EFFECTS OF SIMULATED SOLAR WIND ON POLYMETHYL METHACRYLATE THIN FILM

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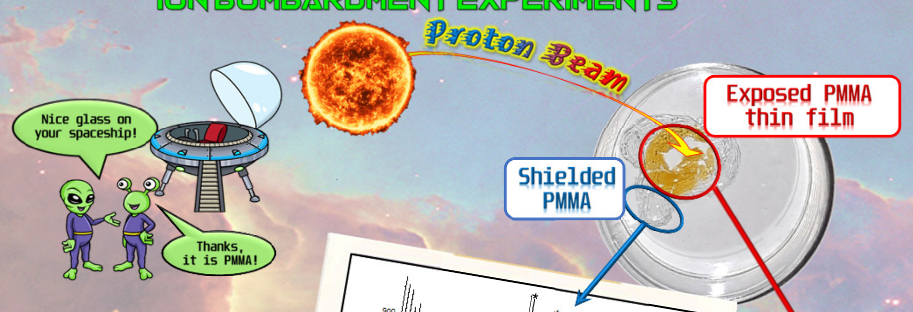
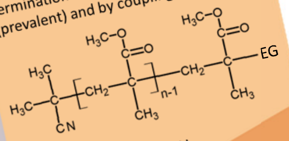
INTRODUCTION

Space exploration missions are currently becoming more frequent as demonstrated by many space missions, for example, NASA's Artemis project. In this landscape, it is extremely important to know the materials' behavior when exposed to space conditions. Thanks to their versatility, polymeric materials are suitable for advanced applications in extraterrestrial environments, despite the effects of space radiation which may cause degradation processes. Polymethyl methacrylate (PMMA) is a thermoplastic polymer with excellent mechanical properties, widely used for different applications, for example, glasses and polymeric-based nanocomposites containing different nanofillers. At now, there are few studies about the degradation mechanisms occurring on PMMA subjected to space conditions. In this work, we shed light on the effects of the simulated solar wind (obtained by proton bombardment) on a PMMA thin film. Hence, the experimental results allowed us to establish the possible degradation pathways and the relative obtained structure.

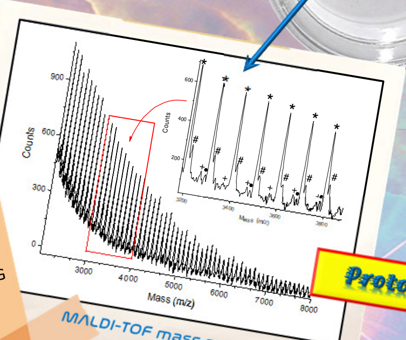
ION BOMBARDMENT EXPERIMENTS



The MALDI-TOF mass spectrum (Fig.2) confirms the structure of the pristine PMMA, showing peaks due to both termination by disproportionation (prevalent) and by coupling mechanisms.



EG=End-Group= H or IBN



MALDI-TOF mass spectrum of the pristine PMMA

Experimental setup

The substrate holder, inclined by 45 degrees with respect to both the ion beam and IR beam directions, is set inside a stainless steel ultrahigh vacuum (UHV) chamber with a base pressure lower than 10^{-9} mbar.

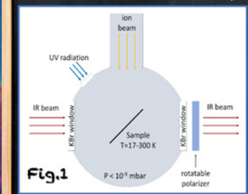


Fig.1

The FT-IR spectrometer is interfaced to the UHV chamber to in-situ acquire the IR spectra of the irradiated sample.

Fast ions, up to an energy of 200 keV, are produced in a separate vacuum line, that is connected to the UHV chamber through a UHV gate valve.

STUDY OF THE STRUCTURAL CHANGES IN PMMA

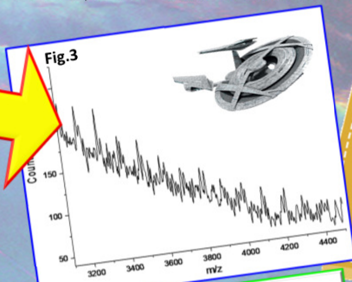
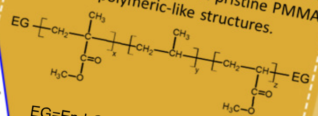


Fig.3

The MALDI-TOF mass spectrum of the bombarded PMMA (Fig.3) shows clusters of peaks belonging to both pristine PMMA and new copolymeric-like structures.



