

Accelerated Polymer Photodegradation

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Abstract: This article presents preliminary results of the accelerated degradation of polymers using concentrated solar radiation. For this purpose, a passive solar concentration prototype was designed, which consists of four trapezoidal mirrors placed in the shape of an inverted truncated square pyramid. The mirrors are placed at an angle of 30° respect to the zenith. The prototype has a square base of 46 cm x 46 cm where the polymers to be irradiated are placed and a geometric concentration ratio, CR_g , of 1.89. The mass change was determined after 30 days of exposure to solar radiation, and the temperature variation of some samples as a function of irradiance was obtained. In addition, a computer simulation was carried out using the free access software Energy2D. Some polymers maintained their flexible mechanical properties, such as PET (type 1), others were partially embrittled, while type 2, 5 and 7 polymers were completely embrittled. It was possible to reduce the degradation time of different types of commercial polymers, while polymers exposed to non-concentrated radiation and without exposure remains intact. Embrittled polymers can be used as waterproof material in slabs and pre-cast walls, as well in applications where they are not exposed to solar radiation. On the other hand, the polymers that remained intact must be used in applications with permanent radiation exposure, such as in flower pots, plastic parts for automobiles, etc.

Keywords: Polymers, Photodegradation, Solar energy, Solar concentration, Energy2D, Sustainable development.

INTRODUCTION

Photodegradation of polymers is an important phenomenon in materials science and environmental chemistry. Polymers can be natural or synthetic and constitute a wide range of materials and used in numerous industrial and everyday applications, which can undergo chemical and physical transformations when exposed to solar radiation or sources of ultraviolet radiation [1]. This photodegradation process can alter the properties and structure of the polymers, which in turn can influence their durability, elasticity, strength and useful life. The interaction of solar radiation with the chemical bonds of polymers can cause the breaking of molecular chains, the formation of functional groups and the modification of mechanical and thermal properties of the material. Photodegradation, in addition to affecting the physical structure of polymers used in industrial and everyday applications, can also have an environmental impact, since polymers without proper handling treatment can release harmful substances into the environment and contribute to waste accumulation [2]. The phenomena of photodegradation and photo-oxidation of different types of polymers in the wavelength spectrum

290 nm to 400 nm, have been widely addressed [3] while the study of the dissociation energy of C-C and C-H bonds, expressed as kcal/mol is analyzed in depth in previous work [4] where the energy for polymers commonly used in the industry is presented. On the other hand, Cacuro *et al.*, (2018) analyze the photodegradation of a single type of polymer (*i.e.*, Polypropylene, PP), they used an apparatus based on UV lamps with high electrical energy consumption [5], although they do not specify details to reproduce the experiment. This work, presents an alternative to accelerate the natural photodegradation process of single-use polymers (*e.g.*, beverage bottles, dairy food containers, etc.), using concentrated solar radiation. The photodegradation study was carried out in an inverted truncated pyramid-type solar concentrator, allowing the tolerance of the polymers to solar radiation to be quantified. It was observed that the change in the mass and mechanical resistance of the samples depends on the quality and nature of the polymers. The photodegradation of polymers is a sustainable and essential alternative to waste treatment technologies. The use of materials according to their final application and mechanical resistance is a characteristic to be considered in the most radiation-resistant polymers where it is required, or promoting the use of polymers that present degradation in a shorter time, in plastics single use.

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THEORY

The manufacture and use of consumer products lead to the generation of various types of waste. These can be represented in three different ways: i) organic and inorganic solids, ii) liquids that dissolve and form part of wastewater, and iii) those that are released in the form of gasses into the environment. Urban solid waste is the waste that we commonly find in productive and everyday spaces as a consequence of domestic activities (containers, packaging, or organic matter). The importance of proper management of these wastes not only lies in the rational use of natural resources, it is also a question of the quantity and composition of the waste and what is done to minimize health and environmental risks [2]. Polymers can be classified as natural and synthetic; they are generally organic compounds of great importance in industry due to their versatile properties and their ability to be molded into different shapes. However, their inappropriate production, use and disposal can have a significant impact on the environment, such as water and soil contamination, ecosystem degradation and threats to human health and biodiversity. One of the big problems with the excessive use and poor management of polymers is the impact on health due to the presence of microplastics in water and in species for human consumption [6]. Polymer recycling is a key strategy to mitigate the environmental impact caused by plastic waste. Among the most used techniques for treatment are: i) waste incineration, in this process they are subjected to high temperatures in controlled incinerators. This method can significantly reduce the volume of waste and generate thermal or electrical energy; ii) plastic shredding is a key stage in the mechanical recycling process. Shredding reduces the size of materials to facilitate handling and transformation into secondary raw materials, although this technique requires a large amount of electrical energy. In the case of incineration, it presents environmental challenges, since gasses and particles are released during combustion that cause

atmospheric damage. The appropriate choice of waste treatment technologies is crucial to ensure efficient and sustainable management of recyclable materials [7].

