

CHEMICAL STABILITY ASSESSMENT OF SOFT MAGNETIC COMPOSITES FOR BIOMEDICAL APPLICATIONS

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Abstract

Silicone-based elastic composites with a metallic filler have been strongly developed in recent years. These materials are considered applicable in many fields of science, including medicine. The advantageous mechanical parameters provided by the NdFeB micropowder reinforcement are balanced by the elasticity and biocompatibility guaranteed by the silicone matrix. So far, there have been several reports regarding such composites' properties important from the biomedical point of view. The article deals with the physicochemical parameters of the new material for medical applications as well as the properties of the incubation liquid. The aim of the work was to determine effects of both the magnetic particles content (0, 30, 50, 70 wt%) and the incubation process under physiological conditions on the physicochemical properties of the material and the solution after incubation. The samples were incubated for various periods of time (8, 16 and 24 weeks) at the temperature of 37°C in a 0.9 wt% NaCl solution. The density, water contact angle, and water absorption of the materials were measured. The electrolytic conductivity, pH value, redox potential, surface tension, and kinematic viscosity were determined for the liquids after the materials incubation. The results obtained for pure silicone and the silicone-based composite reinforced with NdFeB microparticles were compared. The results indicate that incubation affects the samples and liquids, changing their physicochemical properties. For composites, the density decreased, which results in a noticeable concentration of the examined elements in the solutions.

Keywords: *silicone-based composite, magnetic material, physicochemical properties, incubation, ICP-MS analysis*

Introduction

One of the significant directions of progress in biomedical engineering is the need to develop new biomaterials. However, many aspects must be considered to provide safe and useful materials [1]. Despite the chemical composition, the fabrication method is essential in assessing biomaterial's properties [2,3]. In the last few years, there has been an increasing interest in elastic materials endowed with some additional features. Thus, silicones are widely used for applications in medicine. Polydimethylsiloxane (PDMS) is a well-known type of silicone that belongs to the group of siloxanes [4]. It is altered to manufacture stretchable structures, elements of surgical instruments, microfluidic devices, or drug delivery systems [5,6]. PDMS is also used for tissue simulating optical phantoms useful in the development of biomedical engineering technologies [3] and for medical electronics, e.g., electrochemical sensors [7]. Its structural biocompatibility, biostability, and various applications in medicine, were the main reasons for choosing PDMS as a matrix to prepare magnetic powder-based composites in this work [6].

Soft composites can be reinforced with various fillers. One of the groups of filling materials that is becoming increasingly important in materials science is metal alloys with magnetic properties. The balance between the structure flexibility and the ability to move in a magnetic field can be obtained in these composites [8]. Magnetic particles with different shapes and chemical composition are used in biomedical engineering [9-11]. The most popular element showing ferromagnetic behaviour is iron (Fe). Iron is part of many compounds for medical purpose, such as magnetite (Fe₃O₄) or maghemite (γ-Fe₂O₃) [12]. This element is the main component of neodymium magnet (NdFeB). Applications of NdFeB magnets in medical sciences increased in the last decades [11,13,14]. Silicone-based composites reinforced with magnetic particles, especially with NdFeB, are of great interest to researchers from all over the world. Those materials combine elasticity and biocompatibility supported by an organic matrix, and the possibility of the material remote control provided by a filler with magnetic properties. Soft magnetic composites can act as microrobots for precise surgeries. They can also play a role in targeted drug delivery, where precision is crucial [8,15,16]. Many cancer therapies are specific and can be delivered via remotely controlled structures. In this case, drugs are applied to the composite surface. The drug activation may be induced by a magnetic field of a certain value [17,18].

The assessment of new magnetic materials in medicine, apart from their mechanical, thermal and functional properties, also includes their biocompatibility study and impact on the human body. One of the parameters is the influence of physiological fluids on the physicochemical properties of composites. The tendency to release the elements of the magnetic filler from the composite to the environment has to be considered as well. The most commonly used solution for the biomaterials incubation is a sodium chloride solution (0.9 wt% NaCl) [19]. Studies are performed mostly to analyze the material behaviour under specific conditions. The material properties change with the incubation time in the simulated physiological environment is also evaluated [20]. The biomaterial should retain its properties and therefore should not release toxic compounds into the body [21,22].

