Effect of buffer on the optical properties of irradiated hydroxyethyl methacrylate copolymer

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The effect of buffer and γ irradiation on the optical properties of hydroxyethyl methacrylate (HEMA) copolymer was investigated. The transmission of HEMA copolymer decreased with the increase of irradiation dose and/or pH value of the buffer. The cutoff wavelength of HEMA copolymer exhibits a bathochromic shift as the γ-ray dose and/or pH value of buffer increases. The influence of atmosphere during γ-ray irradiation on the optical properties of HEMA copolymer was investigated. The change of optical properties of HEMA copolymer irradiated in air was more pronounced than that irradiated in vacuum. Light was scattered by holes in the polymer. The relationship between scattering intensity (I_s) and incident wavelength (λ) can be described by the formula $I_s \propto \lambda^{-n}$. The span of holes increases with the irradiation dose regardless of radiation atmosphere and pH value in the range of 4.1–6.5. A boundary between the inner and outer layers of HEMA copolymer irradiated in air was observed, separating two differential morphologies of holes.

I. INTRODUCTION

When polymeric materials are irradiated by γ-rays, their chemical structure is changed. A series of reactions results in crosslinking or scission of polymer chains and the creation of color centers, e.g., free radicals and conjugated structures.[1] The color centers adsorb the light of certain wavelengths. The atmosphere of irradiation affects the type and number of color centers. Harmon *et al.* showed that the presence of O_2 during irradiation raises the concentration of color centers.[2] According to Wallace *et al.*, the color centers are classified as two types: one type is a color center that can be eliminated by annealing, and the other is a color center that persists upon annealing.[3] Clough *et al.* found the annihilation rate of color centers depends on the atmsophere of annealing.[4]

Swelling induced by solvent enlarges holes in the polymer, and the holes scatter light. The crosslinking and scission of polymer chains are also related to the atmosphere of irradiation. Sometimes oxygen reacts with free radicals and produces peroxides or hydroperoxides, so that the crosslinking induced by recombination of free radicals is reduced.[5,6] On the other hand, oxygen can promote the degradation of chains for some linear polymers.[6–8] The crosslinking induced by irradiation and ionizing reactions[19] changes the equilibrium swelling ratio and therefore the optical properties of polymer are influenced. According to Rayleigh, the scattering intensity of particles is dependent on the wavelength of incident light.[10] For surface scattering, the scattering intensity is proportional to λ^{-4}, where λ is the wavelength of incident light. In the case of a swollen polymer, holes in polymer matrix are considered as particles and can scatter light. Lin and Lee found that the scattering intensity in methanol-treated polymethyl methacrylate (PMMA) is proportional to $\lambda^{-2.5}$.[11] Chou and Lee observed that the scattering intensity of PMMA treated with mixture of ferric chloride and methanol is proportional to λ^{-n}, where n is in the range of 1.02–3.25 and varies with the concentration of ferric chloride.[12] The value of n different from $n = 4$ is attributed to the fractal behavior of the hole. Wang proposed that the Fourier transfer function of small angle scattering $I(q) \propto q^{-(6-d)}$ for a volume fractal and $I(q) \propto q^{-d}$ for a surface fractal, where q is the wavevector and d is the fractal dimension.[13]

Hydroxyethyl methacrylate (HEMA) copolymer is used in biomaterials[14–16] such as contact lens, drug delivery system, and wound dressings, etc., because of high water content and nontoxicity. In previous research, Chou *et al.* studied the irradiation effect on the mass transport of water in HEMA copolymer and related optical properties.[17] They found that the transmission decreased with the increase of irradiation dose and the cutoff wavelength exhibits a bathochromic shift. Chou *et al.* also analyzed the buffer transport in irradiated HEMA copolymers.[18] This prompted us to study the effect of γ-ray irradiation on the optical properties of HEMA copolymer treated with buffer solution that is close to the encountered bio-environments.

II. EXPERIMENTAL

The HEMA copolymer soft contact lens blanks were obtained from Canadian Contact Lens Laboratories Ltd., Montreal, Quebec, Canada. The high water content of HEMA copolymer is due to the hydroxyl groups on side chains. The HEMA copolymer blanks are disks of 12.8-mm diameter and 6.0-mm thick. These blanks are thinned to 1.5 mm by a bench lathe. The surface of specimen is ground on 600 and 1200 grit emery papers and polished with 1.0 and 0.05 μm Al_2O_3 slurries. The thickness of each specimen was 1.0 mm after final polishing. The specimen was annealed in a vacuum oven at 60 °C for 7 days, and then furnace cooled to room temperature. The residual stresses induced by machining were eliminated via annealing.

Two sets of specimens were exposed on γ-ray irradiation from a 30000Ci cobalt-60 source at the Isotope Center of National Tsing Hua University with the dose rate of 20 kGy/h in air and in vacuum, respectively. Each set of specimens was divided into four groups to irradiate to 100, 200, 300, and 400 kGy.

Nonirradiated and irradiated specimens were immersed in the buffer solution of pH 4.1, 5.6, 6.5, and 7.2. This mass uptake experiment was operated in a thermostatted water bath at 40 °C. The buffers were prepared by the mixture of citric acid anhydrous, sodium phosphate dibasic anhydrous, and water with various concentrations. Citric acid anhydrous and sodium phosphate dibasic anhydrous were obtained from Tedia Company, Fairfield, OH and Showa Chemical Inc., Tokyo, Japan, respectively. The pH value of buffer was determined by a Jenco Electronics (Grand Prairie, TX) digital pH meter at 25 °C. The weight gain of the sample was measured periodically using an Ohaus Analytical Plus digital balance (Pine Brook, NJ) until the equilibrium weight gain was reached. Then these samples were removed from the buffer and desorbed in air at room temperature until the weight loss was insignificant. The spectra of these desorbed samples were measured by a Hitachi (Tokyo, Japan) U-3210/U-3230 spectrometer in the range from 240 to 800 nm.

