CGPM 2020
The First International Conference on "Green" Polymer Materials
05–25 NOVEMBER 2020 | ONLINE
Chaired by PROF. DR. ANTONIO PIZZI and PROF. DR. FRANK WIESBROCK
polymers MDPI

Investigation of surface alteration of microplastics by using UV irradiation

Nina Maria Ainali [1,2] *, Dimitra Lambropoulou [1] and Dimitrios N. Bikiaris [2*]

[1] Laboratory of Environmental Pollution Control, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece

[2] Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece.

* Corresponding author: nsainali@chem.auth.gr; dbic@chem.auth.gr

EPCL...ENVMS Group

ARISTOTLE UNIVERSITY OF THESSALONIKI
BIKIARIS LAB
Faculty of Sciences, Department of Chemistry

Abstract

Microplastics are formed by the degradation of plastic wastes under the action of physicochemical mechanisms in environment, existing as contaminants of emerging concern in recent years due to their adverse impact on living organisms and the environment. When common polymers are exposed to the environment are adversely affected by solar radiation (primarily ultraviolet (UV) UV-B), which initiates photooxidative degradation leading to polymer chain breakdown, causing though the deterioration of their mechanical properties after an unpredictable time. In the present study, to improve understanding of characteristics and mechanism of microplastics, four of the most widely used polymers covering a wide spectrum of applications, due to their excellent chemical inertness and high processability such as **low-density polyethylene (LDPE**), **high-density polyethylene (HDPE)**, **polypropylene (PP)** and **polystyrene (PS)** in the form of thin films were exposed to UV radiation at **254 nm** with constant temperature for several times. After exposure (5, 10, 20, 30, 45 and 60 days), the films were removed from the chamber and UV irradiation influence was evaluated by using **FTIR** (Fourier-Transform Infrared) Spectroscopy, **DSC** (Differential Scanning Calorimetry), **XRD** (X-Ray Diffraction), **Py-GC/MS** (Pyrolysis-Gas Chromatography/Mass Spectroscopy), **SEM** (Scanning Electron Microscopy), while their **mechanical properties** were evaluated.

Keywords: microplastics; degradation; aging; UV exposure

CGPM 2020

Results and Discussion

FTIR

Formation of **ketones**, **esters** and **acids**

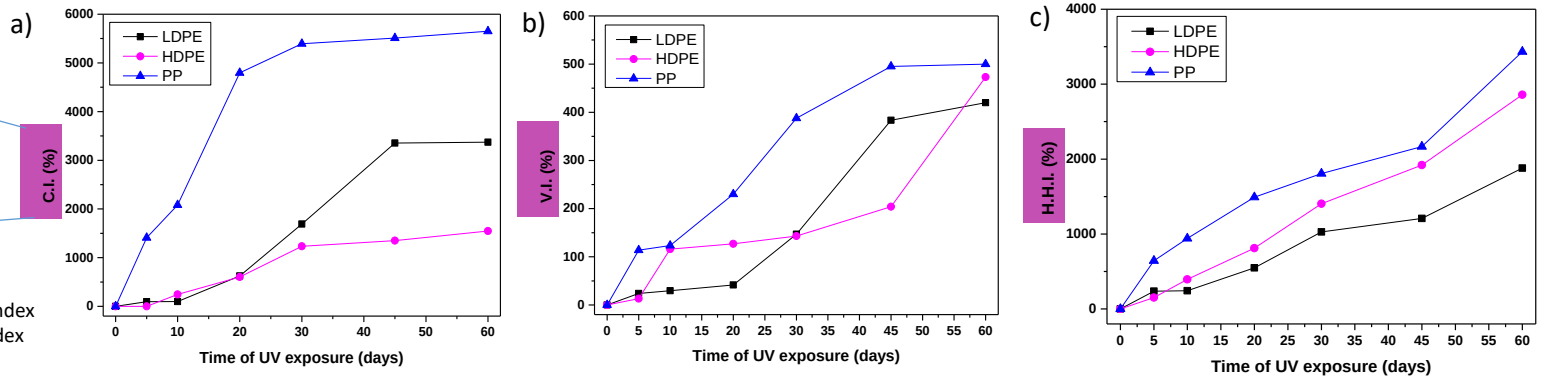
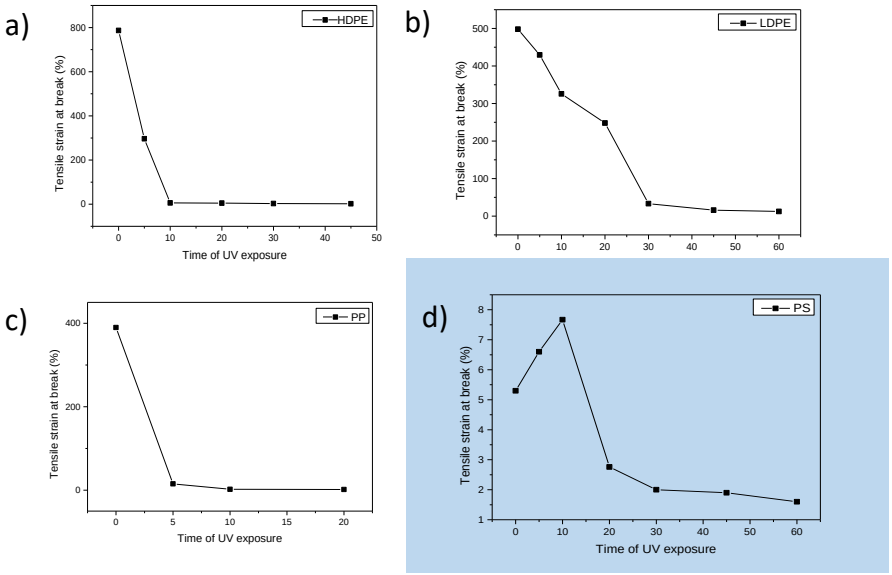


