

Hardness of Irradiated Hydroxyethyl Methacrylate Copolymer at Elevated Temperatures

K. P. Lu,¹ Y. K. Fu,² Sanboh Lee¹

¹Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan

²Institute of Nuclear Energy Research, Lungtan, Taoyuan, Taiwan

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ABSTRACT: The hardness of irradiated hydroxyethyl methacrylate (HEMA) copolymer at elevated temperatures was measured using a microhardness tester. The hardness increases with annealing time, and is attributed to the defects present in the molecular chains. The defects that control the hardness are related to the entanglement of polymer chain and follow a first order kinetics process. The relaxation time satisfies the Arrhenius equation, with constant activation energy of 25 kJ/mol independent of

the irradiation dose. The results were compared with those of PMMA and LiF single crystals reported in the literature. The present findings are useful in the study of soft contact lens, kidney dialysis system, drug delivery system, and artificial liver support system. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 657–661, 2009

Key words: hydroxyethyl methacrylate; gamma ray; hardness kinetics

INTRODUCTION

The 2-Hydroxyethyl methacrylate (HEMA) copolymer and related hydrogels are considered as biomaterials, including the soft contact lens, kidney dialysis system, drug delivery system, and artificial liver support system.^{1–4} The presence of a hydroxyl group and carbonyl group in HEMA permits water uptake similar to the case of living tissue. The hydrogel is inactive to normal biological process and resistive to degradation. Many studies were focused on water uptake including equilibrium swelling^{5,6} and the kinetics of water transport.⁷ In addition to water uptake, the mechanical properties are also very important for the HEMA copolymer when used in making the soft contact lens.

When the polymeric materials are exposed to gamma-ray irradiation, the absorption leads to the production of free radicals or ionic species⁸ and scission or crosslinking in side chain and/or the main chain.⁹ These events can induce significant changes in the optical and mechanical properties of the polymeric material.^{10–17} In the early years, many researchers considered that when the substance was subjected to gamma-ray irradiation, its hardness was related to color centers. Nadeau and Johnston¹⁸

found that for a given concentration of electron excess centers, the irradiated KCl single crystals became harder by a factor of ten than the additive colored ones. Nadeau¹⁹ reported that the flow stress of KCl single crystal is proportional to $n^{1/2}$ where n is the F-center concentration. Lin et al.²⁰ studied optical transmission and hardness of irradiated LiF single crystals at high temperatures. However, the mechanism of change of transmittance and hardness of polymeric materials is different from those of ionic crystals. Lu et al. studied the effect of isothermal annealing on the transmittance²¹ and hardness²² of irradiated PMMA. Lu et al.²³ later reported that the transmittance of irradiated HEMA copolymer decreased with increasing annealing time, a trend opposite to the case of irradiated PMMA. This prompted us to investigate the evolution of hardness of irradiated HEMA copolymer at elevated temperatures. In analogy to color centers for transmittance, we propose here a defect mechanism that would control the hardness variations. A first order kinetic process model is presented to analyze the experimental data. The results obtained are compared with those from the earlier studies on irradiation effects.

EXPERIMENTAL

The poly (HEMA) copolymer was obtained from Canadian Contact Lens Laboratories, Montreal, Quebec, Canada. The chemical composition of HEMA copolymer consists of HEMA, ethylene glycol dimethacrylate (EGDMA), and methacrylic acid (MAA). The

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Correspondence to: S. Lee (sblee@mx.nthu.edu.tw).