[Engineering of Biomaterials 164 (2022) 2-8]

doi:10.34821/eng.biomat.164.2022.2-8

Submitted: 2022-02-15, Accepted: 2022-04-21, Published: 2022-05-05



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NdFeB magnets have already been well-examined for medical applications and are considered to be cytotoxic to certain types of animal or human cells. The tests performed *in vitro* for mucosal fibroblasts showed high cytotoxicity in contact with neodymium [23,24]. Neodymium particles, when not handled with care, can come closer to each other inside the body, causing harmful injuries. It is proven that the presence of neodymium in the human body can damage the liver or cause lung embolism [25,26]. Although, there are no reports regarding the maximum allowable concentration of neodymium, it has to be considered if the component is not rejected by the human or animal body. Iron is an essential element for the proper functioning of the body. It is found in human haemoglobin, cells, and enzymes. Iron deficiency can be dangerous for human health [27]. Boron is a trace element in the human body, delivered with water and food. It can be toxic when the boron intake exceeds 0.75 mg/day for infants, 1.34 mg/day for 50 year-old men, and 1.39 mg/day for nursing mothers [28,29]. Biodegradation and biocorrosion studies for NdFeB magnets defined the neutral or mild behaviour of the material in the microbial environment [13,30].

The main goal of the presented study was to determine physicochemical properties of both the PDMS-based material and the solution after the incubation process. Another goal was to analyze the influence of different powder content on the materials properties. Finally, the research should reveal whether the incubation time affects the chosen characteristics of both the material and the solution.

Materials and Methods

The examined materials were PDMS-based composites with NdFeB micropowder as a filler. A silicone with the trade name Sylgard 184 (Dow Corning, Midland, MI, USA) was used as an organic matrix. This polymer was supplied in a two-component form: an elastomer and a curing agent. The ingredients were mixed in a weight ratio of 10:1. A metallic micropowder with magnetic properties with the trade name MQFP-14-12 (Magnequench, Singapore, Singapore) was used as a reinforcement. The size distribution given by a production company is of $d_{50} = 25 \mu\text{m}$. The chemical composition of the metal alloy is presented in TABLE 1.

The composite manufacturing process started with the silicone matrix preparation. About 20 g of elastomeric liquid was mixed with approximately 2 g of the liquid curing agent to obtain a proper silicone. Then, the material was immediately transferred into four separate Petri dishes. The reinforcement was added to the second, third and fourth dish, in order to obtain composites with 30, 50, and 70 wt% of a filler, respectively. The components for each composite were hand-mixed to obtain a homogenous mixture. In the next step, each material was poured on a PTFE mat and put into a vacuum dryer. Gases entrapped inside the composite were released. The degassed composites were cured in a LabEcon 300 hydraulic press (Fontijne, Vlaardingen, The Netherlands) for 20 min at the fixed temperature (100°C). The cured materials were cut into uniform 9 mm diameter discs of a 1 mm thickness. The prepared samples were weighed before immersing them in a solution.

The solution for the simulation under *in vitro* conditions was 0.9 wt% sodium chloride (NaCl, Sigma Aldrich, St. Louis, MO, USA) in ultrapure Milli-Q water (Merck Milipore, Darmstadt, Germany). The water was mixed with NaCl and then the physicochemical properties of the conditioning liquid were determined to obtain the reference sample characteristics. The composite samples were placed in plastic containers. Each composite and pure PDMS were conditioned separately.

TABLE 1. Chemical composition of the micropowder.

Element	Symbol	Percentage
Neodymium	Nd	26%
Boron	B	1%
Niobum	Nb	1.9%
Iron	Fe	71.1%

TABLE 2. Designation of samples.

