77.78% dissolved	0.815	805.56
6N HCl	0.0	Completely	0.67	644.44
		dissolved		

# 4. Evidence of Drafting

## 4.1. IR Spectroscopy

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In **Figure 11(a)** the IR spectrum of corn starch shows that the characteristic absorption peaks at 1155 cm<sup>-1</sup>, 2929 cm<sup>-1</sup> and 3433 cm<sup>-1</sup> are respectively attributed to C-O, C-H and OH stretching vibration of starch. **Figure 11(b)** shows the IR spectrum of S-g-PAam copolymer (GP 93.32%) which appears the characteristic absorption peak at 1660.41 cm<sup>-1</sup> results from C=O stretching vibration of -CO-NH<sub>2</sub> group. These results prove that starch has been grafted with Aam.



Fig. 11: FT-IR of (a) pure starch, (b) S-g-PAam (Gp 93.32%).

## 4.2. X-Ray Diffractometry

X-ray diffractograms of corn starch, PAam and S-g-PAam (GP 168.57%) were recorded at  $2\theta$  values between 5° and 70° (**Figs. 12a,b,c**). Pure starch shows three different sharp peaks between  $2\theta$  of  $10^{\circ}$  and  $30^{\circ}$  (**Fig. 12a**) which indicates the crystallinity in starch structure. On the other hand, PAam diffractogram (**Fig. 12b**) shows two broad halos in  $2\theta$  range of 7-25°. Moreover, the XRD pattern for S-g-PAam graft copolymer (GP 168.6%) (**Fig. 12c**) shows only two different more broad halos in  $2\theta$  range of 7-25°, indicating the distinct amorphous structure. This finding shows that on grafting, the peaks of starch appear to have changed and broadened. It can therefore be inferred that both the amorphous and crystalline regions are involved in grafting reaction.

#### 4.3. SEM

**Figures 13 a,b** and **c** are the photographs of starch and S-g-PAam copolymers (GP 70% and 193%). Scanning micrograph of the starch granules showed an irregular shape and varied particle sizes with a smooth surface (**Fig. 13a**), while the graft copolymers had a coarse porous structure and broad network (21) (**Figs. 13b** and **13c**). Additionally, the SEM photograph of S-g-PAam copolymer with GP 193% (**Fig. 13c**) shows a hollow structure which may be advantageous for use of this product in the area of super absorption.



Fig. 12: X-ray diffraction patterns of (a) pure starch, (b) PAam and (c) S-g-PAam (GP 168.57%)



Fig. 13: SEM micrographs of (a) Starch, (b) S-g-PAam (GP 70%) and (c) S-g-PAam (GP 193%) at X2000.

#### 4.4. Thermal analysis using TGA and DTA

The data of TGA represented in **Table 5** show that the initial decomposition temperature (IDT) and final decomposition temperature (FDT) of corn starch are 49.04°C and 326.48°C respectively (**Fig. 14**). Whereas in case of S-g-PAam copolymer (GP 300.34%), the IDT and FDT decomposition temperatures are 274.59°C and 693.14°C respectively (**Fig.15**). It is evident from the data in **Table 5** that grafting of Aam onto starch increases their IDT and FDT and this in turn increases its thermal stability. Moreover, in case

of corn starch thermogram (**Fig. 14**) which showed that the decomposition of starch occurs mainly in two stages. The first stage appeared (about 8%) weight loss up to 49°C due to the loss of adhered water, then there was a second sharp weight loss (about 74%) which was extended to 326.48°C due to the loss of the polysaccharide.

		_	-
Sample	GP%	IDT*	FDT**
Starch		49.04°C	326.48°C
Polyacrylamide		286.37°C	589.86°C
S-g-PAam	93.32 %	202.14°C	614.31°C
S-g-PAam	300.34 %	274.59°C	693.14°C

Table 5: TG	A data of	different	polymers
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\*: IDT: Initial decomposition temperature. \*\*: FDT: Final decomposition temperature.

Generally, the main decomposition of the polysaccharides starchs above 200°C (25). On the other hand, the weight loss in S-g-PAam copolymers occurred in four main stages. In case of S-g-PAam (GP 300.34%), its first weight loss (about 9%) was between 218.5°C and 297.59°C, the second weight loss (about 18%) was between 297.59°C and 364.30°C due to the loss of polysaccharides (25)

Table 0. D IN data of different porymers				
Sample	GP%	Exothermic peaks at temperature		
		(µV)		
Starch		318.67°C (6.66 µV)		
		(endothermic)		
Polyacrylamide		535.09°C (34.5 μV)		
Pure Starch + PAam (1:1		556.74°C (43.8 μV)		
w/w) (physical mixture)				
S-g-PAam	93.32%	317.7°C (4.5 µV)		
		, 539.7°C (18 μV)		
S-g-PAam	300.34%	250.93°C (2.2 μV)		
		, 586.97°C (39 μV)		
S-g-PAam S-g-PAam	93.32% 300.34%	317.7°C (4.5 μV) , 539.7°C (18 μV) 250.93°C (2.2 μV) , 586.97°C (39 μV)		

# Table 6: DTA data of different polymers

Moreover, the third weight loss (34.5%) was between 364.3°C and 478.44°C was due to the loss of graft chains in the copolymer (26). But the fourth weight loss was broad (about 19%) and found between 618.84°C and 780.98°C, which may be due to the further loss of graft chains in the copolymer (26,27).

DTA thermograms of Starch showed one endothermic peak at  $318.67^{\circ}C$  (6.66  $\mu$ V) representing gelatinization (**Table 6** and **Fig. 15**). However, in case of S-gPAam copolymer (GP 93.32%) thermogram, there are two exothermic peaks at different temperatures of  $317.7^{\circ}C$  (4.5  $\mu$ V) and 539.7 (18  $\mu$ V). Also, S-

g-PAam copolymer (GP 300.34 %) thermogram shows two exothermic peaks at temperatures of 250.93°C (2.2  $\mu$ V) and 586.97°C (38  $\mu$ V). This obvious difference in the  $\mu$ V values and the peak positions between Starch and S-g-PAam cpoloymers (**Table 6** and **Fig. 15**) tends to suggest the disturbance of the crystalline portion of the starch due to grafting.



Fig. 14: TGA/DTA curve of pure Starch.



Fig. 15: TGA/DTA curve of S-g-PAam (GP 300.34%).

Fig. 16 (a,b and c) shows the comparison between DTA thermograms of PAam, S-g-PAam (GP 300.34%) and the physical mixture of PAam and Starch (1:1 w/w). The comparison indicates that the exothermic peak of PAam at 535.09°C (34.5  $\mu$ V) that was nearly found in the thermogram of physical

mixture at 556.74°C (43.8  $\mu$ V) is virtually disappeared in the thermogram of S-g-PAam copolymer. This trend again confirms the grafting process.



Fig. 16: DTA curve of (a) PAam, (b) S-g-PAam (GP 300.34%), (c) Starch+PAam (1:1 w/w) (physical mixture).

# **5.** Conclusion

In this study, Aam was successfully grafted onto Starch backbone by visible light in air using redox system (FAS/H<sub>2</sub>O<sub>2</sub>) in aqueous medium leading to hydrophilic surfaces. This method provides an easy procedure to incorporate high percentage of PAam onto pure Starch.

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