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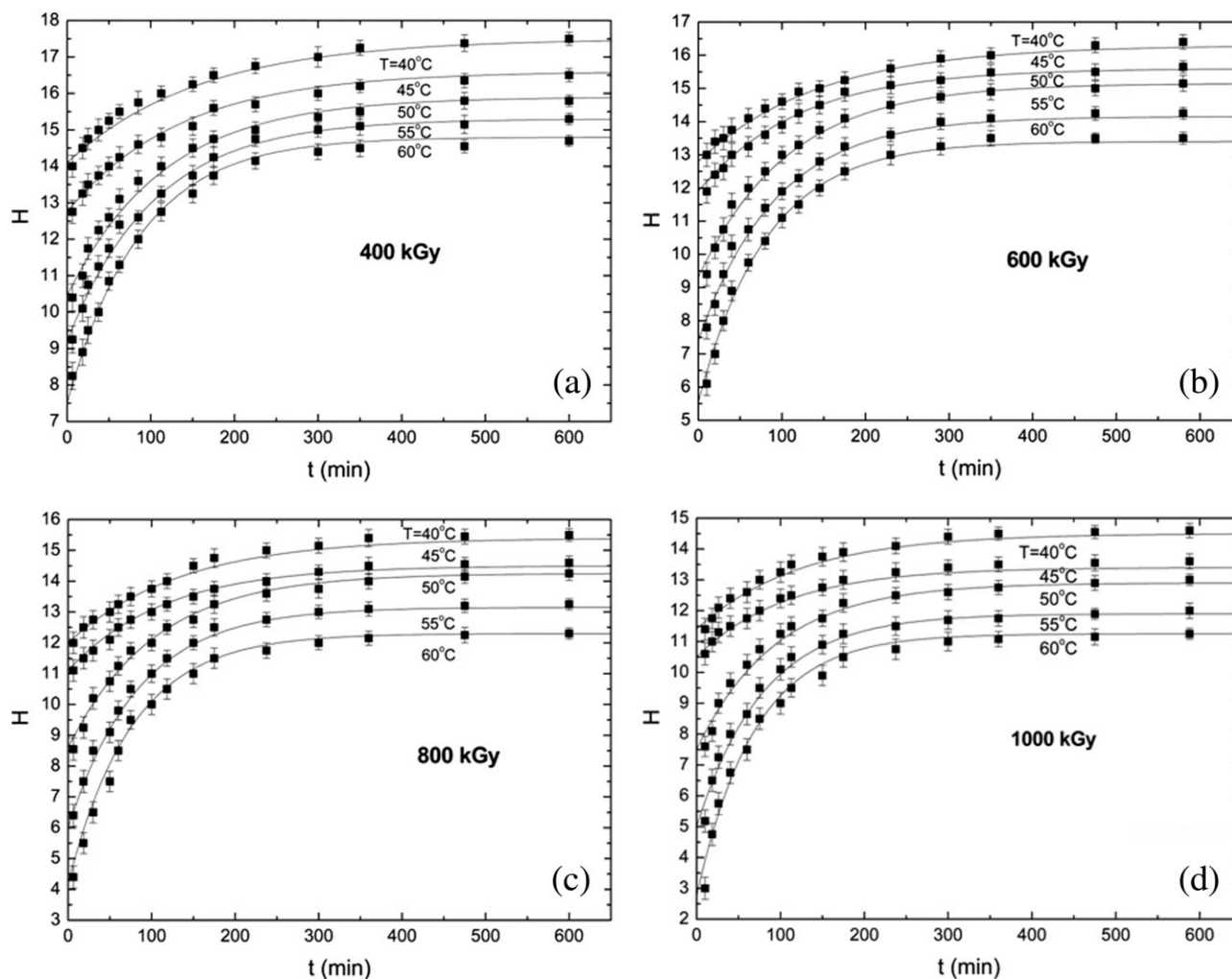


Figure 1 Hardness of irradiated HEMA copolymer as a function of time: (a) 400 kGy; (b) 600 kGy; (c) 800 kGy; and (d) 1000 kGy.

specimens were cut from a sheet to size of 7 mm radius and 4 mm thickness, and then ground with 600, 800, and 1200 grit Carbitet paper and polished with 1.0, 0.3, and 0.05 μm alumina slurries. They were annealed in vacuum at 60°C for 2 days and furnace cooled to room temperature.

The specimens were sealed in glass tubes in air. They were irradiated at room temperature by a gamma-ray source at the Radioisotope Division of National Tsing Hua University with a dose rate 20 kGy/h. The doses were controlled at 400, 600, 800, and 1000 kGy.