Designation	Incubation time [weeks]	Concentration of filler [wt%]
0-0	0	0
0-8	8	0
0-16	16	0
0-24	24	0
30-0	0	30
30-8	8	30
30-16	16	30
30-24	24	30
50-0	0	50
50-8	8	50
50-16	16	50
50-24	24	50
70-0	0	70
70-8	8	70
70-16	16	70
70-24	24	70

Three sets of each type of examined material were prepared for investigating the effects of different incubation times. The samples were immersed in the sodium chloride solution with a weight/volume ratio of 1:10. The samples designations are presented in TABLE 2. It should be noticed that the control samples of solution were incubated in separate plastic containers for the same time periods as the materials for incubation.

The samples were conditioned in a laboratory incubator at a constant temperature of $37 \pm 0.5^\circ\text{C}$ for 8, 16 and 24 weeks. After each period of time, the designated samples were taken out and dried. The control samples i.e. pure silicone and the composite materials were not subjected to the incubation process at all. Having been incubated, the samples were dried in air at the temperature of $22 \pm 1^\circ\text{C}$ and the humidity of 50%. After the materials were removed, the incubation solutions were examined regarding their pH, conductivity, redox potential, surface tension, and kinematic viscosity. The physicochemical properties of materials (density, wettability, water absorption) were evaluated as well.

The SevenMulti (Mettler Toledo, Columbus, OH, USA) multifunctional ionoconductometer with dedicated electrodes was used to measure the pH, conductivity, and redox potential. The surface tension tests were performed using a balance (Mettler Toledo, Columbus, OH, USA) with a platinum ring and the STA1 tensiometer (Sinterface, Berlin, Germany) [31]. The surface tension value (γ) was calculated from the formula (1):

$$\gamma = \frac{F}{4\pi R} \quad (1)$$

where F is the force needed to separate the ring from the solution surface [N], and R is the radius of the measuring ring [m].

The kinematic viscosity of solutions was determined using the iVisc system (LAUDA Scientific, Lauda-Königshofen, Germany) shown in FIG. 1. The system consists of the Ubbelohde glass capillary and a self-priming handle with an optical system for the liquid flow measurement. The capillary was immersed in a thermostat, so the solution temperature was in the same range for all the experiments. The measurements were performed using software connected to a device. The evaluation of kinematic viscosity is person-independent, which makes those calculations very precise. The physicochemical tests were performed at the temperature $25 \pm 1^\circ\text{C}$ and the measurements were repeated five times for each solution.

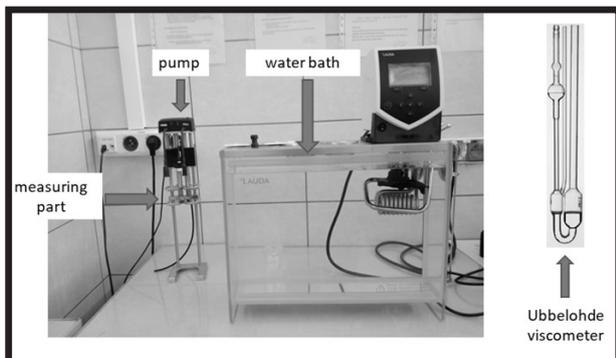


FIG. 1. iVisc system for kinematic viscosity determination.

The elements concentration in the solutions was determined using inductively coupled plasma-mass spectrometry (ICP-MS). This type of spectrometry is used to measure trace elements in biological solutions by comparing their concentration with standards. The ICP-MS analysis of the solutions after conditioning was performed using the Triple Quadrupole ICP-MS (8800 ICP-QQQ, Agilent Technologies, Singapore) fitted with MicroMist nebulizer, Scott-type double pass spray chamber Peltier cooled, nickel sampler and skimmer cones, and collision/reaction cell (octopole reaction system ORS3) [32]. The ICP-MS method was used to determine iron, neodymium, boron, and niobium with interfering elements in the model solutions and the experimental samples.

