

## Effect of acryloylation on superabsorbency of starch copolymers

Aliyu Danmusa MOHAMMED\* and Yusuf HASSAN

*Department of Chemistry, Umaru Musa Yar'adua University, PMB 2218, Katsina, Katsina State, Nigeria*

**Abstract.** Starch is acryloylated and copolymerised without incorporating any vinyl monomer such as acrylic acid or acrylonitrile monomers to produce a superabsorbent copolymer. Fenton's initiation system was used to produce polyacryloylated starch ester with varying degree of substitution. The copolymer from starch ester exhibited improved solubility, and an impressive water, saline, and solvents uptake. The superabsorbency of the samples is affected by the number of acryloyl groups on starch backbone. The starch ester with degree of substitution 0.8 had the highest water absorbency (102 g/g) in this experiment. Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and thermogravimetric (TGA) analyses were used to characterize the products.

**Keywords:** absorbency; acryloylated starch; copolymerization; degree of substitution.

### 1. Introduction

Superabsorbent polymer hydrogels are lightly cross-linked hydrophilic polymers that can absorb, swell and retain aqueous solutions to hundred times their own weight, and they have great advantages over traditional water absorbents such as cotton, pulp, sponge, etc. [1]. The superabsorbents do not dissolve via hydrogen bonds, due to the interconnectivity and electronic nature of the molecules [2]. Superabsorbents are widely used in agriculture, horticulture [3-7], in diapers, hygienic products and pharmaceutical applications for drug delivery [8-11]. Different cross-linkers are used in producing cross-linked superabsorbents from starch based polymers. They include 4,4-divinylazobenzene, N,N'-methylene-bis-acrylamide, ethylene glycol dimethacrylate, sucrose, and photo-induced cross-linked polymers [12]. Superabsorbents produced from direct grafting of acrylic acid onto starch usually come along with some drawbacks. These include poor grafting yield and low superabsorbency. Addition of acryloyl groups on the starch backbone increases the grafting yield, low amount of homopolymers and more superabsorbency. The superabsorbents exhibit structural modification once hydrated. The carboxyl groups of the ester portion split and become negatively charged. The repulsion of the like charges causes enlargement of the overall structure which could allow more aqueous substance to move in and be trapped. Hydrogen bonds from the oxygen of the carboxylate ion and hydrogen atoms from water are formed within the network structure. The swollen- superabsorbent polymer appears like all-water but do not dissolve due to the cross-linking nature of the structure [13]. Superabsorbent polymers are mostly prepared from acrylic acid using cross-linking agent via solution or suspension polymerization. The type of cross-linking agent and its cross-linking density in the polymer matrix determines both the swelling capacity and gel modulus [14].

The concept of osmotic pressure is what explains the phenomenon of superabsorbency and retention. The polymer acts as a semipermeable membrane which controls the flow of charge substituents of the polymer into the surrounding solution. This is based on the concept of ionized monomeric units containing fixed charges which attract and fix ions from the outer solution. Therefore, a charge gradient is set up, in which the concentration of free ions is greater outside the polymer matrix, while the osmotic pressure exerted by the gradient causes the polymer chain to swell as further ions diffuse into the polymer network [15].

Acryloylation of the starch before grafting produces a polymer structure with long comb-like chains that could allow aqueous substance to be trapped within the network of the polymer structure [2]. Application of polysaccharides as superabsorbents is of special interest because of their properties such as biodegradability, renewability, non-toxicity and biocompatibility [16].

On the basis of our previous work on superabsorbency of starch ester grafted with acrylic acid [2, 12], an experiment on absorbency of starch ester copolymer (without addition of any vinyl monomer) and effect of number of acryloyl groups on absorbency of poly starch ester is reported in this work. The ester from starch is polymerized without further grafting with any vinyl monomers such as acrylic acid or acrylonitrile or use of cross-linking agent. In addition, different solvents' uptakes were tested with the samples.

### 2. Experimental

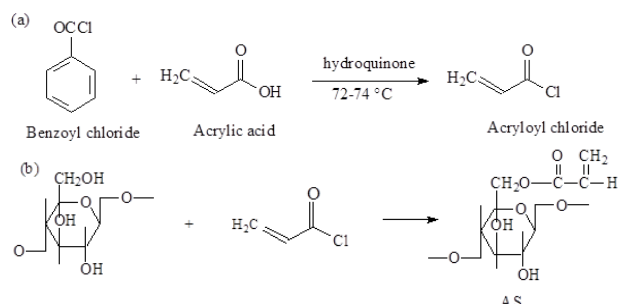
#### 2.1. Materials

Starch from potato and chemicals (from Sigma Aldrich) used in acryloylation reactions (pyridine, ferrous ammonium sulfate, benzoyl and hydrogen peroxides) were used as received. Acrylic acid used in the experiment was obtained by distillation under reduced pressure.

