ABSTRACT

Graft copolymerisation of acrylic acid (AA) onto native starch was carried out in aqueous medium by free radical initiation process. The free radicals were produced by chemical initiation method in the grafting process. It was observed that the percentages of grafting and grafting efficiency were dependent on the concentration of initiator, monomer and reaction temperature. The variables affecting the graft copolymerisation were thoroughly examined. The formation of graft copolymers was confirmed using the gravimetric estimation method. The optimum conditions are defined.

Keywords: sago starch, acrylic acid, persulphate, graft copolymerisation

INTRODUCTION

Starch is one of the most abundant and low cost polymer available in nature. It can be obtained from various natural resources such as rice, cassava, corn, maize, wheat, sago etc. Starch, if chemically modified can find wide application in various industries such as food, textile, paper, plastic and medical industries.

Graft copolymerization of vinyl monomers onto a starch is an excellent method for modifying the physico-chemical properties of starch for its commercial applications. Depending on the type of monomers used in the copolymerization reaction the products may be used as thickeners, absorbents, sizing agents, adhesives, flocculants, resins and plastics.

Graft copolymerisation is a method of addition of new and desirable properties to starch without drastically affecting its basic properties. Grafting of vinyl monomers on to the starches improves their shelf-life against biodegradation and thermal stability and therefore their industrial utility. For conserving the petrochemical resources and reducing environmental pollution, many efforts have been made to develop starch based polymers.

Grafting of vinyl monomers onto natural polymers like gum-guar starch and cereal flour with various initiators has been studied.

Earlier Bayazeed et. al. have described the effect of reaction variables using persulphate to initiate grafting of acrylic acid (AA) onto maize starch and have established certain conditions for optimum graft yield. Similar kind of study was carried by Lele onto potato starch.

Sago starch is extracted from the spongy centre, or pith, of various tropical palm stems (Sago palm), especially Metroxylon sagu. Malaysia is the largest world exporter of sago starch. Sago starch is currently mainly used for food and food related products. Alteration in the sago starch properties by
Graft copolymerization widens the scope of its utilizations which consequently increases its economic importance.

Wan et al. studied grafting of acrylic acid (AA), methyl acrylate (MA), and hydroxyl methyl methacrylate (HEMA) onto sago starch (SG) using ammonium persulphate for generating free radical sites on the starch backbone. Kaur and Sharma employed γ-rays for initiating grafting of acrylic acid (AA) onto SG while Lee et al. used UV rays in grafting of acrylic acid (AA) onto sago starch (SG).

Graft copolymerisation of sago starch has been a recent interest of study. This research paper entails the detailed study of graft copolymerisation of sago starch using potassium persulphate as a chemical initiator and acrylic acid as a monomer.

MATERIALS AND METHODS

Pure sago starch powder (Yiak Say Hang Food Industries(S) PTE Ltd., Singapore) was dried at 70 °C for about 10h to constant weight to make it free of known moisture. Potassium persulphate (AR, S.D. Fine Chemicals, India) and dried starch were stored over anhydrous CaCl₂ in a desiccator to avoid any absorption of moisture. Acrylic acid (AA) (LR, S.D. Fine Chemicals, India) was stored in refrigerator and then brought to room temperature before use.

**Graft Copolymerisation**

Graft copolymerisation reaction was carried out in three steps as follows.

Step 1. Addition of 70 ml of distilled water to 2g of sago starch powder and then stirring it for a while to obtain a uniform slurry.

Step 2. To the slurry a calculated amount of potassium per sulfate was added and then stirred for approximately 10 minutes in order to facilitate the formation of free radical sites on starch backbone.

Step 3. After 10 minutes a known amount of acrylic acid was added to the above mixture and then the total volume was made to 100 ml by further addition of distilled water.

The above reaction mixture was stirred constantly for pre-determined time. The residue so obtained, was filtered through a dry pre-weighed Whatmann paper no. 41. It was then washed with water till it became free of homopolymer, water being the solvent for the homopolymer. The residue now obtained was pure graft copolymer and it was then dried under vacuum.

A control reaction was carried out under similar reaction conditions except for the addition of the monomer.

This procedure was repeated over a range of concentrations of monomer and initiator and at different temperatures.

**Gravimetric estimation**

The weight of the pure starch (W₁), the graft copolymer (W₂) and the monomer (W₃) utilized in the graft copolymerisation reaction were noted and calculations were carried out based on the differences in these weights.

