Mechanical Properties and Gradient Variations of Polymers Under Ultraviolet Radiation

Xue Feng Yao,[1] Dong Liang Liu,[1] Heisen Yang Yeh[2]

[1]*Department of Engineering Mechanics, Tsinghua University, 100084, Beijing, China*
[2]*Department of Mechanical and Aerospace Engineering, California State University, Long Beach, California 90840-8305*

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ABSTRACT: The photodegradable properties and characteristics of poly(methyl methacrylate) (PMMA) polymers were studied experimentally. Some important mechanical parameters under ultraviolet radiation were measured, such as the elastic modulus, Poisson's ratio, fracture strength, and stress–strain relation. Microscopic structural characteristics of photodegradable PMMA were analyzed with scanning electron microscopy. Also, a functionally graded material of PMMA was fabricated with a photodegradable method and characterized. These results were found to have an important role in evaluating the photodegradable properties of PMMA materials and in developing their engineering applications. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3253–3258, 2007

Key words: degradation; mechanical properties; microstructure

INTRODUCTION

Poly(methyl methacrylate) (PMMA) is an important macromolecular polymer material that is widely used in many engineering structures. Photodegradability is an important characteristic of this polymer material, and it can cause crosslinking and average molecular weight degradation (chain scission).[1,2] This kind of chemical effect results in changes in the physical and mechanical properties, such as the elasticity disappearing and the strength decreasing.

Nowadays, studies of the photodegradable properties of PMMA are mainly concentrated on the mechanisms of crosslinking and chain scission and on some basic physical properties. Okudaira et al.[3] studied the radiation damage of PMMA quantitatively, using ultraviolet (UV) photoelectron spectroscopy, which indicated that the main photodegradation could be ascribed to the abstraction of ester groups and the formation of double bonds in the polymer chain. Çaykara and Güven[4] studied the photodegradation of PMMA and vinyltriethoxysilane/methyl methacrylate copolymer films by UV irradiation (λ = 259 nm) and observed that UV irradiation caused changes in the mechanical properties of the PMMA and copolymers. El Shafee[5] studied the effects of photodegradation on β relaxation in PMMA within the temperature range of 60–90°C and within a 20–10^5-Hz frequency band with UV radiation, and he found that increasing the time of UV exposure increased the magnitude of the relaxation and displaced the peak toward a lower temperature, and the apparent activation energy decreased with irradiation. Mansour[6] determined the photostability and optical parameters of styrene/PMMA copolymer films under UV radiation, including the thermal stability, the optical absorption and band gap, the optical transmission and reflection data, the refractive index, and the extinction coefficient. Torikai and Hasegawa[7] studied the wavelength sensitivity of the photodegradation of PMMA in the presence of β-carotene by optical absorption and gel permeation chromatography measurements. Shimoyama et al.[8] studied the photodegradation of PMMA by the use of near-infrared light-fiber spectroscopy. Mikheev and Ershov[9] studied the main route of the photolysis of PMMA, which involves the abstraction of side ester groups and the simultaneous formation of unsaturated bonds. To the best of our knowledge, only a few research works mention the mechanical properties of photodegradable polymers. Abanto-Bueno and Lambros[10] measured the material traction/separation relation for a poly(ethylene carbon monoxide) copolymer subjected to UV irradiation, which exhibited a ductile-to-brittle transition and underwent a change in the failure mechanism from shear yielding to crazing; also, full-field measurements of the in-

Correspondence to: X. F. Yao (yxf@mail.tsinghua.edu.cn).
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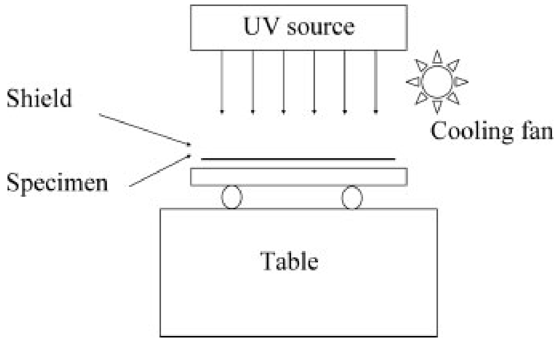


