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Study of the surface modification of the PMMA by UV-radiation

Sophie Eve[a,]* and Juergen Mohr[b]

[a] *ESCTM du CRISMAT – CNRT-Matériaux / ENSICAEN, 6 Boulevard Maréchal Juin, 14050 Caen Cedex 04, FRANCE.*

[b] *Institut für Mikrostrukturtechnik, Forschungszentrum Karlsruhe GmbH, Postfach 3640, 76021 Karlsruhe, GERMANY*

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Abstract

In this paper, we present the evolution of the thermo-mechanical properties of PolyMethylMethAcrylate (PMMA) materials exposed to Ultra-Violet (UV) light. We observed a decrease of the strength and Young's modulus with the increase of the UV irradiation dose, which have been correlated to the physico-chemical degradation of the PMMA and the occurrence of surface damage.

Keywords: *Polymethylmethacrylate; UV irradiation; photo-chemical degradation; mechanical properties; damage evolution.*

I. Introduction

Integrated optics play an important role in optical microsystems as they enable to achieve miniaturization and modularity in the optical information and sensor technology. In recent times expensive classical inorganic basic materials for integrated-optical components, such as glass and semiconductors, have been progressively substituted by polymeric materials, which combine both cost-effectiveness and simple handling and processing [1]. The refractive index of some polymers can be changed by radiation exposure [2]. This intrinsic radiation-induced modification of the optical properties of polymers is extensively exploited for inscribing Bragg gratings in polymer fibers [3]. Moreover, photo-induced fabrication appears to be a useful technique for low cost realization of integrated optical circuits for telecommunication and sensor applications [4], such as planar waveguides. The single polymer layer acts as both substrate and waveguide, and no further etching or development step is required; the waveguide depth is limited through the modification depth of the light [5]. Among others, PolyMethylMethAcrylate (PMMA), which is widely used for a variety of optical devices such as optical lenses and polymer optical fibers (POF), exhibits a significant increase in refractive index after irradiation with Deep Ultra-Violet (DUV) light, as first reported by Tomlinson et al. [6]. Furthermore, it has been shown that optical waveguides can be created in PMMA by the means of ionizing radiation [7] and deep UV radiation [4]. This allows the fabrication of simple components for visible data communication, as well as small stress and temperature sensors, by inscribing Bragg gratings into planar waveguides. For the use of such systems in industrial applications, the thermo-mechanical

* Corresponding author. Tel.: +33-231451314; fax: +33-231451309.
E-mail address: Sophie.Eve@ensicaen.fr.

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reliability, as well as the long-term behaviour in relevant environmental conditions of the polymer material is of great importance. Recently advances have been made in developing surface treatments with ionizing radiation to alter physical and chemical properties of polymer surfaces without affecting bulk properties. But to the best of our knowledge, studies of PMMA subjected to UV radiation are mainly focused on the mechanisms of photo-degradation, such as cross-linking and/or chain scission [8], and on some basic physical properties, such as optical properties [5]. Only limited efforts have been devoted to understanding the evolution of the mechanical properties of PMMA with radiation exposure [9].

The aim of this article is to characterize the effects of UV-radiations on PMMA, in terms of thermo-mechanical behaviour and damage initiation as a function of the UV-radiation dose. These results have been correlated with the chemical modifications induced by the treatment.

II. Experimental

This study has been conduced on a strongly cross-linked PMMA, the HESA Glas HT, commercialized by Notz Plastics AG (Switzerland). The effects of UV illumination on these materials have been investigated by comparing the thermo-mechanical behaviour of each material before and after exposure to different optical power levels and duration of UV illumination. The equivalent radiation doses were 0.5, 0.7, 1, 1.5, 2, 4, 5, 6, 8 and 10 J/cm². The specimens, provided by the IMT/FZK (Germany), consist in circular plates of diameter 100 mm with a thickness of 0.6 mm, produced by hot-embossing. Deep UV (DUV) modification has been performed using the commercial mask aligner EVG 620 (EV Group). The application of DUV-radiation results in a local and controlled increase of the refractive index in the illuminated areas of the polymer surface. This generates the integrated optical waveguide structures in the polymer plate. The refractive index changes reach values up to 0.008 and are characterized by a graded index profile with an exponential decay, which reaches a depth of about 6 to 8 µm (estimated from the refractive index change, which is proportional to 1/e) [3].