Finally, the samples were cleaved using a sharpened blade. The cleaved surface of sample was coated with gold by a sputtering coater. The morphology of cross section of the specimen was observed using a Jeol (Tokyo, Japan) 5200 scanning electron microscope (SEM).

III. RESULTS AND DISCUSSION

A. The optical properties of nonirradiated specimen

The ultraviolet and visible spectra of the nonirradiated specimens treated with buffer are shown in Fig. 1. The transmittance of the polymer decreases with an increase in the pH value of the buffer except for the specimen treated with a buffer of pH 7.2. The cut-off wavelength is 249 nm for all specimens as listed in Table I. This phenomenon implies that chromophores in the specimen do not react with buffer molecules, but the scattering of the holes induced by swelling reduces the transmission of the polymer. The plots of logarithmic light scattering intensity (I_s) versus logarithmic incident wavelength (λ)

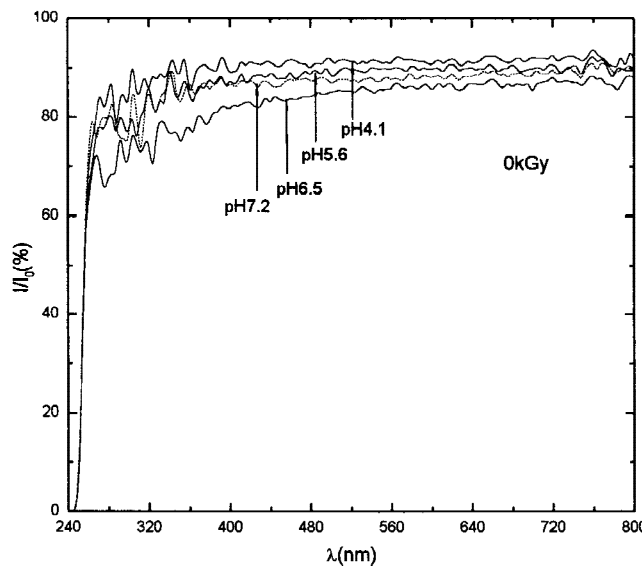


FIG. 1. The ultraviolet and visible spectra of the nonirradiated HEMA copolymer treated with buffer of various pH values. Note that the ordinate is transmittance.

TABLE I. The cut-off wavelengths of nonirradiated and irradiated HEMA copolymers treated with buffers of various pH values at 40 °C (ϕ: irradiation dose). The unit of cut-off wavelength is nm.

pH value	Nonirradiation	Irradiated in vacuum ϕ (kGy) 100	200	300	Irradiated in air ϕ (kGy) 100	200	300	400
4.1	249	249	249	275	249	263	283	284
5.6	249	249	249	275	249	263	287	287
6.5	249	249	267	283	249	275	317	339
7.2	249	249	271	287	249	292	315	323

are shown in Fig. 2. The power n in the relationship between I_s and λ is obtained by linear regression and listed in Table II. The power n increases to a maximum and then decreases with the increase of pH value. The equilibrium swelling ratio of nonirradiated specimens tabulated in Table III increases with decreasing pH value because hydrogen bonds are formed between citric acid and hydroxyl groups, but the increasing amount of equilibrium swelling ratio is not enough to affect the transmission significantly.

The morphology of a cross section of nonirradiated specimen with different pH values is shown in Fig. 3. It is quite noticeable that in some cases the holes have distinct tails in the plane of the cleavage surface, while in other samples there appear to be no tails. The average diameter of holes and the area ratio of maximum hole to minimum hole are listed in Tables IV and V, respectively. Hereafter the span of hole is defined as the ratio of maximum area of hole to minimum. It shows that the diameter and span of holes vary with the pH value and equilibrium swelling ratio. According to Fig. 3, the average diameter of holes corresponding to pH 6.5 is largest.

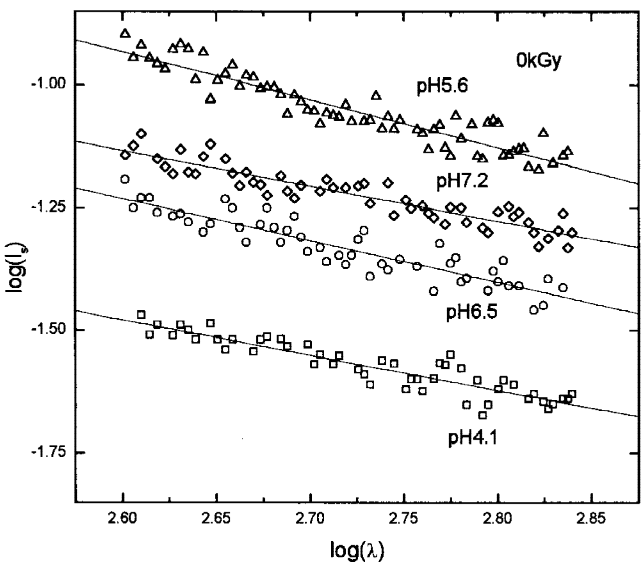


FIG. 2. The plot of log(I_s) versus log(λ) for HEMA copolymer treated with buffer of various pH values where I_s and λ are scattering intensity and wavelength, respectively.

