تأثير التعرض لأشعة جاما على الخصائص الذاتية لبوليمير خلات السليولوز

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الملخص:

الإشعاع المؤين للبوليمرات هي تقنية واعدة وقد وجدت لها تطبيقات في مختلف المجالات مثل حفظ الأغذية، ونتجت لمواجهة المتغيرات في مختلف المجالات مثل حفظ الأغذية، وإنتاج الأدوية والصناعات وغيرها. تمتلك تكنولوجيا التشعيع العديد من المزايا مثل التحكم في درجة التحلل، تكوين توزيع بوزن جزيئي متجانس، توفير المواد الكيميائية وأعمال صناعية للبيئة. وقد أجريت هذه الدراسة لتقييم تأثير التشعيع جاما على الخصائص الفيزيائية والتركيبية لبوليمر خلات السليولوز. تم تكوين أقراص صلبة من خلات السليولوز وتعريضها إلى مصدر الكوبالت 06 لفترات زمنية مختلفة. كما تم تحضير محلال مخففة من البوليمر ودراسة معاملات الإنكسار واللزوجة لكل منها. أظهرت النتائج بأن تعرض خلات السليولوز لأشعة جاما يؤدي إلى انخفاض في قيم كل من الكتلة المولية، الحجم الهيدرودينيميكي، الأبعاد الحقيقية والنمطية والنسب المشروطة لخلاصة السليولوز. وعلى عكس ذلك فإن تشعيع جاما يزيد من قيم ثابت شولتز بلاشكة، التركيز الحرج والتفاعل بين كل من المذاب والمذيب. ومع ذلك، فقد أدى تعرض بوليمرات خلات السليولوز لأشعة جاما في المحاليل المخففة إلى انخفاض قيم معامل الإنكسار، ثابت العزل الكهربائي، متغيرات الدوائيات وكثافة طاقة التماسك.

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The influence of gamma irradiation on the intrinsic properties of cellulose acetate polymers

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Abstract Ionizing radiation of polymers is a promising technique that has found applications in various fields such as food preservation, pharmaceutical production and natural bioactive agent industries. Irradiation technology has several advantages like controlling the degree of degradation, producing uniform molecular weight distribution, saving chemicals and environmentally friendly process. This study was carried out to evaluate the effect of γ-irradiation on the physical and structural properties of cellulose acetate (CA) polymer. Solid disks of CA were exposed to a cobalt-60 source (50 kGy) for different periods of time. Dilute solutions of irradiated and non-irradiated CA were prepared and studied viscometrically and refractometrically. γ-irradiation of CA causes a decrease in the values of relative, specific, reduced and intrinsic viscosities. In addition, there is a reduction in the values of molar mass, hydrodynamic volume, real and ideal chain dimensions and the characteristic ratio of CA. On the contrary, γ-irradiation increased the values of Schulz–Blaschke constant, critical concentration and solute–solvent interaction. However, the values of refractive index, dielectric constant, solubility parameters and cohesive energy density of the polymer in dilute solutions are decreased due to the effect of γ-irradiation.

1. Introduction

Polymers have replaced conventional materials in packaging applications due to their functionality, lightweight, ease of processing, and low cost (Risch, 2009). Thus, research in polymer science is developing to producing a plethora of new elastomers, plastics, adhesives, coatings, and fibers. It has been reported that (Byun et al., 2008) polymers can be degraded by acidic hydrolysis or enzymatic treatment. Although these methods are effective in decreasing the molecular weight, they do have certain disadvantages such as high cost, low yield, long processing time, and acidic wastes from the chemical or enzymatic treatment. Another method used for polymer degradation is irradiation using negative or neutral rays. Irradiation in polymers destroys the initial structure by way of cross linking, free radical formation, irreversible bond cleavages, etc., resulting in the fragmentation of molecules and formation of saturated and unsaturated groups. All these processes introduce defects inside the material that are responsible for change in the physical and chemical properties of the material (Sharma et al., 2007; Alwan, 2012). γ-irradiation is used for the final biological sterilization (Hugo, 1995) of materials that can be subsequently used for
The influence of gamma irradiation on the intrinsic properties of cellulose acetate polymers