Tensile tests have been conducted on a 5566 Instron type testing machine equipped with a 50 kN load cell, at a crosshead displacement rate of 2 mm/min. The dog-bone shape specimens, with a calibrated zone of dimensions $20\times4\times0.6$ mm^3, have been cut from the provided circular plates using a die cutter. The longitudinal deformation of the samples has been followed using an extensometer fixed on the sample. The strength to failure σ_R and the associated ultimate strain ε_R have been measured on the stress-strain curves; the Young's modulus E was evaluated from the slope of the initial linear part of the curves.

Nanoindentation tests have been conduced using a MTS NanoXP system (MTS Systems Corporation, USA), using a Berkovich diamond indenter. Specimens used for the nanoindentation tests consist in small plates of about $30\times22\times0.5$ mm³, which were cut from the circular samples. All these specimens were loaded to a depth of 2 µm, before the load was removed completely. A 3×3 matrix of indentations was performed on each sample, with 100 µm spacing between indents.

III. Results and discussion

Figure 1 shows the tensile stress-strain curves of PMMA HT samples for different UV-irradiation doses. The pristine PMMA HT presents a ductile visco-elastic behavior. By increasing the radiation dose, the materials become less ductile, less deformable and less strong. After an irradiation corresponding to a dose of 4 J/cm², the PMMA HT mostly shows a brittle behavior.

The stress and strain to failure are given as a function of the radiation dose in the Figure 2a. It is shown that these two parameters strongly decrease with an increase of the radiation dose and reach a stable value after a dose of 2 J/cm², indicating that the UV exposure of the PMMA radically changes its mechanical properties from a ductile material to a relatively brittle one. This evolution of the mechanical properties of our samples with the radiation dose is in agreement with some of the results reported in the literature [9]. The strong decrease of the stress to failure of the samples can be linked to the photo-chemical degradation of the polymer material with the UV-irradiation.

Attenuated Total Reflectivity (ATR) FT-IR studies (not reported here [12]) clearly indicate that depolymerization, main chain scission and carbomethoxy side group abstraction are the main reactions after the UV-exposure of the studied PMMA. Due to these degradation reactions, the polymer chains become shorter and more mobile, which facilitate their rearrangements and local conformational changes. It is well known that the mechanical properties of polymers are directly related to their molecular weight. Moreover, the creation of oxidized groups, such as OH, can lead to in-depth changes to the specimens. The efficiency of degradation inside the sample depends on the diffusion and migration of radicals, oxygen and other reactive species. These processes are facilitated by the presence of surface defects, small cracks and micropores. The strong decrease in both stress and strain at failure can thus be correlated to the occurrence of such damages.

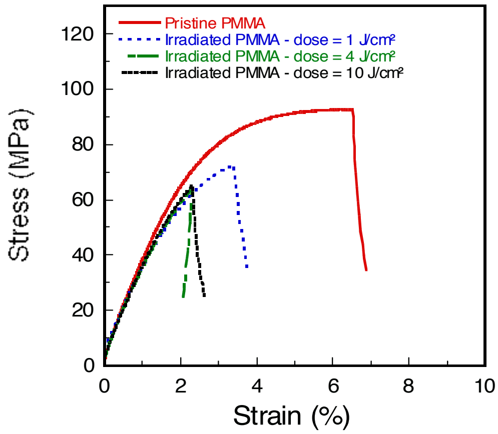
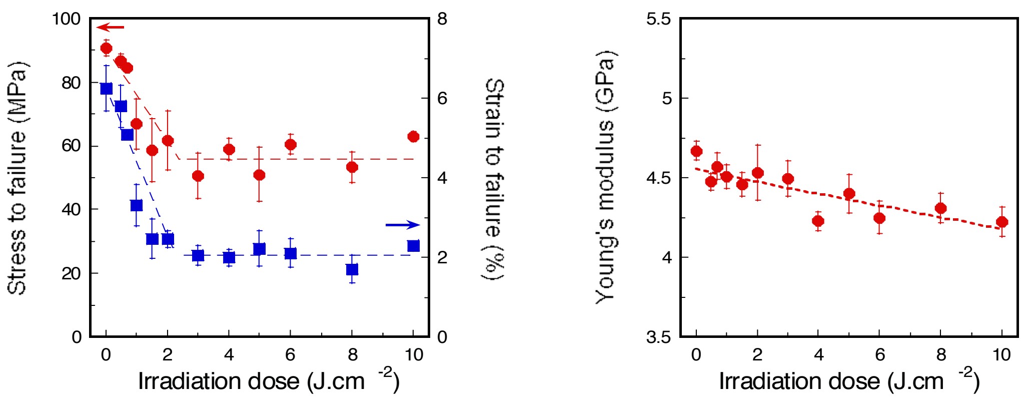


Fig. 1. Stress-strain curves for PMMA HT samples as a function of the UV radiation dose.

