Modification of molecular and optical properties of cellulose triacetate by alpha particles irradiation

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Abstract: Samples from sheets of the polymeric material cellulose triacetate have been exposed to alpha particles in the dose range 20-100 Gy. The modifications induced in the molecular and optical properties of cellulose triacetate samples due to alpha particles irradiation have been studied through different characterization techniques such as intrinsic viscosity, refractive index and color difference studies. The results indicated that the crosslinking is achieved at the dose range 60-100 Gy. This cross linking led to an increase in the value of intrinsic viscosity, indicating an increase in the average molecular mass. This was associated with an increase in the refractive index. Additionally, the non irradiated cellulose triacetate samples showed significant color sensitivity towards Alpha particles irradiation. This sensitivity appeared in the change in the blue color component of the non irradiated cellulose triacetate film to yellow after exposure to alpha particles up to 100 Gy. This is accompanied by a net increase in the darkness of the samples.
[M.M. Abutalib. **Modification of molecular and optical properties of cellulose triacetate by alpha particles irradiation.** *Life Sci J* 2014;11(10):769-773] (ISSN: 1097-8135).http://www.lifesciencesite.com. 124

Keywords: Alpha particles; cellulose triacetate; viscosity, refractive index, color changes.

1. Introduction

The application of radiation in polymer technology is of great importance with a view to achieve some desired improvements in polymer properties [1]. It is obvious that the primary physical interaction of radiations with polymers produces specific damage known as chemical bond scission, free radicals and consecutive cross-linking [2]. Also, passage of heavy particles in these materials creates large scale lattice defects on radiations damage along the path of the particles. This induces formation and transport of reactive species that are able to permanently change the physical and chemical properties of these polymers [3]. The effectiveness of these changes produced in polymers depends on the structure of the polymer as well as the experimental conditions of irradiation. In other words, irradiation of polymers has established itself as one of the most acceptable approach to alter polymer properties significantly [4-7]. Irradiation in polymers destroys the initial structure by way of cross linking, free radical formation, irreversible bond cleavages etc. that results in the fragmentation of molecules and formation of saturated and unsaturated groups. All these processes introduce the so called defects inside the material that are responsible for change in the physical properties of the polymer [8-10]. On the other hand, cellulose triacetate CTA is one of the polymers that have been usefully employed in a number of different fields of science and technology. CTA is manufactured from cellulose and a source of acetate esters, typically acetic anhydride. CTA is typically used for the creation of fibres and film base. It is similar chemically to cellulose acetate, with the distinguishing characteristics being that, during the manufacture of CTA, the cellulose is completely acetylated whereas in regular cellulose acetate or cellulose diacetate, it is only partially acetylated. Thus CTA is significantly more heat resistant than cellulose acetate. Since radiation is known to be one of the major factors that change the structural properties of polymers, it would be worthwhile to study the modifications on molecular and optical properties due to irradiation. Several investigations have been introduced to study the changes in physical properties of polymers due to irradiation [11-15]. The present study deals with the investigation of the effect of alpha particles irradiation on the molecular and optical properties of cellulose triacetate aiming to modify its properties to suit different industrial applications.

2. Experimental

2.1 Samples

Cellulose triacetate polymer used in this study is 0.25 mm thick sheet manufactured by Eastman Kodak Company, Rochester, New York. Its chemical equation is $[C_6H_7O_2(OOCCH_3)_3]_n$.

2.2 Irradiation Facilities

The plastic samples were exposed to a collimated beam of α-particles with initial energy 5.44 MeV using ^{241}Am point source with activity $3.7x10^3$ Bq. The samples were in contact with the collimator.

2.3 Analysis of irradiated samples

2.3.1 Intrinsic viscosity

Solutions of different concentrations (0.2%, 0.4%, 0.6% and 0.8%) were prepared from the irradiated and

non irradiated samples using pure chloroform as a solvent. The viscosity measurements were carried out in Oswald viscometer of the type pinkevitch Size 0 No. 2106, manufactured by Poulten, self, and LEE, LTD, England. This viscometer was calibrated in accordance with the standard method of test for kinematic viscosity specified in ASTM D 445-IP 71. The viscosity measurements were carried out at four different temperatures (35°C, 40°C, 45°C and 50°C) using a bridge controlled thermostat bath E-270 Series III, Pownson, Oxford.

