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# Morphology of Irradiated PMMA Membranes Prepared by Phase Inversion with Supercritical CO2 (Postprint)

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## Abstract

Poly (methyl methacrylate) (PMMA) pellets are irradiated using 60Co gamma-ray in air and successfully formed by hot pressing at constant conditions. The irradiated PMMA membranes are prepared by supercritical carbon dioxide (scCO2) as a physical blowing agent using the pressure quench method. Effects of foaming conditions such as absorbed dose, saturation temperature, and pressure on the morphology and cell size of the microcellular PMMA membranes are investigated in detail. The results showed that the irradiated PMMA membranes possess spherically closed-cell structure with uniform cell size. They have a high cell density compared with virgin PMMA. The cell size uniformity becomes poor at doses lower than 10 kGy, but increases with dose at doses higher than 10 kGy. The mean cell diameter is less than 10  m and the cell density increases with increasing dose. The average cell size of irradiated PMMA membranes decreases and cell density increases with increasing saturation temperature and pressure. The changes in morphology of membranes are attributed to the gamma-ray radiation and scCO2 synergistic effect.

## Full Text

## Preamble

**Morphology of Irradiated PMMA Membranes Prepared by Phase Inversion with Supercritical $CO_2$**

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**Abstract**

Poly(methyl methacrylate) (PMMA) pellets were irradiated using $^{60}$Co gamma-rays in air and subsequently formed into sheets by hot pressing under constant conditions. The irradiated PMMA membranes were prepared using supercritical carbon dioxide ($scCO_2$) as a physical blowing agent via the pressure quench method. The effects of foaming conditions—including absorbed dose, saturation temperature, and pressure—on the morphology and cell size of the microcellular PMMA membranes were investigated in detail. The results showed that the irradiated PMMA membranes possessed a spherically closed-cell structure with uniform cell size and exhibited higher cell density compared with virgin PMMA. Cell size uniformity became poor at doses lower than 10 kGy but improved with increasing dose above 10 kGy. The mean cell diameter was less than 10 m, and cell density increased with dose. The average cell size of irradiated PMMA membranes decreased while cell density increased with elevated saturation temperature and pressure. These morphological changes are attributed to the synergistic effects of gamma-ray radiation and $scCO_2$.

**Keywords:** PMMA, Irradiation, Supercritical $CO_2$, Micropore, Morphology

## Introduction

Poly(methyl methacrylate) (PMMA) is a highly useful flexible material that is inexpensive and readily available in various forms and colors. Many physical properties of PMMA—including electrical, optical, thermal, and mechanical characteristics—are modified after exposure to high-energy radiation. These modifications result from chemical bond scissions and/or cross-linking induced by high-energy radiation. The radiolysis of PMMA has been studied more extensively than that of any other polymer, likely because irradiation produces striking changes in PMMA that can be detected through simple visual examination. Color changes are particularly apparent and easy to monitor spectroscopically. PMMA is also used in dose measurements and aeronautical materials in intense radiation fields due to its perfect optical clarity. It is sensitive to radiation, and its chemical and physical properties are modified after gamma-ray exposure. Wall and Brown reported that the number of bond scissions produced in PMMA for a given dose of gamma irradiation was influenced by the presence of air and benzene as well as by temperature, as measured by the intrinsic viscosity method. Ouano et al. showed that the average molecular weight of PMMA decreased with increasing gamma irradiation dose, as determined by gel permeation chromatography. Subrahmanyam reported that the glass transition temperature of PMMA decreased while the thermal expansion coefficient

increased with irradiation dose. Kudoh demonstrated that the mechanical properties of PMMA were degraded by gamma irradiation. Generally, gamma-ray radiation of PMMA causes main chain scission and hydrogen abstraction from an $\alpha$-methyl or methylene group. The extent of derivative formation resulting from irradiation depends on the physical state of PMMA, which may serve as a model for chain scission without simultaneous cross-linking after gamma-ray exposure.