The samples density (d) was measured by the hydrostatic method. The experiment was conducted using the balance (Mettler Toledo, Columbus, OH, USA) with the special equipment. The procedure is that the weight of the sample is recorded first on a plate in air, then in water. The density was automatically calculated by the balance software. Density tests were performed five times for each sample. The wettability of the materials surface was determined using the Contact Angle Goniometer (Ossila, Sheffield, UK). Wettability is defined by the contact angle (Θ) between the surface of the examined material and a droplet of ultrapure water on the surface. The acquired images of bare PDMS and PDMS-based composites were analyzed with the Ossila Contact Angle software using a tangent method [33]. For each sample, the contact angle was measured five times. The water absorption (W) was determined using a balance with a high sensitivity of 0.01 mg (Mettler Toledo, Columbus, OH, USA). The measurements compared the samples weight before and after incubation. Each sample was weighted before immersion in a medium and after a set incubation time. The experiment was followed by a day of drying at room temperature of $22 \pm 1^\circ\text{C}$ and 50% humidity. The water absorption value is a percentage gain weight of the examined sample.

The obtained results are presented in the form of mean values \pm standard deviations. To determine the significance level for the conducted studies, the one-way ANOVA and Tukey's post-hoc analysis were performed. The statistical analysis was performed with Statistica 13.1 software. The value of $p < 0.05$, and the significance level of $\alpha = 0.05$ were assumed. Probability values less than 0.05 were considered statistically significant.

Results and Discussion

The properties of sodium chloride solutions after the incubation of PDMS-based composites with magnetic powder were determined. In FIG. 2 the results for the pH value (FIG. 2A), electrolytic conductivity (FIG. 2B), redox potential (FIG. 2C) and surface tension (FIG. 2D) measurements of solutions vs time in weeks are presented. These properties are crucial for the material's potential application in biomedical engineering, especially when considering the contact of material with blood and other body fluids. The tests are aimed at verifying the influence of the material on the environment they are supposed to work in. Characterization of the solutions after incubation is essential to identify any biological hazards and show the compliance with regulatory expectations. It is a key issue in terms of accelerating the material or device development in certain conditions.

The initial pH of the sodium chloride was about 7.05 ± 0.02 and it was virtually invariable over the incubation time. An increase in pH of about 0.15 was observed for the solutions after incubation of pure PDMS. With the higher percentage of magnetic filler, the differences were more visible. For the solutions the composites were immersed in, the pH value increased significantly as the incubation time was prolonged. After 24 weeks of incubation, the solution for the 30-24 sample was characterized by the pH increase of about 0.20, the 50-24 sample solution was characterized by the increase of about 0.30 and for the 70-24 solution the pH increase of about 0.50 was observed. The obtained results followed the rule: the higher percentage of magnetic filler, the higher increase in pH value (FIG. 2A), which indicates the interaction between the solution and the incubated composites. The pH value increase can be caused by the chemical processes occurring on the composite surface during the incubation. The oxides, which are formed on the basis of elements separated from the material, might change the pH of the solution. It has to be noticed that the observed pH value was slightly higher than the pH of natural saliva (7.2) [34].

The electrolytic conductivity (k) value of the freshly prepared 0.9 wt% NaCl solution was 13.54 mS/cm. Electrolytic conductivity also showed that the longer incubation time, the higher value of this parameter was obtained. The lowest difference was observed for the control sample with the change of 0.3 mS/cm. The higher changes were noticed for the 70-0 and 70-24 samples solutions differing about 5.1 mS/cm. The interaction between the composite with the 70 wt% of the filler was presumably intensive, hence such changes could have been observed. The lower filler concentration in a composite, the lower changes of the electrolytic conductivity were observed. The change was expected, as the elements in the ionic form could get into solution from the composite.

The redox potential values (E_h) decreased for the solutions after the material incubation, which indicated the intensification of the reduction reactions. For the solutions, where the composites with higher NdFeB content were incubated, the E_h decrease was more significant.