The irradiated HEMA specimens were placed in vacuum at room temperature and then moved into the thermostatted chamber maintained at temperature 40, 45, 50, 55, and 60°C, respectively. The chamber was kept at low humidity of RH 30%. Note that the glass transition temperature of HEMA is 62°C. The hardness study was conducted using a microhardness tester (Akashi MVK) with a load of 100 g and dwell period of 5 s. The specimens were

removed from the thermostatted and humidity-controlled chamber, tested at room temperature (RH = 60–70%) in 30 s, and immediately placed back to the chamber for another period. The process continued until the hardness reaches a constant value.

RESULTS AND DISCUSSION

Polymers change their chemical and physical structures after the gamma-ray irradiation and as a result their mechanical properties are altered. Both chemical and physical structures are unstable and are possibly annealed out or changed to stable structures. The HEMA is softer at higher temperature and humidity. Shultz²⁴ observed that appreciable bubbles occurred when the polymer was heated to or above its glass transition temperature during and/or after irradiation. To prevent the bubbling generation, the annealing temperatures in the present study are kept in the range of 40–60°C, which is below the glass transition point. The full squares in Figure 1(a–d)

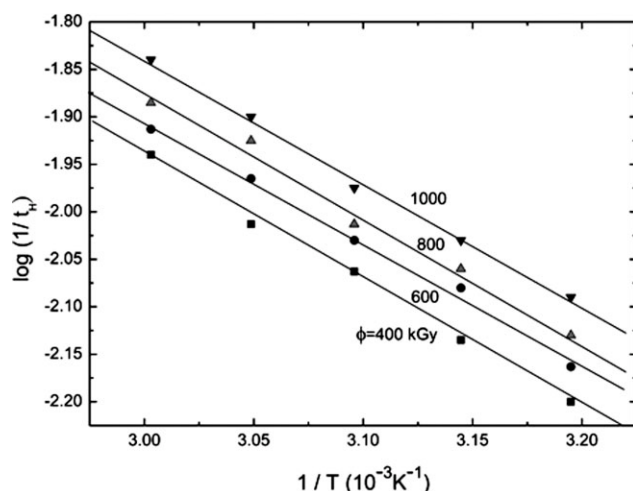


Figure 2 Arrhenius plot of reciprocal of relaxation time versus reciprocal of temperature.

are the experimental hardness data for the irradiated HEMA with different doses at annealing time t . It is seen that the hardness increases with increasing annealing time. The data can be explained using the defect kinetics. The hardness of irradiated HEMA is assumed to be proportional to the concentration, n , of defects that control the hardness. That is,

$$H = H_{\infty} \pm \alpha n \quad (1)$$

where H and H_{∞} are the hardness at time t and time infinity, respectively. Note that α is a proportional constant. The sign before α in eq. (1) depends on the material. For example, the PMMA²² and LiF single crystals²⁰ have negative and positive signs for defect creation and destruction, respectively. If the sign is positive, the defects enhance the hardness of material. Otherwise, they make the material soften. These defects are produced by the high energy particle irradiation and follow a first order annihilation process:

$$dn/dt = -n/\tau \quad (2)$$

where τ is the relaxation time of hardness; eq. (2) with eq. (1) can be solved to yield:

$$H = H_{\infty} + (H_0 - H_{\infty}) \exp(-t/\tau) \quad (3)$$

where $H_0 = H_{\infty} \pm \alpha n_0$ is the hardness at the initial time and n_0 is the concentration of defects at the initial time.

