



## 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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## 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 <sup>1</sup>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 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-benzothiazolesulfenimide (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

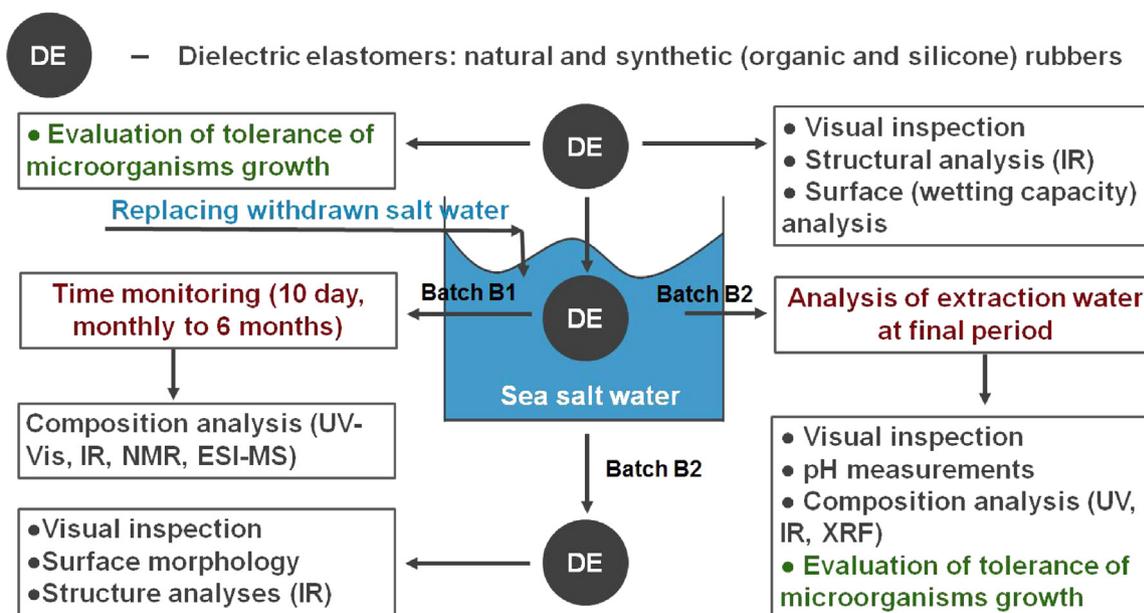


Fig. 1. Schematic representation of the monitoring protocol.

acids (stearic), inorganic oxides (ZnO) as curing activators, talc ( $\text{H}_2\text{Mg}_3(\text{SiO}_3)_4$ ), sulphur compounds (benzothiazole disulphide as vulcanisation accelerator and tetraethyl or tetramethyl thiurame disulphide:  $(\text{C}_2\text{H}_5)_2\text{NCSS}_2\text{CSN}(\text{C}_2\text{H}_5)_2$  or  $(\text{CH}_3)_2\text{NCSS}_2\text{CSN}(\text{CH}_3)_2$ ) as fast vulcanizing accelerator agents [31]. Coloured Styrene Butadiene Rubber (CSBR) is generally produced using recycled tyre rubber which is coated in colour pigments in a trammel mixer to ensure high colour consistency [32]. Nitrile-butadiene rubber (NBR) is a copolymer of acrylonitrile with 15–50% butadiene having also incorporated in general carbon black (up to 90%), hard clay, plasticizer and small amounts of zinc oxide, stearic acid, sulphur, and curing accelerator [33]. Silicone rubber (SR) has as basic component crosslinked polydimethylsiloxane. Inorganic salts (Pd, Al, Zn, Ce) or oxides (Fe, Ti) as heat stabilizers and/or pigments [34] are among usual additives. When highly reinforcing silica fillers are incorporated, processing aids are used that have a softening or plasticizing effect [33]. The silicone elastomers prepared in our laboratory as thick films, have the following characteristics. **SR1**: A polydimethylsiloxane- $\alpha,\omega$ -diol with number-average molecular weight of  $440,000 \text{ g mol}^{-1}$  radicalic cross-linked in presence of 2,4-dichlorobenzoyl peroxide at high temperature [35]. Before crosslinking, 8 wt% silica hydrophobized by surface treatment with octamethylcyclotetrasiloxane in vapour state was incorporated. **SR2**: A polydimethylsiloxane- $\alpha,\omega$ -diol of number-average molecular weight of  $650,000 \text{ g mol}^{-1}$  filled with 15 wt% commercially available barium titanate nanoparticles, surface treated with Pluronic L-81, according to procedure described in ref. [21]. The composite was crosslinked by condensation with methyltriace-toxysilane at room temperature. **SR3**: A polydimethylsiloxane- $\alpha,\omega$ -diol of number-average molecular weight of  $450,000 \text{ g mol}^{-1}$  filled with 5 wt% barium titanate nanorods prepared according to reference [36] and surface hydrophobized by treating with hexamethyldisilazane. The crosslinking was performed with triethoxymethylsilane (TEMS) in presence of dibutyltindilaurate (DBTDL). **SR4**: A polydimethylsiloxane- $\alpha,\omega$ -diol of number-average molecular weight of  $350,000 \text{ g mol}^{-1}$  filled with 2 wt% titanium dioxide nanotubes surface treated with hexamethyldisilazane. The crosslinking was performed with TEMS in presence of DBTDL [37].

## 2.2. Measurements

Water contact angle measurements were performed on the film surface with KSV Instruments Ltd equipment at room temperature. Three measurements were performed for each sample and the average values were taken into account, the results being expressed as mean  $\pm$  standard deviations. UV-vis spectra of the seawater extracts of the polymer films were registered on a Jenway 6505 Spectrophotometer (Watford, UK) in 10 mm optical path quartz cuvettes by using SSW as reference. The infrared measurements for the dried samples (seawater extracts and polymer films) were carried out on a Bruker Vertex 70 spectrometer (Bruker Optics, Ettlingen, Germany). The spectra were recorded in ATR (Attenuated Total Reflectance) mode in the range of  $4000\text{--}600 \text{ cm}^{-1}$  at a resolution of  $4 \text{ cm}^{-1}$ , at room temperature. The  $^1\text{H}$  NMR spectra were recorded on a Bruker Avance DRX 400 MHz Spectrometer equipped with a 5 mm QNP direct detection probe and Z-gradient. Spectra were recorded in  $\text{CDCl}_3$ , with 128 scans, at room temperature. The chemical shifts are reported as  $\delta$  values (ppm) referenced to the solvent residual peak (7.26 ppm). The detection of the presence of heavy metals in the seawater after the immersion of the polymeric films was evidenced using an energy-dispersive X-ray fluorescence (EDXRF) system (EX-2600 X-Calibur SDD). SEM images were taken with an Environmental Scanning Electron Microscope (ESEM) type Quanta 200 operating at 20 kV with secondary electrons (SE) in low vacuum mode. The SEM studies were performed on samples (polymeric films) fixed on copper supports using carbon tape. pH measurements of the aqueous solutions (seawater extracts) were made with a Sensorex pH-meter attached to a Tensiometer Sigma 700. Biological activity tests of the seawater extracts after the immersion of the polymeric films were achieved by standard procedure. The successive dilution procedure has been used to prepare the suspension of microorganisms, final load of as prepared stock inoculum was  $1 \times 10^{-4} \mu\text{g/ml}$ . Microorganisms were provided by American Type Culture Collection (ATCC), USA. The nutrient agar medium was used, from Merck Company (Schwalbach Hesse, Germany). We assessed microbial activity *in vitro* using a suspension of fungi species (*Aspergillus niger*, *Penicillium frequentans*, *Aspergillus flavus*, *Penicillium chrysogenum* and *Alternaria alternata*) and bacteria (*Pseudomonas aeruginosa*, *Microspira*, *Desulfovibrio*, *Bacillus*), some of which are similar to those reported for the