Figure 1 a) Carbonyl index, b) vinyl index and c) hydroxyl/hydroxyperoxide index of LDPE, HDPE and PP during UV exposure for different days.

Mechanical properties



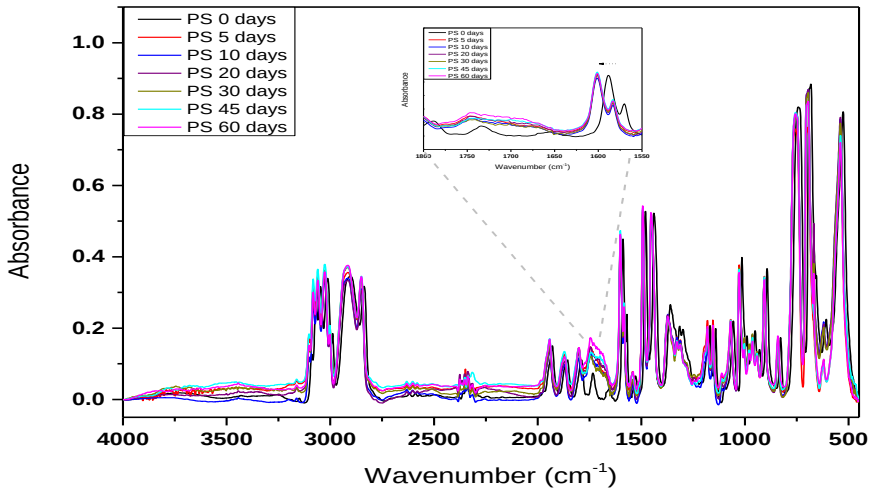


Figure 2 FTIR spectra of neat PS during UV radiation for several times.

Figure 3 Variation of tensile strength at break point for a) HDPE,b) LDPE, c) PP and d) PS during several days of UV exposure.

CGPM 2020

Results and Discussion

DSC

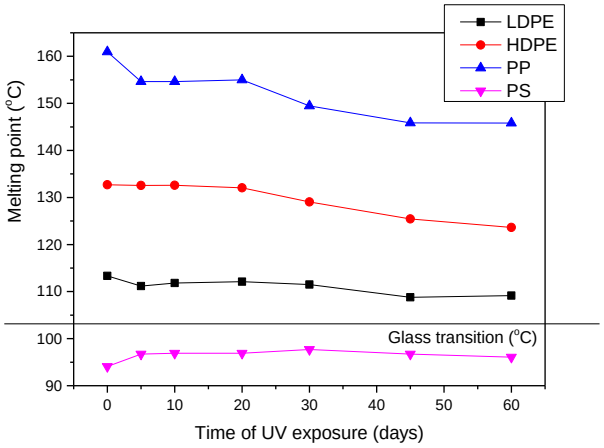


Figure 4 Variation of a) melting point at LDPE, HDPE and PP films, and b)glass transition temperature of PS after UV exposure.

- Progressing shift of PE and PP melting point to lower temperatures, as irradiation time increases.
- Increase in PS T_g till the 30rd day of irradiation, followed by a slight decrease.

Py-GC/MS

- As irradiation time prolongs, the **relative amount of low molecular weight molecules** such as butane and pentane increases.
- UV degradation created more vulnerable sites for thermal decomposition to be initiated, therefore resulting in the evolution of **more small sized hydrocarbons**.

Table 1 Ratios of PE peak areas of the hydrocarbons with more than 10 carbon atoms, to hydrocarbons up to 9 carbon atoms.