B. Optical properties of the specimen irradiated in vacuum

The ultraviolet and visible spectra of the specimens irradiated in vacuum are shown in Fig. 4. The transmittance decreases with increasing irradiation dose. The cutoff wavelength exhibits a bathochromic shift. The γ irradiation changes the structure of HEMA copolymer. The equilibrium swelling ratio decreases with increasing dose for pH 4.1 and increases with increasing dose for pH $\geqq$ 5.6. This is because the pH value of de-ionized water immersed in HEMA decreases to a minimum 4.26.[17] Acidic carboxyl groups are produced so that the equilibrium swelling ratio of the irradiated specimen increases steeply with the pH value.[19,20] The equilibrium swelling ratio increases with increasing diameter and number of holes. The hole scatters light so the transmittance decreased. The scattering intensity (I_s) induced by holes is inversely proportional to the wavelength (λ) with power (n) as shown in Fig. 5. The data of power (n) are listed in Table II. The value of n increases with the increase of pH value with the exception of pH 7.2. The span of hole is in the wide range so that the data of log(I_s) versus log(λ) is scattered. The surface morphologies of

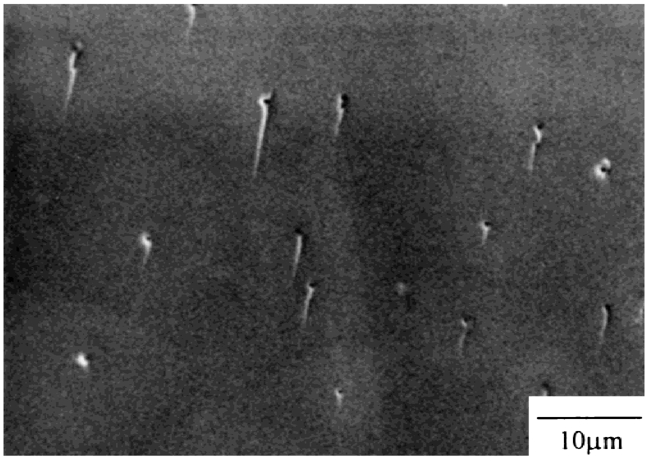
TABLE II. The power n of $I_s \propto \lambda^{-n}$ for the nonirradiated and irradiated HEMA copolymers treated with buffers of various pH values at 40 °C (ϕ: irradiation dose).

pH	Nonirradiation	Irradiated in vacuum ϕ (kGy) 100	200	300	Irradiated in air ϕ (kGy) 100	200	300	400
4.1	0.71 ± 0.04	0.43 ± 0.05	0.51 ± 0.05	0.56 ± 0.08	1.19 ± 0.07	1.70 ± 0.09	0.86 ± 0.06	0.80 ± 0.08
5.6	0.85 ± 0.01	0.47 ± 0.05	0.56 ± 0.05	0.62 ± 0.06	1.18 ± 0.08	1.60 ± 0.07	0.90 ± 0.05	0.88 ± 0.01
6.5	0.97 ± 0.01	0.49 ± 0.05	0.71 ± 0.06	0.73 ± 0.05	0.71 ± 0.03	0.88 ± 0.03	0.93 ± 0.02	0.97 ± 0.03
7.2	0.72 ± 0.01	0.35 ± 0.04	0.73 ± 0.04	0.42 ± 0.03	0.87 ± 0.03	1.18 ± 0.03	0.91 ± 0.05	0.74 ± 0.06

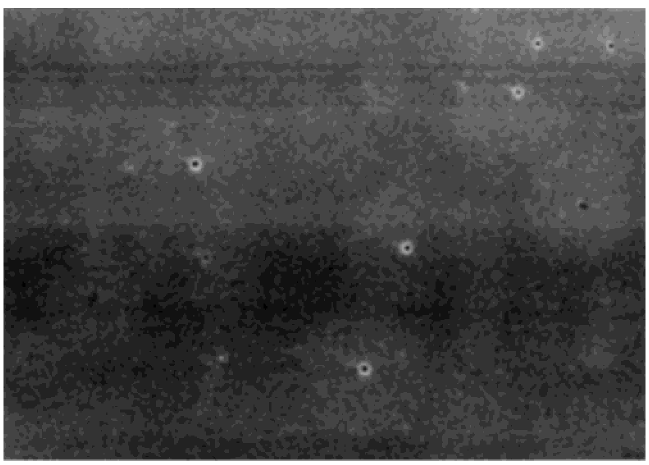
TABLE III. The equilibrium swelling ratio (wt% HEMA) of the nonirradiated and irradiated HEMA copolymers treated with buffers of various pH values at 40 °C (ϕ: irradiation dose). The equilibrium swelling ratio is defined as the ratio of weight of saturated buffer to the weight of dry HEMA.

pH value	Nonirradiation	Irradiated in vacuum ϕ (kGy) 100	200	300	Irradiated in air ϕ (kGy) 100	200	300	400
4.1	50.17	47.50	46.88	45.60	47.47	46.85	45.01	44.50
5.6	49.05	51.40	56.99	66.60	53.94	60.30	71.79	79.00
6.5	47.90	55.85	65.26	101.20	72.79	97.47	150.00	205.49
7.2	45.58	60.48	76.25	113.33	70.28	94.06	135.54	173.54