MATERIALS & METHODS

A photothermal prototype is designed that takes advantage of concentrated solar radiation to accelerate the polymer photodegradation process. The design consists of a square base of 46 cm x 46 cm, four trapezoidal mirrors: A x B x C x D of (44 x 47 x 44 x 87) cm, at 30° with respect to the zenith, placed on the walls of an inverted truncated square pyramid. The opening area ($A_{Ap.}$) and the absorption area ($A_{Abs.}$) are 87 cm and 46 cm, respectively. With this information, the geometric concentration ratio is determined [8]. $CR_g = A_{Ap.} / A_{Abs.}$, $CR_g = 1.89$. The block diagram in Figure 1 presents the stages of development of this study. It begins with the design in the free access computer-aided design program, FreeCAD [9]. Subsequently, the simulation of the thermal behavior of the system is carried out using the free-access program Energy2D [10, 11]. For the simulation, the three heat transfer mechanisms are considered: conduction, convection and radiation, as well as mass convection, and the thermal and optical properties of the materials previously reported are used [12, 13]. Figure 2 shows the design made in FreeCAD, the physical location of the geometric parameters of absorption and aperture, as well as the manufactured prototype.

To characterize the solar resource, a solarimeter (SM-206) was used. The temperature distribution of the absorber was recorded using thermal images obtained with a Flir E5 thermal imaging camera. In this way, it is possible to carry out a precise study of the temperature distribution of the absorber in the hours of exposure to solar radiation. The temperature values of the polymers were obtained using the FLIR Tools application, which allows you to import, edit and analyze the photothermal images to interpret and study the temperature of the samples. To identify the changes in the polymers due

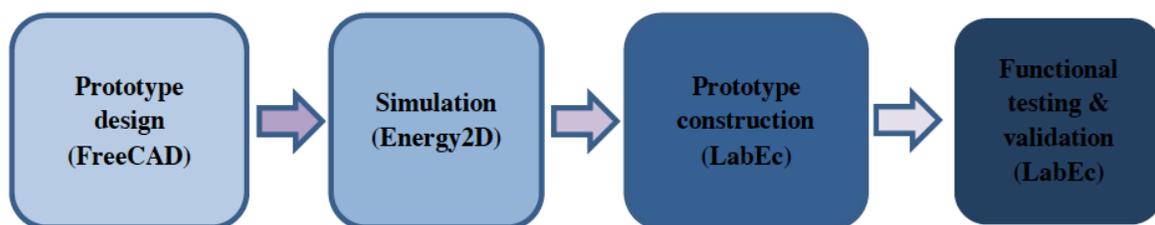


Figure 1: Block diagram of the design, simulation and experimental testing process.

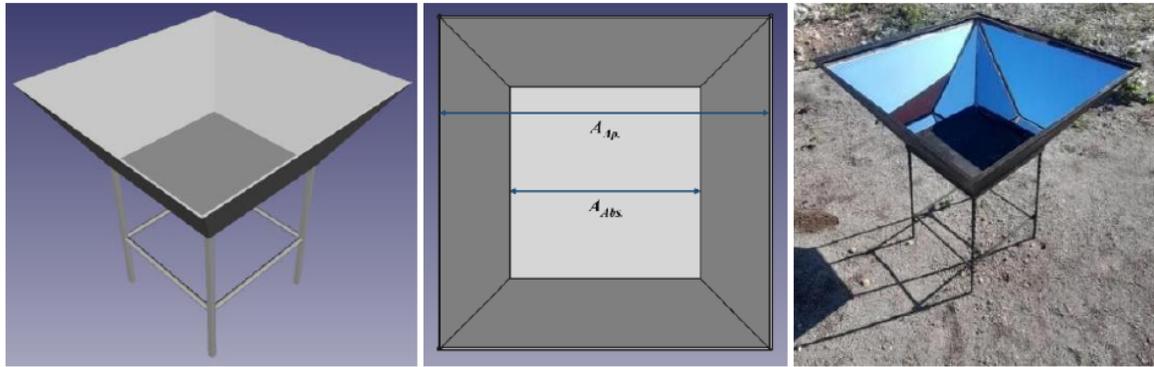


Figure 2: Prototype design using FreeCAD (**left**); top view showing the aperture and absorption area (**center**); photograph of the prototype built in the Ecotechnologies Laboratory, LabEc of the UPEGro (**right**).

