

# Effect of Additive Concentration and Gamma Radiation on the Molecular and Color Properties of Poly(vinyl chloride)

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**ABSTRACT:** The effects of addition of different monomers on the molecular properties of poly(vinyl chloride) (PVC) have been studied. Three different additive monomers from *N*-phenyl maleimide derivatives were added with the same concentration 0.02 gm/1 gm PVC as stabilizers to PVC. These stabilizers are *N*-phenyl maleimide, Para-carboxy *N*-phenyl maleimide, and Para-amide carboxy *N*-phenyl maleimide (PA-NPMI). Their stabilizing efficiencies were evaluated by measuring the intrinsic viscosity of the solution samples. The results reveal that the type of the additive monomer plays a major role in determining the stabilizing potency of these materials. It was found that the PA-NPMI is the most effective stabilizer that improves the intrinsic viscosity of pure PVC from 1.02 to 1.19. So, the effect of its addition with different concentrations was studied. The results indicate that the sample with 0.015 gm PA-NPMI/1 gm PVC has higher

intrinsic viscosity. Thus, this sample was chosen to be a subject for further study to investigate the effect of gamma irradiation on its molecular and color properties. Samples from the 0.015 gm PA-NPMI/1 gm PVC were irradiated with gamma doses in the range 5–100 kGy. It is found that the irradiation in the dose range 20–60 kGy enhances the intrinsic viscosity of the samples. In addition, the transmission of these irradiated samples in the wavelength range 200–2500 nm, as well as any color changes, was studied. The color intensity  $\Delta E$  was greatly increased with increasing the gamma dose, and was accompanied by darkness with a significant increase in the yellow color component. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 3060–3065, 2010

**Key words:** poly(vinyl chloride); additives; gamma irradiation; viscosity; color

## INTRODUCTION

The low cost and excellent performance of poly(vinyl chloride) (PVC) makes it a very attractive and most suitable plastic for a wide variety of applications.<sup>1</sup> 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.<sup>1,2</sup> Possible structure defects in PVC chains are allylic chlorine,<sup>3,4</sup> tertiary hydrogen, and chlorine atoms,<sup>5</sup> end groups such as double bonds,<sup>6</sup> oxygen-containing groups,<sup>7</sup> peroxide residues,<sup>8</sup> head-to-head structures,<sup>1</sup> and the steric order of the monomer units (tacticity) that may have some influence on the degradation.<sup>9</sup> Because of these structure defects,

PVC undergoes rapid autocatalytic dehydrochlorination on exposure to heat<sup>10</sup> and light<sup>11</sup> during its moulding and use, respectively. 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. Also, the action of radiations on polymers leads to several changes in their properties due to the induced degradation and crosslinking. Degradation causes a drastic change in the mechanical properties of the polymer accompanied by a decrease in molecular weight.<sup>12</sup>

In addition, color is the attribute of reflected and transmitted light that, while based on certain arbitrarily agreed upon mathematical notation, is nevertheless scientifically derived from a systematic description of the spectral response of the human eye. The mathematical description of color, or color notation to be more precise, is based on dividing the spectral response of the human eye into three primary colors red, green, and blue (RGB). The vision scientists created a special set of mathematical lights, X, Y, and Z, to replace actual red, green, and blue lights.

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The RGB color space is used in color mixing, color specification, and color difference measurements of colored plastics.

In our previous work,<sup>2,13</sup> para-ethyl carboxy *N*-phenyl maleimide was used as an additive to PVC to investigate the feasibility of enhancing its thermal stability. The results revealed that the addition of this stabilizer by 0.01 gm/1 gm PVC is efficient thermal stabilizer to PVC. The present study deals with the investigation of the effect of additive concentration and gamma radiation on the molecular and color properties of PVC aiming to improve its performance in various industrial fields.

## EXPERIMENTAL

### Samples

PVC (vesolite S 7054) was obtained from Huls Company and freshly distilled tetrahydrofuran (THF) (99.9%) was obtained from Aldrich.

### Preparation of *N*-phenyl maleimides

*N*-phenyl maleimide (NPMI)

NPMI was prepared by the two-step process as previously reported.<sup>14</sup> In this process the aniline (0.5 mol) in chloroform or ether was added to a cold solution of maleic anhydride (0.5 mol) in the same solvents. The resulting *N*-substituted maleamic acid, obtained as a fine precipitate, was treated with fused sodium acetate (0.6 mol) and acetic anhydride (10 mol) for each mol of maleamic acid at 70–80°C for 30 min. The maleimide formed was precipitated with water and crystallized from ethanol.

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.

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

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

Preparation of PVC–Maleimide (MI) films

One gram of PVC and various concentrations from MI were dissolved in Tetrahydrofuran (THF) then poured into a petridish of 6 cm diameter. After nearly 24 h, a film of nearly 0.25 mm thickness was formed.

