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# Microspherical glass additives as coating degradation promoters for UV degradable polymers

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**Abstract.** This study investigates the effect produced by microspherical glass additives on ultraviolet-induced degradation of polymethyl methacrylate films using electrochemical impedance spectroscopy. Ultraviolet exposure accelerates film degradation, which is enhanced by microspherical glass through light concentration and catalytic activity, promoting photoionization and free radical formation. Electrochemical impedance spectroscopy shows reduced impedance and curve flattening in films with microspherical glass after prolonged ultraviolet exposure, indicating faster coating failure than in pure polymethyl methacrylate. These findings support microspherical glass as a safe degradation promoter, aiding sustainable plastic design.

**Keywords:** ultraviolet degradable plastics, biopolymers, microspherical glass, degradation promoters, electrochemical impedance spectroscopy

## Introduction

The problem of plastic waste disposal is one of the most acute problems facing humanity in the 21<sup>st</sup> century. At the root of this problem is the synthetic plastic, whose natural decomposition requires from one hundred to three hundred years (Szaky 2017). Throughout the decomposition process, plastic makes its way from a unit, such as a plastic bottle, to the simplest inorganic molecules, which are water and carbon dioxide. In order to accelerate this process, so-called ‘biodegradable plastics’, or ‘bioplastics’ (Bastioli 2005) are used, which are understood as plastics that can undergo fast decomposition in the natural environment, resulting in harmless components (Ashpina 2014).

UV degradation belongs to one of the four most effective methods of plastics decomposition along with thermal, biological, and mechanical factors. Photooxidation of plastic debris by solar radiation

makes the material prone to subsequent fragmentation. Fragments formed by oxidation can be either other contaminants or non-hazardous products suitable to mechanically-assisted degradation to elemental molecular constituents (Rudin, Choi 2013).

The ideology of the perfect plastic container supposes resistivity to environmental factors on the one hand and the ability to be environmentally decomposable on the other, which, at first glance, seems contradictory. However, requirements can be defined for an ideal plastic material conforming to both of these strategies: a material that is resistant or not exposed to UV light for the duration of its service life yet able to undergo accelerated biodegradation immediately after it. Such biodegradation can be triggered by the 'smart' behavior of the material: the response of the nano-additive to external influences that activates a biodegradation mechanism. Alternatively, it can be considered a material with a built-in bio-clock that is silent for a desired period of time, subsequent to accelerated bio-decomposition after bio-clock activation.

### Spherical micro- and nano-additives and their effect on polymer materials

While nano-additives, such as titanium dioxide particles, can enhance biodegradability, their use in food packaging has been shown to pose potential health risks and should be avoided (Bettini et al. 2017; Peters et al. 2016). Consequently, micro-additives with inert properties, safe for food contact and human ingestion, are preferred. Microspherical glass (MSG) additives are a notable example of such materials.

Microspherical glass (MSG) is a versatile material with numerous practical applications due to its unique properties. It serves as a filler in plastics, rubbers, and adhesives, an additive in lightweight concretes (Chen et al. 2025), microwave absorbers (Yu et al. 2024), and metal reinforcement (Ganesan et al. 2025) to mention just a few.

The light-concentrating properties of glass microspheres are well-documented, particularly in their application as light-blocking and light-scattering modifiers to improve solar cell efficiency (Lee et al. 2015; Sasanpour, Mohammadpour 2014; Tian et al. 2013). MSG enhances LED performance (Zhou et al. 2024) and functions as microspherical lenses (Ling et al. 2023).

Available in various sizes, MSG additives exhibit high crush strength and excellent processability when incorporated into polymers, withstanding most compounding and forming processes. They are compatible with common plastics, including polypropylene, nylon, and polyethylene, and are characterized by water insolubility, high chemical inertness, and non-toxicity.

The rationale for using MSG as a promoter of UV degradation lies in its lens-like ability to concentrate optical radiation and catalytical activity of side groups present at the MSG surface. This high optical energy density accelerates the breakdown of plastic molecules through photoionization, which generates defects and free radicals that disrupt  $\sigma$  bonds. MSG can act as a catalyst and chemical reaction promoter due to its carbonyl and hydroxyl groups (Maity, Polshettiwar 2015; Nechifor et al. 2020). Spectroscopic analysis reveals absorption at  $3320\text{ cm}^{-1}$ , likely due to adsorbed water on the microsphere (Shylesh, Singh 2006), and a peak at  $960\text{--}810\text{ cm}^{-1}$  attributed to the Si-OH group (Launer, Arkles 2013). MSG also exhibits light-absorbing properties in the visible spectrum (Strawbridge, Hallett 1992) and is described as a visible-light photocatalyst (Lin et al. 2024).