Microcellular polymeric materials represent a new class of materials that typically exhibit cell sizes on the order of 10  m and cell densities exceeding $10^9$ cells/cm$^3$. These materials can be obtained without additional post-treatment or solvent-removing processes, offering multiple advantages over solid polymers including reduced material cost and weight, good mechanical properties and chemical resistance, low thermal and electrical conductivity, and excellent sound insulation. They find applications in column chromatography packing, liquid crystal display spacer materials, polymer-supported extractants, catalysts, templates for preparing porous inorganic microspheres, and carriers for enzymes and drugs. In recent decades, supercritical carbon dioxide ($scCO_2$) has been widely used to generate microcellular polymer materials. The products typically possess uniform pore size and high porosity, with pore morphologies controllable by varying $CO_2$ pressure or temperature. Various $scCO_2$ techniques have been developed to prepare microcellular PMMA foams, which exhibit fine microcellular structures with either wholly closed or open pore cells depending on processing conditions and polymer properties. However, foaming of irradiated PMMA using $scCO_2$ has not been previously reported in the literature.

In this work, PMMA samples were irradiated by gamma-ray in air at low doses, and membranes of irradiated PMMA were successfully prepared using $scCO_2$ as the physical blowing agent. The irradiated PMMA membranes possessed spherically closed-cell structures with uniform cell size and higher cell density than virgin PMMA membranes. The average cell size decreased while cell density increased with increasing saturation pressure. Membranes of irradiated PMMA at low dose may find applications as packing materials, polymer-supported catalysts, polymer-immobilized extractants, and related uses.

## 2.1 Materials

PMMA pellets were purchased from CHI MEI Corporation with a density of 1.16 g/cm$^3$ and melt index of 2.0 g/10 min. The pellets were dried at 50°C in a vacuum oven for 24 h and stored in a desiccator prior to use. Carbon dioxide (>99.5% purity) was obtained from Loutang Special Gases of Shanghai. Anhydrous ethanol (analytical grade) was used as received.

## 2.2 Irradiation of PMMA

Gamma-ray irradiation was carried out using the $^{60}$Co source at the Shanghai Institute of Applied Physics. PMMA pellets were irradiated to doses of 5, 10,

and 20 kGy in air at room temperature. The irradiated PMMA pellets were mixed in a mixer (Thermo Haake PolyDrive, Germany) and hot pressed at 200°C and 18 MPa for 5 min into thin sheets 1.0 mm thick. All specimens were cut into 10.0 mm × 10.0 mm pieces for the foaming process.

## 2.3 Membrane Preparation

PMMA sheets were placed in a beaker capped with a porous polyethylene thin film and sealed into a high-pressure stainless steel vessel (500 mL). After preheating the vessel to the desired temperature, $CO_2$ was introduced to purge the vessel for several minutes. The vessel was then pressurized with $CO_2$ using a high-pressure liquid pump. When the desired pressure was reached, the system was maintained at that pressure and temperature for 8 h. This exposure time was sufficient for sc$CO_2$ sorption into the polymer to reach thermodynamic solubility. At the end of this period, the vessel was depressurized by opening the valve and venting the $CO_2$ in less than 30 s. The external temperature of the vessel was maintained constant during depressurization. The temperature inside the vessel decreased as the pressure was rapidly reduced to atmospheric pressure, then was slowly raised to the set value (approximately 20 min) and held for about 5 min before the specimens were removed and cooled to ambient temperature.

## 2.4 Membrane Characterization

Before characterization, all samples were placed in a desiccator for one week to allow $CO_2$ to diffuse out of the polymer matrix. Calorimetric data were obtained using a DSC-7 Perkin-Elmer apparatus equipped with TAS-7 software and a Perkin-Elmer PE-7700 professional computer. The equipment was calibrated with indium (Tm = 156.6°C and $\Delta$Hf = 6.8 cal/g) as the standard. Samples of approximately 10 mg were sealed in aluminum pans and heated from 25–200°C at a rate of 10°C/min in a nitrogen atmosphere.

Microstructures of the microcellular PMMA materials were characterized using a LEO 1530 VP scanning electron microscope at an acceleration voltage of 5.0 kV. Samples were immersed in liquid nitrogen and fractured at cryogenic temperatures, then mounted on stubs. The fractured surfaces were sputter-coated with gold for observation.

Average cell size (D) was determined from SEM images of the foam cross-section using Image-Pro Plus 6.0 software (Media Cybernetics). Cell density (Nf), defined as the number of cells per unit volume of foam, was calculated using Eq.(1):

where n, M, and A are the number of cells in the micrograph, the magnification of the micrograph, and the area of the micrograph ($cm^2$), respectively.