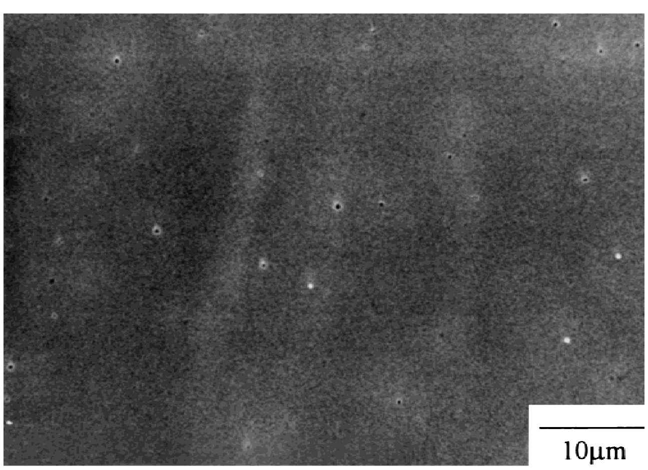
irradiated specimens in vacuum are shown in Fig. 6. Similar to the case of nonirradiated specimens, in some cases the holes have distinct tails in the plane of the cleavage surface, while in other samples there appear to be no tails. The diameter and number of holes are larger than those of nonirradiated specimen. Table V is listed the ratio of maximum area of hole in the irradiated specimen to minimum. These data show that the span of hole in irradiated specimens is broader than that in the nonirradiated specimens.



(a)



(b)



(c)

FIG. 3. The cross section of nonirradiated HEMA copolymer treated with buffer of (a) pH 5.6, (b) pH 6.5, and (c) pH 7.2.

C. Optical properties of the specimens irradiated in air

It can be seen from Table III that the equilibrium swelling ratio of specimen irradiated in air decreases with increasing dose for pH 4.1 and increases with increasing dose for pH $\geqq 5.6$. The pH value of de-ionized water after immersion of HEMA at 40 °C is greater than 4.2.[17] Increased swelling ratio may be expected if the specimen underoges predominantly chain scission upon radiation exposure. This is similar to PMMA, which is well known to be an inherently chain scissioning material due to its backbone structure. Enhanced scission under oxygen is a typical result for most polymer types due to the fact that oxidative free-radical-mediated chemistry usually gives reactions that result in extensive chain scission. The ultraviolet and visible spectra of the specimen irradiated in air are shown in Fig. 7. Comparing Fig. 7 and Fig. 4, the transmission intensity for irradiation in air is smaller than that for irradiation in vacuum because the former has a higher equilibrium–swelling ratio (see Table III). The cut-off wavelength of the former is also longer than that of the latter. The cut-off wavelength increases with

TABLE IV. The average diameter (μm) of holes in the nonirradiated and irradiated HEMA copolymers treated with buffers of various pH values at 40 °C (ϕ: irradiation dose).

		Irradiated in vacuum ϕ (kGy)			Irradiated in air ϕ (kGy)		
	Nonirradiation	100	200	300	200	300	400
pH 4.1	0.19	0.20	0.47	0.28	0.13	0.15	0.15
pH 5.6	0.22	0.35	0.49	0.50	0.31	0.32	0.47
pH 6.5	0.26	0.45	0.63	0.38	0.43	0.34	1.04
pH 7.2	0.20	0.58	0.67	0.41	0.70	0.48	0.67

TABLE V. The ratio of maximum area of hole to minimum in the nonirradiated and irradiated HEMA copolymers treated with buffers of various pH values at 40 °C (ϕ: irradiation dose).

		Irradiated in vacuum ϕ (kGy)			Irradiated in air ϕ (kGy)		
	Nonirradiation	100	200	300	200	300	400
pH 4.1	5.3	6.5	13.1	22.5	4.5	10.1	19.3
pH 5.6	4.6	7.3	18	55.5	5	21.8	24.4
pH 6.5	2.1	8.7	25.1	83.2	24.2	66.6	600
pH 7.2	4.6	8.6	23	76.4	9.0	51	207