### Irradiation facilities

A <sup>60</sup>Co source (manufactured by Atomic Energy of Canada) providing a dose rate of 2.4 Gy/min was used. The measurements were carried out 24 h after irradiation.

### Experimental apparatus

#### Viscosity measurements

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.

#### Color measurement

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:

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

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

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

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

where  $P(\lambda)$  is the value of the spectral power distribution of the illuminant at the wavelength  $\lambda$ .  $R(\lambda)$  is the transmittance factor of the sample at the wavelength  $\lambda$  and  $\bar{x}(\lambda)$ ,  $\bar{y}(\lambda)$ , and  $\bar{z}(\lambda)$  are the CIE color matching functions for the standard observer at the

wavelength  $\lambda$ . 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

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

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,  $\Delta E$  is given by<sup>15,16</sup>

$$\Delta E = [(L_1^* - L_2^*) + (a_1^* - a_2^*) + (b_1^* - b_2^*)]^{1/2}$$

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

## RESULTS AND DISCUSSION

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

Solutions of different loadings (0.2, 0.4, 0.6, and 0.8%) were prepared from the stabilized and nonsta-

**TABLE I**  
Values of Intrinsic Viscosity for the Concentration 0.02 gm of Each Additive/1 gm PVC

Stabilizer monomer (0.02 gm/1 gm PVC)	Intrinsic viscosity
Pure PVC	1.02
NPMI	1.08
PC-NPMI	0.85
PA-NPMI	1.19

bilized samples using THF as a solvent. These diluted solutions were chosen to avoid any attractive secondary interactions between the polymer and solvent molecules, which can be reflected in an increase of the viscosity in ways that accurate measurements cannot be made. 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 ( $\eta_{rel}$ ), 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.

Intrinsic viscosity measurements were performed on samples of 0.02 gm monomer/1 gm PVC (which is the maximum available concentration usually used in industrial applications) and the pure PVC sample. The measurements were carried out at room temperature 30°C. The resultant values are given in Table I. The results indicated that the PA-NPMI additive is the most effective stabilizer that improves the intrinsic viscosity of pure PVC from 1.02 to 1.19. 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 sufficiently 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.

### The dependence of the intrinsic viscosity on the concentration of PA-NPMI

The effect of concentration of PA-NPMI on the intrinsic viscosity of PVC has been investigated. The

**TABLE II**  
Values of Intrinsic Viscosity as a Function of the PA-NPMI Concentration

Concentration (gm PA-NPMI/ 1 gm PVC)	Intrinsic viscosity
0.000	1.02
0.005	1.09
0.010	1.12
0.015	1.27
0.020	1.19

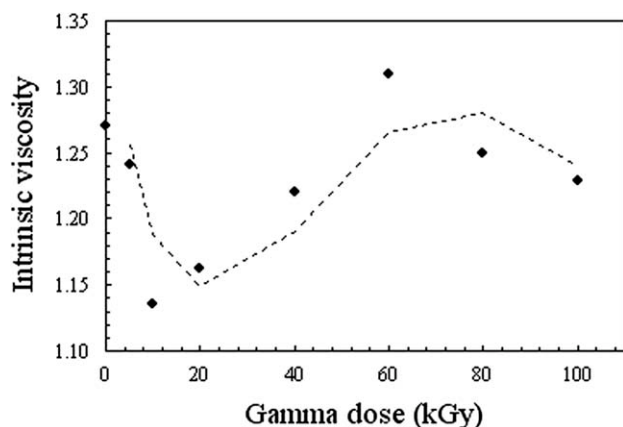
resultant values are given in Table II. The results indicated that the addition of PA-NPMI with 0.015 gm/1 gm PVC enhances the intrinsic viscosity up to 1.27. This is because of the consumption of the stabilizer into the PVC chains, displacing all structure defects for the 0.015 gm PA-NPMI sample. Excess 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 PA-NPMI monomer stabilizer to PVC shows that the sample with 0.015 gm PA-NPMI/1 gm PVC has higher intrinsic viscosity value. Thus, this sample was chosen to be a subject for further study to investigate the effect of gamma radiation on its properties.