2. Experimental

2.1. CA discolor preparation

The powder material of cellulose acetate (CA) has been supplied by a local Libyan company (JOWF) and used without further purification. The samples were ground with a mortar and pestle. The powder samples were spread onto one face of a home-made stainless steel die, in which the die is a Perkin–Elmer product. The powder was placed between two mica sheets to avoid samples sticking to the die, and pressed by a manually operated Perkin–Elmer hydraulic press. After placing the second mica sheet on the top of the powder, the plunger was carefully inserted, and the die cylinder was rotated to remove the air present. The sample was then pressed under a pressure in the range of 3–5 ton/in² for 5 min to produce CA solid disks (0.5 cm thickness and 2.5 cm diameter).

2.2. Solutions preparation

Acetone was used as a solvent for the native and irradiated CA-disks. The solvent was then, also, used to make different concentrations by diluting the native and γ-irradiation mother solutions. The native and γ-irradiation solutions were labeled M₀ and M₁, M₂ and M₃, respectively.

2.3. γ-Irradiation

Irradiated in air at room temperature by a Canadian ⁶⁰Co γ-source (Theratron 780; Theratronics Ltd.) located in the Radiodiagnosis and Radiotherapy Center at Benghazi city. Each CA discolor was exposed to the radiation at a constant dose rate of 50 rad/min for different periods of time. Monitoring the change in each sample was made immediately after irradiation, and at intervals afterward for each sample, by using the solution viscometric technique.

2.4. Measurements

2.4.1. Viscosity measurements

In determining the efflux time of the solutions, methodology stated by ASTM (1989) was used. The efflux time for solvent (tacetone) and cellulose acetate solution (tCA) were measured by glass capillary viscometer made by Brand at W-Germany (Kulicke, 2004). The accuracy of the viscosity measurements was ±0.015.

The measured values have been expressed in terms of relative, η₀s, specific, ηₛ, and reduced, ηₑ, viscosities of dilute cellulose acetate in acetone as follows:

\[ \frac{t_{CA}}{t_{acetone}} = \eta_0 \] (1)
\[ \eta_s = \eta_0 - 1 \] (2)
\[ \eta_r = \frac{\eta_s}{C} \] (3)

where C is the mass concentration of CA in acetone.

2.4.2. Refractive index measurement

Refractive indexes of solutions have been measured by refractometer (Bausch and Lamp, New York) with a precision of 0.01%. The technique is described in detail elsewhere (Kratochvil, 1987). The Measurements have been thermostated to ±0.1 °C; at 25 °C.

3. Results and discussion

3.1. Weight parameters and their kinetic behavior

Fig. 1 shows plot of native (M₀) and irradiative (M₁–M₃) relative viscosity values against mass concentration (Cᵢ). This figure demonstrates that viscosity increases monotonically with the increase of concentration of the CA solution. Furthermore, consideration of the plots indicates that the rate of increment in the viscosity values after γ-irradiation is less than those before irradiation. This could be attributed to the reduction in the polymer chains (O’Donnell, 1991).

Thus it is clear that γ-irradiation produces significant changes in the viscosity of the CA solution and as the absorbed dose increases, the CA solution shows a significant decrease of viscosity. The decrease in the viscosity occurs by the radiolysis of CA. This result is consistent with other studies on starch, agar, alginate, and carrageenan (Aliste et al., 2000; Graham et al., 2002).

The linear plots of Fig. 2 show agree with Schulz–Blaschke equation for native (M₀) and γ-irradiated (M₁–M₃) samples (Schoff, 1999).
where \( \eta_{\text{red}} \) is reduced viscosity, \( [\eta] \) intrinsic viscosity, \( k_{sb} \), Schulz–Blaschke constant and \( \eta_{sp} \), specific viscosity.

