Graft Copolymerization of Acrylonitrile onto Acacia Gum by Manganese (IV)–Nitric Acid as a Redox Initiator in Aqueous Media under Visible Light

E. A. Abdel-Razik *, D. M. Ayaad and A. M. Elbedwehy

Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt

* Author to whom correspondence should be addressed; E-Mail: e.abdelrazik51@gmail.com.

Article history: Received 4 September 2013, Received in revised form 14 October 2013, Accepted 18 October 2013, Published 25 October 2013.

Abstract: Graft copolymerization of acrylonitrile (AN) onto acacia gum (AG) using potassium permanganate (KMnO₄) in aqueous media and in presence of nitric acid under visible light was extensively studied. The optimum grafting conditions were examined as functions of irradiation time and the concentrations of KMnO₄, AN, AG and HNO₃. Grafting parameters such as grafting percentage (GP %), grafting efficiency (GE %), as well as homo polymerization (HP %) all were determined. Highest GP (268%) and lowest homo polymer content (2.47%) were obtained through optimization of the grafting variables. The max absorption of KMnO₄ (λₘₐₓ) was determined via UV spectrophotometer. Graft products of AG-g-PAN copolymers were characterized using FTIR spectroscopy, X-ray diffraction, Scanning electron microscope, thermal analysis such as TGA and DTA. The results are discussed, and the mechanism of grafting was also suggested.

Keywords: Acacia gum; graft copolymerization; Acrylonitrile; thermal resistance; visible-light irradiation.
1. Introduction

AG is a highly heterogeneous complex polysaccharide consists of four sugar units (1, 2) include D-galactose (39–42%), L-arabinose (24–27%), L-rhamnose (12–16%), D-glucuronic acid (15-16%) and protein (1.5–2.6%). AG is a widely natural biopolymer used in many applications, mainly in food, pharmaceutical and cosmetic industries due to its unique physiochemical and functional properties (3, 4). However, like other polysaccharides, it suffers from some drawbacks like biodegradability, thermal instability, etc., which limits its application. Grafting of monomers, especially vinyl monomers onto polysaccharides have received attractive means of chemical modification because grafted copolymers have improved physicochemical properties and industrial applications. Acrylonitrile is one of the most common vinyl monomer used in large scale. This tendency may be resulting from its high activity via grafting onto various natural polymers (5–7), optimizing the thermal resistance of the graft copolymer (8, 9), as well as for obtaining water absorbents by alkaline hydrolysis of the grafted product (10, 11). The ability of the KMnO₄/acidic medium redox initiator in graft copolymerization of some vinyl monomers onto cellulose, starch and others (12–14) have been demonstrated the efficiency of the redox initiator for generation macro-radicals on polysaccharide backbone essentially for grafting. Visible light revealed successful results to induce grafting of many vinyl monomers onto different natural polymers (15–18). However, to the best of our knowledge based on chemical abstracts, no work had been reported on grafting of AN onto AG using a photo-induced (KMnO₄-HNO₃) redox system. This work presents the results of the graft copolymerization of acrylonitrile onto AG using KMnO₄–nitric acid as a redox initiator under visible light.

2. Experimental

2.1. Materials

Acacia gum (A-gum, BDH, England), Acrylonitrile (AN, Sigma-Aldrich, United states) was extracted with aqueous sodium hydroxide – sodium chloride solution to remove the inhibitors, dried over anhydrous calcium chloride, and then was fractionally distilled. Potassium permanganate, nitric acid (AR grade), methyl alcohol and dimethylformamide were supplied by BDH used as received. Laboratory prepared distilled water was used through this study.