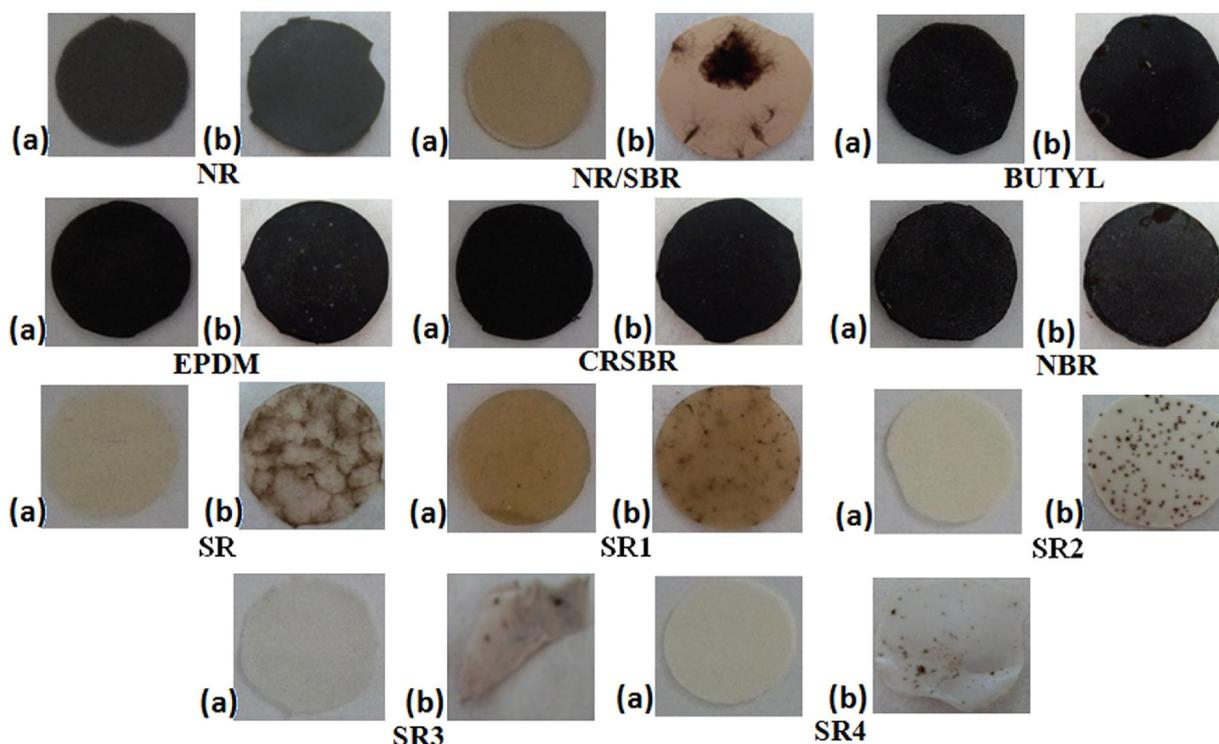


Fig. 2. The aspect of the original elastomer films (a) and after six months of immersion in sea salt water (batch B2) (b).

biodegradation of polyethylene [38]. Observations on the results were made by visual analysis, microscopy and photography, using an Olympus SZY 160 microscope (Olympus Corporation, Shinjuku, Tokyo, Japan). By this protocol, it has been studied the availability of elastomeric membranes for accommodating and development of microbial flora on their surface on the one hand, and the effect that their leakages during films immersion in salt water might have on microbial flora, on the other hand.

### 2.3. Procedures

A series of commercial elastomers used as DE, together with in-house prepared silicone materials, have been tested during six months immersion in SSW, according to the protocol showed in Fig. 1. For this, circular samples with the same diameter (25 mm), and masses between 0.5 and 1 g, depending on film thickness, were cut and submerged in equal volume of SSW (20 ml 3.3 wt% sea salt) placed into polypropylene vials (transparent and sterile, recommended for storage and transportation of liquids, solids and biological materials). Two batches, B1 and B2, were prepared simultaneously. The vessels were closed and kept in the laboratory environment under natural light. Samples consisting in well determined volumes of solutions (3 ml) were extracted from batch B1 at 10 days, 2, 3, 4, 5, 6 months and the withdrawn volumes were replaced each time with fresh salt water. These were analyzed as such by UV-vis spectral method and after evaporating by IR spectroscopy. The protocol allowed the identification of some of the components by comparing with spectral library. In relevant cases, these were also analyzed by  $^1\text{H}$  NMR and ESI-MS. The samples of batch B2 were not opened during the entire six month period, after that, the metal traces, pH and the inhibitory activity for the growth of microorganisms in the used water were determined by specific tests. For pH measurements, SSW and MW were used as control samples. The results are expressed as mean  $\pm$  standard deviations of three independent experiments.

The modifications of the DE materials after six months dipping in salt water (batch B2) were visually inspected and investigated by FTIR, SEM and, in some cases, by EDX.

## 3. Results and discussions

Samples of similar dimensions of elastomers, either commercially available (NR, NR/SBR, BUTYL, EPDM, CRSBR, NBR, SR) or prepared by us (SR1–SR4), with potential application in ocean wave energy harvesting devices were immersed for six months in SSW under room temperature and normal lighting conditions. Two containers, B1 and B2, were prepared for each sample; from batch B1 water samples were extracted periodically and were replaced with fresh solution each time, while the others were not replaced until the end of the monitoring period (B2). After 10 days and then every month for six months, aqueous samples were extracted and analyzed by IR and UV-vis and in a few cases by  $^1\text{H}$  NMR and ESI-MS (B1). At the end of the study period, for the samples in containers which have not been opened during the entire period (B2) there were measured pH, metal traces and biocidal activity of the extraction water, while the changes occurred in elastomer films were investigated visually and also by SEM on surface and in section, EDX and IR-ATR-spectroscopy (Fig. 1).

### 3.1. Analysis of initial elastomer films

#### 3.1.1. Optical aspect

The elastomeric films taken in study were first inspected visually, their optical aspects being showed in Fig. 2a, and their water contact angle and behavior in biological environment were evaluated.

#### 3.1.2. Surface wetting

Contact angle measurements on the surface of the initial films indicate sample NR/SBR as the most hydrophilic ( $84.1^\circ$ ) followed

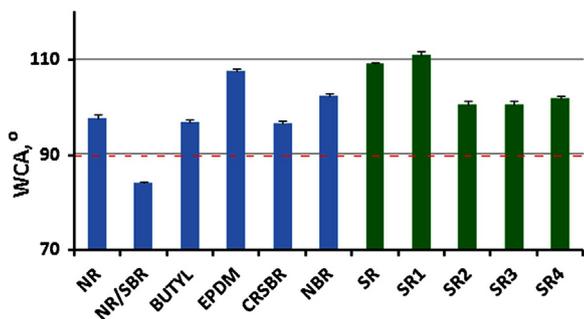


Fig. 3. Comparative values of water contact angle of the elastomer film surface.

by CRSBR (96.7°), BUTYL (96.9°) and NR (97.7°), while the most hydrophobic are, as expected, silicone-based samples SR (109.2°) and SR1 (110.9°) (Fig. 3). Thus, for the latter, the water-surface contact will be minimized, which is expected to limit the accommodation of foreign objects and degradation processes.

### 3.1.3. Behavior in biological loaded environments

Generally, polymers when exposed to sea water, as well as soil or other biotic environments, develop on their surface a microbial rich biofilm due to the reduction in its hydrophobicity [39]. The microbial activity influences the degradation rate of the polymeric material [40]. The behavior of the elastomeric films in their initial state (as prepared or found commercially) was studied in biological loaded environments. The Petri plates with culture media that were previously seeded with a suspension of microorganisms with concentration of  $1 \times 10^{-4}$  µg/ml and trial samples have been incubated. Microbial suspension consists of a mixture of eight microorganisms commonly found in aqueous media. Samples were examined by optical microscopy after 48 h and photo images taken are shown in Fig. S1. From these images, it can be seen that, while the samples BUTYL, EPDM, CRSBR, SR, SR1, SR3 (among these are the samples with highest values for water contact angle) are not affected by the presence of microbial flora in the environment, samples NR, NR/SBR, NBR, SR2, SR4 were covered by a thin layer of microbial flora. At this point, it is difficult to correlate this behavior with the structure or the composition of the materials.