\*Corresponding author. *E-mail address:* aly27moh27@gmail.com (Aliyu Danmusa Mohammed)

## 2.2. Synthesis

2.2.1. *Synthesis of acryloyl chloride and acryloylation of starch.* The methods reported by Mohammed *et al.* [2] were used for the syntheses of acryloyl chloride and starch acryloylation (Scheme 1a and b).



**Scheme 1.** (a) Synthesis of acryloyl chloride and (b) synthesis of acryloylated starch (AS)

2.2.2. *Preparation of poly acryloylated starch copolymer (PAS).* The method reported by Mohammed *et al.* [17] was used. Slurry of starch was formed by adding acryloylated starch (5 g) to water (50 mL) and heated to 60 °C in a three-necked round bottomed-flask to form a slurry. Fenton's initiation system was used to obtain the copolymer.

## 2.3. Characterization

The FTIR spectra of the samples were obtained using Bruker Vertex 80 FTIR spectrophotometer. The spectra were recorded in absorbance mode at a range of 500-4000  $\text{cm}^{-1}$  at room temperature and using ATR Bruker Diamond accessory. The thermal properties and structural characterization were carried out using thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) analyses respectively.

## 2.4. Superabsorbency and degree of substitution

Procedure reported by Mohammed *et al.* [2] was used to calculate the % water absorbency.

The value of water and saline absorbency ( $Q$ ) was obtained from the relation:

$$Q\left(\frac{g}{g}\right) = (w_2 - w_1)/w_1 \quad (1)$$

where  $Q$  is the water or saline absorbency,  $w_2$  is the weight of the swollen sample, and  $w_1$  is the weight of dry sample.

The degree of substitution (DS) was obtained from titrimetric procedure using bromine, iodine and sodium hyposulfite, as reported by Li *et al.* [18]. This involves a reaction of acryloyl groups with bromine and subsequent reaction of the residual bromine with iodine. A further titration of excess iodine with sodium hyposulfite provides the needed information for the determination of the acryloyl groups.

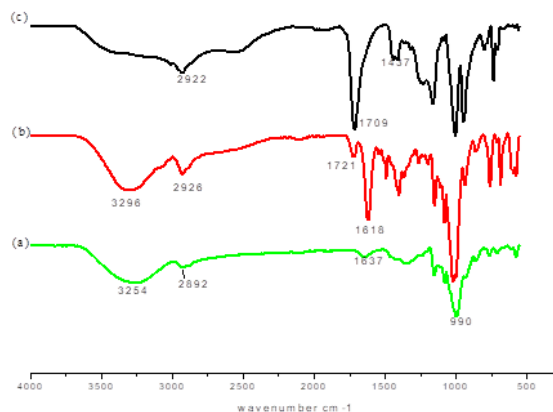
## 3. Results and discussion

### 3.1. FT-IR analysis

FT-IR spectroscopy shows evidence of acryloylation and copolymerisation.

In Fig. 1a, the FT-IR spectrum of starch showed absorption bands at 3254  $\text{cm}^{-1}$  and at 1637  $\text{cm}^{-1}$  due to OH stretching and bending modes respectively, and at

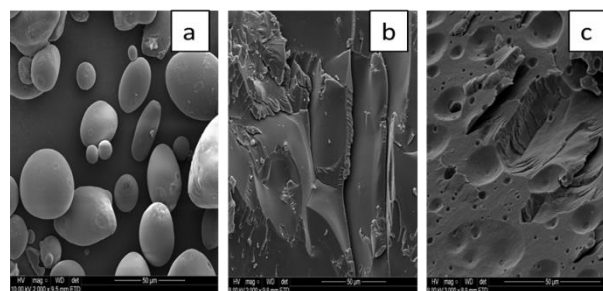
2892 and 1076  $\text{cm}^{-1}$  due to C-H stretching and bending respectively. The acryloylated starch, in Fig. 1b, shows additional peaks at 1721  $\text{cm}^{-1}$  due to C=O from the ester bond formation, and another peak at 1618  $\text{cm}^{-1}$  due to C=C double bond vibration. The copolymer (PAS) in Fig. 3, showed an intensive peak around 1710  $\text{cm}^{-1}$  due to carbonyl stretching and at 2922 due to C-H stretching mode.