Sample name	Ratio	Sample name	Ratio
LDPE 0 days	6.98	HDPE 0 days	7.54
LDPE 30 days	4.83	HDPE 30 days	6.13
LDPE 60 days	1.22	HDPE 60 days	5.42

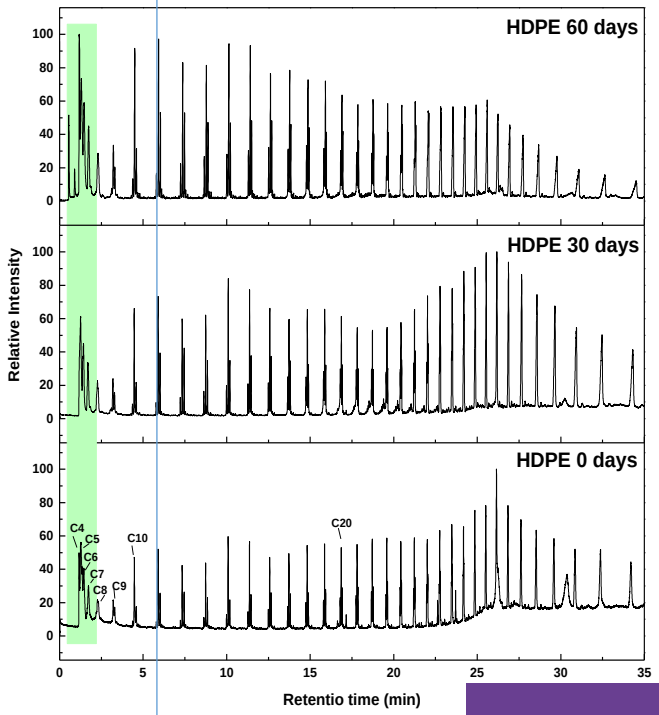


Figure 5 Gas chromatographs of unirradiated HDPE, and after 30 and 60 days of UV exposure.

CGPM 2020

Results and Discussion

Days of UV exposure

SEM

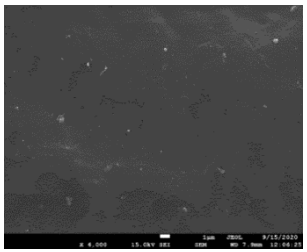
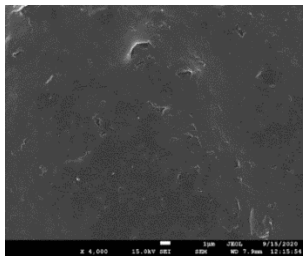
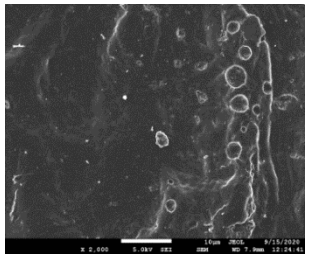
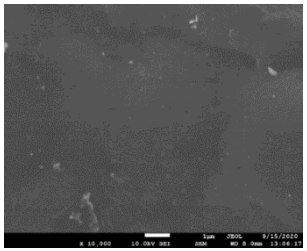
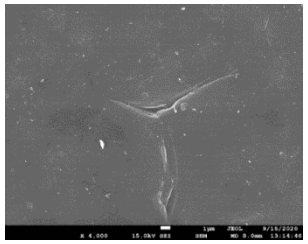
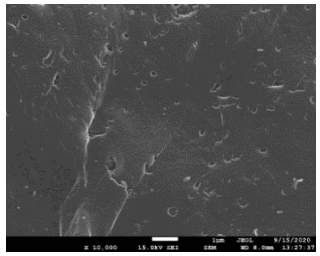
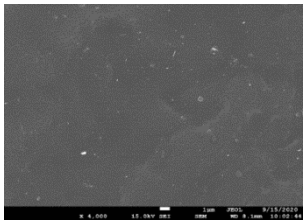
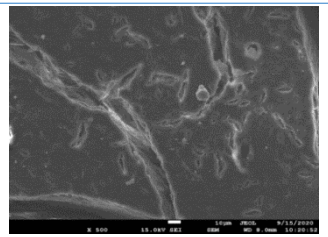
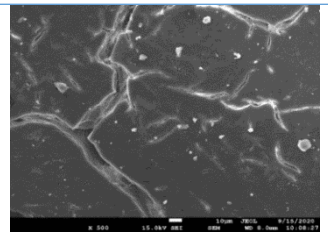
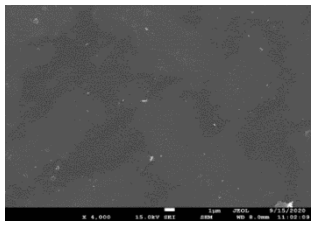
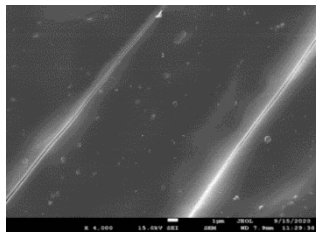
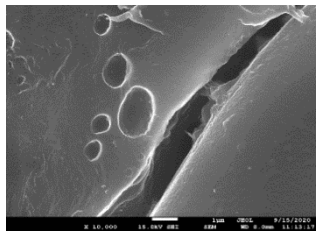
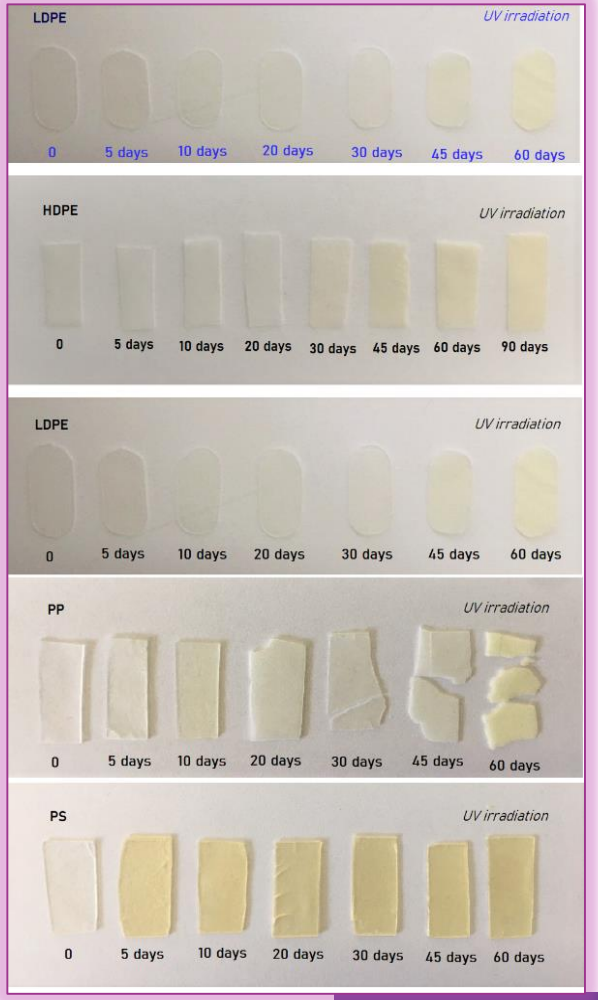
	0	30	60
LDPE			
HDPE			
PP			
PS			