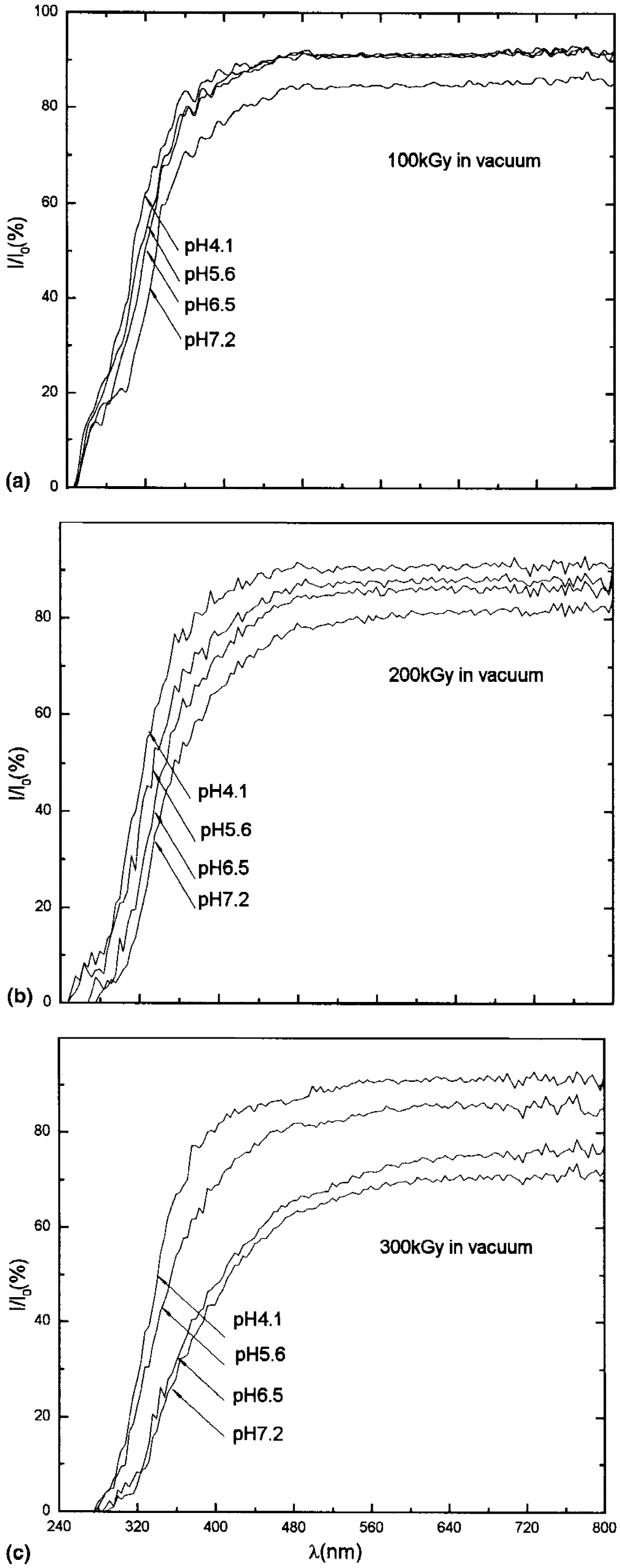


FIG. 4. The ultraviolet and visible spectra of the HEMA copolymer irradiated at (a) 100 kGy, (b) 200 kGy, and (c) 300 kGy in vacuum and then treated with the buffer of various pH values. Note that the ordinate is transmittance.

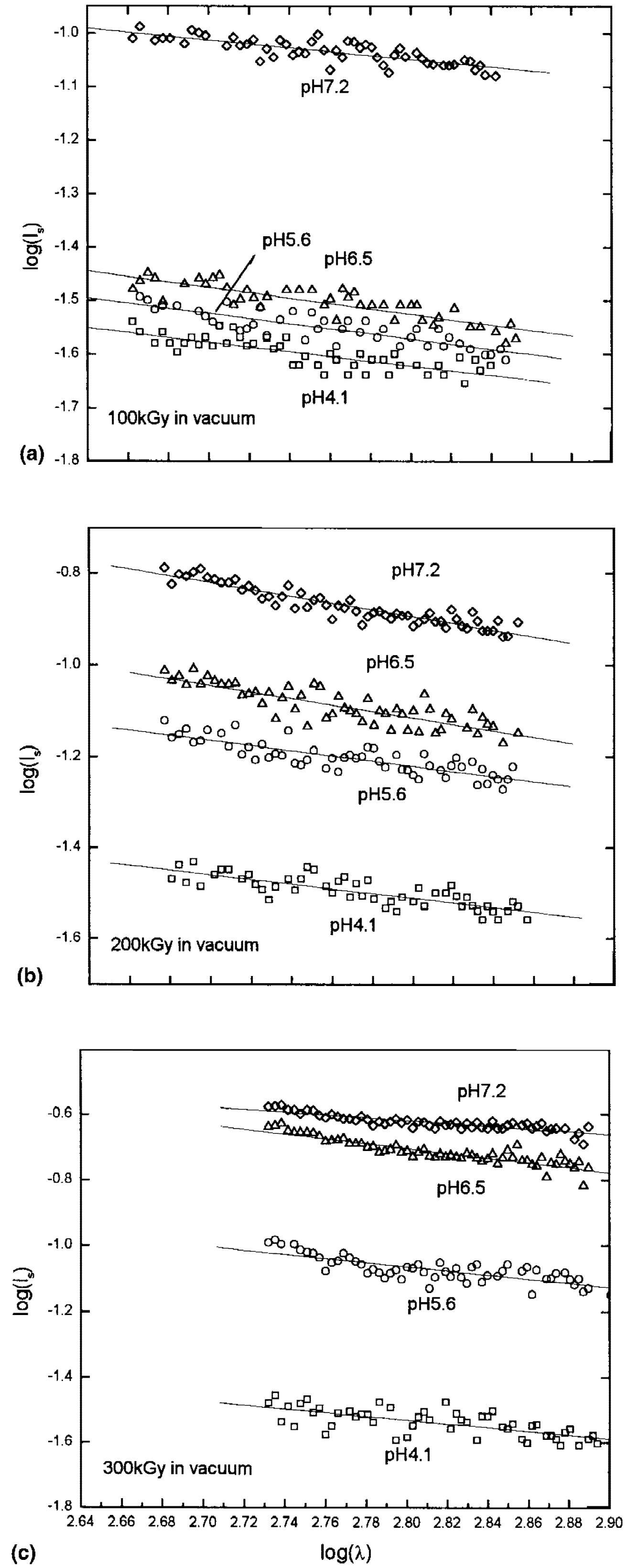


FIG. 5. The plot of $\log(I_s)$ versus $\log(\lambda)$ for HEMA copolymer irradiated at (a) 100 kGy, (b) 200 kGy, and (c) 300 kGy in vacuum and then treated with buffer of various pH values, where I_s and λ are scattering intensity and wavelength, respectively.