2.3.2 Optical properties

2.3.2.1 refractive index

The refractive index measurements were carried out using an Abbe refractometer (Type Reichert; mark II, Model-10480, New York). The accuracy of measuring the values of refractive indices, surface temperature of the prism and the wavelength of the light used were ± 0.0001, 19.4-21.5 °C and 5893 °A, respectively. Several values were measured to the same sample and the average value was considered.

2.3.3.2 Color difference measurements

The transmission measurements were carried out using a Shimadzu UV–Vis–Nir scanning spectrophotometer, type 3101 PC. This unit measures in the wavelength range from 200 to 3000 nm. The Commission International de E'Claire (CIE units *x*, *y* and *z*) methodology was used in this work for the description of colored samples.

Determination and calculation of the tristimulus values

The vision scientists created a special set of mathematical lights, X, Y and Z, to replace actual red, green and blue lights. The color matching functions for the X, Y and Z lights are all positive numbers and are labeled $\bar{x}$, $\bar{y}$ and $\bar{z}$. Every color can be matched using the appropriate amount of X, Y and Z light. The amount of X, Y and Z light needed to match a color are called the color's tristimulus values.

The CIE tristimulus values for a transmitting sample are calculated by adding the product of the spectral power distribution of illuminant, the transmittance factor of the sample and the color matching functions of the observer at each wavelength of the visible spectrum, as shown in the following equations:

$$X = k\sum P(\lambda)\bar{x}(\lambda)T(\lambda),$$

$$Y = k\sum P(\lambda)\bar{y}(\lambda)T(\lambda),$$

$$Z = k\sum P(\lambda)\bar{z}(\lambda)T(\lambda),$$

$$k = \frac{100}{\sum P(\lambda)\bar{y}(\lambda)}$$

Where $P(\lambda)$ is the value of the spectral power distribution of the illuminant at the wavelength λ. $T(\lambda)$ is the transmittance factor of the sample at the wavelength λ and $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ & $\bar{z}(\lambda)$ are the CIE color matching functions for the standard observer at the wavelength λ. The factor k normalizes the tristimulus value so that Y will have a value of 100 for a perfect white diffuser.

The 1976 CIE L* a* b*(CIELAB) color space

A weakness of the CIE X, Y and Z color space is its lack of visual uniformity. Creating a uniform color space would have two major advantages. It would allow plots showing the perceptually relative positions of two or more colors in color space, and it would facilitate the creation of a good color difference ruler between two samples.

The 1976 CIE L^* a^* b^* (CIELAB) color space is widely used in the paint, plastic and textile industries. L^* is correlated with perceived lightness in CIELAB color space. A perfect white would have an L^* of 100, and a perfect black would have an L^* of 0. The coordinates a^* and b^* have their history in the opponent color theory. It was proposed that three pairs of opposing color sensations produce all colors: red & green; yellow & blue; and black & white. The CIELAB coordinate a^* correlates with red ($+a^*$) and green ($-a^*$), while the coordinate b^* correlates with yellow ($+b^*$) and blue ($-b^*$). The CIELAB L^*, a^* and b^* coordinates are calculated from the tristimulus values according to the following equations

$$L* = 116 f(Y/Y_n) - 16,$$

$$a* = 500\left[f(X/X_n) - f(Y/Y_n)\right],$$

$$b* = 200\left[f(Y/Y_n) - f(Z/Z_n)\right].$$

In which X, Y and Z are the tristimulus values and the subscript *n* refers to the tristimulus values of the perfect diffuser for the given illuminant and standard observer; $f(X/X_n) = (X/X_n)^{1/3}$ for values of (X/X_n) greater than 0.008856 and $f(X/X_n) = 7.787(X/X_n) + 16/116$ for values of (X/X_n) equal to or less than 0.008856; and the same with Y and Z replacing X in turn. The CIELAB color difference, ΔE is given by [16]

$$\Delta E = [(L^*_1 - L^*_2) + (a^*_1 - a^*_2) + (b^*_1 - b^*_2)]^{1/2}$$

The subscripts 1 and 2 refer to the irradiated and non irradiated samples.

3. Results and discussion

3.1 Intrinsic Viscosity

Solutions of different concentrations (0.2, 0.4, 0.6 and 0.8 %) were prepared from the non irradiated and irradiated CTA samples using pure chloroform as a solvent. The time of flow (t) was measured five times for each individual solution and the average values were considered. The kinematic viscosity (η_k) of the liquid samples was calculated by the product of the observed time of flow and the capillary constant of the viscometer (C) ($\eta_k = t \times C$). The result is always expressed as relative viscosity (η_{rel}), calculated as the ratio of the viscosities of polymer solutions and the pure solvent. Values of specific viscosity ($\eta_{spc} = \eta_{rel} - 1$), reduced viscosity ($\eta_{red} = \eta_{spc}$ / concentration) and intrinsic viscosity, the limiting viscosity number ($\eta_{in} = \lim \eta_{red}$ when the concentration tends to zero), were calculated.