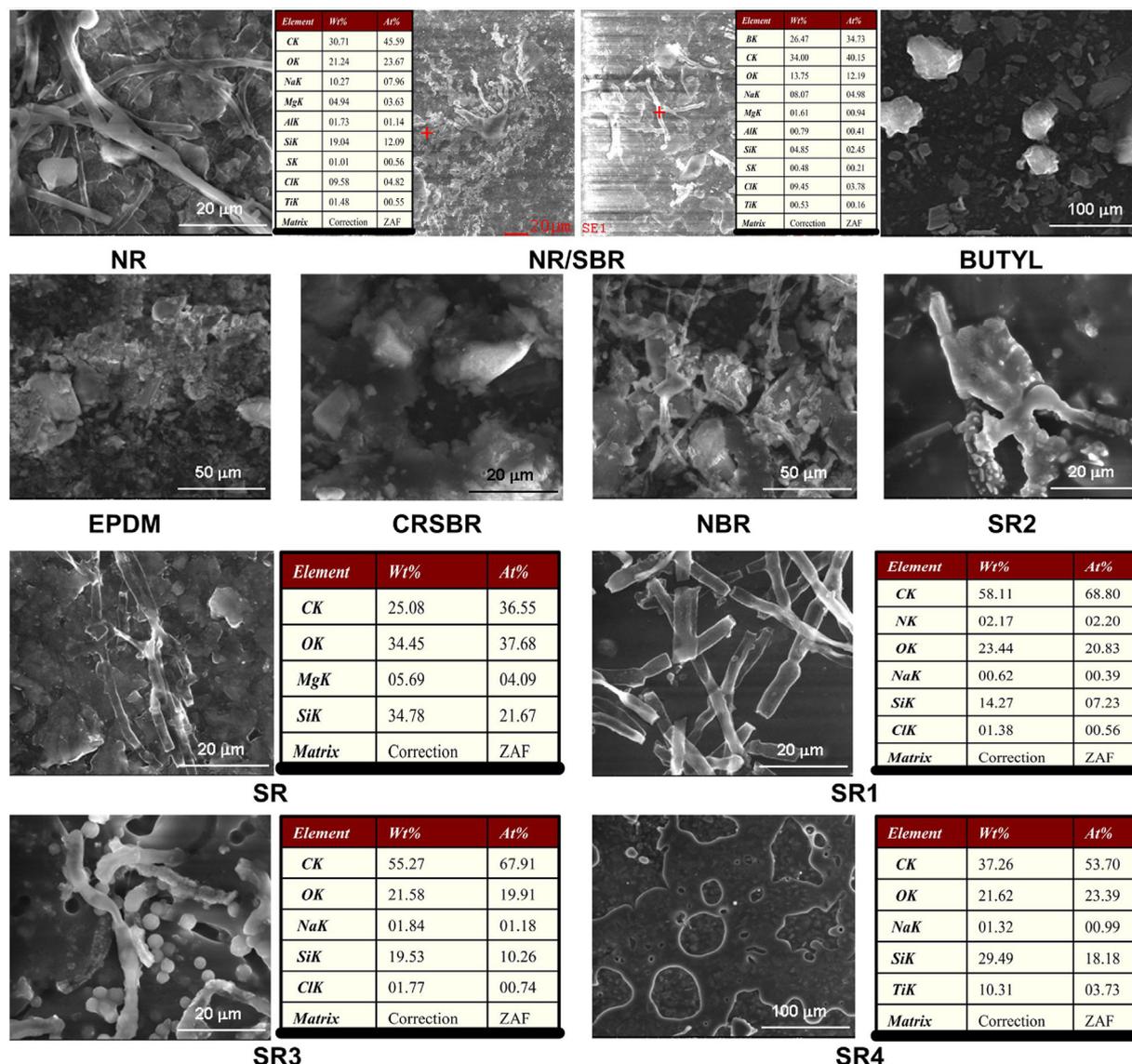
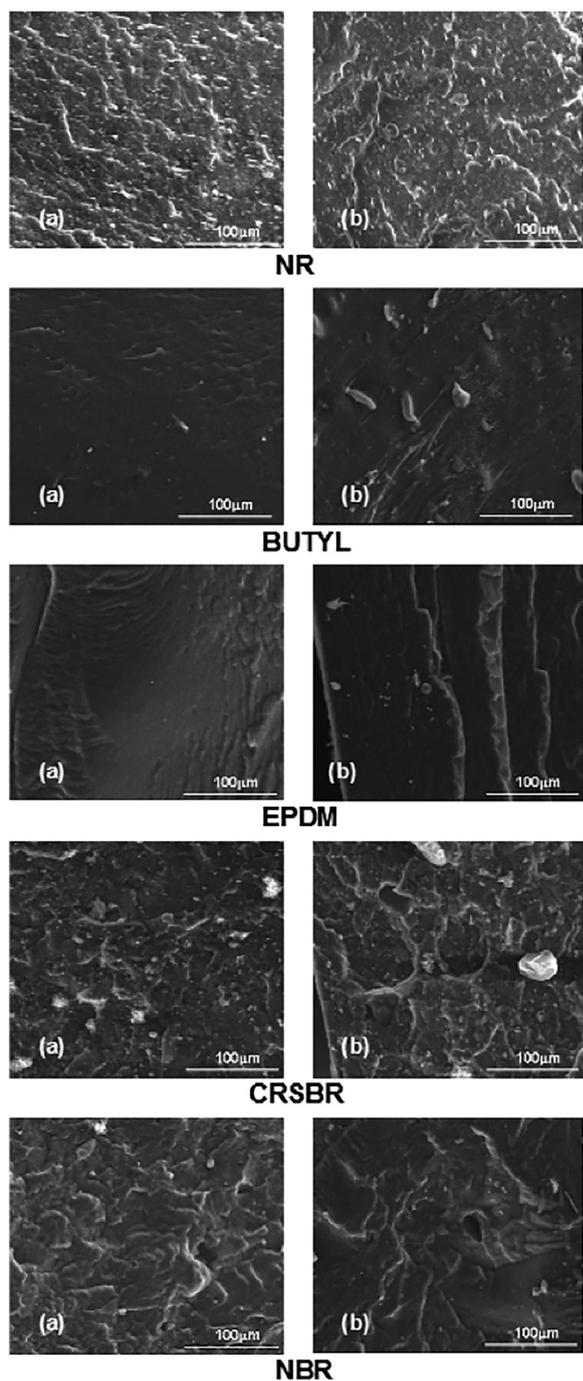


Fig. 4. SEM images of films surface and EDX results for some samples as extracted from salt water after six months (batch B2).



**Fig. 5.** SEM images in fracture section of the samples: NR, BUTYL, EPDM, CRSBR and NBR in the initial state (a) and as resulted from B2 experiments (b).

### 3.2. Changes in elastomeric films induced by the sea salt water over six months (batch B2)

#### 3.2.1. Optical changes

After six months of immersion in SSW, all samples have changed their aspect, presenting different amounts of adhered material with different forms as it can be seen in Fig. 2b. It is supposed that these formations are inorganic salts crystallized from water and/or a combination of salts and organic or inorganic components extracted from the films.

#### 3.2.2. Surface morphology and composition

SEM examination of the films after extraction from salt water reveals the surface structuration, on the one hand due to leaching or reorganization of some components or additives in the aqueous medium and, on the other hand, due to the crystallized salt deposits in various forms, depending on the nature of the surface (Fig. 4).

Thus, large crystalline plates, which co-exist with worm-like formations, were emphasized in the case of NR/SBR sample in which boron is present in large amounts as EDX results show. The presence of boron could probably be due to the presence of boron-containing reinforcing resins in the sample composition [41]. Irregular formations are visible on the surface of films BUTYL, EPDM and CRSBR, while samples NBR, NR, SR1 show a fibrillar structuration on the surface. The in-house prepared silicone rubbers SR2 and SR3 show spherical particles that seem to aggregate into worm-like formations. EDX analysis indicates only small amount of NaCl. A particular case is the sample SR4. At the surface of the film, very little crystalline material is observed; it seems that the salts did not adhere, but rather some fluid component migrated at the surface. This may be due to ineffective cross-linking when part of the polydimethylsiloxane chains remaining free or hanging only one end migrates to the film surface. The elements detected on the surface of sample SR are components of the film and may indicate formation of MgO or MgCO<sub>3</sub>, besides silica particles (that are most probably visible as small points). Thus, based on SEM and EDX results, we concluded that most of the observed formations are of inorganic nature, but in some cases other elements detected indicate leaching of additives.

In order to study the effect of the seawater on the polymer compositions, some of the aged samples were selected for further study. These were the samples for which the extracts taken in B1 series of experiments showed absorption bands in UV spectra, FTIR and <sup>1</sup>H NMR, i.e. NR, BUTYL, EPDM, CRSBR and NBR. After immersion of the samples for six months in seawater, they were placed in distilled water for five days and then repeatedly rinsed with distilled water to remove as much as possible of the salt deposits. SEM examination in fracture section of these samples revealed changes in the materials morphology and salt depositions as a result of the extraction of different organic fragments used as processing aids. The comparison between the selected samples in their original state and after immersion (B2 experiments) and washing can be seen in Fig. 5.