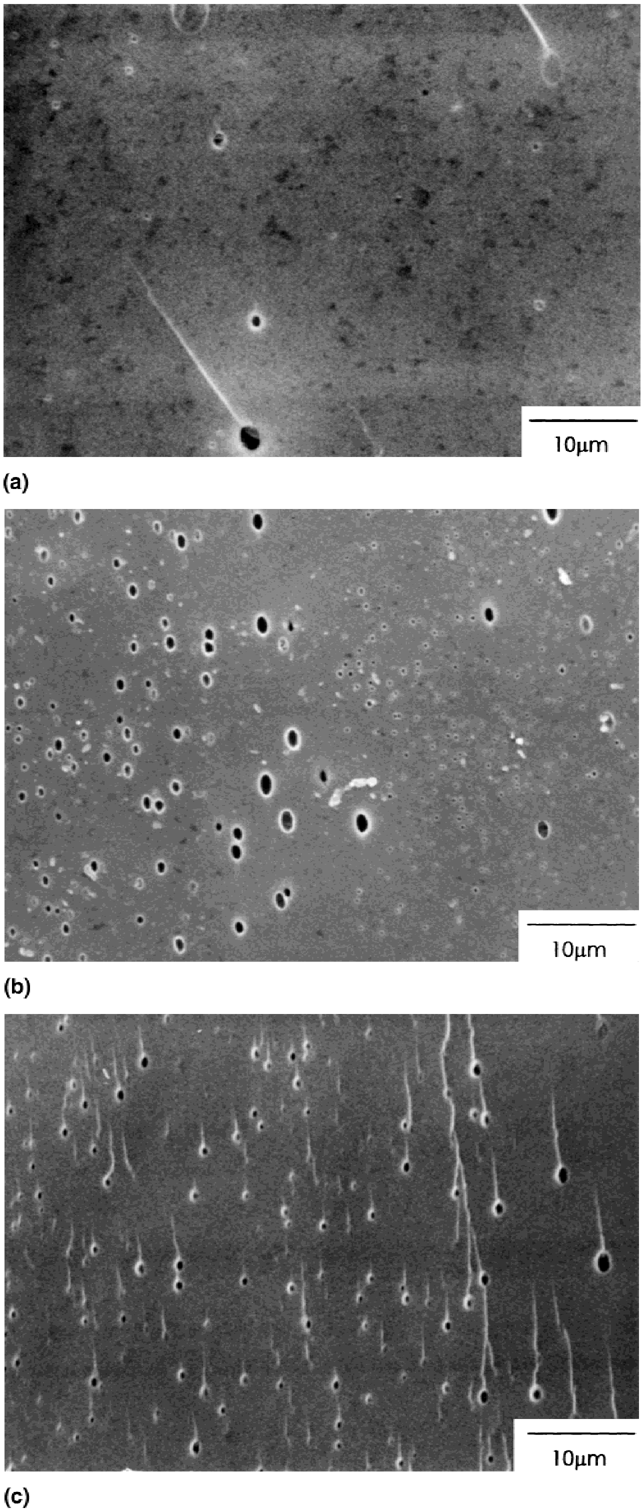


FIG. 6. The cross section of HEMA copolymer irradiated at 300 kGy in vacuum and then treated with buffer of (a) pH 5.6, (b) pH 6.5, and (c) pH 7.2, respectively.

increasing dose. The chromophore groups (or carbonxyl groups) absorb the light of wavelength in the range 240–280 nm. The solvent molecules, especially in the high pH buffer, interact with the molecules of the specimen ionized by irradiation via ion exchange and proton transfer.[21] Therefore, the shift of cut-off wavelength depends on the pH value. The plot of log (I_s) versus log (λ) is shown in Fig. 8. The values of n are obtained by linear regression and listed in Table II. The value of n is greater for the specimen irradiated in air than for the specimen irradiated in vacuum. The holes in the specimen irradiated in air are shown in Fig. 9 where the end of right hand side is exposed in air. It is interesting to find that there is a boundary to separate the inner layer from outer layer at doses 300 and 400 kGy. The number of holes in outer layer is less than that in inner layer, but the trend in the diameter of hole is opposite. The boundary layer observed is due to the oxygen diffusion limited effects, but the evidence must be proved.

D. Analysis of the morphology of holes

According to Tables IV and V, the diameter and ratio of maximum area to minimum area appear extreme at pH 6.5. Thus we focus the morphology of the HEMA specimen in the range of pH 6.5–7.2. For the nonirradiated specimen, the span of hole increases as the pH value of buffer changes from 6.5 to 7.2. The span of hole in the specimen absorbed the buffer of pH 7.2 is close to that in the specimen absorbed the buffer of pH 6.5 after irradiated at 100 kGy in vacuum. The span of hole for pH 7.2 is lower than that for pH 6.5 while the dose is above 200 kGy. For the specimen irradiated in air, the span of hole is also lower for pH 7.2 than for pH 6.5 at all doses. The trend in characteristic parameters of holes in pH 6.5–7.2 is inverted, which is due to the transfer of chemical properties of buffer solution. This pH effect is more significant if the dose is increased. The ionizing acidic group created by irradiation is sensitive to the change of acid–base behavior of buffer. On the other hand, for a given pH value, the span of hole increases with increasing dose. The ionizing effect induced by irradiation is equivalent to the pH effect on the morphology.