Figure 1 UV irradiation of homogeneous PMMA.

plane deformation around the growing crack tip were performed with the optical technique of digital image correlation. Lambros et al.[11] described the design, fabrication, and testing of model functionally graded materials (FGMs) with poly(ethylene-*co*-carbon monoxide), using UV irradiation; they exhibited a Young's modulus that varied from about 160 to 250 MPa and a strain to failure that varied from about 900 to 10% over the width in a 150-mm-wide specimen with continuously and discretely varying mechanical properties. In fact, the variations of the physical and mechanical properties in a polymer due to photodegradation have gradation characteristics because of unequal UV irradiation. Therefore, the study of the mechanical characteristics of graded polymers plays an important role in understanding the photodegradable properties of polymers and designing advanced polymers.[12–15]

In this work, photodegradable properties of a PMMA material were studied under UV irradiation. Some typical mechanical properties, such as the stress–strain relation, fracture load, and elastic constant, were obtained after different irradiation times. The evolution of microscopic structures in PMMA due to the effects of photodegradation was observed. A typical graded polymer material was fabricated through the control of the photodegradation time.

UV IRRADIATION OF HOMOGENEOUS PMMA

A UV-irradiation source (Beijing Optical Instrument Ltd., China) at the selected wavelength of 360 nm was used. The UV intensity was 500 W. An aluminum chamber was made to shield the operator from harmful UV rays. A cooling fan was used to maintain the chamber temperature at about 33°C, which was below the melting point of the PMMA. This experimental configuration is shown in Figure 1.

PMMA strips, nominally 100 mm long, 10 mm wide, and 1 mm thick, were placed on a piece of glass located about 10 mm below the UV source. They were irradiated for various times up to a maximum of 140 h (i.e., 20, 40, 60, 80, 100, 120, and 140 h). The mechanical properties of the homogeneously irradiated PMMA strips were characterized with a uniaxial tension test machine (Changchun Mechanical Instrument Ltd., JiLin, China). At the crosshead speed of 0.05 mm/min, the applied load was recorded with a transducer (Changchun Mechanical Instrument Ltd., JiLin, China). On the other hand, two strain gauges (Hanzhong Strain Instrument Ltd., Baoji, China) were glued along the longitudinal and transverse directions of the irradiated PMMA strip and were used to record the longitudinal and transverse strain history of the irradiated PMMA strips. Finally, the mechanical properties of the irradiated PMMA were obtained, including the stress–strain relation and elastic constant. In this study, four specimens were tested in each irradiated test.

INFLUENCE OF UV ON THE MECHANICAL PROPERTIES OF IRRADIATED PMMA

Figure 2 shows the stress–strain curves of PMMA at different irradiation times. The irradiated PMMA became stronger and stiffer as the irradiation time increased. In addition, the material became less ductile with increasing irradiation time. The raw PMMA specimen had a residual strain 0.8%. After 40 h of irradiation, the plastic effects almost disappeared, and the residual strain after fracture was less than 0.01%, which was within the pure elastic state. Figure 3 shows the stress to failure as a function of the irradiation time; it indicates that UV irradiation could change irradiated PMMA, with respect to the mechanical properties, from a very ductile material to a relatively brittle one. The strength of the irradiated PMMA gradually decreased with an increase in the irradiation time and reached a stable value after 40 h of irradiation.

Figure 4 shows the variation of Young's modulus as a function of the irradiation time for the 30 tests

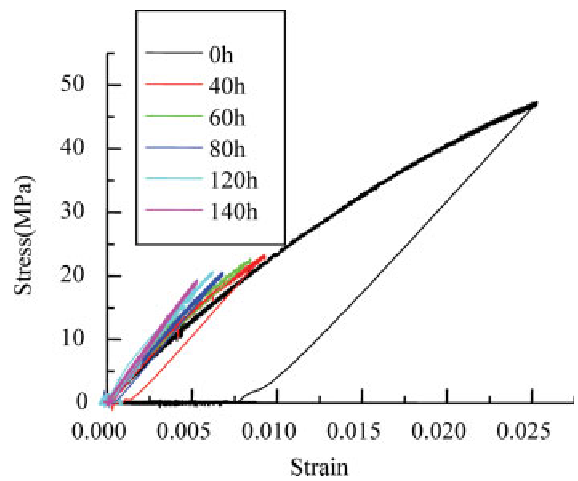


Figure 2 Stress–strain relation of irradiated PMMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