to accelerated solar radiation, the change in mass is measured, expressed as a mass delta (Δm) measured via an Ohaus AX224 precision analytical balance, since due to oxidation processes some polymers generate gasses that modify the mass of the samples. Additionally, as a semi-quantitative test to compare the brittleness of the materials, their response to the application of mechanical stresses exerted manually, is analyzed. This allows classifying the polymers analyzed as: brittle polymers, partially brittle or non-brittle polymers.

RESULTS

The duration of the experiment was 30 days, from July 4 to August 3, 2023. It is worth mentioning that the

experimentation was carried out in real conditions (rain, cloudiness, wind, etc.). On day 14 of the experiment, polymers M2, M6 and M17 began to fracture, while samples M3, M10 and M12 showed signs of fracture on day 21 of the experiment. The complete table with the information on the samples that were fractured is presented in APPENDIX A. To determine the thermal behavior and the effect of the geometry of the solar concentrator, a design was carried out in Energy2D. Regarding the experimental analysis of the operation of the prototype, it consisted of a computer simulation and a comparison with measurements made using a Flir E5 thermal imaging camera, and with post-processing of the thermal images with the help of the Flir Tools application for smart devices. Subsequently,

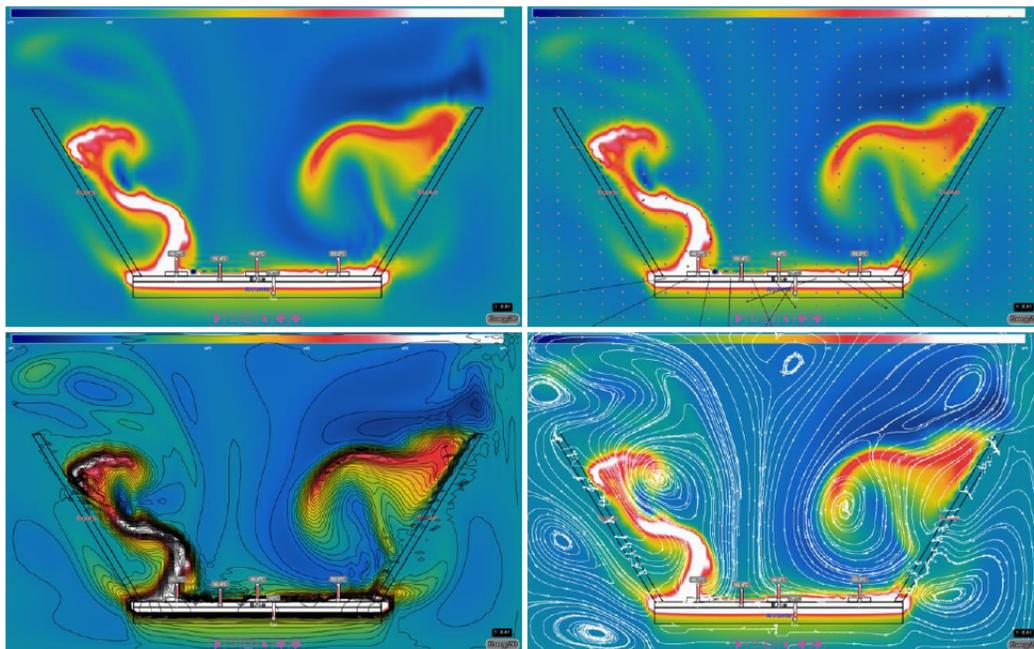


Figure 3: Simulation of radiation absorption on the samples. Natural convection of heat and mass (**top-left**); natural convection showing heat arrows (**top-right**); isotherms (**bottom-left**); and streamlines (**bottom-right**).

simulations of the heating of three polymer samples placed on the surface of the base, denoted TM1, TM2 and TM3, were performed. The heating effect due to the absorption of solar radiation that affects the polymers was analyzed, considering the absorption coefficient of each material [12]. Figure 3 shows a cross-section of the simulated prototype the thermal transfer and distribution are represented by heat flow arrows, isotherms and streamlines.

To evaluate the influence of the angle of incidence on the heat absorption on the samples, simulations were carried out at angles: 60°, 70°, 80° and 90° (i.e., 9 h, 10 h, 11 h, and 12 h) of the sample TM2. The results of this analysis are presented in the graph in Figure 4. The influence of the angle of incidence (directly associated with the time of day) with the increase in temperature of the samples can be seen.