#### 3.2.3. Chemical modifications

The changes in the chemical structure of the polymeric films immersed in sea salt solution were evidenced by ATR-IR spectra. For this study, only the samples whose seawater extracts presented absorption bands in the UV-vis spectra were selected in order to confirm the loss of different organic fragments that have migrated into the aqueous phase. The differences in composition of the polymeric films before and after immersion in salt water were highlighted by using the method of IR spectral subtraction of the samples and the results are shown in Fig. 6. In this case, the resulting subtraction spectrum will correspond to the difference between the spectrum of the initial sample and the spectrum of the same sample after immersion in seawater for six months. Spectra were processed by using Bruker OPUS 6.5 software. It can be seen the loss of some chemical fragments of the initial samples after their immersion in the sea salt solution. These peaks are similar with those found in the seawater extracts (see below Fig. 9) and could be assigned to aliphatic hydrocarbons: C–H stretching vibrations at 2800–3000 cm<sup>-1</sup>, CH<sub>3</sub> and CH<sub>2</sub> deformation vibrations at 1370–1394 cm<sup>-1</sup>, the C–C stretching bands at 1200–1390 cm<sup>-1</sup> (Fig. 6(a) and (b)). The other bands could be attributed to aliphatic ethers, which have characteristic, strong absorption bands in the range 1000–1270 cm<sup>-1</sup> assigned to the C–O–C asymmetric stretching vibration (Fig. 6(c)). This broad band having two absorption

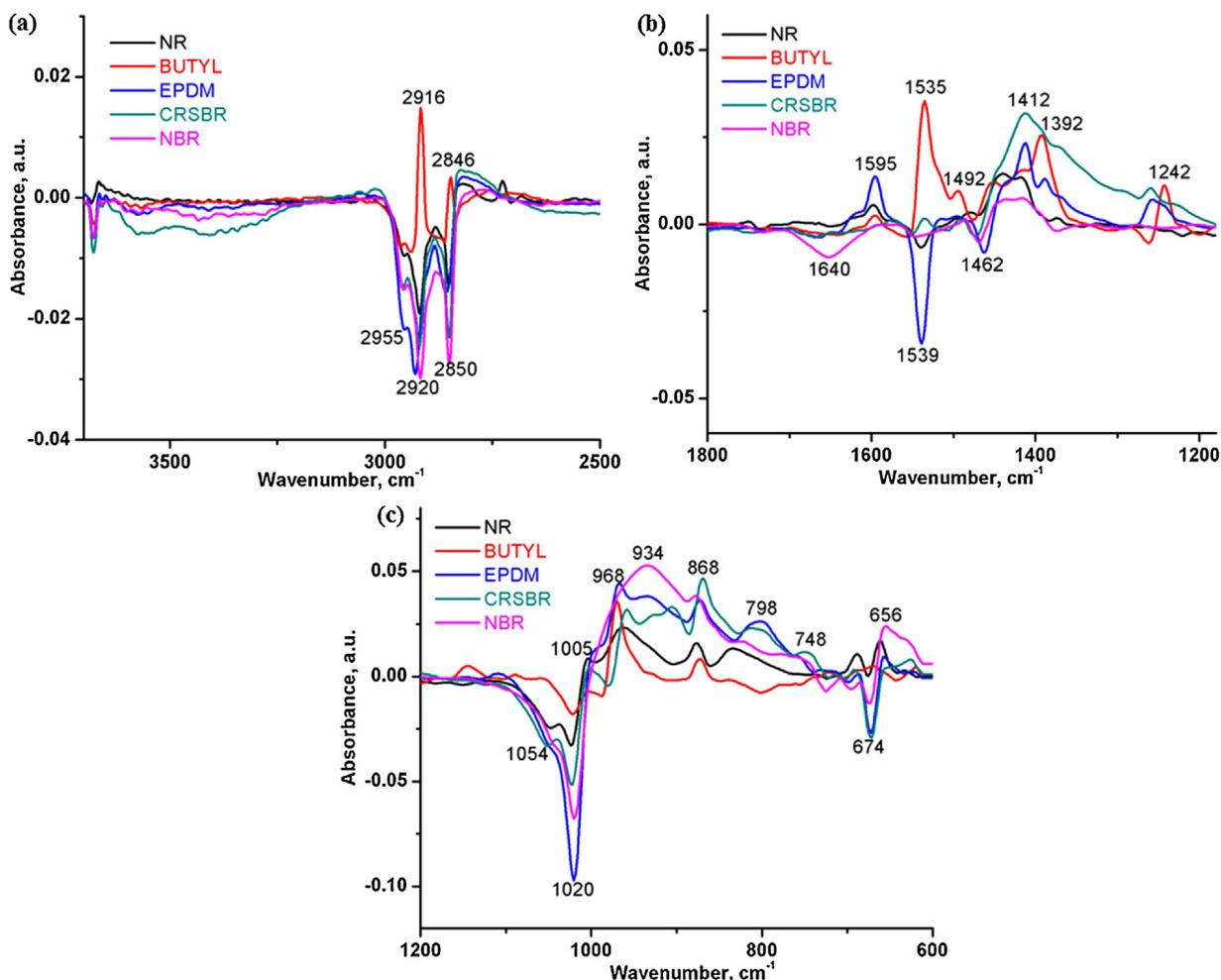


Fig. 6. Subtracted IR spectra of the samples: NR, BUTYL, EPDM, CRSBR and NBR before and after immersion for six months in the sea salt solution.

maxima at 1020 and 1054  $\text{cm}^{-1}$  is characteristic to branched-chain aliphatic ethers and cyclic ethers. The weak bands observed in the region 900–950  $\text{cm}^{-1}$  are due to the symmetric stretching vibration of the C–O–C group. The  $\text{CH}_3$ –O groups for aliphatic ethers are distinguished from the  $\text{CH}_3$ –C groups since they absorb at 1412–1470  $\text{cm}^{-1}$  due to both the  $\text{CH}_3$  symmetric and asymmetric deformation vibrations, whereas the  $\text{CH}_3$ –C group vibrations are observed at 1370–1394  $\text{cm}^{-1}$ . These assignments are consistent with the  $^1\text{H}$  NMR spectra of chloroform extracts of the sea salt water from the same samples (see below Fig. 12). Although the IR spectra of the samples shown in Fig. 6 are quite similar, there is a number of clear differences, especially in the spectrum of sample EPDM in the spectral region 1600–1530  $\text{cm}^{-1}$ , where a strong band at 1539  $\text{cm}^{-1}$  was identified. This band could be assigned to the  $-\text{CH}_2-$  scissoring, in-plane deformation and asymmetric bending deformation vibrations in aliphatic chains as well as to the asymmetric  $-\text{SO}_2$  vibration in aliphatic sulfonates ( $\text{R}-\text{SO}_2-\text{OR}'$ ), esters of sulfonic acid [42,43] or to the specific vibrations of sulfonated carbon black-filled ionomer [44]. These anionic surfactants, beside the inorganic additives are usually used in the preparation of EPDM polymers and are able to interact with the environment in dependence on the polarity of solvents [45]. The subtracted IR spectrum of the sample EPDM also has a weak band at 674  $\text{cm}^{-1}$  which could be assigned to the  $\text{SO}_2$  deformation. Such surfactants are known for their bacteriostatic effect [46–48]. Taking into account the antimicrobial activity of the sea salt water extract of this sample (EPDM) it can be said that its activity is due to the presence in the extract of

such compounds. It is well known that the use of sulfonate additive led to a novel class of thermoplastic elastomers and the plasticization process also has considerable implications on the behavior of sulfonate ionomers in solution [49]. For these approaches there are a variety of patents describing the sulfonation process, elastomer compositions and formulations based on EPDM [50,51].

### 3.3. Investigation of the seawater extracts after the immersion of the polymeric films

The synthetic seawaters in which the films have been dipped were investigated by various methods, either step by step or in final assessment, after six months. In the former case (B1), certain amounts of liquid (3 ml) were withdrawn for analysis at 10 days, 2, 3, 4, 5, and 6 months and replaced each time with the appropriate volume of the stock solution, while in the latter case (B2), the vials have never been opened during the entire period of observation. The analyses that they have been subjected to are summarized in Fig. 1.

