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Effects of gamma ray and sub-cracks on ethanol-assisted crack healing in poly(methyl methacrylate)

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HIGHLIGHTS

- The process of sorption and desorption of ethanol in PMMA can heal crack.
- Crack closure rate is controlled by Case I diffusion in gamma-irradiated PMMA.
- Mechanical strength versus healing time follows the power law with exponent 1/4.
- Gamma irradiation degrades solvent healing while sub-cracks enhance.

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ABSTRACT

The effects of gamma ray and sub-cracks on ethanol-assisted crack healing in poly(methyl methacrylate) (PMMA) were investigated. The transport of ethanol in the gamma-irradiated PMMA was analyzed, using the Harmon model. Both the cracked-gamma-irradiated PMMA and the cracked PMMA with sub-cracks were ethanol-treated at a temperature above the effective glass transition point of the corresponding bulk PMMA. The crack closure rate, which followed the modified Arrhenius equation, increased with increasing gamma ray dose at a given temperature. The fracture strength of the healed PMMA increased with increasing gamma ray dose for short healing time at a given healing temperature, while long healing time led to the decrease of the fracture strength of the healed PMMA with increasing gamma ray dose. The fracture strength of the healed PMMA increased with increasing number of sub-cracks. These results provide the potential to develop self-healing polymeric materials in which structural damage can activate an autonomous healing process without any external stimuli.

1. Introduction

Self-healing of living organisms, in which damage triggers an autonomous healing process with essentially no external intervention, has stimulated the development of self-healing polymeric materials [1,2]. Poly(methyl methacrylate) (PMMA) bone cement is one of promising biomaterials in orthopedics [3]. PMMA acting as space filler holds the stem of an artificial joint replacement with native boney tissue. The damage accumulation and initiation of microcracks under dynamic loading in PMMA bond cement were observed by Culleton et al. [4] and Topoleski et al. [5]. To prolong the life of the PMMA-bond connect, cement was modified by adding cross linking agents, reinforcing metallic wires, or incorporating SiO_2 glass networks to increase tensile strength and fracture toughness [6–9]. Alternatively, autonomous healing of the PMMA-bond cement, where microcracks are arrested and cured, has been utilized. A self-healing system generally consists of microencapsulated healing agents within a catalyst-embedded matrix [10,11]. The propagation of microcracks through the microcapsules causes the release of the liquid healing agents into the damage region which repairs the damage. All of these studies are attractive, while the systems are complex and the healing mechanisms remain elusive.

Crack healing can be categorized as solvent healing, thermal healing, compressive healing, and adhesive healing. The first two healings have been observed in polymeric materials at the healing temperature above the glass transition temperature [12–21]. Wool and O'connor [18] proposed five stages of thermal healing in polymers: (a) surface rearrangement, (b) surface approach, (c) wetting, (d) diffusion, and (e) randomization. The first two stages

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are the incubation period of polymer to be healed. Yu et al. [22] observed and explained the constant closure rate in the wetting stage. The fracture strength of healed polymers is determined by the last three stages and has been found to be proportional to $t^{1/4}$, where t is the healing time [21]. It has been reported that the exponent for the solvent healing is less than 1/4 in the solvent-treated PMMA [14–16] since the effective glass transition temperature of polymers decreases with the increase of the amount of absorbed solvent.

Generally, the transport of solvent in polymers plays an important role in the solvent healing. Alfrey et al. [23] classified the transport in polymers into three categories; Case I diffusion (Fickian), Case II diffusion (stress relaxation), and anomalous behavior (combination of Case I and Case II). Case I diffusion was extensively studied by Crank [24]. The mass uptake is proportional to the immersing time in Case II diffusion, which has been studied by many researchers [25–28]. Kwei and coworkers [29–32] were the first to analyze anomalous transport in polymers, while their results showed the discontinuity of the solvent flux at the center of specimen. Harmon et al. [33,34] modified Kwei's equation and analyzed the anomalous transport in specimens of finite sizes. Harmon's model has been applied to various polymer-solvent systems [14–16,35,36].

It is known that polymer chains undergo scission or crosslinking after exposing polymers to gamma ray, which causes the changes of the microstructures and chain structures of the polymers and affects the physical, chemical, and mechanical properties. There are various studies addressing the effects of irradiation on the physical behavior of PMMA, including the chain scission [37] and the degradation of mechanical properties [38]. It has been shown that the average molecular weight [39], glass transition temperature [40], microhardness [41], and transmittance [42] decrease with increasing gamma-ray dose while the EPR spectra [43] and thermal expansion coefficient [40] increase with increasing irradiation dose. However, there is no study on the effect of gamma irradiation on the crack healing in PMMA. The purpose of this work is to study the ethanol-assisted crack healing of gamma-irradiated PMMA and the effect of sub-cracks.

