

Effect of Additive Concentration and Electron Beam Irradiation on the Molecular and Optical Properties of Poly (Vinyl Chloride)

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Abstract: The effects of addition of different monomers on the intrinsic viscosity of poly(vinyl chloride) PVC have been studied. Three different additive monomers from N-phenyl maleimide derivatives were added with the same concentration 0.015 gm/1gm PVC as stabilizers. These stabilizers are N-phenyl maleimide NPMI, Para-carboxy N-phenyl maleimide PC-NPMI and Para-amide carboxy N-phenyl maleimide PA-NPMI. Their stabilizing efficiencies were evaluated by measuring the intrinsic viscosity of the solution samples. It was found that the PC-NPMI monomer is proved not to be sufficient effective in increasing the average molecular mass. So, the effect of its addition with different concentrations was studied. The results indicate that the sample with 0.01 gm PC-NPMI /1gm PVC has higher intrinsic viscosity. Thus this sample was chosen to be a subject for further study to investigate the effect of electron beam irradiation on its molecular and color properties. Samples from the 0.01 gm PC-NPMI /1gm PVC were irradiated with electron beam doses in the range 50-300 kGy. It is found that the irradiation in the dose range 50-250 kGy enhances the intrinsic viscosity and the color response of the samples.

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1. Introduction

Poly(vinyl chloride), PVC, is very attractive and most suitable plastic for a wide variety of applications [1]. It stands second in the world after polyethylene concerning the production and consumption of a synthetic material. However, in spite of its enormous technical and economic importance, PVC possesses many problems accompanied by instability in its physical properties. Structure defects that are formed in the polymer chain during the polymerization process are thought to be responsible for this instability [2]. Possible structure defects in PVC chains are allylic chlorine, tertiary hydrogen and chlorine atoms, end groups such as double bonds, oxygen-containing groups, peroxide residues, head-to-head structures and the steric order of the monomer units (tacticity) that may have some influence on the degradation [3, 4]. Therefore, the stabilization of a PVC polymer using a variety of additives is required. On the other hand, radiation processing is a useful technology to induce suitable modifications of polymers. In particular, it is an important way to achieve some desired improvements that promise many applications in a wide range of industrial fields. Several investigations were performed on the field of polymer additives or irradiation aiming to annihilate the structure defects, improving the performance of the polymer in industrial applications [5-13]. The present study deals with the investigation of the effect of additive concentration and electron beam irradiation on the molecular and color properties of

poly(vinyl chloride) aiming to improve its performance in various industrial fields.

2. Experimental

2.1. Samples

Poly(vinyl chloride) (vesolite S 7054) was obtained from Huls Company and freshly distilled tetrahydrofuran (THF) (99.9%) was obtained from Aldrich, USA.

Preparation of N-phenyl maleimides

(i) N-phenyl maleimide (NPMI)

NPMI was prepared by the two-step process as previously reported [2]. In this process the aniline (0.5 mole) in chloroform or ether was added to a cold solution of maleic anhydride (0.5 mole) in the same solvents. The resulting N-substituted maleamic acid, obtained as a fine precipitate, was treated with fused sodium acetate (0.6 mole) and acetic anhydride (10 moles) for each mole of maleamic acid at 70-80 °C for 30 minutes. The maleimide formed was precipitated with water and crystallized from ethanol.

(ii) Preparation of para-carboxy N-phenyl maleimide (PC-NPMI)

The same procedure was used to prepare (PC-NPMI) with para-carboxy aniline as a primary amine.

(iii) Preparation of para-amide N-phenyl maleimide (PA-NPMI)

PC-NPMI was treated with thionyl chloride (1 mole) and then (1 mole) of ethanol to obtain the corresponding derivative PA-NPMI.

(iv) Preparation of PVC – Maleimide (MI) films

One gram of PVC and various concentrations from MI were dissolved in Tetrahydrofuran (THF) then poured into a Petri-dish of 6 cm diameter. After nearly 24 hours, a film of nearly 0.3 mm thickness was formed.