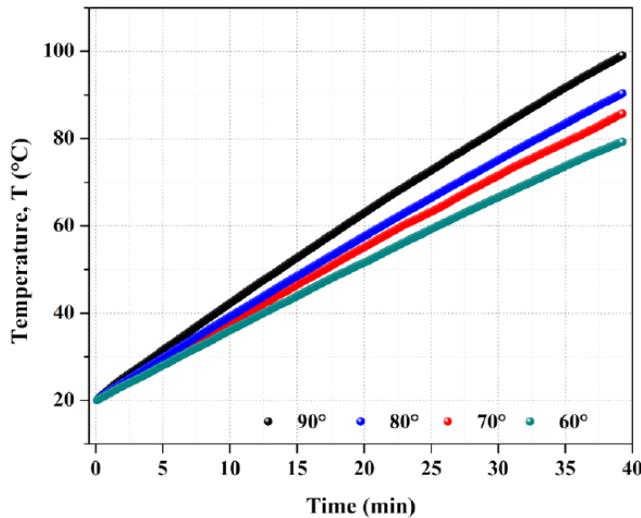


Figure 4: Temperature variation of a polymer sample placed in the center of the base.

The theoretical study regarding the effect of the angle of solar incidence on the polymers, provided a quantitative basis on the rate of heating by absorption and the most suitable solar exposure schedule for the photodegradation process, to favor the physicochemical effect in the different polymers analyzed.

4.1. Thermographic Analysis

In Figure 5, two thermal images are presented, on the left the distribution of the temperature corresponding to 9:06 h is observed, the blue area is the one with the lowest temperature in that image (i.e., 36.9 °C), it can be seen that solar radiation does not yet hit the surface evenly. To the right of that same image, a better temperature distribution can be seen, and it is observed that the highest temperature rises to 92.3 °C, the effect of concentrated solar radiation being notable.

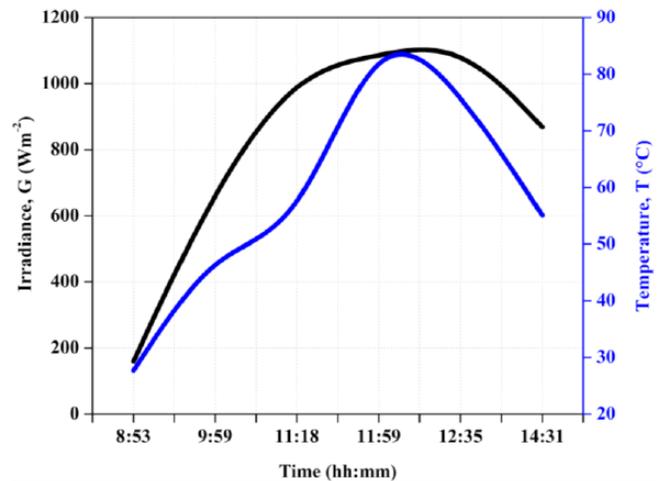


Figure 6: Variation of solar irradiance and temperature of a sample exposed to radiation.

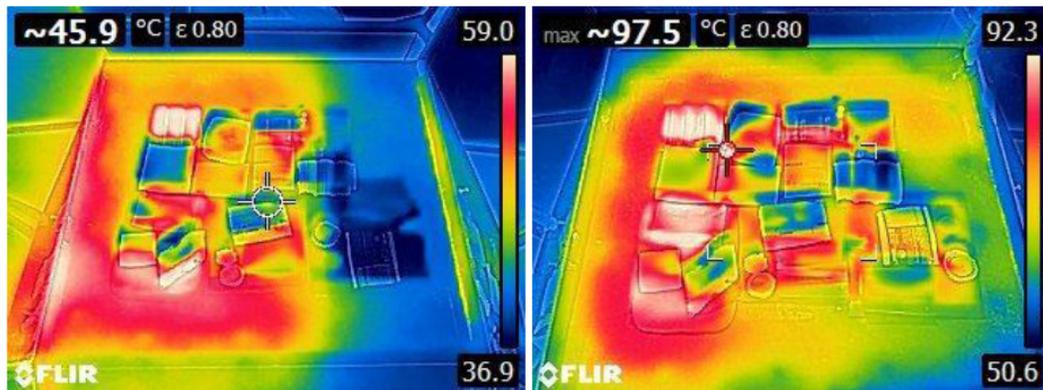


Figure 5: Thermal images from July 4, 2023; photograph taken at 9:06 a.m. (left) and 1:44 p.m. (right).

