Conversion of Polyacrylonitrile to Poly amidoxime and Substitution with Maleic Anhydride, Itaconic Acid, Methyl Nadic Anhydride and Acetylchlorid

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ABSTRACT

The aim of this research is to modified and graft poly acrylonitrile to poly amidoxime [A] for dental fillers, because some of the prepared graft copolymers can be molded to a solid, such as maleicanhydride, itaconic acid, methyl nadic anhydride, acetylchlorid. New properties of the substrate of useful derivatives as material were formed through chemical reactions. Due to their structural diversity and stability, onto backbone of polymers. The prepared polymers were characterized by Fourier Transforms Infra-Red (FTIR) spectroscopy and thermal analysis were considered. It was found the prepared graft copolymers can be changed to a white solid, to be suitable for dental fillers, which gave high thermal resistance with more stabilities, the degree of swelling was convenience for dental applications.

Keyword: Polyacrylonitrile, Poly amidoxime, Substitution with maleic anhydride, Itaconic acid, Methyl nadic anhydride

INTRODUCTION

Copolymerization is used to change the some properties of known manufactured polymers to get specific requires, and to reduce crystallinity, modify glass transition temperature or to enhance the mechanical or physical properties [1,2]. Graft copolymerization is a technique for modifying the chemical and physical properties of natural and synthetic copolymers such as alternating, periodic and block copolymers which generally linear chains. Some applications of graft copolymers include [3-5], membranes for the separation of gases or liquids compatibilizers for polymer blends [6-8], Impact resistant plastics, thermoplastic elastomers, hydrogels drug carriers polymer [9,10].

Polyacrylonitrile (PAN) nanofibers [11-13] were prepared by electro spinning and they were modified with hydroxylamine to synthesize Amidoxime Polyacrylonitrile (AOPAN) chelating nanofibers, which were applied to absorb copper and iron ions. The conversion of the nitrile group in PAN was calculated by the gravimetric method. The structure and surface morphology of the AOPAN nanofiber were characterized [14,15]. Copolymerization is used to modify the some properties of known manufactured polymers to get specific requires, to reduce crystallinity, modify glass transition temperature or to improve solubility and to enhance the mechanical or physical properties [16], graft copolymerization is a technique for modifying the chemical and physical properties of natural [13] and synthetic copolymers [17] such as alternating, periodic, and block copolymers which generally linear chains. Some applications of graft copolymers include membranes for the separation of gases or liquids compatibilizers for polymer blends. Impact resistant plastics [18,19].Thermoplastic elastomers, Hydrogels, Drug carrier polymers. The uranium concentration in seawater is 3 μg/l with an estimated 5 × 10^8 tons of uranium in the oceans, in solution as the tricarbonato complex. Any extraction process will encounter the problems attendant on this high dilution, the only possible techniques currently being ion exchange on chelating resins [20,21] or sorption onto inorganic materials [22-24]. Poly(amidoxime)/poly(hydroxamic acid) chelating resin has been produced with high uranium sorption from neutral solutions containing the metal as the tricarbonato complex, and the results of a study of the behavior of this resin towards seawater are given. High chemical and biochemical stability and fast sorption which can sorb 68 per cent of the uranium present using a 24 s resin to seawater contact time [25-29]. The main objective of the research is to synthesis and study of copolymers as fillers of dental or other uses by some synthetic and natural polymers.

MATERIALS AND METHODS

Polyacrylonitrile, maleicanhydride, itaconic acid, methylnadicanhydride were used from Fluka, and Hydroxyl ammonium chloride were purchased from BDH. Fourier Transform Infrared (FTIR) spectra were recorded by testing Shimadzu FTIR 8000 series spectrophotometer; Al- Thermal analyses were performed using Differential Scanning Calorimeter (DSC) and Thermogravimetry (TGA). Softening points were determined using Thermal Microscope (Kofler-method), and Reichert thermovar. SP.100/25, 160. The degree of swelling was calculated for each sample after 24 h, using the following Equation 1.
Where, \(m_0\) is the weight of a dry polymer at \(t=0\), \(m_t\) is the swallowed polymer after 24 h.

Conversion of PAN with hydroxyl ammonium chloride to (poly amidoxime) \((A_1)\)

10 g of PAN dissolved in 20 ml of THF was placed into the flask and hydroxyl ammonium chloride solution was added to the flask, the reaction was carried out at 70°C for 2 h, shaking gradually, the product was separated from the solution by filtration and washed several times with deionized water until no further \(\text{NH}_2\text{OH}\) remained in the solution. It gave polyamidoxime \(A_1\).