2.2 Irradiation facilities

The electron beam irradiation was carried out in the electron accelerator facility of NCRRT, AEA, Cairo, EGypt (1.5MeV and 25 kW) in which the conveyer speed was adjusted at 20 mm/min. The thickness of the sample does not exceed 1mm to ensure complete penetration of the accelerated electrons. The dose was determined by the FWT₆₀₋₀₀ dosimeter that was calibrated using the CERIC/CEROUS dosimeter.

2.3 Experimental apparatus

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 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 reflecting or transmitting sample are calculated by adding the product of the spectral power distribution of illuminant, the reflectance or 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

$$\begin{aligned} X &= k \sum P(\lambda) \bar{x}(\lambda) T(\lambda) \\ Y &= k \sum P(\lambda) \bar{y}(\lambda) T(\lambda) \\ Z &= k \sum P(\lambda) \bar{z}(\lambda) T(\lambda) \\ k &= \frac{100}{\sum P(\lambda) \bar{y}(\lambda)} \end{aligned}$$

Where $P(\lambda)$ is the value of the spectral power distribution of the illuminant at the wavelength λ . $R(\lambda)$ 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, while the 1976 CIE L* u* v* (CIELUV) color space is widely used in the television and video display industries.

L^* correlates 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

$$\begin{aligned} L^* &= 116f(Y/Y_n) - 16 \\ a^* &= 500[f(X/X_n) - f(Y/Y_n)] \\ b^* &= 200[f(Y/Y_n) - f(Z/Z_n)] \end{aligned}$$

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 [14]

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

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

3. Results and discussion

3.1 The dependence of the intrinsic viscosity on the type of stabilizer

Solutions of different concentrations (0.2, 0.4, 0.6 and 0.8 %) were prepared from the stabilized and non stabilized PVC samples using THF as a solvent. The kinematic viscosity of the liquid samples can be calculated by the product of the observed time of flow and the capillary constant of the viscometer. The result is always expressed as relative viscosity (η_{rel}), calculated as the ratio of the viscosities of polymer solution and the pure solvent. Additional values may be calculated such as specific viscosity ($\eta_{spc} = \eta_{rel} - 1$), a reduced viscosity ($\eta_{red} = \eta_{spc} / \text{concentration}$) and intrinsic viscosity, the limiting viscosity number ($\eta_{in} = \lim \eta_{red}$ when the concentration tends to zero) that is related to the average molecular mass of the dissolved polymer.

The intrinsic viscosity measurements were performed on samples of 0.015 gm monomer/1gm PVC and the pure PVC sample. The measurements were carried out at 35 °C. The resultant values are given in Table 1. The results indicated that the PC-NPMI additive is the most effective stabilizer that decreases the intrinsic viscosity of pure PVC from 1.09 to 0.92. The interpretation of these results can be that the addition of NPMI stabilizer monomer to PVC leads to the formation of a bond between the carbon atom and the monomer molecule. This reduces the formation of HCl and the formation of double bonds along the chain and thus increasing the average molecular mass. While, the PC-NPMI stabilizer monomer contains groups which are acidic in nature and give H^+ in the medium which increases the probability of producing HCl and thus this monomer is proved not to be sufficient effective in increasing the average molecular mass. On the other hand, the PA-NPMI stabilizer monomer contains groups which have a very weak acidic character and thus the probability of formation of HCl is small. So, PA-NPMI is the most effective stabilizer for increasing the average molecular mass.

3.2 The dependence of the intrinsic viscosity on the concentration of PC-NPMI

The effect of concentration of PC-NPMI on the intrinsic viscosity of PVC has been investigated. The resultant values are given in Table 2. The results indicated that the addition of PC-NPMI with 0.01 gm/1gm PVC enhances the intrinsic viscosity up to 1.27. This is due to the consumption of the stabilizer into the PVC chains, displacing all structure defects for the

0.01gm PC-NPMI sample. Excess stabilizer may lead to a detachment of the stabilizer moieties previously incorporated into the polymeric chains due to steric hindrance.

