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Impact of radiation induced crosslinking on structural, morphological, mechanical and optical properties of Polymethylmethacrylate thin films

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ABSTRACT

This project is dedicated to investigate the optimal fluence of laser produced X-rays for crosslinking in thin Polymethylmethacrylate (PMMA) films. These films were deposited at room temperature using Pulsed Laser Deposition (PLD) technique. These deposited films were then irradiated with various X-ray fluence (produced from Laser induced Plasma) ranging from 2.5 to 5.76 mJ-cm^{-2}. X-ray Diffractometer, Optical microscope, hardness tester and UV-VIS spectroscopy techniques have been employed to characterize the films. The X-ray fluence 4.48 mJ-cm^{-2} comes out to be the optimal fluence for crosslinking that not only improved the crystallization of the films but also caused the generation of new phases. The surface exhibited larger fragments at this fluence. A sharp enhancement in hardness as well as in absorption in the UV–vis range have also been observed at this fluence. These cross linked PMMA films have their potential applications in biomedical, optoelectronic, lithography, coating, packing and medical field.

1. Introduction

Polymer thin films play a vital role in various fields of science and industry [1]. Polymethylmethacrylate (PMMA) is most frequently used polymer among the Methacrylate family [2] and it is being widely studied (both as bulk and as a thin film) [2–4]. PMMA thin film has many applications in chemical sensing, lithography, optoelectronics, data display and storage, etc. [2–6].

Irradiation of species like X-rays, γ-rays, electrons and ions is being widely used for modification of polymers [2,7,8]. The irradiation results in the breakage of covalent bonds, promotion of cross linkages, formation of carbon clusters, liberation of volatile species and, in certain cases, creation of new chemical bonds [9,10–13]. The applicability of polymers has greatly increased due to possibility of selective surface modifications without any changes in bulk characteristics [2]. However, for particular-application, the knowledge about polymer radiation resistance (maximum and minimum dose/fluence) is very important. Generally, two important mechanisms responsible for change in properties of polymers are cross-linking and scissioning reactions [14].

Radiation induced crosslinking is one of the convenient, clean and cost effective methods to improve the mechanical, thermal and physicochemical properties of polymeric materials [15,16]. The crosslinking level can be adjusted by irradiation fluence [17]. The dimensional and thermal stability, toughness, modulus, surface hardness, viscosity, wear and chemical resistance can be improved by controlling the crosslinking [15–20].

The radiation induced crosslinking plays a significant role in the practical use of the polymer material. The applications of polymer crosslinking include the processing of heat shrinkable products for food packaging, electrical connections, the curing of resins used in coating applications, polymer foams and high purity O-ring [15,16,18,20–22]. Crosslinked heat resistant wires and cables insulation can be used in motors, automobiles, household appliances, computers and other electronic equipment [20,21].

Promising new applications in this category may include radiation crosslinking of high- end engineering polymers and high performance polymers, green (biobased and biodegradable) polymers, recycled polymers and polymer blends [16]. Radiation crosslinking improves the thermal stability and process ability of biopolymer. Shape memory polymer (SMPs), a representative of heat shrinkable tubing, are being applied in medical devices such as splints, surgical staples and intra-arterial catheters [16]. The outstanding biomedical applications are

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wound dressings, controlled drug delivery systems, hydrogels [21], and orthopedic implants [16,18,20,22]. In the field of nanotechnology, emerging applications of polymer crosslinked systems are three dimensional nanostructures. They can be utilized for high capacity optical data storage or 3-D holographic recording devices [20].

Although polymer with methyl group such as PMMA would more likely undergo degradation with radiation, cross linking can occur under high irradiation fluence [23]. Optical, structural, morphological and mechanical properties of the materials can be tailored for various applications by adjusting the irradiating X-rays fluence [16,24]. Radiation crosslinked PMMA has found applications in biomedical (cardiovascular stents) [16], optoelectronic devices, lithography [2–6], packing and dentistry [25].

This project is an attempt to find the Laser produced X-rays threshold fluence of crosslinking of PMMA thin films. This is the continuity of our previous work [2], in which irradiation only caused the amorphousness in PMMA thin films deposited at 300 °C. In this paper, we report PMMA thin films deposited at room temperature after irradiation exhibit crosslinking.

2. Experimental details

The experiment was performed in two steps. In the first step, thin films of PMMA were deposited on glass substrate at room temperature using PLD technique. In the second step, these films were exposed to X-rays produced from laser induced plasma. The details of both setups are given in the following.

2.1. Experimentation for pulsed laser deposition

A standard PLD chamber has been used for the deposition of polymeric thin films [26]. A KrF Excimer laser (248 nm, 20 mJ) was focused with 40 cm focal length lens on PMMA target placed under vacuum of the $\sim 10^{-6}$ Torr using turbo molecular pump. The glass substrate was placed at 1 cm away from the target surface. The films were deposited by taking 15,000 laser shots on the PMMA target. The target was rotated by a programmable stepper motor at 12 rpm to bring the fresh surface for each laser exposure (to avoid the crater formation). The films were deposited at room temperature.