**Figure 1.** FT-IR spectra of (a) starch, (b) AS, and (c) polyacryloylated starch

### 3.2. SEM

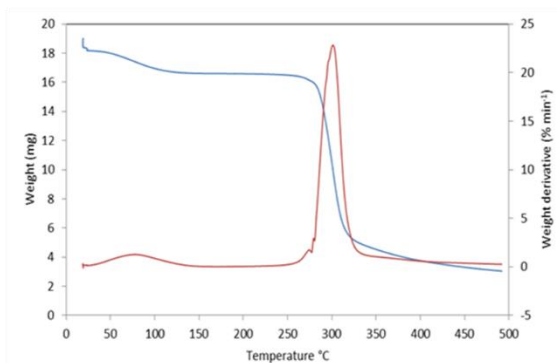
The surface morphology of starch, AS and PAS are shown in Fig. 2. The smooth surface and irregular oval shape of the granular starch is clearly seen in Fig. 2a. In Fig. 2b, the starch morphology is disrupted, and a thick coated surface is formed. This results from chemical modification of starch by acryloylation reaction. The polymer PAS shows a different morphology, whereby the thick-coated surface changes to a clearly porous structure (Fig. 2c). This justifies why the copolymer could absorb and retain large quantity of aqueous substance within its network.



**Figure 2.** SEM images of (a) starch, (b) AS and (c) polyacryloylated starch

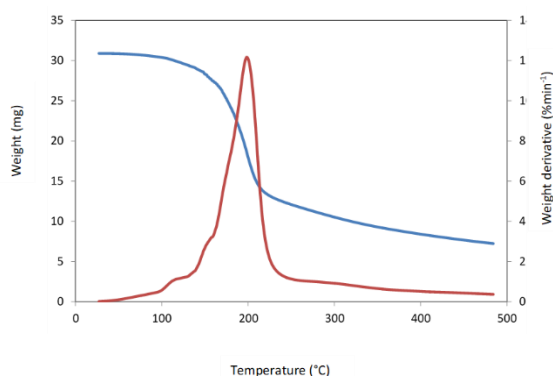
### 3.3 Thermogravimetric analysis

The thermal stability and the degradation pattern of starch, acryloylated starch and polyacryloylated starch are shown in Fig. 3. In the thermal analysis curve of starch, there is decomposition at around 90 °C due to evaporation of moisture.



**Figure 3.** Thermal analysis curve of starch

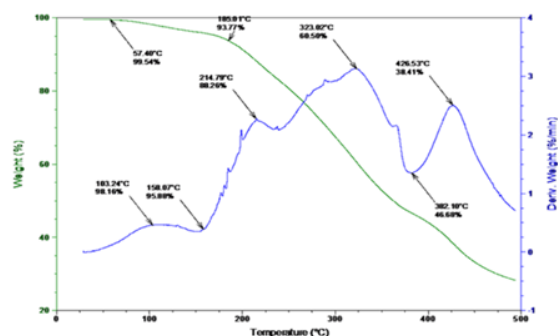
The first stage of decomposition is due to evaporation of absorbed moisture which results in a slight loss in weight. The second step is rapid and accounts for the highest weight-loss (75%) with a temperature of maximum decomposition of 300 °C as can be seen in the weight-derivative curve. The final stage is a slow decomposition, probably, of some volatile compounds formed at higher temperature [2].



**Figure 4.** Thermal analysis curve of acryloylated starch

The AS, Fig. 4, shows the decomposition of the starch ester. There is a slow decomposition followed by a major decomposition at 105 °C and at around 200 °C respectively. These resulted in 43% weight loss. Subsequent decompositions could be from some volatile compounds formed at higher temperatures. There is decrease in the number of hydrogen bonds due to substitution of free OH in the starch molecule by acryloyl groups, hence, lower thermal stability of the sample.

There is however, a different pattern of decomposition of the polymer sample (PAS, Fig. 5), the initial decomposition observed from 60 to 150 °C is due to dehydration showing about 6% weight loss. The second stage pattern of decomposition occurs at a temperature range of 160–214 °C whereby about 40% weight loss is observed. The third stage shows decomposition at 427 °C with a char yield of 38%, this could be mainly from the decomposition of some compounds formed at higher temperature from the cross-linked network of PAS copolymer. The trend in the decomposition pattern of the samples goes as follow: PAS > Starch > AS. This shows an increase in thermal stability from ungrafted starch to the copolymer.