The intrinsic viscosity of the CTA solutions was measured at different temperatures (35, 40, 45 and 50 ^{o}C). Figure 1 shows the dependence of intrinsic viscosity on the alpha particles dose. The intrinsic viscosity shows a decrease until a minimum value around the 60 Gy irradiated sample, followed by an increase on increasing the dose up to 100 Gy. The dose range in which the intrinsic viscosity decreases can be explained by the formation of shorter molecules as a result of degradation which causes both a random breaking of bonds and the formation of stable molecules with a lower molecular weight [17]. While the increase in intrinsic viscosity in the dose ranges 60-100 Gy, indicates an increase in the molecular mass of the polymer due to crosslinking.

The effect of temperature on the intrinsic viscosity of CTA polymer was investigated (Figure 2). The results indicated that the intrinsic viscosity decreases with temperature. This can be attributed to the temperature that causes a simple thermal activation.

3.2 Refractive index

The refractive indices of solid sheets of CTA, were measured. Figure 3 illustrates the variation of the refractive index with alpha particles dose. The refractive index showed a decrease in magnitude until a minimum value at around 60 Gy followed by an increase on increasing the dose up to 100 Gy. This behavior can be explained in terms of degradation and cross-linking induced by alpha particles irradiation. Such behavior facilitates the formation of free radicals that are chemically active. This allows the formation of covalent bonds between different chains (crosslinking), and in turn minimizes the anisotropic character of the CTA polymer, leading to the increase in refractive index.

3.3 Color changes

The transmission spectra of the irradiated and non irradiated CTA samples, in the wavelength range 350-800 nm, have been investigated in Figure 4. Using these transmission data, both the tristimulus values and chromaticity coordinates were calculated. Figure 5 shows the variation of tristimulus values (X, Y, Z) with the dose. From the figure it is clear that X, Y and Z exhibited the same trend, where they decreased on increasing the dose up to 100 Gy. Figure 6 shows the variation of chromaticity coordinates (x, y, z) with the dose. From the figure it is clear that x and y exhibited the same trend, where they increased with increasing the dose up to 100 Gy. The chromaticity coordinate z exhibited the opposite trend with the dose.

The variation of color intercepts ($L^*$and b^*) with the alpha particles dose is shown in (Figure 7). The accuracy in measuring L^* is $\pm$ 0.05 and $\pm$ 0.01 for a^* and b^*. It can be seen that the color parameters L^* and b^* were significantly changed after exposure to alpha particles irradiation. The blue ($-b^*$) color component of the non irradiated film was changed to yellow ($+b^*$) after exposure to alpha particless up to 100 Gy. This is accompanied by a net increase in the darkness of the samples ($-L^*$). At the same time, the red ($+a^*$) color of the non irradiated sample was not affected by the alpha particles dose.

The color intensity ΔE (color difference between the non irradiated sample and those irradiated with different alpha particles doses) were calculated and are plotted in Figure 8 as a function of alpha particles dose. From the figure it is seen that ΔE increased with increasing the dose. This indicates that the CTA polymer has a response to color change by alpha particles irradiation. These changes in color can be attributed to the trapping of the excited free radicals that are formed by ionization. Also, the trapped free radicals resulting from radiation induced rupture of polymer molecules have electrons with unpaired spin; such species may also give optical coloration [17].

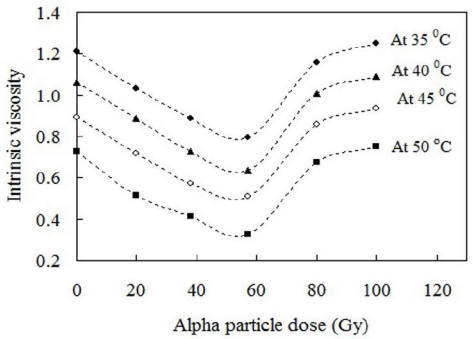

Figure 1 Variation of the intrinsic viscosity of cellulose triacetate samples with the alpha particles dose.