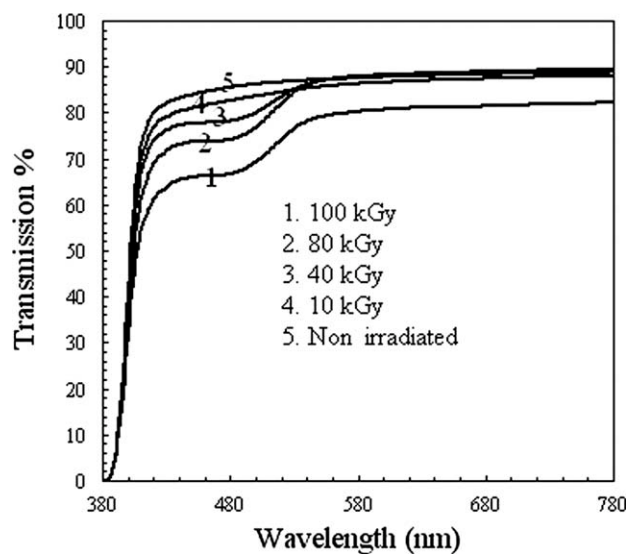
#### Effect of gamma dose on the molecular and color properties of the 0.015 gm PA-NPMI/1 gm PVC polymer

##### Intrinsic viscosity

Samples from the 0.015 gm PA-NPMI/1 gm PVC were irradiated with gamma doses in the range 5–100 kGy. The intrinsic viscosity of the nonirradiated and irradiated samples could be measured. Figure 1 shows the variation of intrinsic viscosity with the gamma dose. From the figure it is clear that the intrinsic viscosity shows a decrease until a minimum



**Figure 1** The variation of intrinsic viscosity of the 0.015 gm PA-NPMI/1 gm PVC sample with the gamma dose.

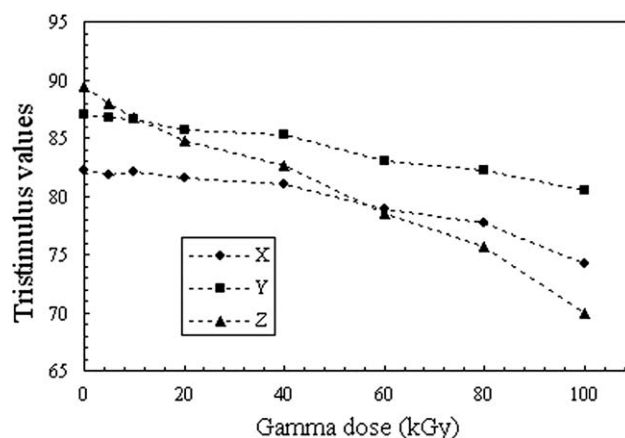


**Figure 2** The transmittance of the nonirradiated and gamma irradiated 0.015 gm PA-NPMI/1 gm PVC samples in the wavelength range 380–780 nm.

value around the 10 kGy irradiated sample, followed by an increase on increasing the gamma dose up to 60 kGy. Above 60 and up to 100 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 20–60 kGy, indicates an increase in the average molecular mass of the polymer because of crosslinking process.

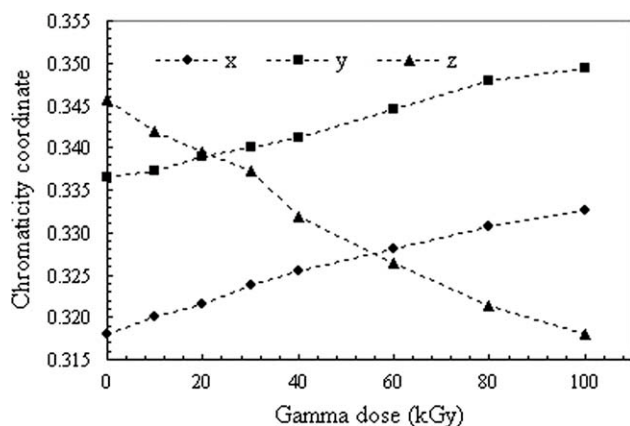
##### Color changes

Figure 2 shows the transmittance of the nonirradiated and gamma irradiated 0.015 gm PA-NPMI/1 gm PVC samples in the wavelength range 380–780



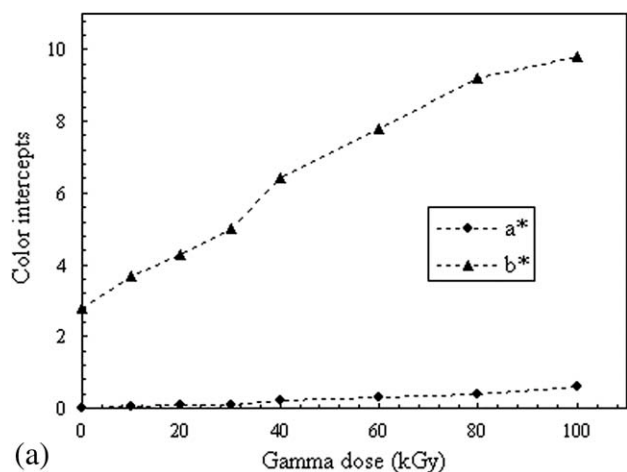
**Figure 3** The variation of tristimulus values (X, Y, Z) with the gamma dose.