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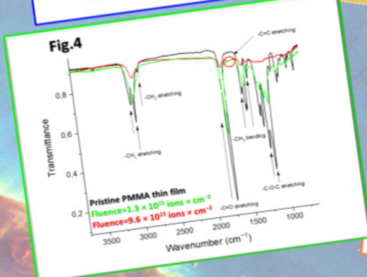


Fig.4

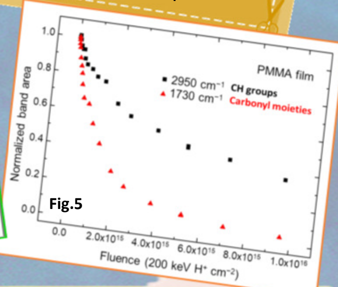
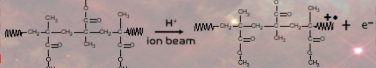


Fig.5

The 200 keV proton irradiation steps were performed in the fluence range from 6.25×10^{12} ions × cm^{-2} to a total fluence of 9.6×10^{15} ions × cm^{-2}. The variations of the signals in the FT-IR spectra (Fig.4 and Fig.5) and in the mass spectrum (Fig. 3) could be interpreted as a partial modification of the polymer, due to reactions inducing the loss of methyl and carboxy-methyl pendant groups, as showed in the PMMA Degradation Pathway scheme. The appearance of a signal at 1605 cm^{-1} (conjugated C=C stretching) could suggest the formation of unsaturated moieties. While the residual spectrum of the irradiated PMMA (Fig.4, red line) could be due to the formation of an olefinic-like structure

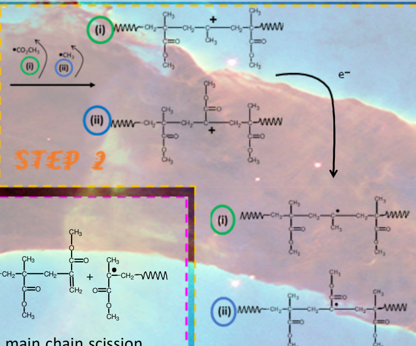
PMMA DEGRADATION PATHWAY

STEP 1



Step 1: the proton beam impinging on the polymeric thin film generates a radical cation on the main chain, causing the ejection of an electron.

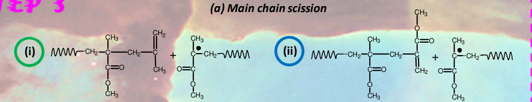
STEP 2



Step 2: the expulsion of methyl-ester radicals (path i) and/or the α-methyl radicals (path ii) generates a tertiary carbocation on the main chain, which can be converted into a radical by capturing an electron.

STEP 3

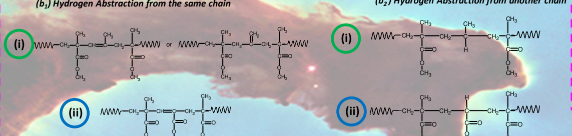
(a) Main chain scission



a) the presence of the radical could lead to the main chain scission, causing a lowering of the molecular weight of the polymer

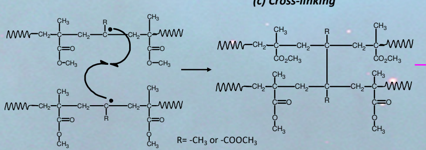
(b) Hydrogen Abstraction

(b₁) Hydrogen Abstraction from the same chain — *(b₂) Hydrogen Abstraction from another chain*



b) the polymeric chain could be stabilized by hydrogen abstraction from the same chain or from a different polymeric chain

(c) Cross-linking



c) if two radicals are close enough, they could collapse leading to branching. The eventual recurrence of this mechanism could lead to the crosslinking of the polymer matrix, justifying the reduced solubility of irradiated PMMA than that of pristine polymer.

HIGHLIGHTS

- PMMA exposed to proton beam undergoes a gradual breakdown with the consequential formation of olefinic and/or partial cross-linked structures.
- The structural modification leads to the loss of the starting properties of the material.
- It is possible to study the degradation effects of the proton beam on PMMA via common analytical techniques such as mass spectrometry and in-situ FT-IR.

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