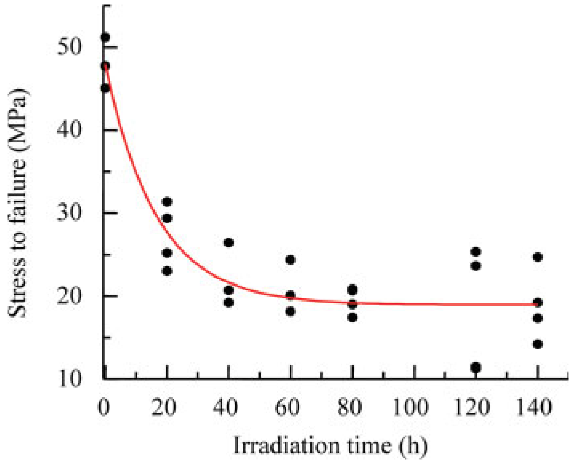


Figure 3 Failure stress of irradiated PMMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

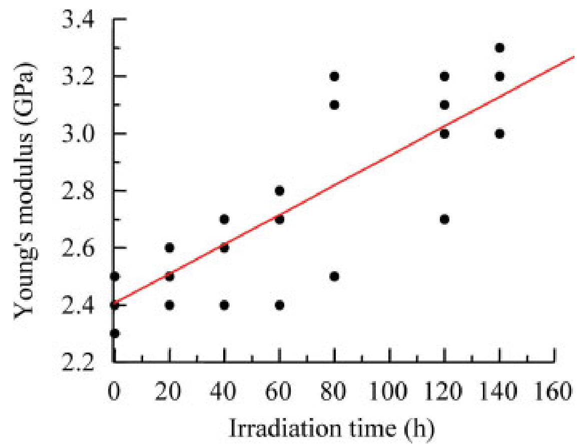


Figure 4 Young's modulus of irradiated PMMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

conducted. The solid line in the figure is a polynomial approximation to the experimental data. Although the data show a fairly high degree of scattering, which is inherent to this type of polymer irradiation measurement, Young's modulus increased over 32% after 140 h of irradiation. Young's modulus increased quickly in the beginning stages of the irradiation.

On the other hand, after Poisson's ratio was measured for almost 40 specimens, it could be seen that Poisson's ratio was not changed, as shown in Figure 5, and Poisson's ratio could be regarded as a constant (0.32). Figure 6 shows the microscopic characteristics of the fracture surface of irradiated PMMA at different irradiation times. With an increase in the irradiation time, the fracture surfaces of the irradiated PMMA showed higher toughness.

MICROSCOPIC CHARACTERIZATION OF IRRADIATED PMMA

Figure 7 shows the surface appearance of an irradiated specimen after different irradiation times. With an increase in UV irradiation, the specimen surface took on a concave–convex configuration at 40 h. The inanition of stomatics appeared at 80 h. At 140 h, a large number of inanition of stomatics developed and filled the specimen surface. These phenomena could be attributed to the photodegradable degree of the polymer material after different irradiation times. In principle, the degradation of PMMA under UV irradiation lies in the rupture of the chemical bond. The polymer, with macromolecular quanta, was decomposed into a low-molecular-weight polymer, which led to a solid low polymer and molecule gaseity (see Fig. 8). Some important characteristics of photodegradation were revealed, such as the main-chain scission reaction of the polymer and atom separation and substitution in the polymer. The chemical reaction led to the variation of the physical and mechanical properties of the polymer.