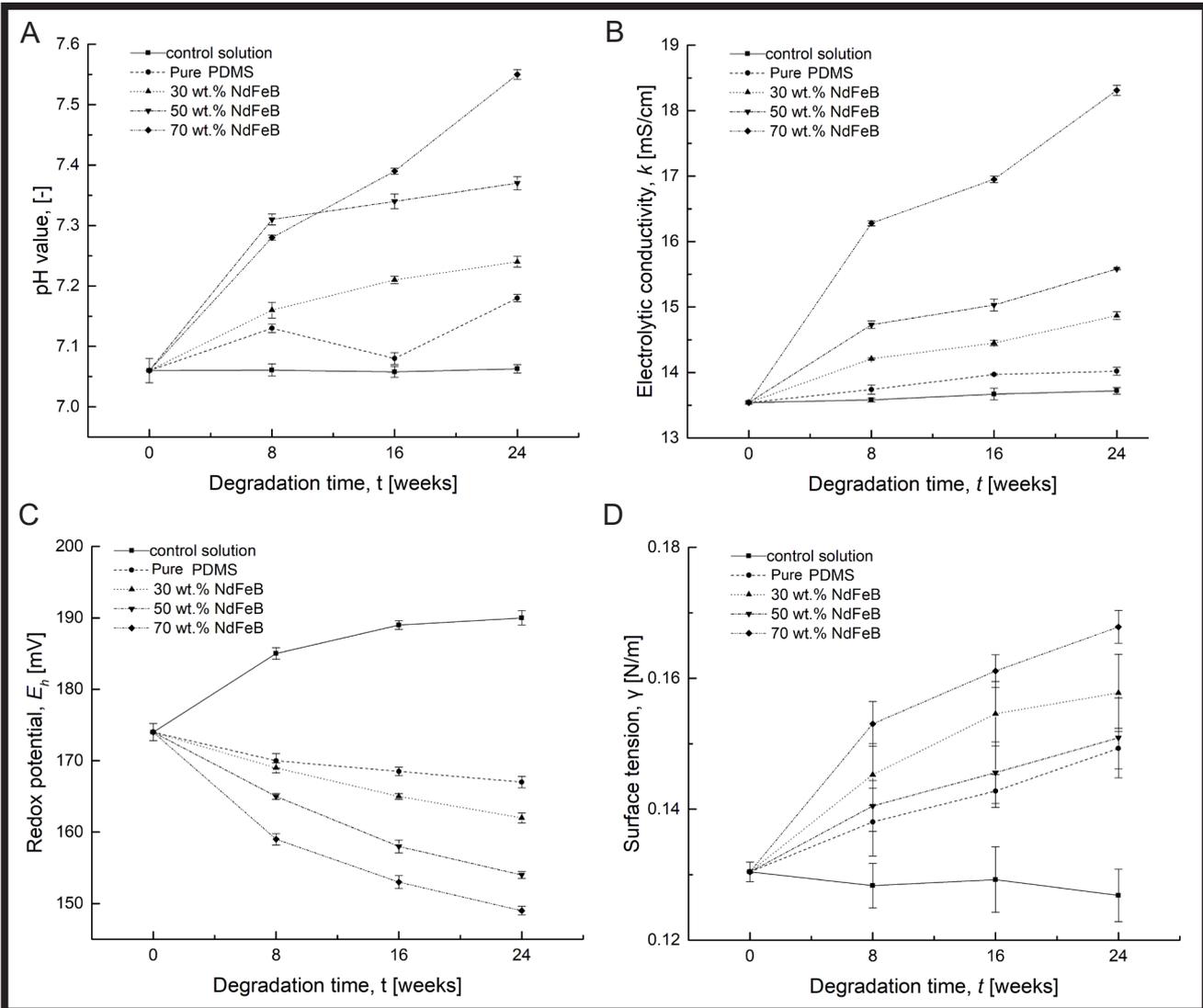


FIG. 2. Results of physiochemical properties of solutions vs incubation time: (A) pH value; (B) Electrolytic conductivity; (C) Redox potential; (D) Surface tension.

This change is connected with a higher concentration of elements in solutions that may undergo oxidation or reduction. For the 70-24 solution, E_h was about 25 mV lower, for the 50-24 solution it was 20 mV lower and for the 30-24 solution 10 mV lower in comparison to the freshly prepared solution. The inverse relationship i.e. the E_h value increase was observed for the control sample, where mainly oxidation reactions occurred. For the control solution incubated for 24 weeks ($T = 37^\circ\text{C}$) the E_h value increased by approximately 15 mV. The lower E_h indicates the tendency to perform oxidation reactions, caused by the electron loss in the solution.