2.2. Graft Copolymerization and Parameters

Grafting reaction was carried out in closed Pyrex cells. For each experimental calculated amount of AG was dissolved in a limited volume of water with stirring until
obtaining homogenous solution, (total volume of all reactions was kept constant). Then, freshly prepared solution of KMnO₄ in nitric acid was added and stirred for 10 min. The zero reaction time was at the time of monomer addition. Polymerization experiments were mainly studied under photo-inducing with visible light by placing the cells between a pair of tube fluorescent lambs (40 W) for definite time periods (0.5-3h). Initially some polymerization experiments were also done in similar systems in the dark at room temperature. The polymerization process was finally terminated by pouring the reaction mixture in methanol for precipitation. The crude copolymer that obtained was dried to constant weight under vacuum at 40ºC. The dried product was extracted with dimethylformamide for 48h to remove the homopolymer (polyacrylonitrile). Obtained pure graft copolymer was dried under 40ºC until constant weight. GP%, GE%, WC% and HP% were calculated according to the following expressions:

\[
\text{Grafting percentage (GP %)} = \frac{A-B}{B} \times 100
\]

\[
\text{Grafting efficiency percentage (GE %)} = \frac{A-B}{C} \times 100
\]

\[
\text{Weight conversion percentage (WC %)} = \frac{A}{B} \times 100
\]

\[
\text{Homopolymer percentage (HP %)} = \frac{\text{wt of homopolymer}}{C} \times 100
\]

Where A, B, C are the weight of graft product, AG and monomer respectively. Weight of homopolymer is A-B.

2.3. Instrumental Analysis

The UV spectrum of potassium permanganate was measured by UV spectrophotometer (Perkin Elmer Lambda 3B) and its (λₘₐₓ) in the visible region was also determined. Chemical structure of the grafted product was examined by IR spectrophotometer (Perkin Elmer 1430) using KBr to prepare its disks. The thermal analysis of AG and graft copolymer was determined using thermal analyzers (Shimadzu DTA-50 and Shimadzu TGA-50H) under nitrogen atmosphere. Powder samples of some polymers were subjected to (X-ray Diffraction - D8 Advance X-Ray diffractometer; Bruker AXS) using Cu Kα radiation. The scattering angle 2θ was varied from 5° to 60°. The morphology of samples was studied by scanning electron microscopy (SEM), dried samples were coated with a thin layer of palladium-gold alloy and imaged using (JEOL-JSM 5300).
3. Results and Discussion

3.1. Comparison

For comparison, some grafting experiments were carried out both in dark and under visible light to check the efficiency of (KMnO₄-HNO₃) redox initiator in the presence of visible light maintaining constant the concentration of the initiator, polysaccharide and monomer (Table 1). The results indicated that the grafting percentage in the dark for 24h gave 74%, but in presence of visible light was 150% during only 2h. This means that the rate of grafting highly increase in presence of visible light.

Table 1. Graft copolymerization of AN onto AG in aqueous medium, AG (83.33g/l), AN (6.36 mole/l), initiator system KMnO₄ (0.0169 mole/l) and HNO₃ (0.129 N).

<table>
<thead>
<tr>
<th>Initiator system</th>
<th>condition</th>
<th>GP%</th>
<th>GE%</th>
<th>WC%</th>
<th>HP%</th>
</tr>
</thead>
<tbody>
<tr>
<td>KMnO₄ + HNO₃</td>
<td>Dark (24hr)</td>
<td>74%</td>
<td>18.3%</td>
<td>174%</td>
<td>13.3%</td>
</tr>
<tr>
<td>KMnO₄</td>
<td>Dark (24hr)</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>HNO₃</td>
<td>Dark (24hr)</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>KMnO₄ + HNO₃</td>
<td>Visible (120min)</td>
<td>150%</td>
<td>37%</td>
<td>250%</td>
<td>4.5%</td>
</tr>
<tr>
<td>KMnO₄</td>
<td>Visible (120min)</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>HNO₃</td>
<td>Visible (120min)</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

Therefore, the determination of UV spectrum of KMnO₄ became essential to know its absorption in the visible region. The UV spectrum of KMnO₄ showed absorption peaks at wavelengths 392nm, 524nm and 542nm. This prevails that KMnO₄ has obviously specific absorption in the visible region and this is in turn may be explained its activity under visible-light irradiation.