#### 3.3.1. Periodic monitoring (Batch B1)

3.3.1.1. *Optical observations.* After the immersion of the films in SSW during six months, inorganic deposits or anaerobe microorganisms have been observed in solutions (Fig. 7a). The amount of these deposits differed in rather large limits between samples, from very low in samples EPDM (consisting of ethylene-propylene-diene rubber) to very high in samples NR and SR2 (consisting in natural

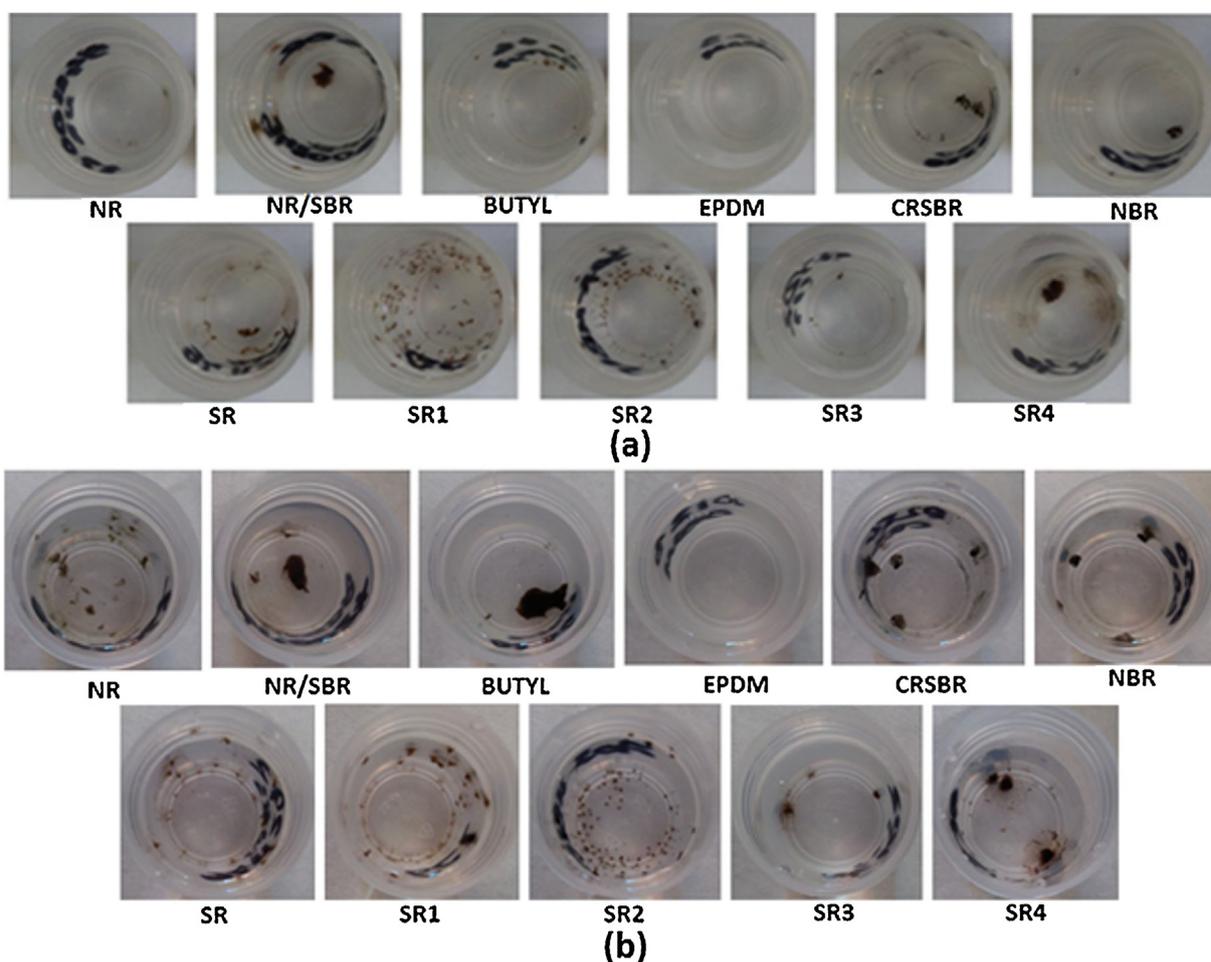


Fig. 7. The aspect of the sea salt solutions of: (a) – batch B1; (b) – batch B2 after six months from the immersing of rubber samples, after these have been removed.

and barium titanate filled silicone rubber, respectively). The same deposits were identified in the sea salt solutions opened first time after six months (Fig. 7b). It is noticeable the absence of deposit formation on the film surface or in the seawater solution in the case of EPDM. For this solution, the antimicrobial tests have shown a bacteriostatic activity, which can be attributed to the additives used in the preparation of the polymeric films, identified as sulphonate derivatives by IR spectroscopy.

### 3.3.1.2. The detection of organic materials in salt water extracts.

**3.3.1.2.1. UV-vis spectrometry.** UV-vis spectra of the sea salt solutions were measured after 10 days from the immersion of the films and then each month by using the initial sea salt water solution as reference (Fig. S2). The spectra showed absorption maxima in the case of the solutions containing samples BUTYL, NR, EPDM, NBR and CRSBR, which can be assigned by the position of the maxima to the electronic transitions  $n \rightarrow \sigma^*$  at values of 200–260 nm characteristic for saturated compounds with heteroatoms (especially O) in the structure (Fig. 8). Other maxima could be attributed to the electronic transitions  $\sigma \rightarrow \sigma^*$  specific for saturated hydrocarbons (alkane and cycloalkane) at about 200 nm. The conjugations of the chromophores in the structure of the organic seawater extracts contribute to the hypsochromic shifts of the maxima (in the case of sample EPDM) or to the appearance of new bands at higher wavenumbers assigned to the electronic transitions  $\pi \rightarrow \pi^*$  (diene, EPDM) or  $n \rightarrow \pi^*$  at 270–300 nm (NR and EPDM) [52].

In most samples, the organic compounds concentration increased in time as the UV-vis spectra recorded monthly sug-

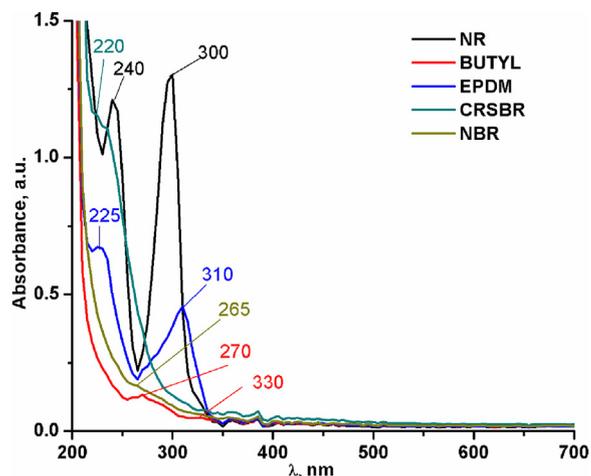


Fig. 8. UV-vis spectra of the sea salt water solutions after six months of immersion of the samples BUTYL, NR, EPDM, NBR, CRSBR (batch B1).

gest (Fig. S2). However, replacing the solution with fresh salt water might alter the result of the next sampling. For example, in the case of BUTYL sample, the absorption band assigned to organic extract (270 nm) exhibited a maximum after 3 month, after which it decreased, due to dilution. This would indicate different extraction kinetics, compared with other samples. Comparative UV spectra plotted for sea salt solution after six months of immersion of elastomeric samples from batches B1 and B2 indicate small differences