The glass transition temperature (Tg) provides valuable information on molecular structure changes. To investigate characteristic changes in irradiated PMMA

samples, typical DSC curves of virgin and irradiated PMMA specimens are shown in [Figure 1: see original paper]. The Tg value of virgin PMMA is 105.3°C. The Tg of irradiated PMMA decreases with increasing dose from 5 kGy to 10 kGy; however, the Tg of specimens irradiated at 20 kGy shows a slight increase.

## 3.1 Effect of Irradiation on Structural Change

PMMA is a well-known degradative polymer whose main chains undergo random degradation upon radiation exposure. Previous research on PMMA demonstrated that the most significant effect of gamma radiation is polymer chain degradation. Subrahmanyam reported that the Tg of PMMA decreases with increasing dose, confirming that main chain fracture occurs randomly at room temperature, causing a decrease in molecular weight with increasing dose without monomer production. It has been proposed that for each main chain scission, a lateral group is disrupted with 83% probability. Changes in molecular structure induced by gamma radiation are reflected in modifications of thermal properties. However, the Tg value of PMMA irradiated at 20 kGy is 105.5°C, indicating the possibility of double bond formation due to higher energy radiolysis. Chemical changes in PMMA are promoted by radiation. The melting temperature of irradiated PMMA decreases with increasing dose, as shown in [Figure 1: see original paper]. A decrease in melting point implies molecular chain scission after irradiation. This analysis indicates that gamma-ray irradiation causes structural change and chain scission even after 20 kGy. While lower dose irradiation does not substantially alter the molecular structure of PMMA, higher doses do modify it. The molecular weight decreases with increasing dose, as evidenced by the decrease in melting point of irradiated PMMA.

## 3.2 Effect of Irradiation on Membrane Morphology

The morphology of irradiated PMMA membranes formed at various doses was investigated using SEM. SEM images of pristine PMMA membranes are shown in Figure 2: see original paper for comparison. Figures 2(b–d) show SEM images of PMMA membranes foamed under different doses at constant saturation temperature (80°C) and pressure (20 MPa). Although micropores were formed, they were not perfectly spherical. As revealed in Figure 2: see original paper, the micropore cells are discrete, nearly spherical, and surrounded by thick walls. The micropore depth is heterogeneous and shallow, with deep and small micropores distributed throughout the virgin PMMA membranes. Micropore formation is likely due to desorption of some $CO_2$ during low-pressure quench, which creates a low $CO_2$ concentration near the membrane surface and restricts nucleus growth. The number of micropores changes with increasing dose, and the sample depth decreases with dose from 5 kGy to 10 kGy. However, the depth and cell size of irradiated PMMA membranes at 20 kGy show a slight increase, and homogeneity improves, as shown in Figs. 2(b–d).

[Figure 3: see original paper] shows the effect of dose on cell morphology parameters. The average cell size of PMMA membranes first decreases with increasing dose below 10 kGy but increases with dose above 10 kGy. Cell density increases with dose below 10 kGy but decreases with increasing dose above 10 kGy. Cell size uniformity becomes poor at doses below 10 kGy but improves with increasing dose above 10 kGy. The mean cell diameter is less than 10  m, and cell density increases with dose. These morphological changes are attributed to radiation effects on the molecular structure of PMMA. Radiation causes structural changes including chain scission and hydrogen abstraction from $\alpha$-methyl or methylene groups. Chain scission leads to decreased macromolecular chain length, resulting in lower melt strength and viscosity. During irradiation, gamma rays produce excited atoms and ions, and Coulombic interactions among these ions can cause excessive bond stretching or breakage, while nuclear reactions can cause atomic displacement. Both processes lead to release of pendant atoms and groups such as -H, -$CH_3$, and $CH_3OOC$-, as well as main chain scission. Various gaseous molecular species are released during irradiation, with the most prominent being hydrogen, molecular scission products from end groups and pendant groups, and their reaction products. Radicals or dangling bonds are created by release of pendant atoms such as hydrogen and by loss of pendant groups. The micropore morphology changes in irradiated PMMA result from these complex molecular structural changes.