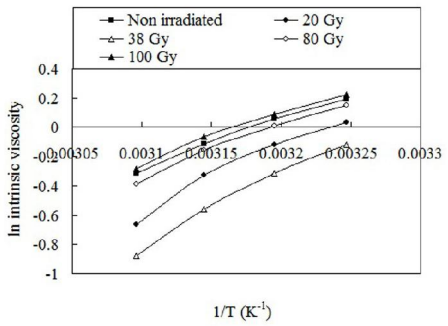

Figure 2 Variation of the intrinsic viscosity of the non irradiated and irradiated cellulose triacetate samples with temperature.

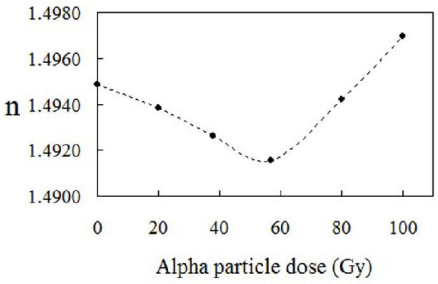

Figure 3 Variation of the refractive index of cellulose triacetate polymer with the alpha particles dose.

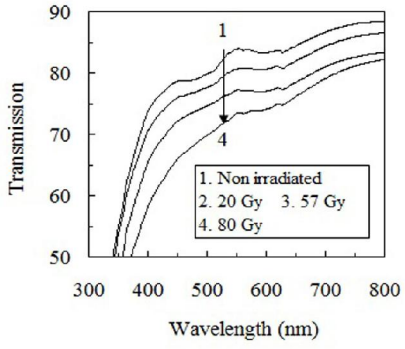

Figure 4 The transmission spectra, measured in the wavelength range 350-800 nm, for the non-irradiated and irradiated cellulose triacetate samples.

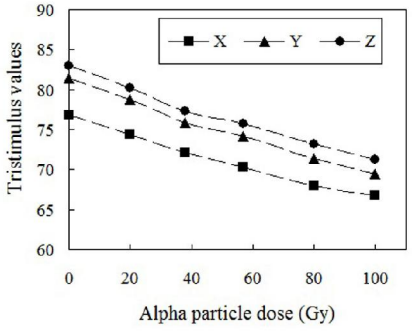

Figure 5 Variation of tristimulus values (X, Y, Z) of Cellulose triacetate polymer with the alpha particles dose.

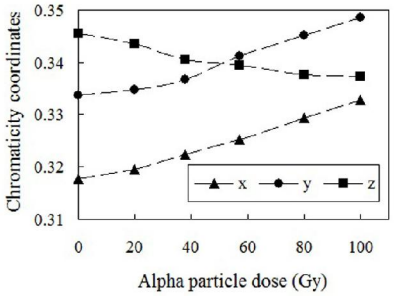

Figure 6 Variation of chromaticity coordinates (x, y, z) of cellulose triacetate polymer with the alpha particles dose.

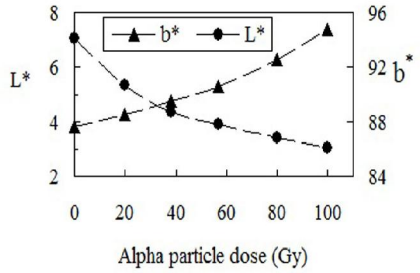

Figure 7 Variation of color intercepts L^* and b^* of cellulose triacetate polymer with the alpha particles dose**.**

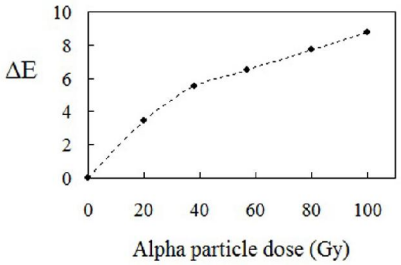

Figure 8 Variation of color intensity ΔE of cellulose triacetate polymer with the alpha particles dose**.**

Conclusion

From the study of the effect of alpha particles irradiation on the molecular and optical properties of cellulose triacetate polymer, one can draw the following conclusions.

The alpha particles irradiation in the dose range 60-100 Gy led to a more compact structure of cellulose triacetate polymer, which resulted in an increase in the average molecular mass and refractive index.

The non irradiated cellulose triacetate samples are nearly colorless; however, they showed significant color sensitivity towards alpha particles irradiation that appeared clearly in the change in the blue color component of the non irradiated cellulose triacetate film to yellow after exposure to Alpha particles up to 100 Gy. This is accompanied by a net increase in the darkness of the samples.

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7/26/2014