The solid lines in Figure 1(a–d) are obtained using eq. (3) to fit the experimental data with the relaxation time and final hardness shown in Figures 2 and 3, respectively. The experimental data are in good agreement with the theoretical prediction. It can be seen from Figure 2 that the reciprocal of relaxation time satisfies the Arrhenius equation. The associated activation energy is 25 kJ/mol and is the same for

all irradiation doses. This implies that the dose of gamma rays does not affect the energy barrier for the annihilation of defects that control the hardness. However, the pre-exponent factor of $1/\tau$ increases with increasing dose. Note that the color centers responsible for the transmittance loss in irradiated HEMA copolymers follow a first order annihilation process and its activation energy is 17.37 kJ/mol regardless of the radiation dose.²³ For polymeric materials, the color center arises from free radicals and unsaturated double bonds^{10–12} whereas the hardness is contributed by both the length and crosslink of the polymer chains. In other words, the former and the latter are respectively related to the changes in the chemical and the physical structures. Although both the defects for controlling the hardness and transmittance have the same order kinetic process and are generated by the same gamma-ray irradiation, their annealing mechanisms are different.

The evolution of hardness of irradiated PMMA at temperatures in the range of 40–80°C was studied by Lu et al.²² The hardness of irradiated PMMA increases with increasing annealing time, a result similar to that for irradiated HEMA. This is because that the polymeric chains of both PMMA and HEMA are rearranged to entangle to each other. They found that the defects that control the hardness follow a first order kinetic process. The activation energies are 45.1, 41.5, 38.2, and 36.8 kJ/mol at the doses 400, 600, 800, and 1000 kGy, respectively. Comparing both activation energies of hardness for HEMA and PMMA in the same range of dosage, the effect of gamma ray irradiation on evolution of hardness is more significant for PMMA than for HEMA. Lin et al.²⁰ investigated the recovery of hardness of

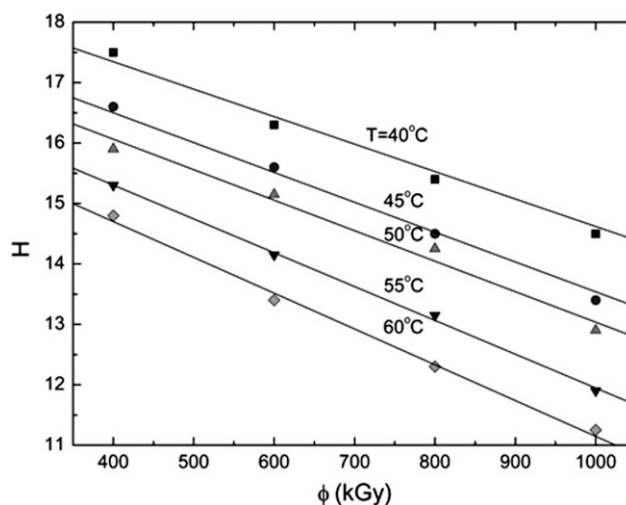


Figure 3 The hardness of HEMA copolymer annealed at long times as a function of irradiation dosage at different temperatures.

irradiated LiF single crystals at temperatures 400–520°C. Some Li and F ions are displaced to unstable positions during gamma ray irradiation and the hardness increases. These unstable atoms in the LiF single crystal will return back to the equilibrium positions at elevated temperature and decrease the hardness with increasing time. However, in polymeric materials a group of atoms are bounded in the chain. An atom affected by the other atoms in the same chain is more pronounced than that in the other chains. The rearrangement of the molecular chain, unlike the atomic displacement in crystal lattice, commonly takes place in polymeric materials at elevated temperature. This is because that the polymeric materials are stabilized by van der Waal bonding, whereas the ionic crystals by ionic bonding. Therefore, the mechanism of hardness applied to LiF single crystal must be excluded when we study the hardness of polymeric materials.