2.2. Experimentation to irradiate films with X-rays

Fig. 1 shows a schematic of the setup used for the irradiation of PMMA thin films by laser produced X-rays from Tungsten target. The Tungsten (W) was chosen as a target because it produces 56.4 keV X-rays [27] which is expected to be more than sufficient to induce changes in the polymeric thin films. In order to produce X-rays, the target was mounted on the target holder and an Excimer laser (248 nm, 20 mJ) was tightly focused on the target with the help of a 40 cm focal length lens. PMMA thin films (used as substrate) were positioned parallel to the target (W) at a distance 5 cm. Hard X-rays (56.4 keV) produced from tungsten target [27] were filtered by placing an Al-filter of thickness 24 μm in front of the films. The films were irradiated with various X-ray fluence ranging from 2.56 to 5.76 mJ-cm^{-2}. The experiment was performed under vacuum $\sim 10^{-6}$ Torr.

Table 1
Calculated value of X-ray energy falling on the substrate, Fluence, LET, Energy deposited per atom and Corresponding Pressure.

Number of Shots	X-ray energy falling on the substrate (MeV) × 10^{10}	Fluence (mJ-cm^{-2})	LET (eV/nm) × 10^{15}	Energy deposited per atom (eV)	Pressure (Gpa)
4000	1.6	2.56	3.63	5	6.4
5000	2.0	3.2	4.54	6.25	8
6000	2.4	3.84	5.45	7.5	9.6
7000	2.8	4.48	6.36	8.75	11.2
8000	3.2	5.12	7.27	10	12.8
9000	3.6	5.76	8.18	11.25	14.4

Table 1 gives the calculated values of fluence, energy deposited per atom and exerted pressure using formulas from [2] and Linear Energy Transfer (LET in eV/nm) is also given by [2]

$$\mathrm{LET} = \frac{E}{L_O} \tag{1}$$

where E is X-ray energy and L_o is penetration depth.

Structural analysis and investigations on surface modifications were performed by X-ray Diffractrometer (PANAlytical X'Pert PRO Diffractrometer) and Optical (Olympus STM-6), respectively. The hardness of films was determined by Hysitron-Ubi1 nanoindentation system. UV–visible Spectrophotometer (U-2800) was used to obtain information about absorption spectra of the films.

3. Results and discussion

3.1. XRD patterns of PMMA thin films (before and after irradiation)

The XRD patterns of Bulk PMMA (for reference) and PMMA thin film deposited at room temperature are shown in Fig. 2. The broad band in XRD pattern of PMMA indicates the amorphous nature of PMMA.

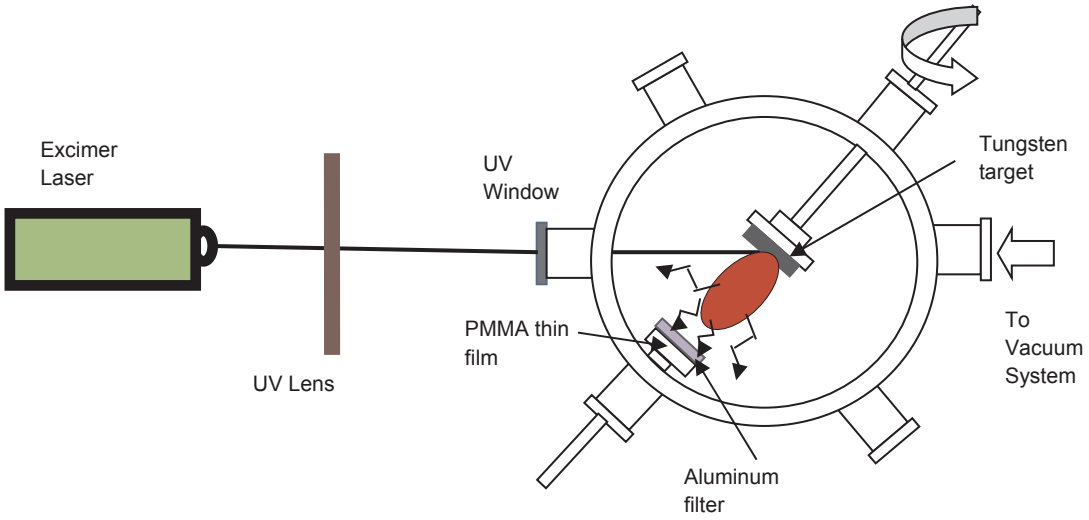

Fig. 1. A Schematic of experimental setup used for X-rays irradiation on PMMA thin films.