Rayleigh found that when the diameter of particle is smaller than the visible wavelength, the scattering intensity is proportional to the square of electric field arising from the particle.[10] The electric field due to the surface scattering of particle is proportional to the reciprocal of square of visible wavelength. As a result, the scattering intensity is proportional to λ^{-4}. That is, the power is 4 for surface scattering. Assume that a hole is a particle and its surface dimension is of a fraction (not an integer). The power n smaller than 4 is believed due to the fractal surface of hole.[13] The fractal surface dimension of a hole is n/2. The value of n depends on the span and diameter of hole, so as the fractal surface of hole. Therefore, the average diameter and span of holes is influenced by equilibrium swelling ratio. The correlation of parameters of the hole (Tables IV and V), and the various values of n

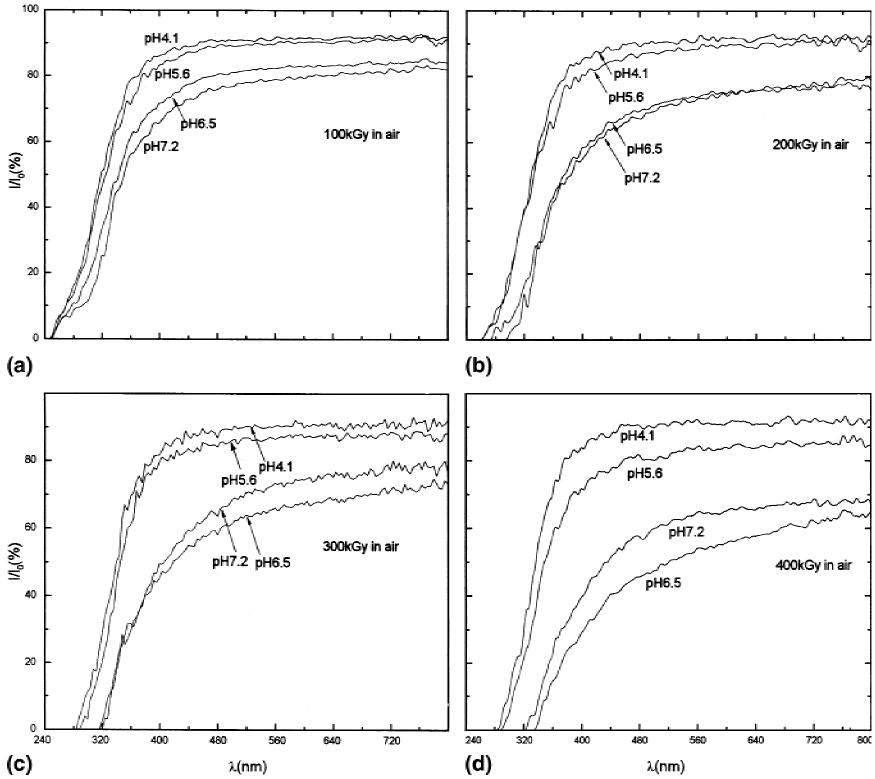


FIG. 7. The ultraviolet and visible spectra of the HEMA copolymer irradiated at (a) 100 kGy, (b) 200 kGy, (c) 300 kGy, and (d) 400 kGy in air and then treated with buffer of various pH values. Note that the ordinate is transmittance.

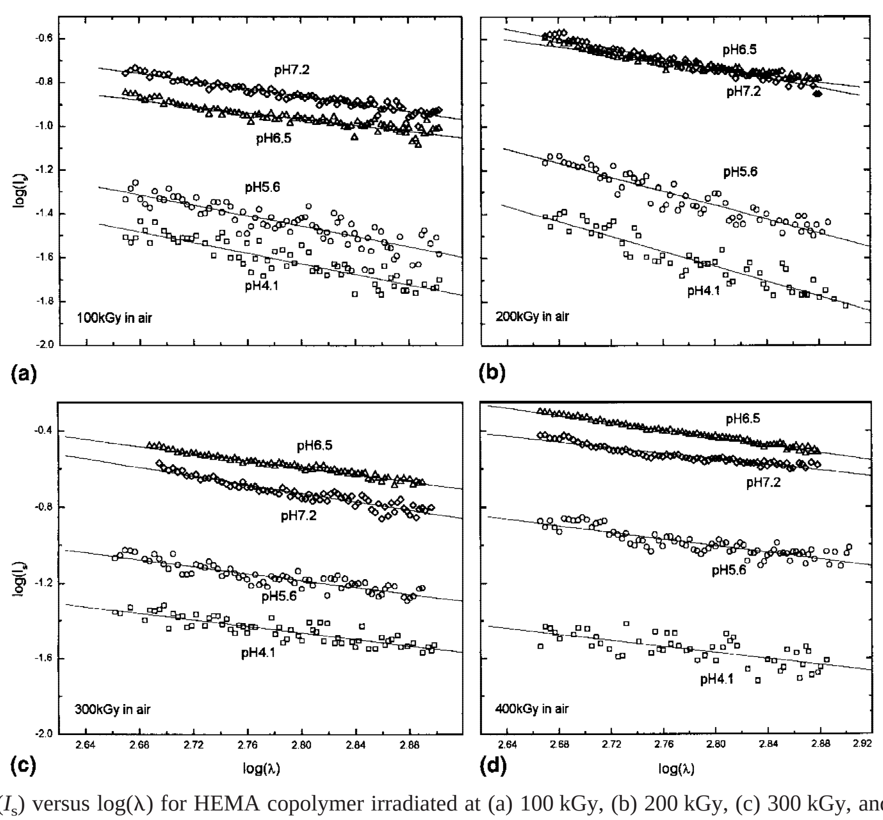


FIG. 8. The plot of $\log(I_s)$ versus $\log(\lambda)$ for HEMA copolymer irradiated at (a) 100 kGy, (b) 200 kGy, (c) 300 kGy, and (d) 400 kGy in air and then treated with buffer of various pH value where I_s and λ are scattering intensity and wavelength, respectively.