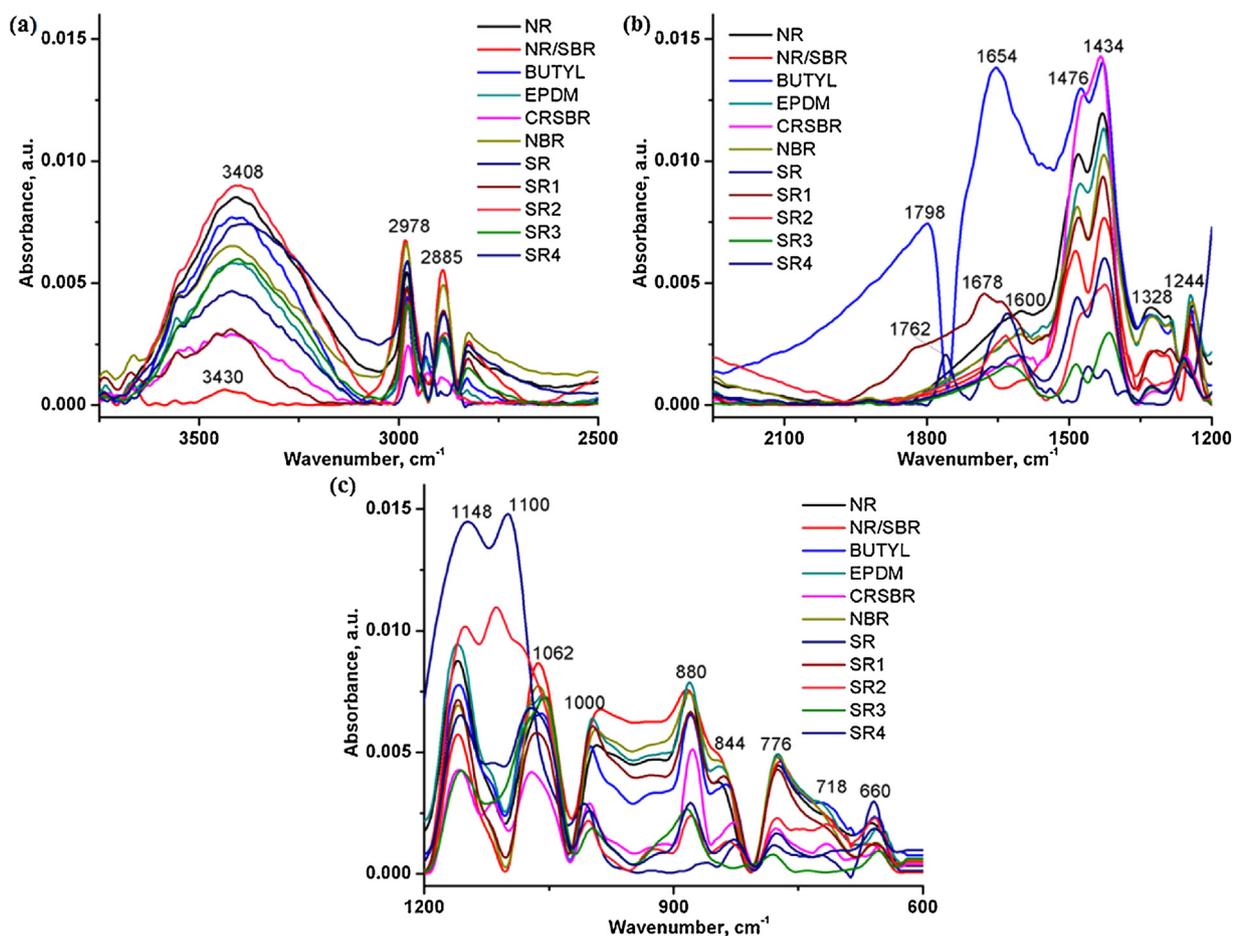


Fig. 9. ATR-IR spectra of the salt water extracts after six months of immersion of the elastomer samples (batch B1).

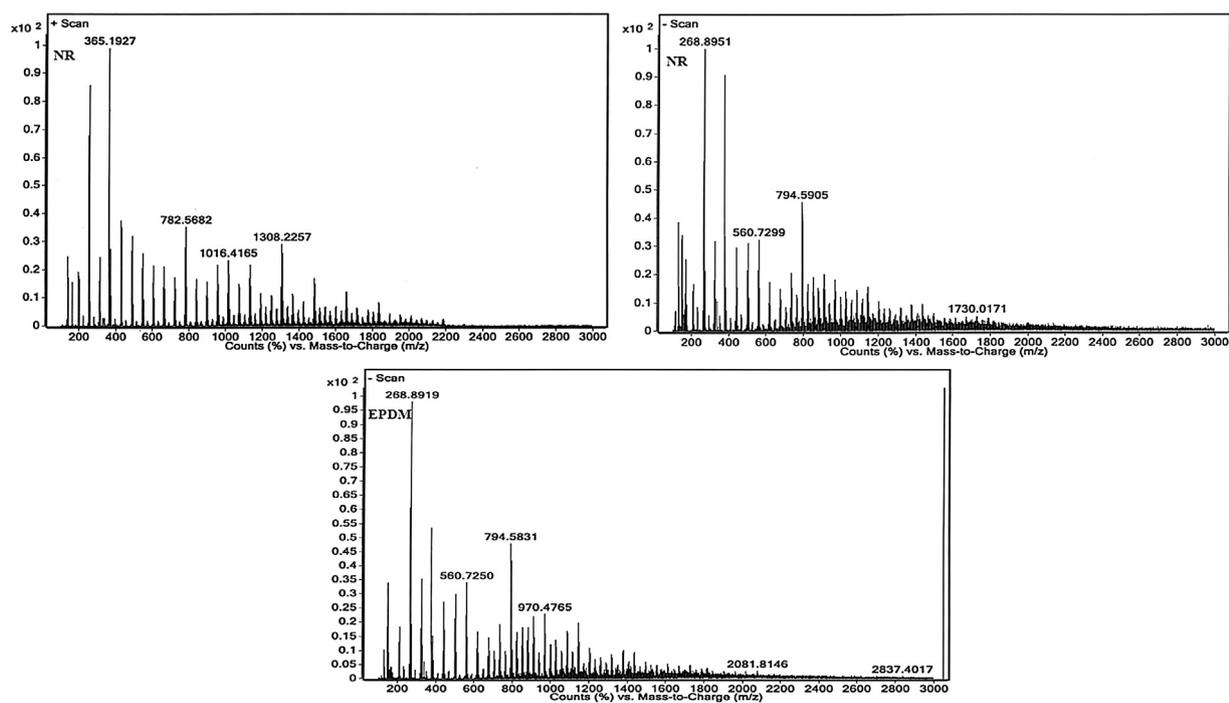


Fig. 10. ESI-MS spectra in positive and negative modes of the sea salt solutions of the samples: NR and EPDM after 10 days.

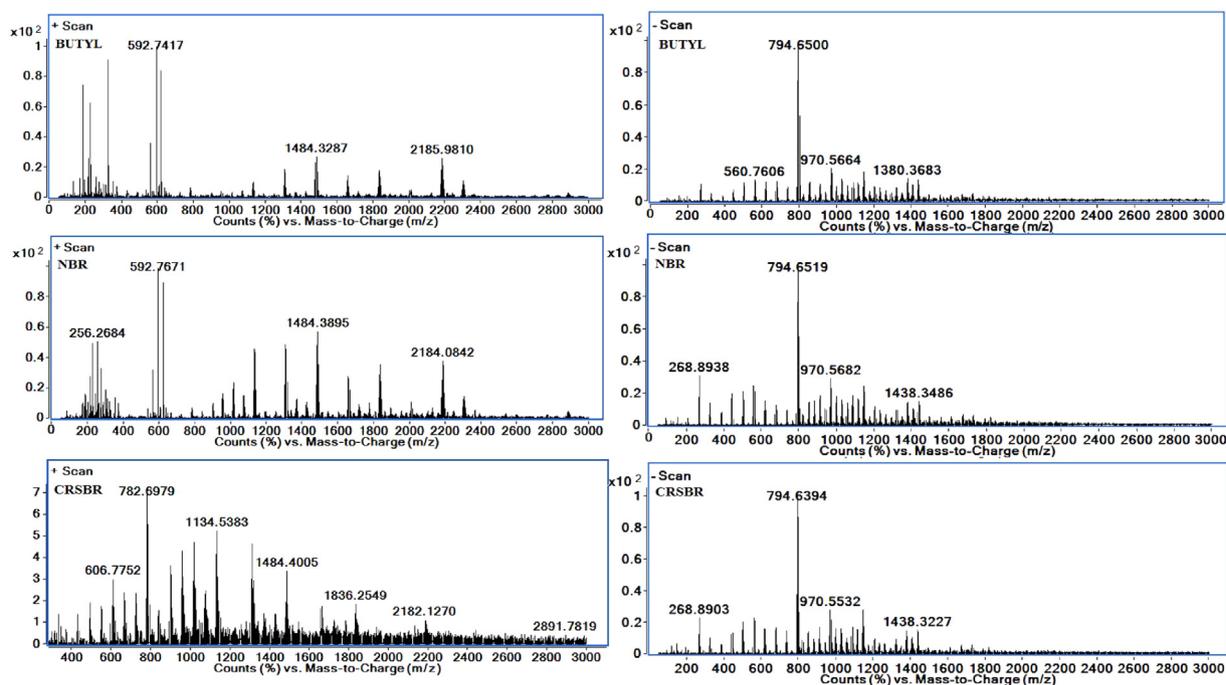


Fig. 11. ESI-MS spectra in positive and negative modes of the sea salt solutions of the samples: BUTYL, NBR and CRSBR after two months.