2. Experimental detail

The PMMA, Lucite L, of an inherent viscosity of 0.237 dL/g was obtained from Du Pont (Wilington, DE) in the form of a cast sheet of 6.1 mm in thickness. Following the procedure used in the work of Wang et al. [15] and Lin et al. [16], the PMMA samples for studying the mass transport and crack healing of irradiated PMMA were prepared. Briefly, the samples of 80 × 6.1 × 1 mm^3 and 40 × 6.1 × 1 mm^3, as shown in Fig. 1, were cut from the sheet for the crack healing and the mass transport, respectively. Fig. 1a and b shows the geometric configuration of the samples for the measurement of crack closure rate and tensile test, and Fig. 1c shows the geometric configuration of the samples with sub-cracks for tensile test. The samples were ground on 600 and 1000 grid cabinet papers and followed by final polishing with 1 μm and 0.3 μm alumina slurries. The samples were then annealed in air for 24 h at 120 °C and furnace-cooled to 25 °C. The samples for the gamma ray treatment were placed in an air-filled glass tube. These samples were exposed to gamma ray at 24 °C with the irradiation doses of 15, 25, and 35 kGy, respectively, using a Co-60 gamma ray source at Radiation Application Technology Center in the Institute of Nuclear Energy Research (Tauyuan, Taiwan) at a dose rate of 30 kGy/h. For the irradiation doses of 15, 25, and 35 kGy, the corresponding time was 30, 50, and 70 min, respectively.

The sorption study was conducted by measuring the weight gain of the samples periodically. Only one sample was used for the sorption study under each testing condition. The samples were preheated to the sorption temperature and immersed in an ethanol solvent bath maintained in a water bath at 40–55 °C. The mass gain was measured on a Kern 870 digital balance. After the measurement, the samples were placed back immediately to the solvent bath for the next measurement. For the gamma-irradiated sample, a crack was created via a sharpened blade, and the crack was allowed to propagate until the ligament length reached about 0.3 mm. The crack closure was recorded, using a Nikon camera to monitor the receding crack tip of the irradiated, cracked samples during the ethanol treatment. For the sub-crack study, a pair of fractured surfaces with several sub-cracks perpendicular to the fractured surfaces was created, using a utility knife. To heal the damaged samples, both the cracked surfaces with sub-racks were faced to each other and immersed in an ethanol bath which was maintained at a constant temperature (40–50 °C) over a period of time. The healed PMMA samples were placed in a vacuum chamber at a temperature, which was the same as that for the ethanol treatment, until most of the ethanol desorbed from the samples. The samples were then machined to remove the regions covering the main cracks and the other end. The fracture strength of the healed samples was measured, using a universal tensile test machine with a cross head speed of 0.014 mm/s at 25 °C. The values of the fracture stresses measured were the average of three samples.

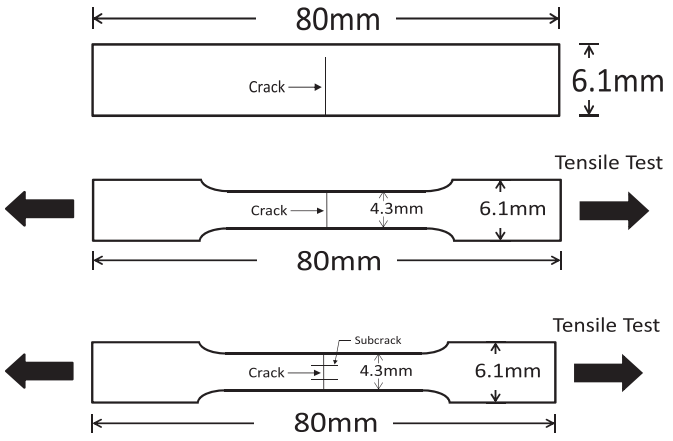

Fig. 1. Top view of the healed sample dimensions; (a) with gamma ray irradiation for crack closure rate measurement, (b) with gamma ray irradiation for tensile test, and (c) with sub-cracks for tensile test. The thickness of healed sample is 1 mm.

The samples for the study of glass transition temperature, which had similar structures to the material for the study of the crack healing, were obtained from Chi-Mei Chemical Corporation (Tainan, Taiwan). The sample preparation was the same as that for the crack healing. Samples of ca. 10 mg were obtained and then exposed to the gamma ray source in air at 24 °C with the irradiation doses of 15, 25, and 35 kGy, respectively. The glass transition temperature of the irradiated PMMA was characterized, using a Netzsch DSC 200F3 differential scanning calorimeter (Selb, Germany). The samples were heated to 200 °C at the rate of 10 °C/min and maintained for 5 min, quenched to 0 °C at a cooling rate of 40 °C/min and isothermed for 10 min, and finally heated again at the rate of 10 °C/min. The last trace was used to determine the glass transition temperature.

3. Results and discussion

3.1. Ethanol transport

Fig. 2 shows the temporal evolution of the mass in the un-