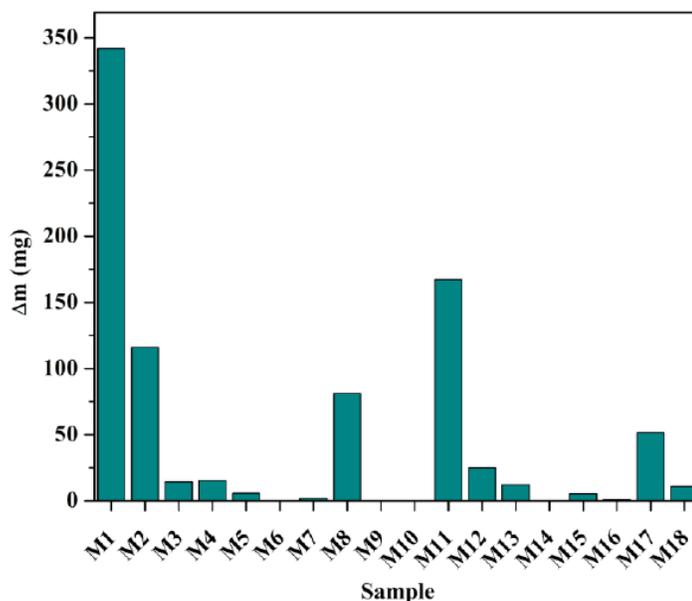


Figure 7: Mass delta of the polymer samples.

The heating of some samples was also analyzed due to the effect of absorption of solar radiation as a function of time. Figure 6 shows the representative graph of this process corresponding to August 8, 2023, of sample M18, a type 2 plastic, considering the solar irradiance and the temperature of the sample. In the same sense, the change in mass experienced by the samples at the end of the study is presented in Figure 7.

4.2. Photodegradation

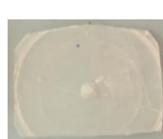
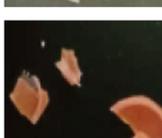
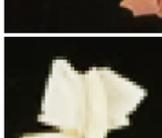
As a reference parameter, the change in mass of each sample was determined at the beginning and end of the experiment. It is observed that sample M1 is the one with the greatest change in mass, probably due to the discoloration of the sample. Some samples did not present a change in mass (*i.e.*, M6, M9 and M14). Similarly, a semi-quantitative assessment of the fragility of the polymers after exposure to solar radiation was carried out. 50% of the samples became completely fragile to the touch; 44% of the samples showed no brittleness, and 6% were partially brittle.

DISCUSSION & CONCLUSIONS

A preliminary study of the accelerated degradation of different types of commercial polymers using concentrated solar radiation is presented, for which a passive solar concentration device with a geometric concentration ratio $CR_g = 1.89$ was designed, manufactured and tested. The theoretical analysis of

the effect of the angle of incidence of solar radiation on polymers provides a quantitative basis for the heating rate and the ideal solar exposure schedule that favors and accelerates the photodegradation process. In this sense, after 9:00 a.m., the mirrors placed at 30° with respect to the zenith perform their function of projecting radiation onto the samples to be degraded, even though the prototype presented does not have a solar tracking system. It is observed that 50% of the samples exposed to concentrated solar radiation presented a total fracture, while 44% remained intact in a visual analysis and semi-quantitative mechanical fracture test, the rest presented partial fracture. Some polymers suffered discoloration and others were partially burned. The types of plastic that presented greater photo-degradation and fracture are types 2, 5 and 7. Plastics 1 and 3 did not show signs of fracture and their color remained without significant changes. This innovative equipment allows the use of concentrated solar radiation, which reduces operating costs, in addition to reducing the environmental impact of the use of typically polluting energy. It is essential to use materials according to their final application, among other aspects, their duration in the short, medium, or long term. Mechanical resistance is an important characteristic to consider in polymers permanently exposed to solar radiation. Likewise, knowledge of their behavior in the face of solar radiation makes it possible to promote the use of polymers that degrade in a shorter time, such as plastics 2, 5 and 7 in disposable packaging.

APPENDIX A

Sample	Polymer	Δm (mg)	Initial photo	Final photo
M2	7	116.1		
M3	7	14.4		
M6	5	0.0		
M10	5	0.1		
M12	5	25.0		
M14	5	0.0		
M16	2	0.8		
M17	2	51.7		

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