However, \( [\eta] \) and \( k_{sb} \) before and after \( \gamma \)-degradable CA were estimated from the typical linear plot of Schulz–Blaschke.

The values of relative average viscosity molar mass \( <M_v> \) in Tables 1–3 were calculated according to the following form of Mark–Houwink equation (Johnston and Sourirajan, 1973).

\[
[\eta] = 4.46 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1} <M_v>^{0.731}
\]

Reduction in the values of intrinsic viscosity and average relative molar mass could be attributed to the marked scission effect on the polymer chain (Reichmanis et al., 1993).

Thus for the CA in acetone solution, the solute–solute contact is greater than that for degradable one and consequently, for irradiated CA, the solute–solvent interaction is greater than that of the non-irradiated one (Kurata and Tsunashima, 1999; Fujita, 1997).

The linearity increases in the Logarithm of relative average viscosity molar mass vs. Logarithm of intrinsic viscosity of CA in acetone solution in the plot of Fig. 3 verifying Mark–Houwink equation.

Fig. 4 shows plot of Schulz–Blaschke constant \( k_{sb} \) values against exposure time, it reflects how far the values of Schulz–Blaschke constant of the polymer increase with increasing the exposure time. This could be attributed to scission on the polymer chains.

### 3.2. Size parameters and their kinetic behavior

The values of hydrodynamic volume \( (V_h) \), average number of bonds \( (n) \), root-mean-square end-to-end distance \( <r^2>^{1/2} \), and

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**Table 1** Mark–Houwink parameters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>t_exposure/min</th>
<th>[\eta]/cm(^3)g(^{-1})</th>
<th>&lt;M(_v)&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(_0)</td>
<td>0.00</td>
<td>1656.6</td>
<td>1784583.73</td>
</tr>
<tr>
<td>M(_1)</td>
<td>30.00</td>
<td>1232.2</td>
<td>1190420.7</td>
</tr>
<tr>
<td>M(_2)</td>
<td>60.00</td>
<td>857.2</td>
<td>724613.973</td>
</tr>
<tr>
<td>M(_3)</td>
<td>90.00</td>
<td>622.3</td>
<td>467566.682</td>
</tr>
</tbody>
</table>

**Table 2** The average number of bonds for CA in acetone at 25 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(_0)</td>
<td>6890.30</td>
</tr>
<tr>
<td>M(_1)</td>
<td>4596.22</td>
</tr>
<tr>
<td>M(_2)</td>
<td>2797.74</td>
</tr>
<tr>
<td>M(_3)</td>
<td>1805.30</td>
</tr>
</tbody>
</table>

**Table 3** The characteristic ratio for CA in acetone at 25 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C(_\infty)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(_0)</td>
<td>195.57</td>
</tr>
<tr>
<td>M(_1)</td>
<td>160.96</td>
</tr>
<tr>
<td>M(_2)</td>
<td>157.74</td>
</tr>
<tr>
<td>M(_3)</td>
<td>152.37</td>
</tr>
</tbody>
</table>

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**Figure 1** Relative viscosity vs. concentration for native and different degradable CA in acetone solution at 25 °C.

**Figure 2** Reduced viscosity vs. specific viscosity for native and different degradable CA in acetone at 25 °C.

**Figure 3** Mark–Houwink plot for CA in acetone at 25 °C.

**Figure 4** Schulz–Blaschke constant \( k_{sb} \) values against exposure time.
root-mean-square radius of gyration \(< S^2 >^{1/2}\) of CA in acetone were calculated according to the following mathematical expression, respectively (Debye, 1946; Flory, 1949):

\[ V_h = \frac{(2/5) \eta}{M_v > / N_A} \]  
\[ n = 2 < M_v > / M_w \]  
\[ [\eta] = \Phi < r^2 >^{3/2} / < M_v > \]  
\[ < S^2 >^{1/2} = < r^2 >^{1/2} / (6)^{1/2} \]

where \(M_w\) is the molar mass of CA repeating unit, and Flory viscosity constant, \(\Phi\), is defined as (Kurata and Tsunashima, 1999):

\(\Phi = 2.1 \times 10^{-23} \text{ mol}^{-1}\) before irradiation and \(\Phi = 2.7 \times 10^{23} \text{ mol}^{-1}\) after irradiation.