The results of the surface tension for the solutions after incubation are presented in FIG. 2D. The tested parameter increased with the materials incubation time and with the higher percentage content of the powder filler. Between the initial value and the value for the 70-24 solution the difference was about 0.035 N/m. Lower differences were observed for solutions where the composites of 50 and 30 wt% addition were incubated. The surface tension of the control NaCl solution decreased with the incubation time for about 0.005 N/m. The change in the surface tension value is affected by the changes in the intermolecular forces system in the examined solution. That might be caused by the release of elements from the composite to the solution. The surface tension increase means that the wettability decreases and causes less adhesion.

The primary value of the kinematic viscosity for the control solution was of $0.00959 \text{ cm}^2/\text{s}$ and it increased over time. The value grew significantly for the solutions after incubating the 70 wt% NdFeB composite over time (for approximately $0.0025 \text{ cm}^2/\text{s}$). The difference for the solutions after incubating the composites of 30 wt% and 50 wt% was of $0.0014 \text{ cm}^2/\text{s}$ and $0.0018 \text{ cm}^2/\text{s}$, respectively. The kinematic viscosity changed with the incubation time, presumably due to the change in the chemical composition of the solutions and the ions diffusion into the solution. The kinematic viscosity was in a linear correlation to the pH value. The data presented in FIG. 3. show the correlation between the kinematic viscosity of solutions (ν) and pH value. The data prove the relationship: the higher pH value, the higher kinematic viscosity. Due to the Pearson's r (0.88) and adjusted R-square (0.76) coefficients, the data fit the linear regression model. The data for pH value vs kinematic viscosity are correlated. At the higher pH values, the solutions viscosity is expected to increase due to the new compounds in the incubation liquid and the presence of ions.

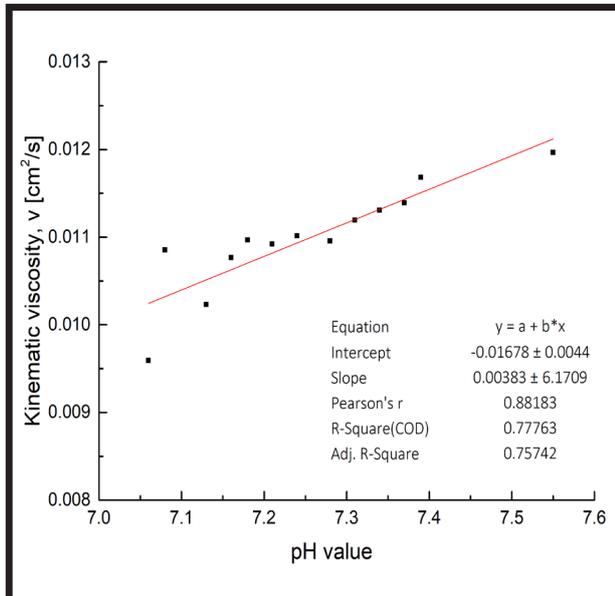


FIG. 3. The correlation between the kinematic viscosity (v) and pH value of examined solutions.

The chemical composition and concentration of selected elements in the solutions after the material incubation were investigated. The results of the ICP-MS analysis are presented in TABLE 3. The presence of Nd, Fe, B, and Nb in the solution after incubation was caused by the release of elements. The concentrations of each element varied and the following changes were observed. For boron, the lowest concentration was observed for the solution after 24 weeks incubation of the composite with 70 wt% NdFeB reinforcement. The highest value was noticed for the solution after conditioning the composite for 16 weeks. Surprisingly, the concentration of Fe in the solutions after incubation of the 70 wt% composites, despite repeated experiments, was under the detection limit for this element and the method combined.