3.2. Effects of the Grafting Variables

3.2.1. The reaction time

Fig. 1 presents the relationship between the reaction time and grafting parameters such as WC%, GP % and GE % as well as HP % within a given time range (30-180 min). It was found that the
values of WC %, GP %, and GE % increased and reached to optimum condition at 120 min, beyond it, they slightly decreased.

Fig. 1. Effect of time on the photo-induced grafting of AN onto AG in presence of KMnO₄/HNO₃ as initiator

The initial rate of grafting was determined to be 0.8%/min (19). The increase observed in WC %, GP % and GE % may be due to the increase in the number of grafting sites in the initial stage of grafting reaction (20, 21). The decrease in contents for both KMnO₄ and AN as the reaction proceeds explains the decrease observed in grafting parameters. Moreover, in case of HP %, it increases by the time then decrease by time increase and finally levels off. Similar time dependency of grafting was reported by other workers (19-21).

3.2.2. The acrylonitrile (AN) concentration

The effect of AN concentration on the grafting parameters and HP % was studied (Fig. 2). The AN concentration was ranged from 1.27 to 8.91 mole/l. The results indicated that the increasing in AN content was accompanied by increasing in grafting parameters until reached the optimum at AN content 6.36 mol/l and after that, it markedly decrease by increasing AN content. This finding may be ascribed to the greater availability of grafting sites to AN, whereas in case of HP %, it initially rapid decreases then finally increases. It is also known that the grafting reaction mainly depends on the ratio between the monomers and initiator content (19, 21).
Fig. 2. Effect of AN content on the photo-induced grafting of AG onto AN in presence of KMnO$_4$/HNO$_3$ as initiator in aqueous medium: AG 83.33g/l, KMnO$_4$ 0.0063 mole/l, HNO$_3$ 0.13 N and time 120min.

3.2.3. The KMNO$_4$ initiator concentration

Grafting dependence on KMnO$_4$ concentration can be seen in (Fig.3). The grafting parameters WC %, GP % and GE % were increased by increasing KMnO$_4$ content until reaching to optimum condition at KMnO$_4$ concentration of 0.0327 mol/l whereas HP % content was only 2.96. Additionally, it was observed that the increase in KMnO$_4$ content beyond 0.031 mole/l, lead to decrease in values of grafting parameters. As a result, the increased amounts of free radicals on the AG were compensated by partial termination of macro radicals, and this explains the decrease observed in grafting parameters (12-14).

It has been reported (22) that radical formation occurs during a polymerization initiated by KMnO$_4$ in the presence of an acid through the reduction of Mn (IV) to Mn (III) and/or Mn (II). Thus, during vinyl polymerization onto AG under the catalytic influence of KMnO$_4$ in the presence of an acid (HR), formation of a free-radical species occurs as follows:

\[
\text{Mn (IV) + HR} \rightarrow \text{Mn (III) + H}^+ + \cdot R \quad (1)
\]

\[
\text{Mn (IV) + H}_2\text{O} \rightarrow \text{Mn (III) + H}^+ + \cdot \text{HO} \quad (2)
\]

When free radicals species (R') are created, they generate an AG macroradicals

\[
\text{AG-OH + R'} \rightarrow \text{AG-O}^+ + \text{RH} \quad (3)
\]
AG macroradicals may also be formed by direct attack of Mn (IV) or Mn (III) ions on the AG molecule via abstraction of a hydrogen atom:

\[
\text{AG-OH} + \text{Mn (IV)} \rightarrow \text{Mn (III)} + H^+ + \text{AG-O}^\cdot \quad (4)
\]

\[
\text{AG-OH} + \text{Mn (III)} \rightarrow \text{Mn (II)} + H^+ + \text{AG-O}^\cdot \quad (5)
\]

Fig. 3. Effect of KMnO₄ content on the photo-induced grafting of AG onto AN in presence of KMnO₄/HNO₃ as initiator in aqueous medium: AG 83.33g/l, HNO₃ 0.13N, AN 6.36 mole/l and time 120min.