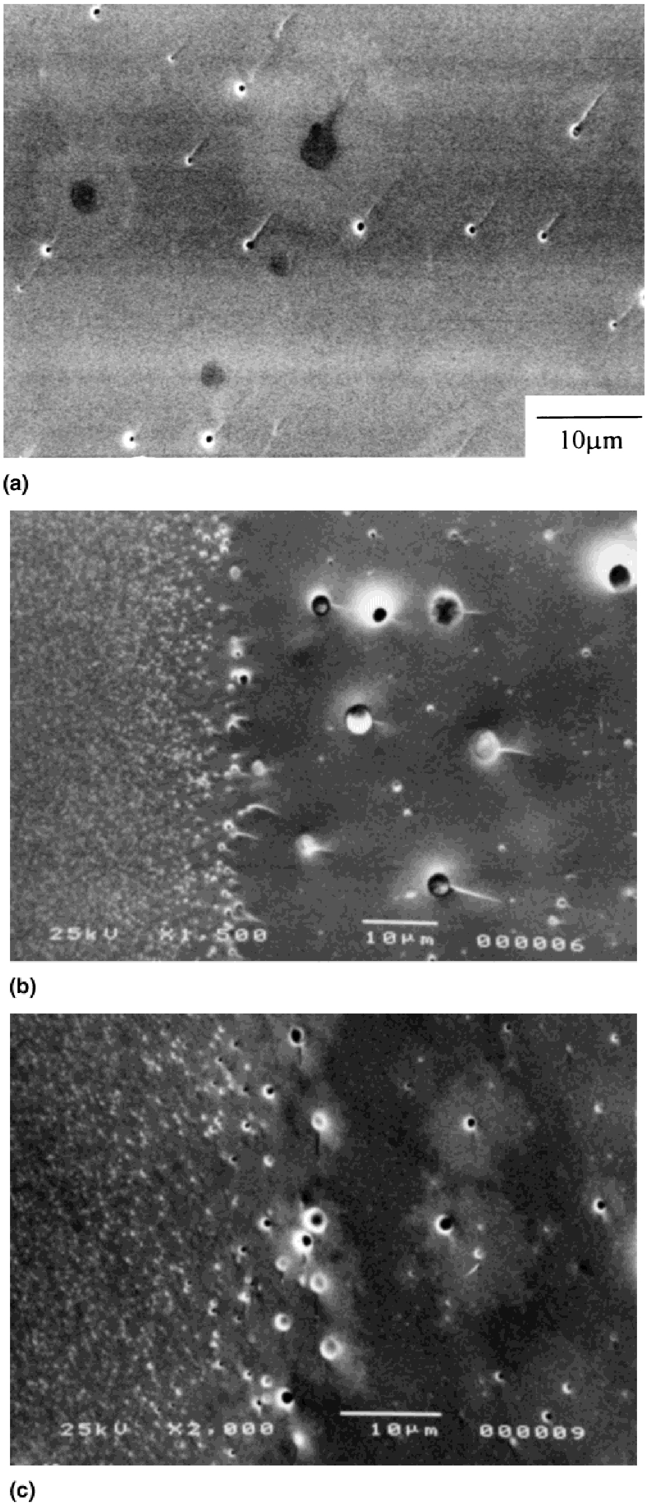


FIG. 9. The cross section of HEMA copolymer irradiated at 400 kGy in air and treated with buffer of (a) pH 5.6, (b) pH 6.5, and (c) pH 7.2.

(Table II) are considered. It can be seen from Tables II and V that the span of the hole increases with increasing *n* for pH 4.1–6.5. While the spans of holes are close to each other, the value of *n* increases with increasing diameter of holes, if the specimens irradiated with 200 kGy and 300 kGy in vacuum and treated with the pH 6.5 and 7.2 of buffer are considered.

IV. CONCLUSIONS

The transmittance of specimen was reduced by the buffer treatment due to the scattering of holes induced by swelling. The HEMA is subject to a greater equilibrium swelling ratio and hence lower transmittance after irradiation. The changes in swelling ratio and transmittance were greater when the material was irradiated in air than in vacuum. The cut-off wavelength of irradiated specimen exhibits a bathochromic shift after buffer treatment due to the creation of color centers, for example, carboxyl groups. The cut-off wavelength of the specimen irradiated in air shifted more than that of the specimen irradiated in vacuum. The scattering intensity satisfied the formula of $I_s \propto \lambda^{-n}$ where $n = .35$ to 1 and λ was the wavelength. The value of *n* depended on the span and diameter of hole. The characteristic parameters of holes were influenced by the pH value of buffer, dose and irradiation atmosphere. The span of hole had a maximum at pH 6.5 for the irradiated specimen and at pH 7.2 for the nonirradiated specimen, respectively. The irradiation treatment influenced the pH effect on the morphology of holes. The cross section of the specimens irradiated in air at 400 kGy was divided into two layers. The holes were small and dense in the inner layer, and large and scarce in the outer layer.

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