PREPARATION AND CHARACTERIZATION OF GRADIENT PMMA

To fabricate gradient PMMA with photodegradation, PMMA strips, nominally 100 mm long, 40 mm wide, and 1 mm thick, were used. On the other hand, a special experimental electronic apparatus was designed, as shown in Figure 9, and it included a precise motor, a plane table, and a computer with control software. It could be automatically moved at a uniform speed. The electronic control system was used to control a slow rotation. In this study, the specimen, placed on the experimentation table, moved along the width direction of the specimen at a very slow speed of 0.01 m/h. Under the irradiation of UV light, the motion of the specimen resulted in different irradiation times. Finally, the mechanical properties of the specimen led to graded variations along the width of the specimen.

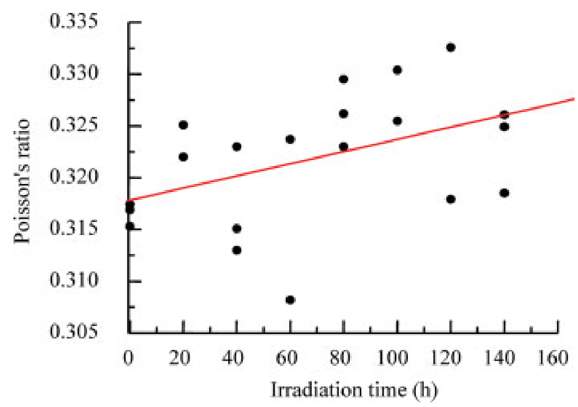


Figure 5 Poisson's ratio of irradiated PMMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

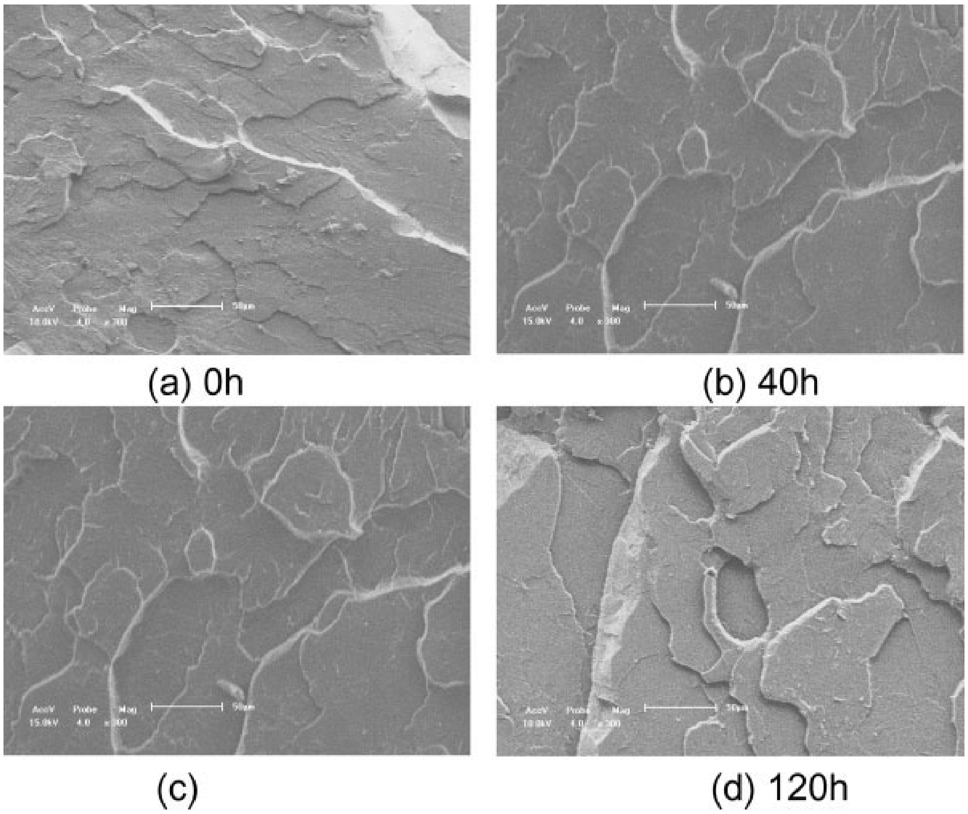


Figure 6 Fracture surfaces of irradiated PMMA.