In conclusion the study of the effect of concentration of added PC-NPMI monomer stabilizer to PVC shows that the sample with 0.01 gm PC-NPMI/1gm PVC has higher intrinsic viscosity value. Thus this sample was chosen to be a subject for further study to investigate the effect of electron beam irradiation on its properties.

3.3 Effect of electron beam dose on the molecular and color properties of the 0.01 gm PC-NPMI /1gm PVC polymer

3.3.1 Intrinsic viscosity

Samples from the 0.01gm PC-NPMI /1gm PVC were irradiated with electron beam doses in the range 50-300 kGy. The intrinsic viscosity of the non irradiated and irradiated samples could be measured. Figure 1 shows the variation of intrinsic viscosity with the electron beam dose. From the figure it is clear that the intrinsic viscosity shows a decrease until a minimum value around the 50 kGy irradiated sample, followed by an increase on increasing the dose up to 250 kGy. Above 250 and up to 350 kGy it decreases again. 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. While the increase in intrinsic viscosity in the dose range 50-250 kGy, indicates an increase in the average molecular mass of the polymer due to crosslinking process.

3.3.2 Color changes

Figure 2 shows the transmittance of the non irradiated and electron beam irradiated 0.01gm PC-NPMI /1gm PVC samples in the wavelength range 380-780 nm. Using these transmission data, both the tristimulus values and chromaticity coordinates were calculated. Figure 3 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 show an increase up to a maximum value around the 200 kGy irradiated sample, followed by a decrease on increasing dose up to 350 kGy.

The variation of chromaticity coordinates x, y and z with the electron beam dose is shown in figure 4. The chromaticity coordinates x and y increased with increase in dose up to 350 kGy, while z exhibited the opposite trend.

The variation of color intercepts (L^* and b^*) with the electron beam dose is shown in Figure 5. The accuracy in measuring L^* is + 0.05 and + 0.01 for b^* . It can be seen that the blue ($-b^*$) color component of the non irradiated film was changed to yellow ($+b^*$)

after exposure to doses up to 350 kGy. This is accompanied by an increase in the darkness of the samples ($-L^*$).

Figure 6 shows the variation of the color intensity ΔE (color difference between the non irradiated sample and those irradiated with different doses) with the electron beam dose. From the figure it is seen that ΔE was greatly increased with increasing the dose, and accompanied by a significant increase in the yellow color components ($+b^*$) and darkness of the samples ($-L^*$). This indicates that the 0.01 gm PC-NPMI /1gm PVC stabilized polymer has more response to color change by electron irradiation. These changes in color can be attributed to the trapping of the excited free radicals that are formed by ionization [15]. 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.

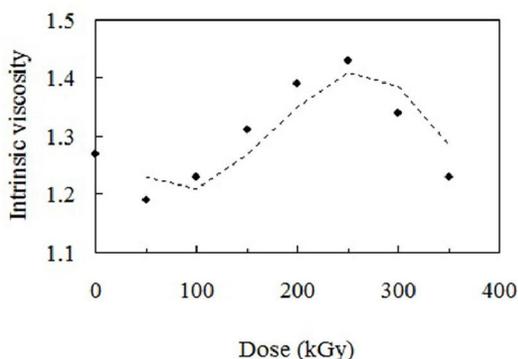


Figure 1. Variation of the intrinsic viscosity of the 0.01gm PC-NPMI /1gm PVC polymer with the electron beam dose.

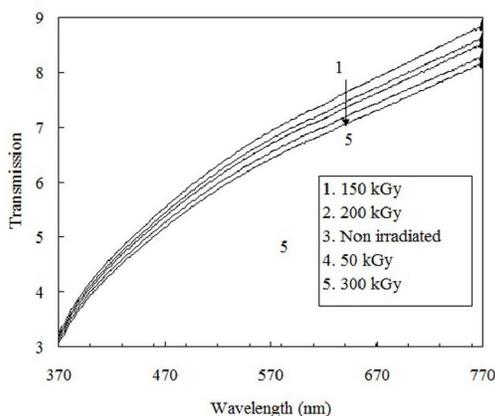


Figure 2. The transmittance spectra of non irradiated and some of the electron beam irradiated 0.01 gm PC-NPMI /1gm PVC polymer, measured in the wavelength 380-780 nm.

