Hardness of irradiated poly(methyl methacrylate) at elevated temperatures ⊘

K.-P. Lu; Sanboh Lee; Cheu Pyeng Cheng

Check for updates

View Online

Export Citation

23 August 2024 09:52:29

Hardness of irradiated poly(methyl methacrylate) at elevated temperatures

K.-P. Lu and Sanboh Lee[a)]
Department of Materials Science, National Tsing Hua University, Hsinchu, Taiwan

Cheu Pyeng Cheng
Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan

The decrease in hardness induced by gamma irradiation in poly(methyl methacrylate) (PMMA) has been investigated. The hardness is assumed to decrease linearly with the concentration of radiation-induced defects. Annealing at high temperatures induces defect annihilation as tracked by an increase in hardness. The annihilation follows first-order kinetics during isothermal annealing. The dependence of hardness on the reciprocal of the time constant satisfies the Arrhenius equation, and the corresponding activation energy of the kinetic process decreases with increasing dose. The hardness of postannealed PMMA decreases linearly with increasing dose. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1388573]

I. INTRODUCTION

When polymeric materials are exposed to high-energy particles, the backbones undergo scission or cross linking.[1–4] Cross linking leads to an increase in molecular weight while scission decreases molecular weight. Polyethylene, polypropylene, poly(methyl acrylate), polystyrene, etc., belong to the former, and polyisobutylene, poly(methyl methacrylate) (PMMA), poly(vinyldine chloride), polycarbonate, etc., belong to the latter. Fujisawa *et al.*[5] reported that the hardness of ultrahigh molecular weight polyethylene increases with gamma radiation dose and wear is improved by gamma-ray irradiation. Wallace *et al.*[6] studied the transmittance of irradiated polystyrene as a function of time at elevated temperatures. Poly(methyl methacrylate) is one of the most extensively studied among the above polymeric materials. Experiments have documented the effect of copolymerization and plasticization on transient color centers.[7–9] The oxygen permeability of PMMA was related to the annealing rate of color centers due to oxygen quenching.[9] UV/visible spectroscopy, differential scanning calorimetry, dynamic mechanical analysis, and gel permeation chromatography were used to characterize the effect of ionizing radiation on the properties of PMMA and fluorinted derivatives.[10,11]

Wall and Brown[12] monitored intrinsic viscosity and calculated the number of scissions events in PMMA per unit dose of radiation. Ouano *et al.*[13] analyzed the molecular weight distribution in PMMA arising from gamma irradiation by the gel-permeation chromatography technique. Knappe and Yamamoto[14] studied the effect of dose on color center formation. Todd[15] and David, Fuld, and Geuskins[16] tested the volatile products in PMMA arising from gamma radiation. Lin and Lee[17] studied the optical transmission of irradiated PMMA. Lu, Lee, and Cheng[18] analyzed the recovery of the optical transmittance in irradiated PMMA at elevated temperatures.

Lin and Lee[17] and Lu, Lee, and Cheng[18] studied the thermal annealing of the transmission of irradiated PMMA qualitatively and quantitatively. Lin[19] studied the electron paramagnetic resonance (EPR) spectra of irradiated PMMA at elevated temperatures.

Our laboratory is currently interpreting radiation effects in PMMA in terms of a defect model. This article focuses on relating the microhardness values to the defect concentrations induced by radiation of the polymer matrix. The effect of thermal annealing on the hardness of irradiated PMMA is characterized. The overall goal of this research is to clarify the mechanism behind the kinetic processes responsible for changes in microhardness.

II. EXPERIMENT

Poly(methyl methacrylate), with an inherent viscosity 0.237 dl/g, was obtained from Du Pont, Delaware, in the form of a 6.35-mm-thick Lucite L-type cast acrylic sheet. Specimens of $15\times10\times6.35$ mm were cut from the acrylic sheet. They were ground with 600, 800, and 1200 grit emery papers and then polished with 1.0, 0.3, and 0.05 μm alumina slurries. The specimens were annealed in air for 24 hr at 93 °C and then were slow cooled to room temperature.

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

The irradiated PMMA samples were annealed below the glass transition temperature at 40, 50, 60, 70, and 80 °C. The microhardness study was conducted using an Akashi MVK-E microhardness tester with a loading of 100 g and a dwell period of 5 s. The specimens were removed from the furnace, tested at room temperature within 30 s, and then immediately returned to the furnace for the next measurement.