Substitution \((A_1)\) with maleicanhydride, itaconic acid, methyl nadic anhydride, acetylchloride \((A_2-A_5)\)

1 g polyamidoxime \((A_1)\) dissolved in (5 ml) of acetone and few drops DMF. 1 g maleic anhydride dissolved in (5 ml) acetone, or itaconic acid or, methyl nadic anhydride or acetylchloride. The mixture was heated at 50°C using water bath for 1 h. The solvent was evaporated under vacuum; the product was washed three times with ether, dried in a vacuum oven at 50°C (Table 1).

Table 1: Physical properties of prepared polymers \((A_2-A_5)\)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Monomer M</th>
<th>Copolymer</th>
<th>Conversion (%)</th>
<th>(\mu) in dl/g</th>
<th>Color</th>
<th>S.P. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2</td>
<td><img src="image" alt="Cyclopentadiene" /></td>
<td><img src="image" alt="Cyclopentadiene" /></td>
<td>76</td>
<td>0.68</td>
<td>Brown</td>
<td>Viscous</td>
</tr>
<tr>
<td>A3</td>
<td><img src="image" alt="Maleic Anhydride" /></td>
<td><img src="image" alt="Maleic Anhydride" /></td>
<td>80</td>
<td>0.64</td>
<td>Brown</td>
<td>=</td>
</tr>
<tr>
<td>A4</td>
<td><img src="image" alt="Itaconic Acid" /></td>
<td><img src="image" alt="Itaconic Acid" /></td>
<td>77</td>
<td>0.55</td>
<td>Black</td>
<td>=</td>
</tr>
<tr>
<td>A5</td>
<td><img src="image" alt="Methyl Nadic Anhydride" /></td>
<td><img src="image" alt="Methyl Nadic Anhydride" /></td>
<td>70</td>
<td>0.59</td>
<td>Black</td>
<td>=</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Conversion of polyacrylonitrile with hydroxyl ammonium chloride to (polyamidoxime) \([A_1]\) and substitution \([A_1]\) with maleicanhydride, itaconic acid, methyl nadic anhydride, acetylchloride \([A_2-A_5]\) (Table 2 and Schemes 1-5). The amidoxime were obtained by treatment of nitrile groups with hydroxylamine at 70°C, giving rise to a selective functional group. The poly(amidoxime) was synthesized by conversion of the nitrile groups of PAN copolymers into amidoxime groups by a reaction with hydroxylamine. Four new polymers were prepared by substitution of \([A_1]\) with different compounds, as shown below:
Scheme 1: Reaction polyacrylonitrile with hydroxyl ammonium chloride \([A_1]\)

\[
\text{[H}_2\text{C-CONitrile]} + \text{NH}_2\text{OH.HCl} \xrightarrow{70^\circ C} \text{[H}_2\text{C-C-Nitrile with OH]} \]

Scheme 2: Substitution \([A_1]\) with maleic anhydride \([A_2]\)

\[
\text{[H}_2\text{C-CONitrile]} + \text{Maleic anhydride} \xrightarrow{\Delta} \text{[H}_2\text{C-C-Nitrile with Maleic anhydride]} \]

Scheme 3: Substitution of \([A_1]\) with itaconic acid \([A_3]\)

\[
\text{[H}_2\text{C-CONitrile]} + \text{Itaconic acid} \xrightarrow{\Delta} \text{[H}_2\text{C-C-Nitrile with Itaconic acid]} \]

Scheme 4: Substitution of \([A_1]\) with methyl nadic anhydride \([A_4]\)

\[
\text{[H}_2\text{C-CONitrile]} + \text{Methyl nadic anhydride} \xrightarrow{\Delta} \text{[H}_2\text{C-C-Nitrile with Methyl nadic anhydride]} \]

Scheme 5: Substitution of \([A_1]\) with acetylchloride \([A_5]\)

\[
\text{[H}_2\text{C-CONitrile]} + \text{Acetylchloride} \xrightarrow{\Delta} \text{[H}_2\text{C-C-Nitrile with Acetylchloride]} \]
Polyamidoxime

The structures of polymers [A₁-A₅] were confirmed by FTIR (Figures 1-5).

Figure 1: FTIR spectrum of polymer A₁ showed absorption peaks at 2970 cm⁻¹ of \( \nu(\text{CH}_2) \) aliph. 3105 cm⁻¹ of (N-H), \( \nu(\text{OH}) \) 3400-3500 cm⁻¹ stretch and 1666 cm⁻¹ (strong), \( \nu(\text{C}=\text{N}) \) of (polyamidoxime).