Figure 6 SEM micrographs of LDPE, HDPE, PP and PS films after 0, 30 and 60 days of UV exposure, respectively.

CGPM 2020

Conclusions

- ✓ UV exposure provokes **yellowing** and **embrittlement** of the studied polymers; in PS case the yellowing starts after only 5 days of irradiation.
- ✓ **Deterioration of mechanical properties** as irradiation proceeded; PP mechanical weakening started after 5 days of UV exposure.
- ✓ **FTIR** spectra displayed significant alterations at **vinyl**, **carbonyl** and **hydroxyl** bands for PE and PP during irradiation, with the relative carbonyl index in PP being more abrupt for the first 30 days of UV irradiation; degree of chain scission and cross-linking reactions could not be estimated from PS spectra since small alterations were noticed.
- ✓ **DSC** analysis depicted a gradual drop in melting point for PE and PP, revealing the correlation between crystallinity and UV degradation process.
- ✓ **SEM** micrographs outlined cracks and holes at films' surface, after only the 30 days of UV exposure.
- ✓ **Py-GC/MS** indicated that with progressive UV exposure, the relative amount of low molecular weight compounds is boosted; the occurring UV degradation creates more susceptible sites for thermal decomposition to be originated.



CGPM 2020

Acknowledgements

This research was financially supported by the Greek Ministry of Development and Investments (General Secretariat for Research and Technology) through the research project "Intergovernmental International Scientific and Technological Innovation-Cooperation. Joint declaration of Science and Technology Cooperation between China and Greece" (Grant no: T7ΔKI-00220).

EPCL...ENVMS Group https://users.auth.gr/dlambro/

ARISTOTLE UNIVERSITY OF THESSALONIKI
BIKIARIS LAB
Faculty of Sciences, Department of Chemistry
https://bikiarislab.wixsite.com/bikiarislab

https://www.researchgate.net/profile/Nina_Maria_Ainali

nsainali@chem.auth.gr

European Commission

GSRT
GENERAL SECRETARIAT FOR RESEARCH AND TECHNOLOGY

CGPM 2020