## 3.3 Effect of Saturation Temperature and Pressure on Membrane Morphology

The effect of saturation temperature was examined at constant saturation pressure (20 MPa) and absorbed dose (10 kGy). [Figure 4: see original paper] shows the effect of saturation temperature on cell morphology. At 60°C, cell size and depth are heterogeneous, with large pore cells that are discrete, nearly spherical, and surrounded by thick walls. Different micropore sizes are distributed throughout the PMMA membranes. The number of micropores increases with temperature, and micropore size becomes more homogeneous with increasing saturation temperature. Micropore depth decreases with temperature from 60°C to 80°C but increases at 90°C.

[Figure 5: see original paper] shows the effect of saturation temperature on cell morphology parameters. As temperature increases, the number of smaller cells increases while the number of larger cells decreases. The average cell size of PMMA membranes first decreases with increasing temperature below 80°C but increases above 80°C. Cell density increases with temperature below 80°C but decreases at 90°C. When exposed to high sc$CO_2$ pressures, the sample creates a depletion layer near the surface where gas concentration is too low for nucleation and growth. However, in the core region, after rapid depressurization of the $CO_2$-saturated polymer, $CO_2$ solubility decreases and more $CO_2$ molecules separate. If the degree of supersaturation is sufficiently high, the energy barrier for nucleation is overcome and new stable nuclei develop. In the absence of

supersaturation, $CO_2$ molecules diffuse into preexisting bubbles, causing them to grow. These competitive processes depend on factors such as the quantity of $CO_2$ molecules available for nucleation, the rate of $CO_2$ availability, the physical characteristics of the polymer-rich phase, and interactions between the two phases. Thus, an open cellular structure is formed. The formation process of open cellular micropores is mainly related to processing conditions such as saturation pressure, temperature, and time. At a given temperature, nucleation and growth of micropores are initially slower than $CO_2$ diffusion, but nucleation growth increases at temperatures above 80°C. These factors lead to cell growth and decreased cell sizes.

As saturation temperature increases, the viscosity of the substrate material decreases, reducing the retractive force restricting cell growth and increasing $CO_2$ diffusivity within the substrate. As reported in the literature, micropore formation during foaming can be attributed to gas molecules near the sample surface diffusing out faster than they can join nuclei. Rapid diffusion out of the solution creates a depletion layer near the surface with insufficient gas concentration for nucleation and growth.

The effect of saturation pressure was studied at 80°C and 10 kGy, with results shown in [Figure 6: see original paper]. At 10 MPa, some micropores are present in the membrane with heterogeneous cell size and depth. The number of micropores gradually increases with saturation pressure, while cell size and depth decrease with increasing pressure. The micropores are discrete, nearly spherical, and surrounded by thick walls.

[Figure 7: see original paper] shows the effect of saturation pressure on cell morphology parameters. As $scCO_2$ saturation pressure increases, average cell size decreases while cell density increases. Microcellular PMMA membranes can be produced by foaming polymer with $CO_2$ using the pressure quench method. The amount of $CO_2$ incorporated into PMMA increases with saturation pressure, resulting in higher supersaturation upon pressure release and likely leading to a large population of nucleated cells. Classical nucleation theory predicts that as the magnitude of the pressure drop increases, the energy barrier to nucleation decreases, leading to more cells being nucleated within a given volume. Consequently, irradiated PMMA micropores can be extensively foamed due to $CO_2$ diffusion. It is common to generate a closed-cell microcellular core structure encased by a nonporous skin during $scCO_2$ foaming of bulk polymers.

## 4 Conclusion

The membrane morphology of gamma-ray irradiated PMMA was investigated using $scCO_2$ as a physical blowing agent via the pressure quench method for the first time. PMMA is a well-known degradative polymer. The Tg of irradiated PMMA decreases with increasing dose below 10 kGy but increases with dose above 10 kGy. The melting transition temperature of irradiated PMMA decreases with increasing dose. The irradiated PMMA membranes possess spher-

ically closed-cell structures with uniform cell size and higher cell density than virgin PMMA membranes. Cell size uniformity becomes poor at doses below 10 kGy but improves with increasing dose above 10 kGy. The mean cell diameter is less than 10  m, and cell density increases with dose. The average cell size of irradiated PMMA membranes decreases while cell density increases with saturation temperature and pressure. Membranes of irradiated PMMA at low dose may find wide application in industrial fields.

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