Figure 2: FTIR spectrum of polymer A₂, absorptions appeared at 1728, 1670 cm⁻¹ (C=O) (strong) of maleamic acid, 1070 cm⁻¹ (C-O) stretch and 1354 cm⁻¹ of (C-N), 1728, 1670 (C=O) (strong) maleamic acid.
Figure 3: FTIR spectrum of polymer A showed absorption peaks at (1166) cm\(^{-1}\) (C-O) stretch of itaconic acid, 1398 cm\(^{-1}\) (C-N), (3450, 2900) (OH), 1705 (C=O) itaconic acid.

Figure 4: FTIR spectrum of polymer A showed absorption peaks at 1384 cm\(^{-1}\) (C-N), 1761, 1680 (C=O) methyl nadamic acid.
Figure 5: FTIR spectrum of polymer A3 showed absorption peaks at 1383 cm\(^{-1}\) (C-N), 1670 (C=O) ester.

Table 2: FTIR Spectral data for compounds [A1-A5]

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>(\nu(\text{N-O})) (cm(^{-1})) (Polyamidoxime)</th>
<th>(\nu(\text{OH})) (cm(^{-1})) stretch (Polyamidoxime)</th>
<th>(\nu(\text{C=O})) (cm(^{-1})) (Polyamidoxime)</th>
<th>(\nu) other (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>974</td>
<td>3400-3500</td>
<td>1666 (strong)</td>
<td>1728, 1670 (C=O) (strong) maleamic acid</td>
</tr>
<tr>
<td>A2</td>
<td>962</td>
<td>3408</td>
<td>1622</td>
<td>(3450, 2900) (OH), 1705 (C=O)itaconic acid</td>
</tr>
<tr>
<td>A3</td>
<td>966</td>
<td>3380</td>
<td>1635</td>
<td>1761, 1680 (C=O) methyl nadamic acid</td>
</tr>
<tr>
<td>A4</td>
<td>950</td>
<td>3380</td>
<td>1700</td>
<td></td>
</tr>
<tr>
<td>A5</td>
<td>962</td>
<td>3600</td>
<td>1672</td>
<td>1670 (C=O) ester</td>
</tr>
</tbody>
</table>

The thermal stability study

The thermal stability of some selective prepared co polymers were investigated technique is based on measuring the weight loss as a function of time at constant temperature or as a function of temperature at constant rate of heating by measuring the sample weight, and the change at a programmed rate of heating. The change in weight was measured as a function of temperature which gave valuable information about the thermal stability of the prepared polymers such as (A3-A4) was taken 10-20 mg from the prepared polymers use Helium as inert gas in rat 20 ml/min). The thermo-grams were recorded and analyzed, as shown in Tables 3-8 which indicated the high thermal resistance and showed the steps of weight loss-temperature. This high thermal resistance indicated the high interaction between hydrogen bonding of polar groups through the co polymer chains.

Table 3: DSC of polymer (A3) first stage

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset point</th>
<th>Offset point</th>
<th>Point of reaction</th>
<th>Peak maximum</th>
<th>Enthalpy</th>
</tr>
</thead>
<tbody>
<tr>
<td>A3</td>
<td>163.4°C (13 min)</td>
<td>212.9°C (18 min)</td>
<td>-19.937 mw at 164.2°C (13 min)</td>
<td>-26.019 mw at 196.9°C (16 min)</td>
<td>-31.93 J/g</td>
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</table>

Table 4: DSC of polymer (A3) second stage

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset point</th>
<th>Offset point</th>
<th>Point of reaction</th>
<th>Peak maximum</th>
<th>Enthalpy</th>
</tr>
</thead>
<tbody>
<tr>
<td>A3</td>
<td>276.4°C (25 min)</td>
<td>310.0°C (28 min)</td>
<td>-31.049 mw at 295.7°C (27 min)</td>
<td>-32.565 mw at 300.5°C (27 min)</td>
<td>-78.06 J/g</td>
</tr>
</tbody>
</table>

Table 5: DSC of polymer (A3) third stage

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset point</th>
<th>Offset point</th>
<th>Point of reaction</th>
<th>Peak maximum</th>
<th>Enthalpy</th>
</tr>
</thead>
<tbody>
<tr>
<td>A3</td>
<td>312.0°C (28 min)</td>
<td>330.7°C (30 min)</td>
<td>-26.475 mw at 313.6°C (29 min)</td>
<td>-31.801 mw at 321.0°C (29 min)</td>
<td>-46.25 J/g</td>
</tr>
</tbody>
</table>
CONCLUSION

It was concluded that the prepared graft copolymers can be molded and then changed to a white solid, to be convenience for dental, with a suitable cost, beneficial thermal safety, extended life of useful as dental fillers, because the preparing conditions which gave high thermal resistance with more stabilities. The degree of swelling was calculated for each sample after 24 h=zero, was convenience for dental uses. The best one was A3 as a dental filler.

REFERENCES