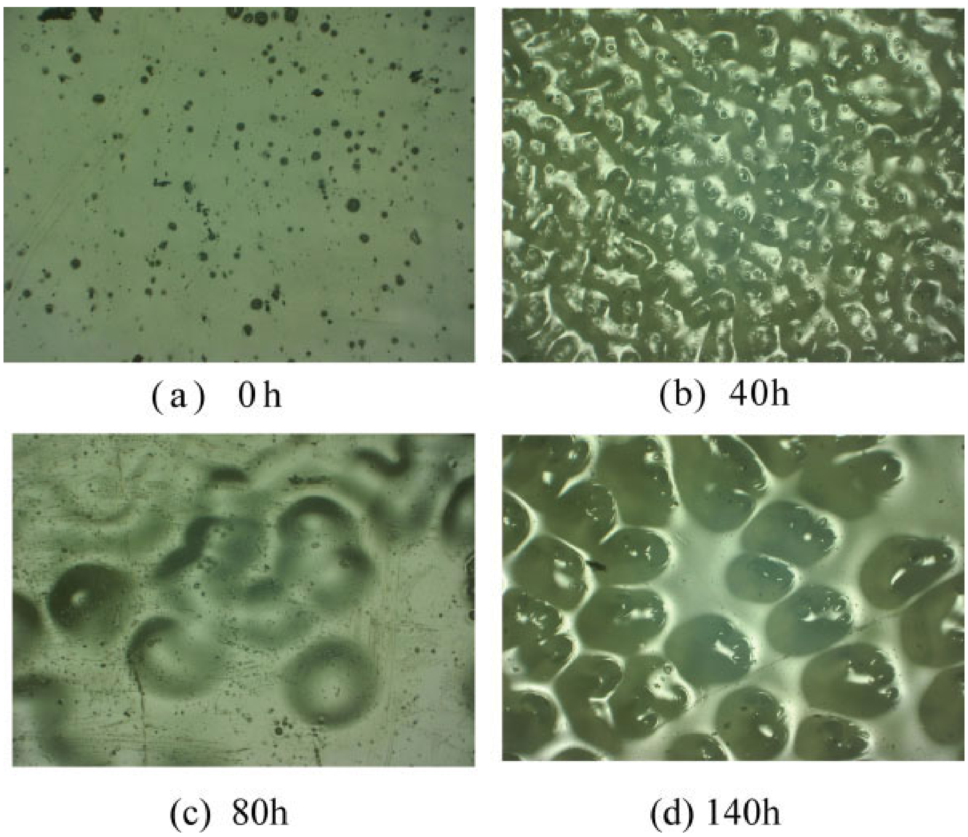
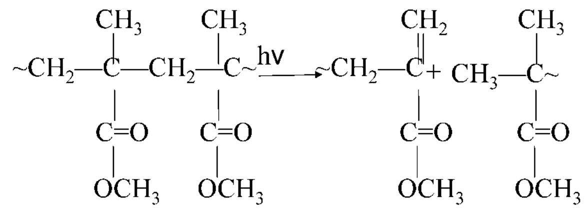
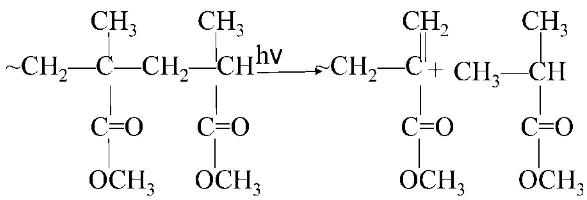


Figure 7 Surface appearance of an irradiated specimen (magnification = 100×). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

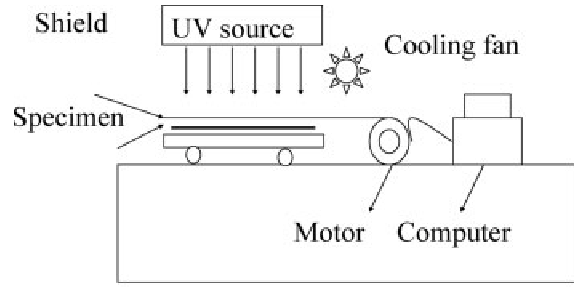


(a)



(b)

Figure 8 Photodegradation of irradiated PMMA.