The hardness of polymeric materials arises from both length and crosslinking of polymer chains. The longer (or the more the entanglement of) the polymer chain is, the stronger the polymer. When a polymer is exposed to gamma ray, the polymer chains undergo scission or crosslinking. Thus the polymer chains are unstable during and after gamma ray irradiation. Lin et al.²⁵ studied annihilation of radicals in irradiated HEMA copolymer at elevated temperatures using EPR spectra. They observed three radicals Ra, Rb, and Rc. Radical Ra was identified as methyl radical and/or methylene radical with two similar hyperfine coupling constants. Radical Rb was a methylene radical produced by main-chain scission. Radical Rc was the free radical without hyperfine coupled to any proton. These radicals followed a second order kinetics and were spent ca. 35 h to be annealed out. The annihilation of radicals increased the length of polymer chain. However, in the present case, the hardness shown in Figure 1 reaches the steady state within 10 h and the defects present follow a first order kinetics. On the basis of the above argument, the annihilation of radicals is not dominant in the evolution of hardness of the HEMA specimen at elevated temperatures. The mobility of polymer chain increases with increasing temperature. The unstable polymer chains are easy to rotate and rejoin or cross link at elevated temperatures so that the length or crosslink of the polymer chain increases with time until equilibrium is reached. For HEMA copolymers, the entanglement of polymer chains is more important than the length increment of polymer chain because of the annihilation of radicals. Therefore, the hardness of irradiated HEMA increases exponentially with annealing time and is saturated at time infinity. In addition to gamma ray irradiation, thermal annealing also plays an important role on crosslink of polymer chains.

TABLE I
Constants a and b in eq. (4) for Hardness in Irradiated HEMA after Annealing

Temperature (°C)	a (10^{-3} GPa/kGy)	b (GPa)
40	3.56	15.20
45	3.70	14.14
50	4.55	12.10
55	6.77	11.68
60	7.90	10.53

However, the entanglement of polymer chain is not understood at the present time. This issue needs to be studied.

The hardness values of the irradiated HEMA after annealing are shown in Figure 3. It can be seen that the hardness decreases with increasing temperature and dose. This is because a lower temperature would give the polymer chains a greater rigidity and consequently a higher hardness. According to Chou et al.,¹³ scission dominates at high doses of irradiation and results in a shorter length of polymer chains in HEMA copolymers and a shorter chain reduces the hardness. The result is different from that of hardness variation in the ultrahigh molecular weight polyethylene where the hardness increases with increasing dose.¹⁴ In the latter case, the crosslink dominates during the gamma ray irradiation and it makes the ultrahigh molecular weight polyethylene harden. The experimental hardness data shown in Figure 3 can be fitted with a linear equation:

$$H_{\infty} = b - a\Phi \quad (4)$$

where H_{∞} is the hardness of the material after annealed at time infinity and Φ is the irradiation dosage. Parameters a and b are the rate of change in hardness per dose and the hardness of non-irradiated specimen, respectively. The solid lines in Figure 3 are obtained by data fitting using eq. (4) where the values of a and b at different temperatures are listed in Table I. It is found that a increases with increasing temperature, but b has an opposite trend to a . Because the rigidity of the polymer chain increases with decreasing temperature, the hardness of non-irradiated HEMA increases with decreasing temperature.

SUMMARY AND CONCLUSIONS

HEMA copolymers are biomaterials used in soft contact lens, drug delivery system, artificial liver system, and kidney dialysis system.^{1–4} The understanding of mechanical properties of HEMA is therefore important to improve and expand the above applications. The hardness of the HEMA copolymer after gamma-ray irradiation was measured at temperatures 40–60°C. The hardness increased

exponentially with increasing time. The result is due to the presence of defects that harden the polymer. These defects are related to the entanglement of polymer chain and thus enhance the hardness of the polymer. The experimental data are in good agreement with the theoretical model based on the first order kinetic process of the defects. The reciprocal of relaxation time satisfies the Arrhenius equation with activation energy of 25 kJ/mol for all irradiation doses. Although the variation in transmittance for HEMA copolymer at elevated temperatures has an opposite trend to that for PMMA, the behavior of hardness of HEMA copolymer at elevated temperatures is similar to that for PMMA. The activation energy of defect kinetics for hardness of HEMA copolymer is the same for all irradiation doses, whereas in the case of PMMA it varies with the dose.

NOMENCLATURE

a, b	Parameters
H	Hardness at annealing time t
H_{∞}	Hardness at annealing time infinity
H_0	Hardness at the beginning of annealing
n	Number of defects to control the hardness
n_0	Number of defects to control the hardness at the beginning of annealing
dn/dt	The differentiation of n with respect to time
α	Constant
τ	Relaxation time

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