The glass transition temperature measurement was conducted with a Seiko II differential scanning calorimeter. Cubes irradiated, approximately 10 mg, were enclosed in a
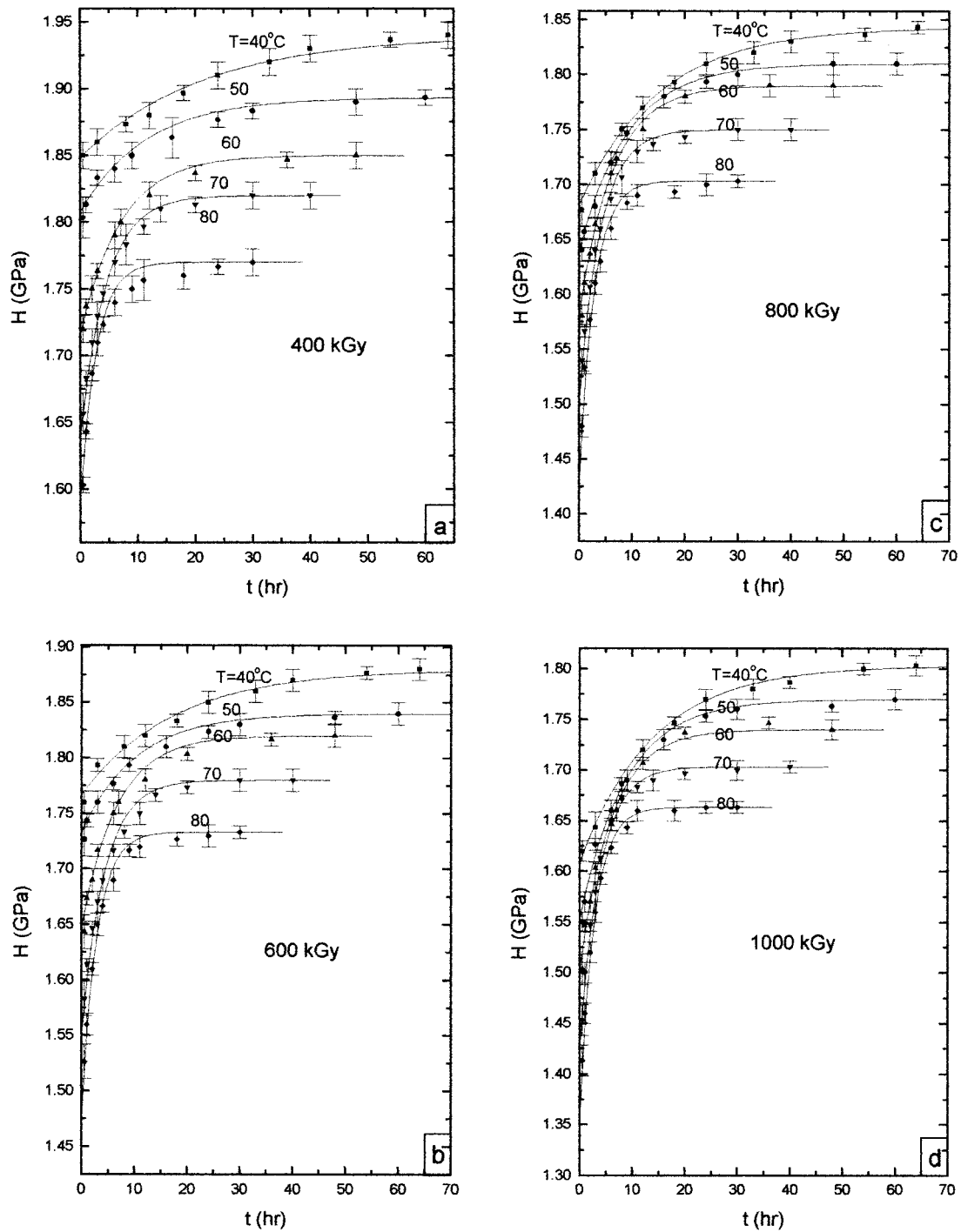
FIG. 1. Hardness of irradiated PMMA as a function of annealing time: (a) $\Phi = 400$ kGy, (b) $\Phi = 600$ kGy, (c) $\Phi = 800$ kGy, and (d) $\Phi = 1000$ kGy, at temperatures of 40, 50, 60, 70, and 80 °C.

regular aluminum pan and moved heated from room temperature to 120 °C at a heating rate of 5 °C/min under a nitrogen flow of 40 ml/min. Changes in heat flow versus temperature were recorded.