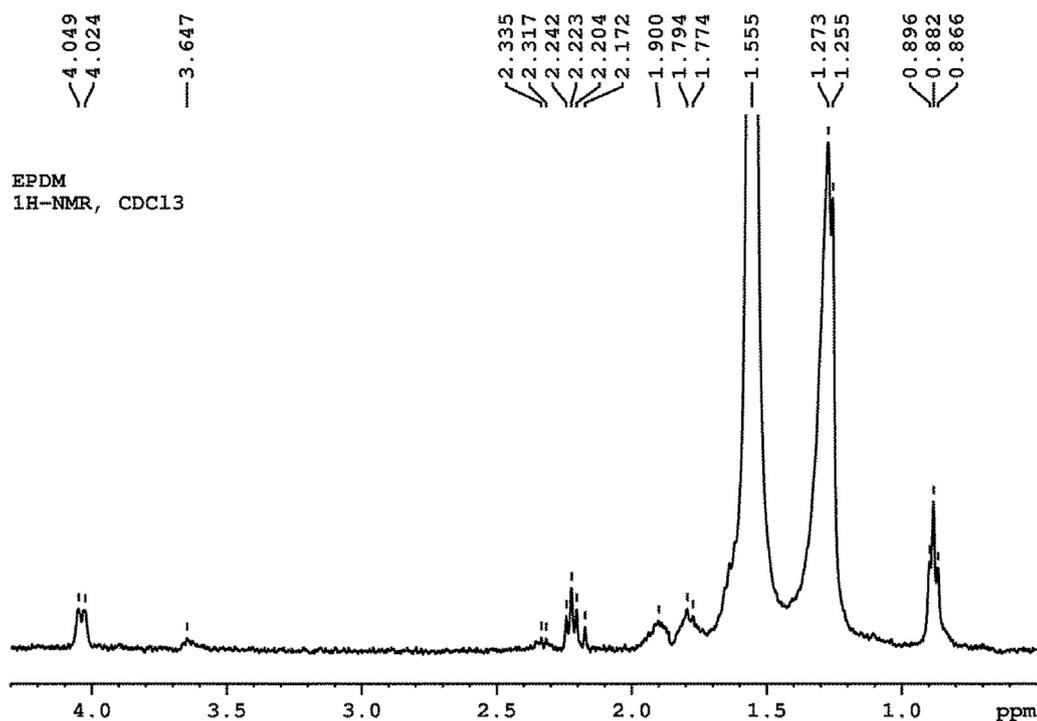


Fig. 12.  $^1\text{H}$  NMR spectrum of the organic extract in  $\text{CDCl}_3$  of the EPDM immersion salt water after three months.

between the intensity of the absorption bands only for samples NR and CRSBR (Fig. S3). No material with UV–vis absorption was extracted from the silicone films (SR, SR1–SR4).

**3.3.1.2.2. ATR-FTIR spectroscopy.** The salt water samples withdrawn at certain time intervals during the half year (batch B1) were dried in ambient conditions and the resulted residues were analyzed by IR spectroscopy in ATR mode. For the assignments of the characteristic bands, the Search Library database for IR spectra was used [53]. The results indicated the presence of different organic compounds, especially hydrocarbons and polyethers in the

solid extracts. Besides the strong absorptions of water O–H vibrations, which could be observed as broad bands at about  $3400\text{ cm}^{-1}$  and  $1630\text{ cm}^{-1}$  for all samples, other bands observed in the range  $1270\text{--}1060\text{ cm}^{-1}$  are usually associated with C–O–C asymmetric stretching vibrations. For saturated aliphatic ethers, this band may be found at  $1150\text{--}1060\text{ cm}^{-1}$ . In the case of branched-chain aliphatic ethers, two peaks may be observed. For aliphatic chain, a weak band is observed in the region  $930\text{--}900\text{ cm}^{-1}$  but sometimes found as high as  $1140\text{ cm}^{-1}$ . Other specific bands in the IR spectra of the sample are assigned to the  $-\text{CH}_2-$  asymmet-

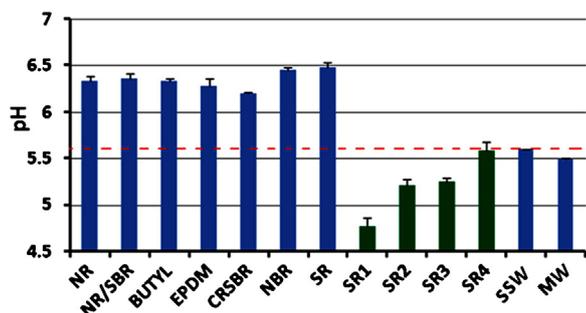


Fig. 13. pH values of the dipping salt water after six months as compared with initial one.

ric ( $2978\text{ cm}^{-1}$ ) and symmetric ( $2885\text{ cm}^{-1}$ ) stretching vibrations (Fig. 9(a)), asymmetric and symmetric  $-\text{CH}_2-$  deformation vibrations at  $1476\text{--}1434\text{ cm}^{-1}$  or rocking vibrations of the same groups at  $1200\text{--}1100\text{ cm}^{-1}$  (Figs. 9(b) and (c)). The IR spectra of the sea-water extracts of all samples during six months can be seen in Figs. S4 and S5). The residual alkyl groups are found in a large number of samples. Four types of vibrations are normally observed for this class, i.e. the stretching and deformation of the C–H and C–C skeletal bonds. The C–H vibration frequencies of the methylene groups result in bands in the spectral region  $3000\text{--}2800\text{ cm}^{-1}$  while the C–C stretches occur in the range  $1300\text{--}600\text{ cm}^{-1}$ . These bands are often overlapped by the  $-\text{CH}_2-$  vibrations, the IR spectra being quite similar (Figs. 9, S4 and S5) [54].

**3.3.1.2.3. ESI–MS analysis.** By this method only the sea salt solutions which showed strong bands in the UV–vis spectra were analyzed. The spectra of the samples BUTYL, NR, EPDM, NBR and CRSBR in positive and negative modes indicated the presence of different organic fragments in the seawater extracts at  $m/z$  between 365 and 3683 (Figs. 10 and 11), which may belong to the different molecular weight extracted compounds (supposed polyethers). These results are well correlated with the  $^1\text{H}$  NMR, IR and UV data.

**3.3.1.2.4.  $^1\text{H}$  NMR spectroscopy.** For detecting traces of organic materials in SSW extracts of the samples, which showed absorption bands in the UV–vis and mass spectra, the extracts of the interest samples after three months were extracted with chloroform for 72 h. The organic part (in chloroform) was then evaporated and analyzed by  $^1\text{H}$  NMR spectroscopy. The  $^1\text{H}$  NMR spectra of the organic extracts of the samples NR, BUTYL, EPDM, CRSBR and NBR (Fig. S6) show characteristic peaks for methyl and/or methylene protons from aliphatic chains at  $0.8\text{--}3\text{ ppm}$  and some signals attributed to ethers, esters, linear and cyclic olefins at  $3.5\text{--}5.5\text{ ppm}$ . In addition to these peaks, the  $^1\text{H}$  NMR spectrum for sample CRSBR shows peaks at  $7.3\text{--}7.4\text{ ppm}$ , characteristic to aromatic protons. In the  $^1\text{H}$  NMR spectrum of EPDM, the peaks at  $4.03$  and  $3.65\text{ ppm}$  can be attributed to ethers or esters, the peaks between  $1.25$  and  $2.33\text{ ppm}$  to methylene protons from aliphatic chains and the peak at  $0.88\text{ ppm}$  can be attributed to methyl protons from aliphatic chains (Fig. 12).

### 3.3.2. Analysis of salt water extraction after half a year (batch B2)

**3.3.2.1. pH measurements.** The pH was measured for the salt water after six months immersion of the polymeric films (batch B2) and the recorded values presented some modifications compared with the stock solution (Fig. 13). All samples showed pH values above 6 compared to 5.6 and 5.5 of salt water and Millipore water, respectively, except, the aqueous samples in contact with in-house prepared silicones that had slightly lower pH values, of 5.2 (samples SR2 and SR3) or 4.8 (sample SR1), while the sample SR4 has a value identical to the salt water. The explanation for the lower pH values of the water samples in contact with silicone lies in the composition of the elastomer. In the case of the sample SR1, incomplete postvulcanization procedure could lead to the per-

sistence of 2,4-dichlorobenzoil peroxide decomposition products (2,4-dichlorobenzoic acid and 2,4-dichlorobenzene) [33,35]. For the other samples (SR2, SR3, SR4), the acid by-products (acetic acid) generated from methyltriacetoxysilane cross-linking agent in sample SR2 or the acid crosslinking catalyst (DBTDL) used in samples SR3 and SR4 could be released after long time immersion in water. The acidity is suppressed in the case of SR4 sample due to nature of the filler ( $\text{TiO}_2$  nanotubes) born from basic medium.