This work investigated the effect of MSG on the UV degradability of polymers. Electrochemical impedance spectroscopy (EIS) was chosen as a control method indicative of polymer coating properties (Iroh, Levine 2003).

### Materials and methods

Samples of calibrated microspheres were provided by the Power Engineering Faculty of the Polytechnic University named after Peter the Great (Saint Petersburg, Russia). MSG was obtained by processing river sand in atmospheric plasma (Dresvin, Amouroux 2007) with subsequent sieving through calibrated sieves. For the experiment, a fraction of  $100\text{--}170\text{ }\mu\text{m}$  was chosen.

Polymethyl methacrylate (PMMA) with a molecular weight of 88000 was provided by lab. 3 of the branch of the Kurchatov Institute — Institute of Macromolecular Compounds.

To obtain polymer PMMA films, PMMA was dissolved in acetone at a concentration of 0.1 w %. The solution was cast and dried at stainless steel electrodes in quantity enough to obtain films of  $100\text{--}150\text{ }\mu\text{m}$  thickness. To obtain MSG-added polymer films, MSG was stir-added to a PMMA polymer solution

in the amount of  $0.1 \text{ g/cm}^3$ , followed by casting and drying. As a result, electrodes were coated with films adhered to its surface (Fig. 1).

Stainless steel plates coated with films served to working electrodes as bottoms of cylindrical EIS cells.

A total of 10 samples were made, 5 of which were PMMA films without additives and 5 PMMA with MSG additives. The samples were kept at laboratory conditions between the experiments.

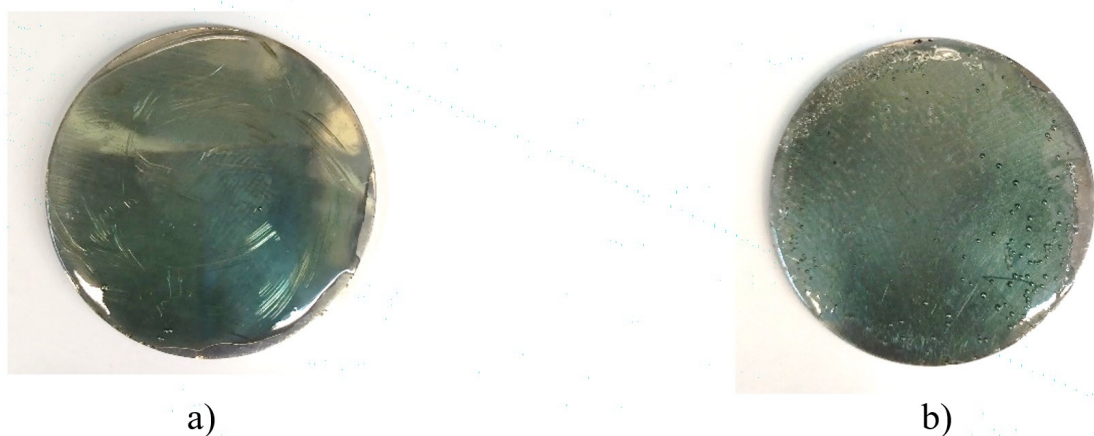


Fig. 1. Photographic image of the studied samples a) with MSG, b) without MSG

A 20 W UV light bulb with a peak intensity at 380 nm was used as a UV source. UV exposure was conducted at a distance of 10 cm from the bulb on samples submerged in distilled water, with a 1 mm water layer maintained above the film surface.

Following UV exposure, samples were transferred to a single-compartment electrochemical cell containing a  $0.1 \text{ M Na}_2\text{SO}_4$  aqueous electrolyte solution. The cell configuration included sample-coated steel as the working electrode, a platinized grid as the counter electrode, and an  $\text{Ag}/\text{Ag}^+$  wire as the reference electrode.