**Figure 5.** Thermal analysis curve of polyacryloylated starch (PAS)

### 3.4. Absorbency and degree of substitution

Introducing hydrophobic acyl groups onto starch backbone affects solubility and swelling effects of starch ester in water. High number of acyl groups (DS) per starch molecule decreases the solubility and swelling behavior of starch ester in water [19-21]. However with polymerization of the ester, the properties are remarkably improved. This is because a comb-like structure is built upon the starch backbone which allows aqueous substance to move-in [2]. Table 1 shows the water and saline absorbency of the samples. The absorbency is observed to be highest with a DS of 0.8 and decreases when increased to 0.9. The formation of polymeric network from the starch ester allows aqueous substance to move into the porous surface and become enveloped in the matrix. When the number of acryloyl groups increases (DS > 0.8), a dense network of the molecules are formed which hinders easy passage of aqueous substance to get into the matrix, hence lower absorbency. All the samples show excellent absorbency under load (AUL), this property is ascribed to the nature of the monomeric units and the tight structure being formed after polymerization.

**Table 1.** Water retention ability of samples for different degrees of substitution (DS)

| DS   | Water absorption (g/g) | Saline soln. absorption (g/g) | Saline soln. AUL (g/g) | Retention (%) water | Retention (%) saline soln. |
|------|------------------------|-------------------------------|------------------------|---------------------|----------------------------|
| 0.05 | 42                     | 2                             | 1                      | 100                 | 100                        |
| 0.20 | 69                     | 5                             | 3                      | 100                 | 100                        |
| 0.32 | 73                     | 12                            | 5                      | 100                 | 100                        |
| 0.50 | 88                     | 16                            | 6                      | 100                 | 100                        |
| 0.80 | 102                    | 20                            | 8                      | 99                  | 99                         |
| 0.90 | 99                     | 18                            | 7                      | 99                  | 100                        |

The solvent uptake of the samples is shown in Table 2. Dimethylformamide is absorbed most while hexane is the least absorbed. Like water and saline absorbency, the sample with DS of 0.8 has taken up more solvents than other samples in this experiment. 1500 % and 68% of DMF and *n*-hexane were absorbed by the polymer samples respectively. The change in DS from 0.8 to 0.9 doesn't show much difference in the solvents' uptake. Although there is no decrease in absorbency in some samples with DS from 0.8-0.9, it can be deduced that the solvents uptake leveled-up when the DS is 0.8. The

polarity and dielectric constants determine the solvents uptake by each sample [12]. In this experiment, polar solvents with high dielectric constant are taken up more than the non-polar with low dielectric constants.

**Table 2.** Solvent uptake of the samples (% uptake) for different degrees of substitution

| DS   | Aceto-nitrile | DMF  | Hexane | Toluene | DCM |
|------|---------------|------|--------|---------|-----|
| 0.05 | 520           | 650  | 30     | 34      | 43  |
| 0.20 | 640           | 900  | 41     | 42      | 51  |
| 0.30 | 680           | 1190 | 48     | 51      | 67  |
| 0.50 | 770           | 1250 | 62     | 65      | 72  |
| 0.80 | 890           | 1500 | 68     | 71      | 83  |
| 0.90 | 889           | 1500 | 67     | 69      | 81  |

#### 4. Conclusion

In conclusion, we have prepared a superabsorbent polymer with good retention ability and absorbency under load using copolymerization of acryloylated starch. The morphology and thermal stability of the products were investigated using SEM and TGA analyses respectively. The method provides an advantage over other techniques that require cross-linking agents or further grafting with other vinyl monomers such as acrylic acid and acrylonitrile. Thus, the cost to produce the superabsorbent in this study is lower compared to the previous works reported in literature. The water absorbency and solvents' take up are affected by the number of acryloyl groups present in starch molecule. The lower cost of production (since no cross-linker and acrylic acid monomer are required) coupled with the impressive ability of the samples to absorb under load, retention of aqueous substance under pressure and ability to absorb solvents with relatively high dielectric constants, could make application of these superabsorbents a promising venture in pharmaceutical, horticultural and cosmetics industries.

#### Acknowledgment

The authors gratefully acknowledge the financial support of Tertiary Education Trust Fund (TETFUND), Nigeria.

#### Conflict of interest

Authors declare no conflict of interest.

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*Received:* 12.02.2020

*Received in revised form:* 23.02.2020

*Accepted:* 26.02.2020