**Grafting parameters**

The following formulae were applied to calculate the percentage grafting and grafting efficiency.

\[
\% GE = \frac{100(W_2 - W_1)}{W_3}
\]

\[
\% G = \frac{100(W_2 - W_1)}{W_1}
\]
RESULTS AND DISCUSSIONS

Grafting was monitored gravimetrically. Grafting percentage (%G) gives graft copolymer yield with reference to weight of starch (backbone polymer), while grafting efficiency (%GE) gives yield with reference to weight of monomer in feed.

Effect of initiator concentration

The %GE initially increases with the increase in initiator concentration, however it decreases gradually with further rise in concentration of the initiator.

The decrease in %GE beyond optimum conditions can be attributed to the following reasons:

- Formation of unstable complex between initiator and starch
- Dominance of the termination reaction
- Reduction of the active sites exposed to the monomer
- Homopolymerization

Table 1. Effect of initiator concentration on the grafting of AA onto SG

<table>
<thead>
<tr>
<th>Concentration of initiator (mol/L)</th>
<th>%G</th>
<th>%GE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0005</td>
<td>0.35</td>
<td>0.3330</td>
</tr>
<tr>
<td>0.001</td>
<td>1.10</td>
<td>1.0470</td>
</tr>
<tr>
<td>0.002</td>
<td>2.30</td>
<td>2.1900</td>
</tr>
<tr>
<td>0.003</td>
<td>0.70</td>
<td>1.4200</td>
</tr>
<tr>
<td>0.004</td>
<td>1.50</td>
<td>1.0000</td>
</tr>
<tr>
<td>0.006</td>
<td>1.05</td>
<td>0.0950</td>
</tr>
<tr>
<td>0.01</td>
<td>0.10</td>
<td>0.3330</td>
</tr>
</tbody>
</table>

Starch = 2g; [AA ]= 0.2775 mol/L in each case in 100mL of distilled water at 30°C for 180 min

Effect of monomer concentration

%GE was observed to increase for monomer concentration from 0.1 to 0.3 mol/L but there was decline in %GE for concentrations beyond 0.3 mol/L. The increase can be attributed to the greater availability of monomer in the proximity of starch macro radicals, however the decrease in grafting yield at a later stage may be owing to the wastage of initiator molecules in the formation of large amounts of homopolymer.
Table 2. Effect of monomer concentration on the grafting of AA onto SG

<table>
<thead>
<tr>
<th>Concentration of monomer mol/L</th>
<th>%G</th>
<th>%GE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06935</td>
<td>0.750</td>
<td>2.857</td>
</tr>
<tr>
<td>0.1387</td>
<td>1.600</td>
<td>3.047</td>
</tr>
<tr>
<td>0.2775</td>
<td>3.875</td>
<td>3.690</td>
</tr>
<tr>
<td>0.4163</td>
<td>1.950</td>
<td>1.238</td>
</tr>
<tr>
<td>0.5550</td>
<td>0.975</td>
<td>0.464</td>
</tr>
<tr>
<td>0.6840</td>
<td>0.650</td>
<td>0.247</td>
</tr>
</tbody>
</table>

Starch = 2g; [PPS]= 0.002 mol/L in each case in 100mL of distilled water at 30°C for 180 min.

Effect of reaction temperature

The %GE has a maximum value at reaction temperature of 35°C. The increase in %GE up to 35°C was possibly due to the higher rate of diffusion of monomer molecules to starch macro radicals. However the decline in %GE beyond 35°C can be explained on the basis of increased rate of homopolymerisation which was evident from the increase in viscosity of medium.

Table 2. Effect of polymerisation temperature on the grafting of AA onto SG

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>%G</th>
<th>%GE</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>2.050</td>
<td>1.952</td>
</tr>
<tr>
<td>30</td>
<td>2.850</td>
<td>2.710</td>
</tr>
<tr>
<td>35</td>
<td>7.300</td>
<td>6.950</td>
</tr>
<tr>
<td>40</td>
<td>5.750</td>
<td>5.470</td>
</tr>
<tr>
<td>45</td>
<td>3.850</td>
<td>3.666</td>
</tr>
</tbody>
</table>

Starch = 2g; PPS = 0.002 mol/L; [AA] = 0.2775 mol/L in each case in 100mL of distilled water at 30°C for 180 min.
CONCLUSION

It is possible to graft acrylic acid onto sago starch using chemical initiation method. The reaction parameters namely concentration of initiator & monomer and polymerization temperature were optimized to obtain maximum grafting.

The optimum conditions for effective grafting of acrylic acid onto 2g of sago starch have been established as [AA] = 0.2775 mol/L, [PPS] = 0.002 mol/L and temperature= 35°C.

REFERENCES