Electrochemical impedance spectroscopy (EIS) measurements were performed using a Gamry PC3 potentiostat over a frequency range of 5000 Hz to 0.02 Hz. Each sample was measured after 5 minutes of contact with the electrolyte. UV exposure durations were 30 minutes, followed by additional intervals of 60 and 120 minutes. After each exposure step, the samples were transferred to the EIS cell for measurement.

## Results and discussion

EIS patterns for films with and without MSG are presented in Figs. 2 and 3. The sample without MSG exhibited a slight decrease in impedance, suggesting the onset of UV-induced degradation of the polymer film. Notably, during the initial stages of exposure, the impedance slightly increased. This behavior, observed in both PMMA and PMMA with MSG, was previously reported in polyimide films subjected to corrosion testing (Levine et al. 2012). A decreasing impedance, accompanied by the disappearance of EIS curvature, is a well-established indicator of degradation (Yang et al. 2002). The samples containing MSG displayed a similar pattern up to 90 minutes of exposure. However, at 210 minutes of UV exposure, the EIS curvatures showed significant flattening, indicating a pronounced coating failure due to MSG additives promoting accelerated degradation (Fig. 2).

To assess the role of MSG as a promoter of UV degradation, the imaginary ( $\text{Im}(Z)$ ) and real ( $\text{Re}(Z)$ ) components of impedance at 0.02 Hz were selected. This frequency was chosen as a balance between minimizing experiment duration and achieving quasi-steady-state conditions for the coating. Figs. 4 and 5 present data averaged from five samples, showing the behavior of  $\text{Im}(Z)$  and  $\text{Re}(Z)$ . The primary sources of error were the inhomogeneous distribution of MSG and variations in film thickness.

The  $\text{Im}(Z)$  parameter reflects the film capacitance ( $C$ ), as described by the relation  $\text{Im}(Z) = 1/(\omega C)$ . As shown in Fig. 3,  $\text{Im}(Z)$  values for UV-treated samples with MSG significantly decrease compared to those without MSG, indicating an increase in capacitance. This increase, consistent with the behavior of a two-plate capacitor, suggests coating thickening due to decomposition.

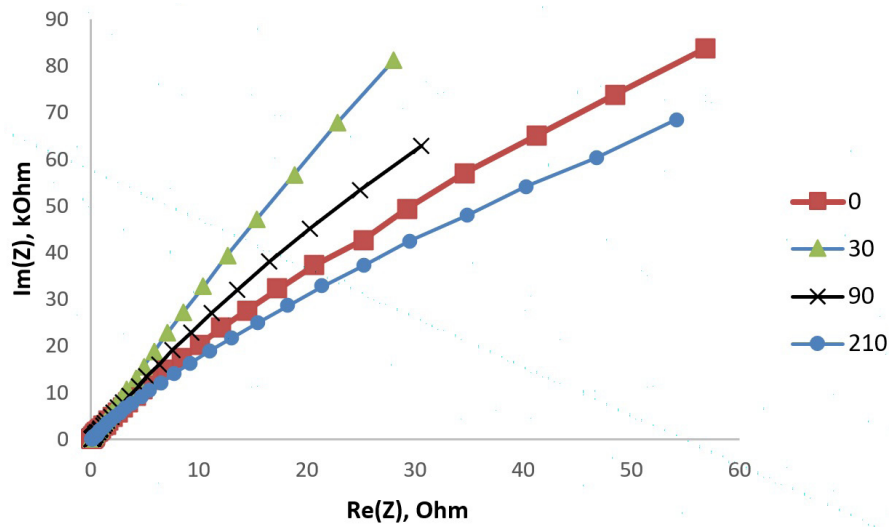


Fig. 2. Typical EIS pattern of a polymer film without MSG after different periods of UV exposure, min