Indeed, the study of the relation of real root-mean-square radius of gyration vs. \(\gamma\)-exposure time for CA, in acetone at 25 °C, demonstrates the reduction in root-mean-square radius of gyration with increasing \(\gamma\)-time. This is in accordance with the previously discussed results on this work.

Fig. 5 represents the linear plot of Stockmayer–Fixman equation (Van Krevelen, 1997):

\[ [\eta] / < M_v >^{1/2} = K_o + B < M_v >^{1/2} \]

in which the intercept \((K_o = 0.5433 \text{ cm}^3 \text{ g}^{-1})\) is the ideal Mark-Houwink constant and the slope \((B = 0.5 A_2 = 5 \text{ cm}^3 \text{ kg}^{-1})\) is the interaction parameter, while \(A_2\) is the second virial coefficient.

Therefore, the values of hydrodynamic expansion factor, \(x_o\), ideal intrinsic viscosity \([\eta]_o\), ideal root-mean-square end-to-end distance \(< r^2 >^{1/2}\), and ideal root-mean-square radius of gyration \(< S^2 >_o^{1/2}\) of CA in acetone were calculated according to the following expression (Kulicke, 2004), the subscript zero is used to indicate unperturbed dimensions.

\[ a^h_o = \frac{1 + B < M_v >^{1/2}}{K_o} \]  
\[ a^\eta_o = \frac{[\eta]}{[\eta]_o} \]  
\[ < r^2 >^{1/2} = a_o < r^2 >_o^{1/2} \]  
\[ < S^2 >_o^{1/2} = \frac{< r^2 >_o^{1/2}}{(6)^{1/2}} \]

The relation between hydrodynamic expansion factor and \(\gamma\)-exposure time for CA, in acetone at 25 °C, demonstrates the reduction in the hydrodynamic expansion factor with increasing \(\gamma\)-irradiation time, due to the marked scission on polymer chains (O’Donnell, 1991). This is in accordance with the average number of bond, \(n\), characteristic ratio, \(C_e\), calculated from the following expression (Kulicke, 2004).

\[ C_e = \frac{< r^2 >}{\eta^2} \]  
\(l\) is the bond length = 1.43 \(\times 10^{-8}\) cm.

Table 3 illustrated the decrease in the characteristic ratio by increasing \(\gamma\)-irradiation due to the decrease in the short-range interactions.

3.3. Cohesion parameters and their kinetic behavior

Refractive index, dielectric constant, solubility and cohesive energy density parameters are related with each other as follows (Sun, 1994):

\[ \varepsilon_r = n^2 \]  
\[ \delta = (30.3) \frac{(\varepsilon_r - 1)}{(\varepsilon_r + 2)} \]  
\[ \delta = (C.E.D.)^{1/2} \]

where, \(n_r, \varepsilon_r\), is the refractive index, dielectric constant, \(\delta\), is the solubility parameter, \(C.E.D.,\) is cohesive energy density of native and irradiated CA in acetone.

Fig. 6 shows linear increase in the values of cohesive energy density with increasing concentration at 25 °C. However, further consideration of the plots in Fig. 6 indicates that the \(\gamma\)-irradiation has a reduction effect on such values due to scission effect on the CA chain. This is in accordance with the values of viscosity parameters described above.

4. Conclusion

From the obtained data, one can notice that cellulose acetate undergoes random chain scission due to the effect of \(\gamma\)-irradiation. The periods of exposure time have considerable...
influence on the amount of scission and consequently on the intrinsic properties and their parameters. The intrinsic properties play a major role in the kinetics of cellulose acetate degradation.

References