On the other hand, the Young's modulus calculated from the stress-strain curves, remains somewhat constant with the UV-treatment. It has to be reminded that the UV-treatment results in a modification of the PMMA material along a thickness which has been estimated to about 6 to 8μm. The tensile samples have been cut into the all thickness of the plates, of about 600 μm, so that the modified layer corresponds to about 1% of the sample thickness. This is consistent with the stability of the tensile Young's modulus. In order to investigate the mechanical properties of the modified layer, with respect to its small thickness, nanoindentation tests have been performed.

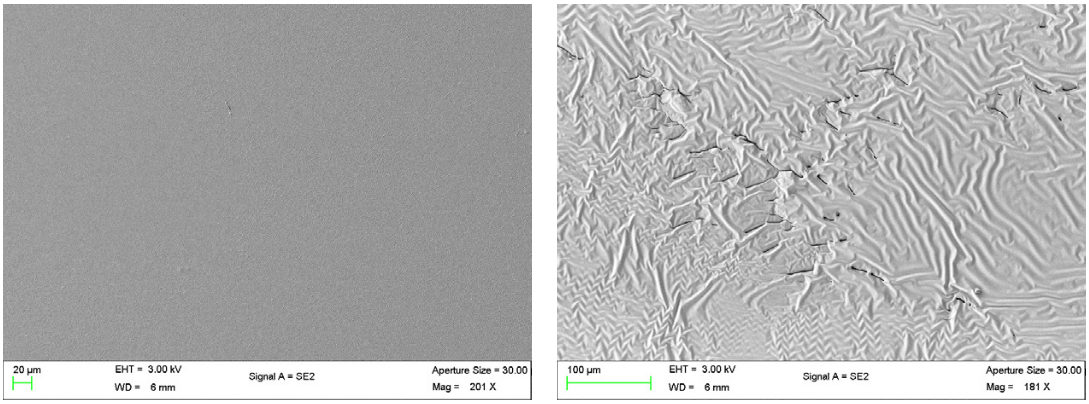


(a) (b)

Fig. 2. Evolution of the mechanical properties of the PMMA as a function of the radiation dose: (a) failure stress and strain, (b) Young's modulus

Figure 2b shows the evolution of the elastic modulus as a function of the radiation dose. The Young's modulus of the PMMA gradually decreases with the radiation dose, as the hardness remains somewhat stable. This behaviour has to be related to the chemical modifications induced into the polymer structure by the UV light. During the UV-radiation exposure, a competition between two mechanisms takes place [10, 11]: (i) at lower radiation doses a

radical cross-linking takes place; (ii) at higher radiation doses the polymer chains break between the carbonyl chains and the ester groups. As the PMMA is initially strongly cross-linked, no further cross-linkage can be induced by UV radiation, and degradation progress begins immediately with the UV exposure, resulting in the decrease of the Young's modulus, as well as a slight decrease of the hardness of the samples.
Figure 3 depicts the surface damage observed by SEM on pristine and irradiated (dose = 10 J/cm²) PMMA HT sample. The exposure of the PMMA surface to UV light results in a significant roughening of the sample surface, as well as in the appearance of cracks. These surface modifications led to an important variation of the mechanical properties of the PMMA.



(a) (b)

Fig. 3. SEM observations of the surface damage evolution of the PMMA with the UV exposure: (a) non-exposed sample, (b) exposed sample (dose = 10 J/cm²)

IV. Conclusions

In this work, thermo-mechanical properties of PMMA have been studied for different UV radiation doses. Typical mechanical parameters, such as the stress-strain curves and elastic constant have been obtained. It has been shown that the exposure of the PMMA to UV radiation leads to a reduction of its ductility, the PMMA presenting a rather brittle behaviour after a dose of 2 J/cm². The failure strength and the strain at rupture strongly decrease with the increase of the irradiation dose (over 30%), and reach a stable value for a dose of 2 J/cm². The modification of these mechanical parameters has been correlated to the reduction of the molecular weight of the polymer material, resulting from the photo-induced chain scission, and to the occurrence of surface damage, consisting in surface roughening, and in the appearance of holes and cracks. The Young's modulus of PMMA HT decreases with the increase of the radiation dose, as a chain scission process takes place upon the UV exposure.

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