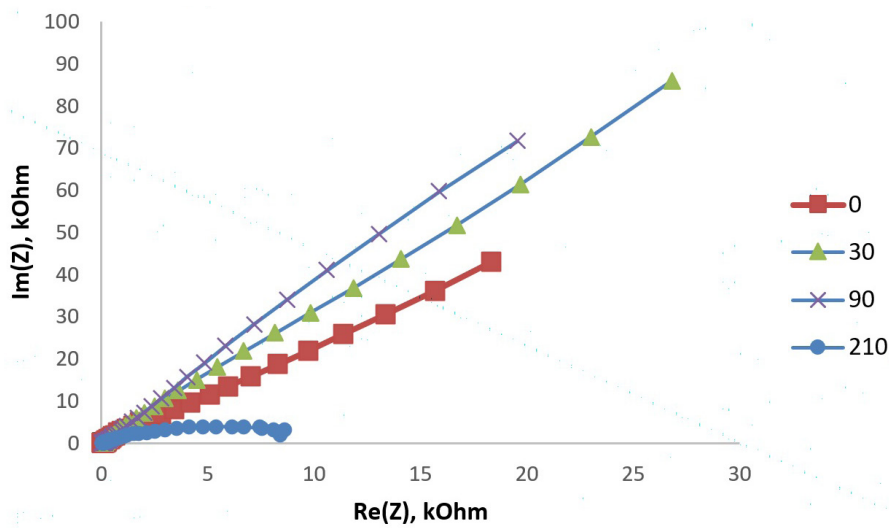


Fig. 3. Typical EIS pattern of a polymer film with MSG after different periods of UV exposure, min

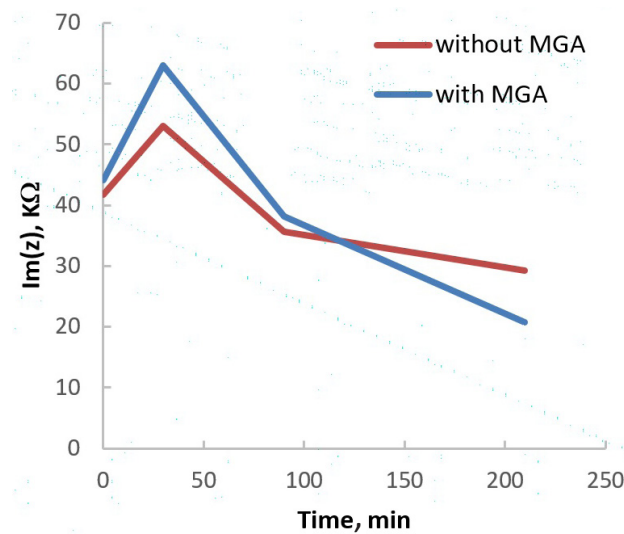


Fig. 4. Evolution of the imaginary part of the impedance ( $Im(Z)$ ) under different periods of UV exposure



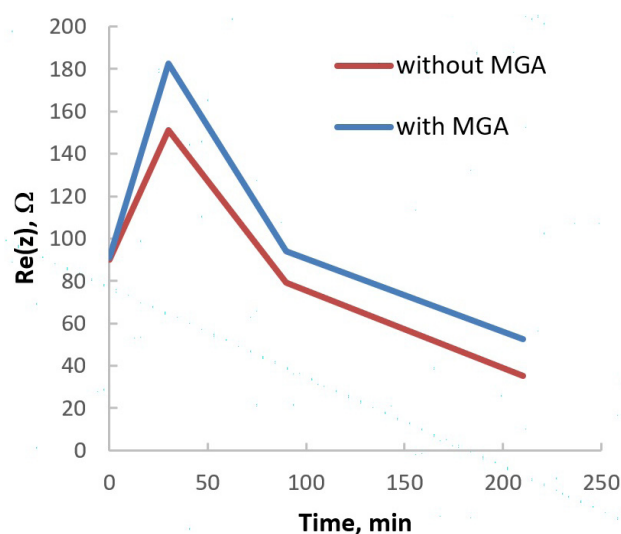


Fig. 5. Evolution of the real part of the impedance ( $Re(Z)$ ) under different periods of UV exposure

In contrast,  $Re(Z)$  data at the same frequency exhibit similar trends regardless of UV exposure. Initially,  $Re(Z)$  curves for all samples align, with differences emerging after 30 minutes of the exposure. These differences remain constant with the prolonged exposure. This behavior may reflect electrolyte saturation within the coating, primarily indicating interface properties rather than bulk characteristics, rendering  $Re(Z)$  less informative for studying the phenomenon.

## Conclusions

The study concludes that MSG significantly influences the UV-degradable properties of polymer films, acting as a promoter of UV-induced degradation. These findings are practically significant for developing UV-degradable plastic packaging with accelerated solar-induced decomposition, offering a novel 'green technology' approach to combating plastic pollution.

## Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

## Author Contributions

All the authors contributed equally to this work.

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