In the presence of vinyl monomer as AN, the AG macro-radicals are reacted with the double bond of AN with the creation of a free radical on the monomer when a chain start initiated and then the initiated chain propagates grafting onto the AG:

\[
\text{AG-O}^\cdot + \text{CH}_2=\text{C} \rightarrow \text{AG-O}^\cdot \text{C} - \text{C}\cdot \quad (6)
\]
3.2.4. The acid concentration

The influence of HNO$_3$ concentration on the grafting parameters and HP% was studied (Fig. 4). It was found that values of WC %, GP%, and GE % increase with increasing HNO$_3$ concentration attaining a maximum at 0.18N. The decrease observed in grafting parameters beyond this concentration could be attributed, firstly, due to the coagulation of colloidal homopolymer in the solution. This retards the diffusion of both the monomer and the initiator. Secondly, due to the side reaction given in equation (10) that increases at higher acid content it also leads to a constant production of inhibiting oxygen (22). On the other hand, the values of HP % often increase by increasing HNO$_3$ concentration.

$$\text{MnO}_2 + 2\text{H}^+ \longrightarrow \text{Mn}^{(II)} + \text{H}_2\text{O} + 0$$

3.2.5. The AG content

The grafting dependence on AG content is shown in (Fig. 5). Other variables kept constant. It was found that the values of WC% and GP % increase by increasing AG content until reach a maximum grafting condition at AG content 100g/l then decrease by increasing in AG content. Whereas GE % gradually increases thereafter levels off by increasing AG content.
Fig. 4. Effect of KMnO$_4$ content on the photo-induced grafting of AG onto AN in presence of KMnO$_4$/HNO$_3$ as initiator in aqueous medium: AG 83.33, KMnO$_4$ 0.0327 mole/l, AN 6.36 mole/l and time 120 min.

Moreover, the HP % markedly decreases by AG increase. The observed rising in grafting parameters is attributed to the availability of more radicals sites for initiation the graft copolymerization. However, further increase in AG content caused an increase in viscosity of the medium and this in turn restrict the movements of macro-radicals, thereby lead to decrease in the WC % and GP% values. This finding may also be attributed to deactivation of the macro-radicals growing chains (e.g., by transfer reactions, combination, and/or interaction with the primary radicals) shortly after their formation (19-21).

4. Evidence of Grafting

4.1. IR Spectroscopy

IR spectra of AG and PAN-g-AG copolymer show in (Fig. 6). The AG spectrum showed a broad peak at 3405 cm$^{-1}$ due to stretching vibration of OH and a moderate peak at 2924 cm$^{-1}$ attributed to C-H stretching vibrations. Furthermore, a large broad peak at 1074 cm$^{-1}$ assigned to stretching vibrations of C-O-C bond (Fig.6a). The occurrence of grafting is confirmed by the existence of an intense sharp at 2244 cm$^{-1}$ that is attributed to CN stretching absorption (Fig.6b).
Fig. 5. The Effect of AN content on the photo-induced grafting of AG onto AN in presence of KMnO₄/HNO₃ as initiator in aqueous medium: KMnO₄ 0.0327 mole/l, HNO₃ 0.18 N and time 120 min.

Fig. 6. FT-IR spectra of (a) AG, (b) PAN-g-AG (GP 192%)
4.2. Thermal Analysis Using TGA and DTA

The data of TGA found in (Table 2) shows that the initial decomposition temperature (IDT) and final decomposition temperature (FDT) of AG are 224.77°C and 446.31°C respectively (Fig. 7). Whereas in case of PAN-g-AG copolymer (GP 128%), its IDT and FDT decomposition temperature was 289.81°C and 651.38°C respectively (Fig. 8). It is confirmed from the data in (Table 2) that grafting of AN onto AG increases their IDT and FDT decomposition temperatures and this lead to increase its thermal stability. Moreover, in case of AG thermogram (Fig. 7) which showed that the decomposition of AG occurs in three stages as was reported (23). So the first stage appeared (~ 8%) weight loss up to 132°C due to the loss of adhered and bound water, then there was a second sharp weight loss (~ 52%) which was extended to 366°C and was followed by a broad weight loss (~ 23.6%) up to 582.6°C due to the loss of the polysaccharide (24).