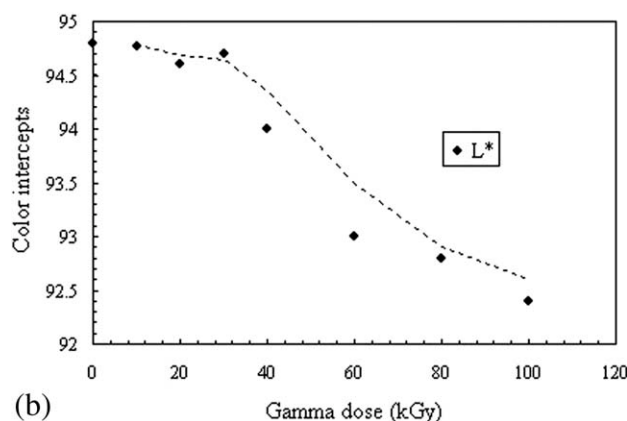


**Figure 4** The variation of chromaticity coordinates  $x$ ,  $y$ , and  $z$  with the gamma dose.

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 gamma dose. From the figure it is clear that  $X$ ,  $Y$ , and  $Z$  exhibited the same trend, where they show a decrease on increasing dose up to 100 kGy.

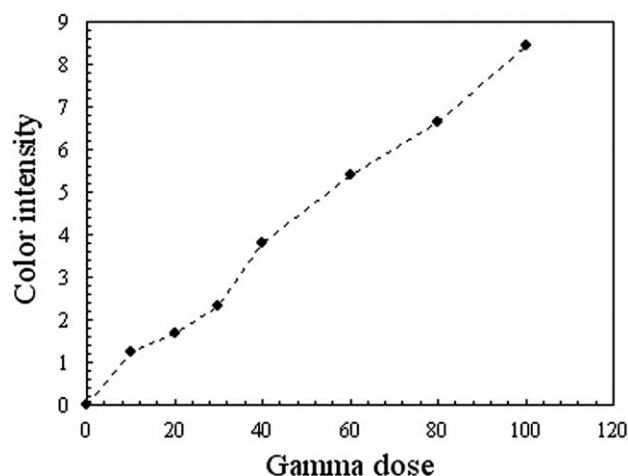


(a)



(b)

**Figure 5** The variation of color intercepts ( $a^*$  and  $b^*$ ) with gamma dose. The variation of color intercept  $L^*$  with gamma dose.



**Figure 6** The variation of the color intensity  $\Delta E$  with the gamma dose.

The variation of chromaticity coordinates  $x$ ,  $y$ , and  $z$  with the gamma dose is shown in Figure 4. The chromaticity coordinates  $x$  and  $y$  increased with increase in gamma dose up to 100 kGy, while  $z$  exhibited the opposite trend.

The variation of color intercepts ( $L^*$ ,  $a^*$ , and  $b^*$ ) with gamma dose is shown in Figure 5(a,b). 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  $b^*$  and  $L^*$  were significantly changed after exposure to gamma irradiation. The blue ( $-b^*$ ) color component of the nonirradiated film was changed to yellow ( $+b^*$ ) after exposure to gamma doses up to 100 kGy. This is accompanied by an increase in the darkness of the samples ( $-L^*$ ). At the same time, the green ( $-a^*$ ) color component of the nonirradiated sample was slightly changed to red ( $+a^*$ ).

Figure 6 shows the variation of the color intensity  $\Delta E$  (color difference between the non irradiated sample and those irradiated with different gamma doses) with the gamma dose. From the figure it is seen that  $\Delta E$  was greatly increased with increasing the gamma dose, and accompanied by a significant increase in the yellow color components ( $+b^*$ ) and darkness of the samples ( $-L^*$ ). This indicates that the 0.015 gm PA-NPMI/1 gm PVC stabilized polymer has more response to color change by gamma irradiation. These changes in color can be attributed to the trapping of the excited free radicals that are formed by ionization.<sup>17</sup> 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.

## CONCLUSIONS

From the previous study one can draw the conclusion that the intrinsic viscosity in the polymer samples is dependent on both the PA-NPMI

concentration and the gamma dose. Also, the PVC polymer stabilized with 0.015 gm PA-NPMI/1 gm PVC and irradiated with 60 kGy gamma dose has the maximum average molecular mass.

The nonirradiated 0.015 gm PA-NPMI/1 gm PVC polymer showed significant color sensitivity toward gamma irradiation. The sensitivity in color change toward gamma irradiation appeared clearly in the change in green and blue color components to red and yellow, accompanied by an increase in the darkness of the polymer samples.

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