(a)

(b)

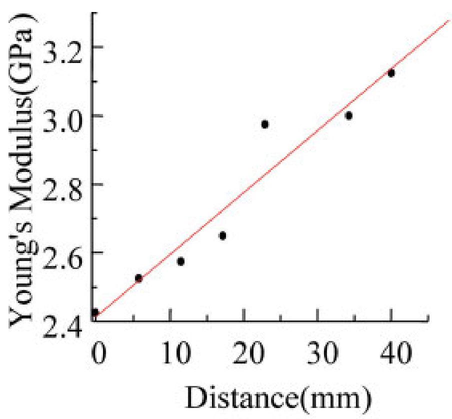
Figure 9 UV irradiation of FGM: (a) the experimental setup and (b) gradient PMMA.

According to the aforementioned experimental results for the mechanical properties of irradiated PMMA, the mechanical properties of the gradient PMMA are presented in Figure 10, which shows the gradient variation of the elastic modulus along the width direction of the specimen. This kind of gradient variation of the elastic modulus can be expressed in the form of linear and exponent patterns as follows:

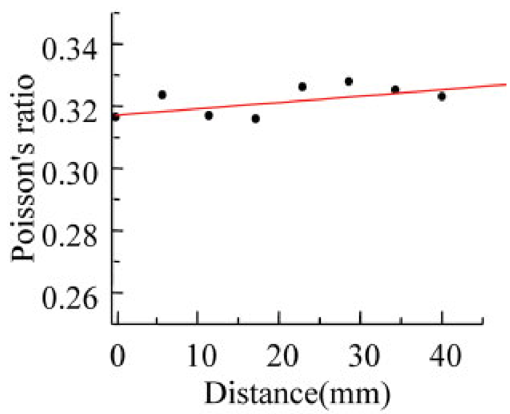
$$E_{line} = 2.39 + 18x \quad (1)$$

$$E_{exp} = 2.39(6.47x) \quad (2)$$

where x represents the coordinate position along the width of the specimen and E_{line} and E_{exp} are the elastic moduli fitted in the form of the linear and exponent patterns, respectively. On the other hand, Poisson's ratio along the width of the specimen can be regarded as a constant in this kind of FGM. Over a distance of 40 mm in the direction of increasing photodegradation time for the FGM, the elastic modulus increased by 32%. This kind of phenomenon reveals that photodegradation results in the rupture of the chemical bond and finally leads to the variation of the physical and mechanical properties of the polymer. After the fabrication and mechanical characterization of the FGM are finished, fracture experimentation with the FGM can be performed, and this will be published in the future.



(a)



(b)

Figure 10 Evaluation of the gradient properties of PMMA: (a) Young's modulus of irradiated PMMA and (b) Poisson's modulus of irradiated PMMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

In this work, the photodegradable properties and characteristics of PMMA polymers were studied experimentally. Some valuable results are listed as follows:

1. The mechanical parameters of a PMMA material subjected to different amounts of UV irradiation were characterized, such as the elastic modulus, Poisson's ratio, fracture strength, and stress–strain relation. The strength of the irradiated PMMA gradually decreased with an increase in the irradiation time and reached a stable value after 40 h of irradiation; Young's modulus increased over 32% after 140 h of irradiation. Poisson's ratio could be regarded as a constant. The microscopic structural characteristics of photodegradable PMMA were determined with scanning electron microscopy photography.
2. The variation of the mechanical properties of photodegradable PMMA resulted from the rupture of the chemical bond in the polymer. Also, the polymer with macromolecular quanta was decomposed into a low-molecular-weight polymer, which led to a solid low polymer and molecular gaseity. Some important characteristics of the photodegradation were revealed, such as the main-chain scission reaction of the polymer and atom separation and substitution in the polymer.
3. An FGM of PMMA was fabricated and characterized, and it showed gradient variation of the elastic modulus along the width direction of the specimen due to unequal UV irradiation. Over a distance of 40 mm in the direction of increasing photodegradation time of the FGM, the elastic modulus increased by 32%.

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