**Table 2. TGA data of different polymers**

<table>
<thead>
<tr>
<th>Sample</th>
<th>GP%</th>
<th>IDT*</th>
<th>FDT**</th>
</tr>
</thead>
<tbody>
<tr>
<td>AG</td>
<td>---</td>
<td>224.77°C</td>
<td>446.31°C</td>
</tr>
<tr>
<td>PAN</td>
<td>---</td>
<td>286.70°C</td>
<td>611.66°C</td>
</tr>
<tr>
<td>PAN-g-AG</td>
<td>128%</td>
<td>289.81°C</td>
<td>651.83°C</td>
</tr>
</tbody>
</table>

*: IDT: Initial decomposition temperature.
**: FDT: Final decomposition temperature.

![Fig. 7. TGA/DTA curve of AG](image-url)
Generally, the main decomposition of the polysaccharides starts above 200°C (23). On the other hand, the weight loss in PAN-g-AG copolymer occurred in three major stages as was found before in AG but at higher IDTs and FDTs (Table 3). In case of PAN-g-AG (GP 128%), its first weight loss (13.4%) was between 289.81°C and 346.82°C, the second was broad weight loss (12.63%) between 346.98°C and 481.34°C due to the loss of gum (23), whereas the third very broad weight loss (28.47%) was between 651.83°C and 796.27°C was due to the loss of graft chains in the copolymer (24).

DTA thermogram of AG showed two exothermic peaks; the first was small at 343.37°C (9 µV) and the second was sharp at 472.75°C (42 µV) as were shown in (Table 3 and Fig. 8). However, in case of PAN-g-AG copolymer, its DTA thermogram showed three exothermic peaks at 302.18°C (13 µV), 450.79°C (10 µV) and 670.9°C (16.2 µV). This find presented in the thermogram of PAN-g-AG, which showed three clear exothermic peaks was found in difference when compared with the thermogram of AG and PAN that both have two exothermic peaks at different temperatures (Table 3). So, the previous results also confirm the grafting reaction.

4.3. X-RAY Diffractometry
X-ray diffractograms of PAN, AG and PAN-g-AG are shown in (Fig. 9). In the case of PAN (spectrum a), the crystalline peaks appear in $\theta = 16.6^\circ$ and $29.2^\circ$ (25). AG showed an amorphous nature (26) with two broad haloes at maximum $\theta = 18.47^\circ$ and $7.92^\circ$ (spectrum b). Graft copolymerisation of AN onto AG lead to considerable shift of $\theta$ from $18.47^\circ$ to $17.1^\circ$ with a high intense crystalline peak, more ordering also arisen for shifted $\theta$ from $7.92^\circ$ to $8.68^\circ$ and the new small peak appears at $29.15^\circ$ (spectrum c). It is worth mentioning that graft copolymerisation exhibits (53%) relative crystallinity (27). This finding led to conclusion that grafting of AN made observable ordering in the original amorphous structure of AG.

Fig. 9. XRD patterns of (a) PAN, (b) AG, and (c) AG-g-PAN (268%).

4.4. Scanning Electron Microscopy

Morphological surface examination of AG and grafted copolymer was carried out at the same conditions. From (Fig. 10a), AG has scattered and varied particle sizes with slightly bores on some surfaces and this clearly different from that of the parent graft copolymer, which has irregular larger particles and this indicate that graft of AN make polysaccharide particles join with each other (Fig10b). Comparison of these figures also supports the grafting of AN onto the AG.
5. Conclusion

In the present study, AN was successfully grafted onto AG in air using redox system (KMnO₄-HNO₃) induced by visible-light irradiation. This method provides an easy procedure to incorporate a high percentage of grafting (268%) with only homopolymer content (7.4%). Grafting was confirmed by IR, scanning electron microscopy, x-ray diffraction and thermal analysis techniques. Results indicated that grafting of AN success to improve characteristics of AG involve increasing its thermal stability and crystallinity.

References