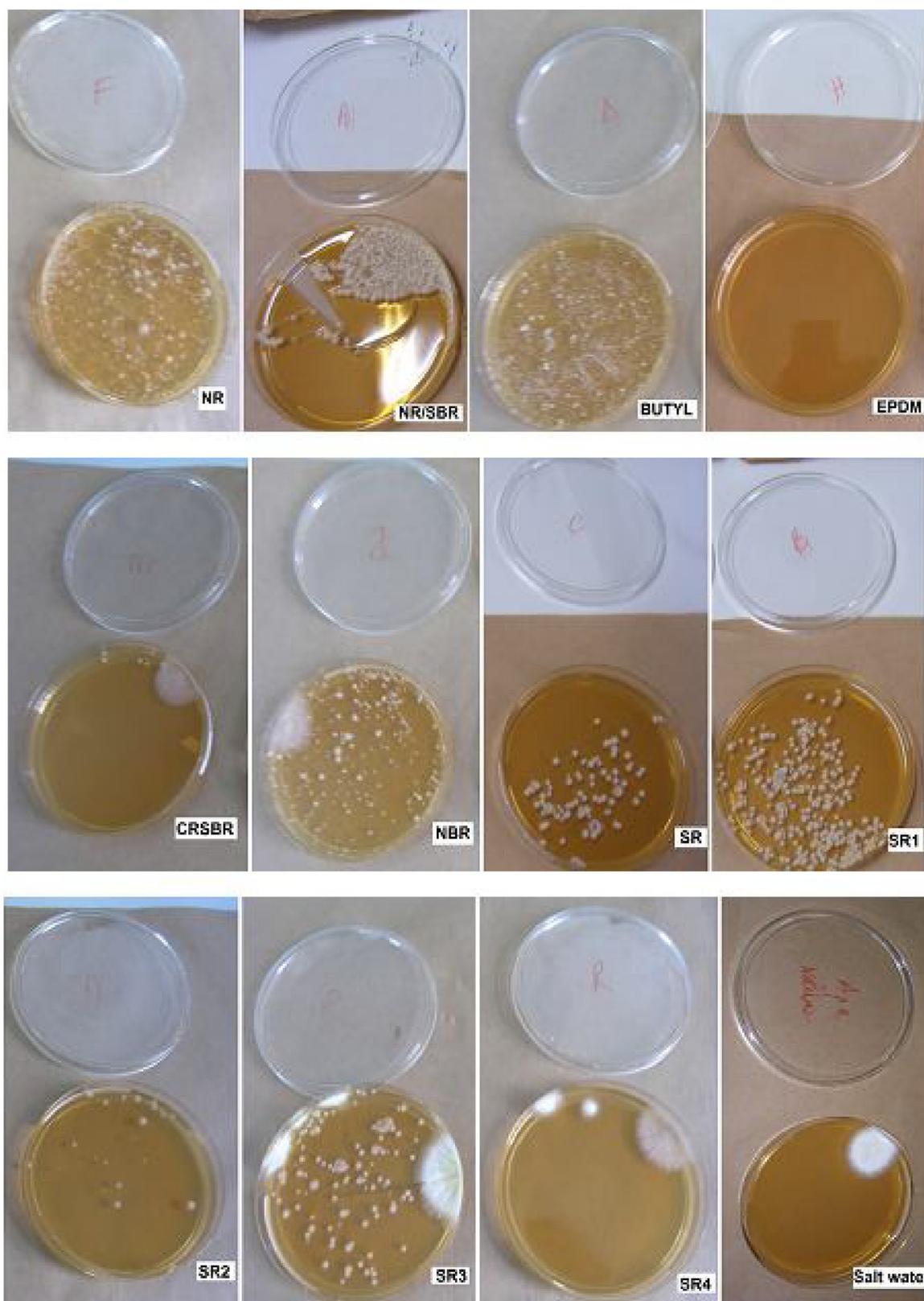
**3.3.2.2. Screening for heavy metals.** The presence of heavy metals in water was checked by XRF, assuming that certain additives containing metals might migrate from the polymeric films. The spectra were recorded on samples of batch B2 and were compared with the starting sea salt water. No heavy metal was detected at this concentration, although the method is very sensitive allowing detection of ppm traces. The XRF spectra of all water samples after immersion of the polymeric films are identical to the initial salt solution. A representative XRF spectrum of the salt water after immersion of sample BUTYL, in comparison with the initial solution, is presented in Fig. S7.

**3.3.2.3. Biological activity of the immersion sea salt water.** For testing biological activity of the SSW extracts, Petri dishes with growth medium consisting in agar – agar Sabouraud – dextrose 4% (SDA) and agar – agar (nutrient agar for the bacterial growth) from Merck, Germany were used. The successive dilution method was utilized for seeding biological agent on Petri plates, the final concentration of microorganisms suspension being  $1 \times 10^{-4}\text{ }\mu\text{g/ml}$ . The culture medium was seeded with 1 ml of microorganisms suspension and 1 ml test sample (B2 batch) and incubation was carried out at  $30^\circ\text{C}$  for six days. The first readings were performed at 48 h after seeding and the last in the seventh day. It was found that only the water extract of the sample EPDM shows inhibitory activity on the development of microbial flora seeded, the others being favourable to life (Fig. 14). Thus, although according to UV–vis, IR and ESI–MS, different components leached out from many polymeric films, most of the materials tested are non-dangerous for living organisms as it could also be marine biota (Fig. 14).

The IR, UV–vis data and ESI–MS spectra revealed the presence of some anionic surfactant fragments in the water extract of the sample EPDM. Due to their physicochemical characteristics, anionic surfactants have been used in pharmaceutical and biotechnological processes and showed a remarkable biological activity by binding to different bioactive molecules (peptides, DNA or cell wall constituents). Besides the beneficial effects in the industrial scale production and applications, they show marked toxicity and can cause marked environmental pollution. The molecular basis of their biological and toxicological activity is not mentioned until now [55]. For the water extract of the sample EPDM, the hydrophobic interaction with the cell membrane appears to be the most important mechanism involved in anionic surfactants adsorption and, as a result, its biocidal activity [56]. In this case the pH does not play any role on adsorption process, the water extract for EPDM sample indicating a pH 6.5.

## 4. Conclusions

A protocol involving sensitive analysis techniques (UV–vis, IR with IR spectral subtraction method,  $^1\text{H}$  NMR, ESI–MS and XRF spectroscopies), as well as microscopy and biological tests, has been applied and has been shown to be effective in detecting and identification of chemicals released in the marine environment by a series of dielectric elastomers. As a result of the immersion in synthetic seawater, in all cases it has been observed the formation of inorganic deposits on the elastomer film surface. In the case of samples based on styrene-butadiene, it was found a large quantity of boron



**Fig. 14.** Biological activity of the salt water after immersion of the elastomeric films for six months (batch 2).

on surface probably from boron based hardener resin sometimes used in rubber formulation. The losses of some chemical fragments (hydrocarbons or polyethers compounds) as a result of the samples immersion in the synthetic seawater were emphasized by UV-vis and IR analysis. Inorganic deposits or anaerobe microorganisms

have been also observed in solutions after six months. All commercial samples have slightly increased the pH value of the salt water, while our samples have lowered it. The latter effect is attributed to the presence in the material of acid traces resulting from the decomposition of the catalysts. No heavy metals were detected

at this concentration, although the XRF method is very sensitive. The IR results interpreted by reference to IR Search Library database indicated the presence of different organic compounds, especially hydrocarbons and polyethers in the solid extracts. The immersion sea salt water for all commercial samples, except those based on silicones showed UV absorption bands characteristic for saturated compounds with heteroatoms (especially O) in the structure and others specific for saturated hydrocarbons (alkane and cycloalkane).  $^1\text{H}$  NMR corroborated with MS data confirmed these informations. The biological test results showed that only in one of the cases studied (sample based on ethylene-propylene rubber) the immersion water inhibits the growth of microorganisms living, the other being favourable to their life.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2017.07.068>.

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