



## Research Paper

# Assessment of chemicals released in the marine environment by dielectric elastomers useful as active elements in wave energy harvesters



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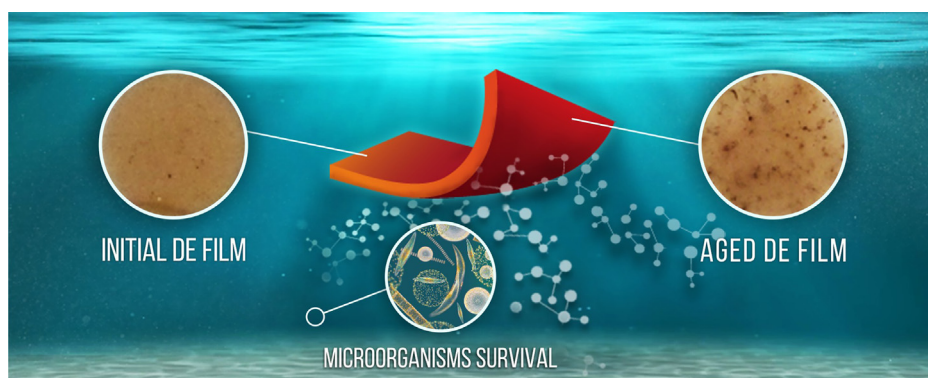
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## HIGHLIGHTS

- Rubbers suitable for wave energy dielectric elastomer transducers are taken in study.
- The chosen elastomers are studied for assessing their hazard risk on marine environment.
- A sequence of techniques is applied to analyze salt water in which rubbers were immersed.
- Chemicals released by rubbers for half a year of immersion in salt water are assessed.
- The activity of the rubber releases in salt water on the microbial flora was assessed.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A series of elastomers, either natural or synthetic (some of them commercial, while others prepared in the laboratory), suitable for use as active elements in devices for wave energy harvesting, were evaluated concerning their behavior and effects on the marine environment. In this aim, the elastomer films, initially evaluated regarding their aspect, structure, surface wettability, and tolerance of microorganisms growth, were immersed in synthetic seawater (SSW) within six months for assessing compounds released. There were analyzed the changes occurred both in the elastomers and salt water in which they were immersed. For this, water samples taken at set time intervals were analyzed by using a sequence of sensitive spectral techniques: UV-vis, IR, and in relevant cases <sup>1</sup>H NMR and electrospray ionization mass spectrometry (ESI-MS), able to detect and identify organic compounds, while after six months, they were also investigated from the point of view of aspect, presence of metal traces, pH, and biological activity. The changes in aspect, structure and morphology of the dielectric films at the end of the dipping period were also evaluated by visual inspection, IR spectroscopy by using spectral subtraction method, and SEM-EDX technique.

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## 1. Introduction

Dielectric elastomers are electroactive materials, which became of great interest in the last two decades for one of the main fields

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of human creativity developed on the border between chemistry and mechanics of materials, an emerging field that uses soft active materials to create soft machines. The operating principle of these materials can be summarized as follows: when a voltage is applied, their thickness is reduced in the direction of the applied field but, due to the material incompressibility, the area extends, thus a mechanical work is performed. This is called “actuation mode”, and is used in dielectric actuator – DEA, and for broad applications, including soft robots, adaptive optics, Braille displays, etc. [1]. When they return from a mechanical deformation and an initial charge, dielectric elastomers can function as generators – DEGs, similar with the principle of electrostatic energy conversion [2]. Different mechanical forces could be used, e.g., human motion, wind, wave, etc. The use of dielectric elastomer generators (DEGs) consisting in elastomeric thin films coated with compliant electrodes [3], to convert ocean-wave power in electrical energy, is an alternative for a few still immature, pre-commercial systems in operation around the world, having as potential advantages, among others, large energy densities, cyclic operation, good efficiency, high shock and corrosion resistance, noiseless operation and reasonable costs [4]. Natural, butyl, styrene–butadiene, ethylene–propylene, acrylic, and silicone rubbers and polyurethanes, and their different modifications are used as dielectric elastomers [5].