III. RESULTS AND DISCUSSION

The evolution of hardness of irradiated PMMA annealed at $T = 40$, 50, 60, 70, and 80 °C irradiated to various doses is plotted in Figs. 1(a)–1(d). The hardness increases with annealing time for a given temperature and dose. The following

model is used to explain the experimental data in Fig. 1. The hardness is assumed to decrease linearly with increasing concentration of defects. That is,

$$H = H_\infty - \alpha n, \qquad (1)$$

where H, H_∞, and n are the hardness at time t, hardness at time infinity, and concentration of defects that control hardness, respectively. α is constant. Note that H and n are func-

TABLE I. Time constant τ(h) of the hardness annealing process of irradiated PMMA.

	400 kGy	600 kGy	800 kGy	1000 kGy
40 °C	21.25	17.57	14.97	13.84
50 °C	11.45	10.23	9.13	8.73
60 °C	7.12	6.70	6.39	6.05
70 °C	4.53	4.32	4.02	3.89
80 °C	2.98	2.88	2.84	2.78

TABLE II. Glass transition temperature T_g of postannealed PMMA and activation energy Q of the hardness annealing process.

Φ (kGy)	400	600	800	1000
T_g (°C)	94.1	91.1	87.1	82.4
Q (kJ/mol)	45.1	41.5	38.2	36.8

tions of time. The concentration of defects controlling hardness during isothermal annealing is assumed to follow the first-order kinetic process,

$$dn/dt = -n/\tau, \tag{2}$$

where τ is a time constant. Solving Eq. (2) with Eq. (1), one obtains the hardness at time t as

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

where $H_0(=H_\infty - \alpha n_0)$ is the hardness of PMMA at $t=0$. Note that n_0 is the concentration of defects controlling hardness at $t=0$ and n is zero at time infinity.

Equation (3) is in excellent agreement with the experimental data shown in Figs. 1(a)–1(d). The corresponding time constant τ is tabulated in Table I. The reciprocal of time constant $1/\tau$ satisfies the Arrhenius equation, as shown in Fig. 2,

$$\frac{1}{\tau} = C \exp(-Q/RT), \tag{4}$$
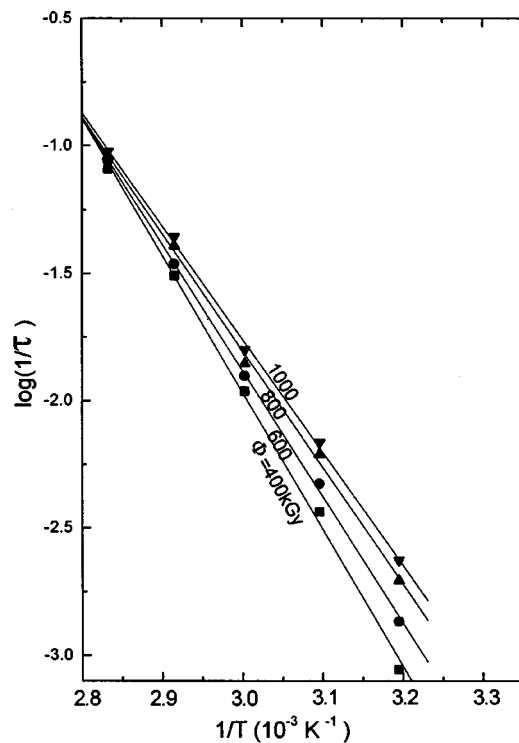
FIG. 2. Arrhenius plot of rate constant $1/\tau(\mathrm{h}^{-1})$ vs $1/T(\mathrm{K}^{-1})$ for various doses $\Phi = 400$, 600, 800, and 1000 kGy.

where C and Q are the preexponent factor and activation energy, respectively, and R and T are the gas constant and temperature in kelvin. From Fig. 2, the activation energies for different doses are obtained and listed in Table II. It is found that the activation energy decreases with increasing dose. This kinetics is different from that determined for optical transmittance annealing of irradiated PMMA.[18] The recovery of transmittance in PMMA during isothermal annealing follows a second-order kinetic process for the annihilation of transient color centers. The activation energies for color center annealing are 51.15, 48.91, 45.69, and 44.27 kJ/mol for $\Phi = 400$, 600, 800, and 1000 kGy, respectively. This trend in activation energies with irradiation dose is the same as that for hardness recovery. The kinetic behavior for hardness recovery is different from that of free-radical annealing as detected in the EPR spectra of irradiated PMMA.[19] EPR spectra at elevated temperatures consist of three kinds of radicals. EPR spectra are more complicated than both optical transmittance and hardness. The time constant for the disappearance of each radical is much shorter than that determined from hardness studies. It is interesting to find that although hardness defects, color centers, and radicals of PMMA are generated by gamma irradiation, their annihilation rates at elevated temperatures are different. Therefore, the mechanism for the kinetic process of hardness recovery is different from those determined via optical transmittance and EPR studies. Unfortunately, the complete understanding of the nature of the hardness defects, color centers, and radicals are unknown. The effect of these parameters will be studied in the near future.