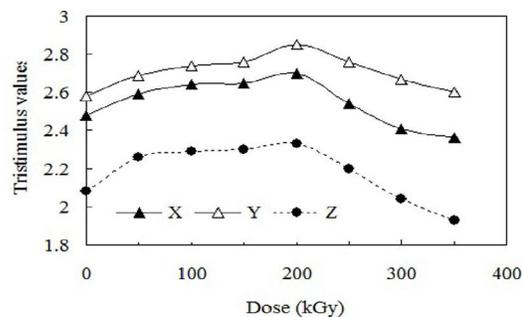


Figure 3. Variation of the tristimulus values X, Y and Z of the 0.01gm PC-NPMI /1gm PVC polymer with the electron beam dose.

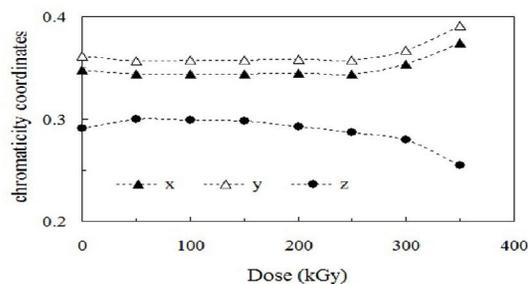


Figure 4. Variation of the chromaticity coordinates x, y and z of the 0.01gm PC-NPMI /1gm PVC polymer with the electron beam dose.

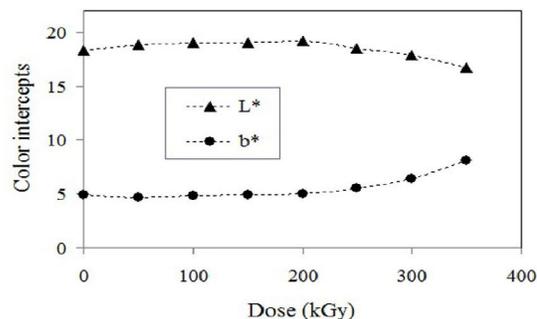


Figure 5. Variation of the color intercepts L^* and b^* of the 0.01gm PC-NPMI /1gm PVC polymer with the electron beam dose.

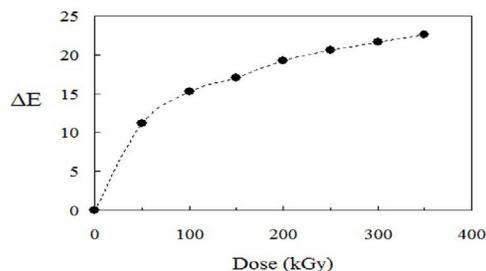


Figure 6. Variation of the color difference ΔE between the non irradiated and irradiated 0.01gm PC-NPMI /1gm PVC polymer with the electron beam dose.

Table 1 Values of intrinsic viscosity for the concentration 0.015gm of each additive /1gm PVC

Stabilizer monomer (0.02 gm/1gm PVC)	Intrinsic viscosity
Pure PVC	1.09
NPMI	1.18
PC-NPMI	0.92
PA-NPMI	1.29

Table 2 Values of intrinsic viscosity as a function of the PC-NPMI concentration.

Concentration (gm PC-NPMI / 1gm PVC)	Intrinsic viscosity
0.000	1.09
0.005	1.16
0.010	1.27
0.015	0.92
0.020	0.81

Conclusion

From the previous study one can draw the conclusion that the intrinsic viscosity in the polymer samples is dependent on both the PC-NPMI concentration and the electron beam dose. Also, the PVC polymer stabilized with 0.01gm PC-NPMI/ 1gm PVC and irradiated with 250 kGy electron beam dose has the maximum average molecular mass.

The non irradiated 0.01gm PC-NPMI/ 1gm PVC polymer showed significant color sensitivity towards electron beam irradiation, appeared clearly in the change in the green and blue color components to red and yellow, accompanied by an increase in the darkness of the polymer samples.

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