Polymers in general and especially rubbers are widely used in marine environments due to their excellent properties and good weathering resistance [6]. However, they are rarely used in pure form and almost all commercial plastics include a wide variety of chemical additives, which may be incorporated during manufacture as processing aids, to change their properties or extend their life [6–9]. Fillers and pigments are often added to polymers, their type significantly influencing the behavior of polymers [10]. Some additives are designed to stabilize the polymers and make them more resistant towards degradation [7], by providing thermal (e.g. polybrominated diphenyl ethers), photo, oxidative (e.g. nonylphenol) and microbial (e.g. triclosan) resistance but the amounts used in plastic products vary [6–9,11,12]. In recent years, biodegradable polymers play an essential role in solving or mitigating the problem of plastic waste [13,14]. In this context, additives are an alternative to confer biodegradability to synthetic polymeric materials [15,16]. Generally, additives are not chemically bonded to the polymer matrix so they can migrate easily into the environment, whether it is air, soil or water, and can thus be up taken by living organisms with disastrous effects on them [17]. In addition, additives are low molecular compounds and are more reactive than polymers, generating by-products which can migrate out of the polymer matrix [18]. Thus, the products resulted from the degradation of the plastics are not the only chemicals released by polymeric materials during weathering. Additives are also released and they can be themselves dangerous or these may also degrade to form other environmental pollutants [7]. Besides the fact that they may leach out introducing potentially hazardous chemicals to biota, additives are also an environmental concern because, in some cases they can extend the degradation times of plastic [8,9,17]. Phthalates, bisphenol A and brominated flame retardants, although are the most used additives, they are the highest risk to the environment because they are considered to be biologically active. In addition, they are resistant to photo- and bio-degradation, thus presenting potential for accumulation and persistence. Therefore, efforts are being made to carefully monitor or replace them with less dangerous products [17]. For example traditional brominated additives commonly used to increase their fire resistance and often detected in environmental samples [19] are increasingly being replaced by halogen-free flame retardants [17]. Phthalates are commonly used as plasticizers that soften plastics by reducing the affinity between molecular chains within the synthetic polymer matrix. In some cases (e.g., PVC), phthalates can account for up to 50% of their mass [7,8]. But

they are chemically stable in a wide range of temperatures; they migrate easily from the polymer and are easily soluble in the water, polluting it [17]. An alternative to the addition of extractable phthalates is the use of lower toxicity plasticizers (i.e., natural-based plasticizers) or to resort to the use of flexible polymers that require less or no plasticizer [20]. Such flexible polymers are silicones that do not require the addition of plasticizer and are therefore more environmentally friendly.

As mentioned above, the using of dielectric elastomers in units of wave energy conversion is just at the beginning. The performance of these materials and, more so, their impacts on the marine environment are not fully confirmed. Therefore, concomitantly with on-going research to develop chemical structures and formulations suitable for dielectric elastomers, our interest is also in the study of their behavior and impact on the marine environment. In a previous paper [21], we studied modifications of mechanical and dielectric properties of specially designed, in-house prepared dielectric silicone elastomers induced by their exposure in salt water with or without UV irradiation.

In this paper, we focused on the influence that various dielectric elastomers (commercial or prepared by us) with potential in energy generators could have on the marine environment. For this, the samples were immersed into SSW, which is ion-exchanged water containing 3.3 wt% sea salt [22]. The potted samples were maintained in the laboratory conditions and monitored by different methods during half a year, a period similar to that used by Sudhakar et al. [23] to study the biodegradation of the polyolefins in ocean waters. The releases were evaluated monthly by IR and UV spectroscopies and, in certain cases by  $^1\text{H}$  NMR and ESI–MS, while at the end of the period considered, the metal traces, pH and biological activity of the extraction solution were measured to assess the possible effect induced to the marine biosystem. The changes in the structure and morphology of the dielectric films occurred as a result of their dipping in sea salt solution were also verified by IR using spectral subtraction method and SEM–EDX, respectively.

## 2. Experimental

### 2.1. Materials

The synthetic seawater (SSW) was prepared by dissolving sea salt commercially available (Solaris Plant S.A.) in 3.3 wt% [22] in Millipore water (MW).

The studied samples are thick films/foils of commercially available rubbers with partly disclosed composition and synthetic details as follows. Natural rubber (NR) is a polyisoprene in *cis* conformation with minor impurities of other organic compounds (up to 5% reported to the dry rubber mass consists in proteins, fatty acids, resins), inorganic salts and water; it also can contain up to 50% filler (i.e., carbon black) [24–28]. Natural rubber/styrene butadiene rubber (NR/SBR) is a blend of the two rubbers with their usual additives: zinc oxide, stearic acid, morpholine benzothiazol sulphonamide (MOR), cyclohexyl-2-benzothiazyl (CBS-N), trimethyl dihydroquinoline (TDQ), sulphur [29]. Butyl rubber (BUTYL) is generally produced by copolymerizing isobutylene with small amounts of isoprene. Usually, these are incorporating carbon black (0–55 pph), zinc oxide/stearic acid or other fatty acid as curing accelerator/activator and processing aid, respectively, elemental sulphur with *N-t*-butyl-2-benzothiazoylesulfenimide (TBSI) or sulphur donor cure systems consisting in tetramethylthiuram disulfide (TMTD) and dithio dimorpholine (DTDM) [30]. Ethylene-propylene-diene rubber (EPDM) is, as its name shows, a terpolymer of ethylene, propylene and diene, in which in general the ethylene is the major component. The commercial formulations generally contain, besides copolymer, paraffinic oil, fatty

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