The evolution of hardness in irradiated LiF single crystals at temperatures from 400 to 520 °C was studied by Lin, Tsai, and Lee.[20] The hardness of LiF increases with increasing dose in the range 100–1000 kGy and decreases with increasing annealing times at elevated temperatures. These trends are opposite to those of the hardness of irradiated PMMA. The hardness annealing data of LiF single crystals depends on the irradiation dose. Nevertheless, the hardness is always proportional to the concentration of the defect controlling the hardness. For a 100 kGy dose, the hardness accompanying annealing follows a first-order kinetic process, similar to that in irradiated PMMA. For doses greater than or equal to 250 kGy, the kinetics follows a biexponential behavior. Chiang, Hu, and Lee[21] analyzed the transmittance of irradiated polystyrene at elevated temperatures and found that the color center annihilation follows a second-order kinetic process for vacuum annealing and a first-order kinetic process for air annealing. The activation energy is 54.29 kJ/mol for the former and 56.62 kJ/mol for the latter.

The hardness of irradiated PMMA after annealing is a function of dose Φ shown in Fig. 3. According to Fig. 3, the
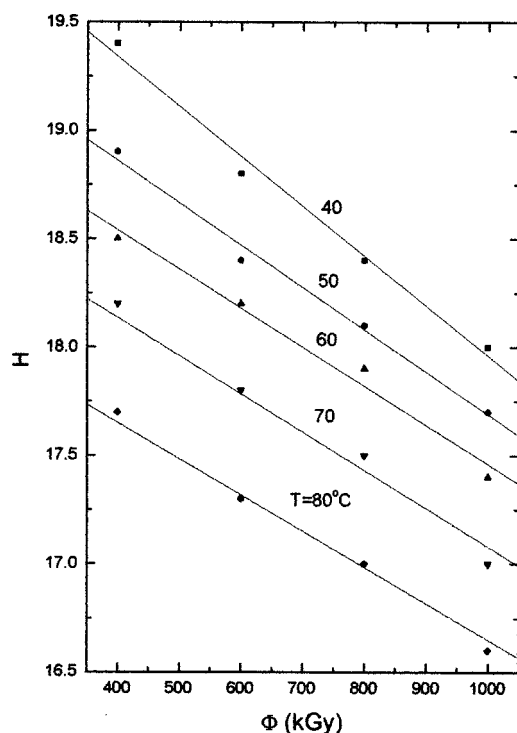
FIG. 3. Hardness of irradiated PMMA after annealing, as a function of dose.

hardness of postannealed PMMA decreases with increasing temperature for a given dose. The hardness decreases with increasing dose, which is opposite to the hardness of ultra-high molecular weight polyethylene, which increases with increasing dose.[5] The former and the latter are likely due to the effect of gamma irradiation on these two polymer materials; the former is chain scission and the latter is chain cross linking.

The experimental data for our PMMA study can be fitted with a straight line,

$$H_\infty = a\Phi + b, \tag{5}$$

where a and b are constant. The corresponding a and b are listed in Table III. The slope a (a is negative) decreases with increasing temperature. This implies that the effect of gamma irradiation on hardness is pronounced at high doses.

After complete annealing at elevated temperatures, the glass transition temperatures of gamma-irradiated PMMA with different doses are listed in Table II. Note that the glass transition temperature of nonirradiated PMMA is 104 °C.[22] The glass transition temperature of PMMA decreases with increasing dose. Thus, at the same annealing temperature, the specimen with a high dose is closer to the glass transition

TABLE III. Constants a and b in Eq. (5) for hardness of postannealed PMMA.

Temperature (°C)	a (10^{-3} GPa/kGy)	b (GPa)
40	−2.30	20.26
50	−1.95	19.64
60	−1.80	19.26
70	−1.76	18.99
80	−1.67	18.41

temperature than that with a low dose. Chemical aging such as gamma ray-induced degradation is different from physical aging. The former and the latter involve the chemical reaction and the arrangement of molecular chains, respectively. Physical aging is defined as a physical process involving microstructural rearrangement when the polymer is heated at a temperature close to (but not at) the glass transition temperature. At this temperature, the process of chain rearrangement is accelerated. Narin et al.[23] found that the hardness of polycarbonate increases with increasing time during physical aging. Their hardness increases from 1.32 to 1.47 GPa for an annealing time of 240 h at 123 °C. The glass transition temperature of polycarbonate is 145 °C. The period of specimen heating in this study is shorter than that operated by Narin et al.,[23] but the recovery of hardness in this study is more pronounced than that reported by Narin et al.[23]

IV. SUMMARY

The isothermal annealing of irradiated PMMA has been investigated. The evolution of hardness immediately after irradiation was measured at temperatures of 40–80 °C. The hardness was assumed to be linearly dependent on the concentration of defects controlling hardness. The defect concentration controlling hardness follows a first-order annihilation process during annealing. The reciprocal of the corresponding time constant for the annealing process satisfies the Arrhenius equation and the activation energies for the process are 45.1, 41.5, 38.2, and 36.8 kJ/mol for $\Phi=400$, 600, 800, and 1000 kGy.

ACKNOWLEDGMENT

[1] R. Simha, Trans. NY Acad. Sci. **14**, 151 (1952).
[2] A. A. Miller, E. J. Lawton, and J. S. Balwit, J. Polym. Sci. **XIV**, 503 (1954).
[3] E. J. Lawton, H. M. Bueche, and J. S. Balwit, Nature (London) **172**, 76 (1953).
[4] S. Andjelic and R. E. Richard, Macromolecules **34**, 896 (2001).
[5] A. Fujisawa, S. Masuda, H. Oonishi, Y. Ikada, I. C. Clarke, and V. Good, Seitai Eairyo **16**, 29 (1998).
[6] M. B. Wallace, M. B. Sinclair, K. T. Gillen, and R. L. Clough, Radiat. Phys. Chem. **41**, 85 (1993).
[7] J. P. Harmon and J. Gaynor, J. Polym. Sci., Part B: Polym. Phys. **31**, 235 (1993).
[8] J. Gaynor, V. Fischer, J. K. Walker, and J. P. Harmon, Nucl. Instrum. Methods Phys. Res. B **69**, 332 (1992).
[9] J. P. Harmon, J. F. Gaynor, and A. G. Taylor, Radiat. Phys. Chem. **41**, 153 (1993).
[10] J. Gaynor, G. Schueneman, P. Schuman, and J. P. Harmon, J. Appl. Polym. Sci. **50**, 1645 (1993).
[11] P. Bertolucci, E. Biagtan, E. P. Goldberg, P. Schuman, W. Schuman, and J. P. Harmon, Polym. Eng. Sci. **38**, 699 (1998).
[12] L. A. Wall and D. W. Brown, J. Phys. Chem. **61**, 129 (1957).
[13] A. C. Ouano, D. E. Johnson, B. Dawson, and L. A. Pederson, J. Polym. Sci., Polym. Chem. Ed. **14**, 701 (1976).
[14] W. Knappe and O. Yamamoto, Kolloid Z. Z. Polym. **240**, 775 (1970).
[15] A. J. Todd, J. Polym. Sci. **42**, 223 (1969).
[16] C. David, D. Fuld, and G. Geuskins, Makromol. Chem. **139**, 269 (1970).
[17] C. B. Lin and S. Lee, J. Appl. Polym. Sci. **44**, 2213 (1992).

[18] K. P. Lu, S. Lee, and C. P. Cheng, J. Appl. Phys. **88**, 5022 (2000).
[19] Y. S. Lin, Master thesis, National Tsing Hua University, Hsinchu, Taiwan (2000).
[20] H. Y. Lin, Y. Z. Tsai, and S. Lee, J. Mater. Res. **7**, 2833 (1992).
[21] I. J. Chiang, C. T. Hu, and S. Lee, Mater. Chem. Phys. **70**, 61 (2001).
[22] C. B. Lin, S. Lee, and K. S. Liu, Polym. Eng. Sci. **30**, 1399 (1990).
[23] K. M. Narin, R. L. Walters, G. P. Simon, and A. J. Hill, Mater. Forum **16**, 167 (1992).

23 August 2024 09:52:29