The content of elements in the solutions after incubation of all the tested composites (30, 50 and 70 wt% of magnetic powder) and the total content of all the elements for each tested composite are presented in FIG. 4. The highest diffusion of elements into the solutions was noted for the samples indexed as 30-24, 50-8, and 50-16. The boron concentration was relatively high (5 $\mu\text{g}/\text{ml}$ or more) for all the solutions (18 $\mu\text{g}/\text{ml}$ or more). The iron concentration was high for the solutions indexed by 30-24, 50-8, and 50-16. The neodymium content was the highest for the 70-16 solution. The time of exposure did not affect the chemical composition of the solution.

TABLE. 3. Results for ICP-MS analysis (LOD is the limit of detection).

Solution Sample	B	Fe	Nd	Nb
	Concentration [$\mu\text{g}/\text{ml}$]	Concentration [$\mu\text{g}/\text{ml}$]	Concentration [$\mu\text{g}/\text{ml}$]	Concentration [ng/ml]
0-0	0.00	<LOD	0.018	<LOD
0-8	0.00	<LOD	0.035	<LOD
0-16	0.07	<LOD	0.035	<LOD
0-24	0.00	<LOD	0.087	<LOD
30-8	14.26	7.16	1.614	3.83
30-16	12.13	4.05	0.673	1.37
30-24	15.00	18.01	1.203	1.01
50-8	10.69	18.73	0.928	0.33
50-16	10.75	20.04	0.860	4.54
50-24	14.95	2.70	0.698	0.27
70-8	17.40	<LOD	0.251	0.30
70-16	20.59	<LOD	8.112	9.61
70-24	4.63	<LOD	0.249	1.49

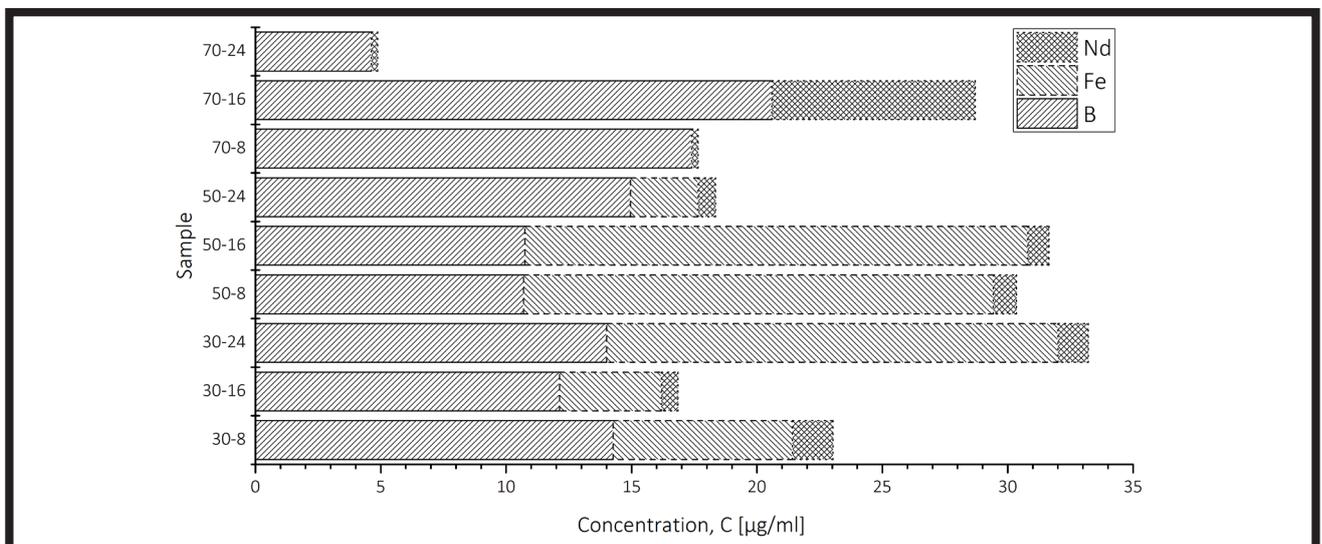


FIG. 4. Concentration of Nd, Fe and B in solutions for different materials and incubation times.

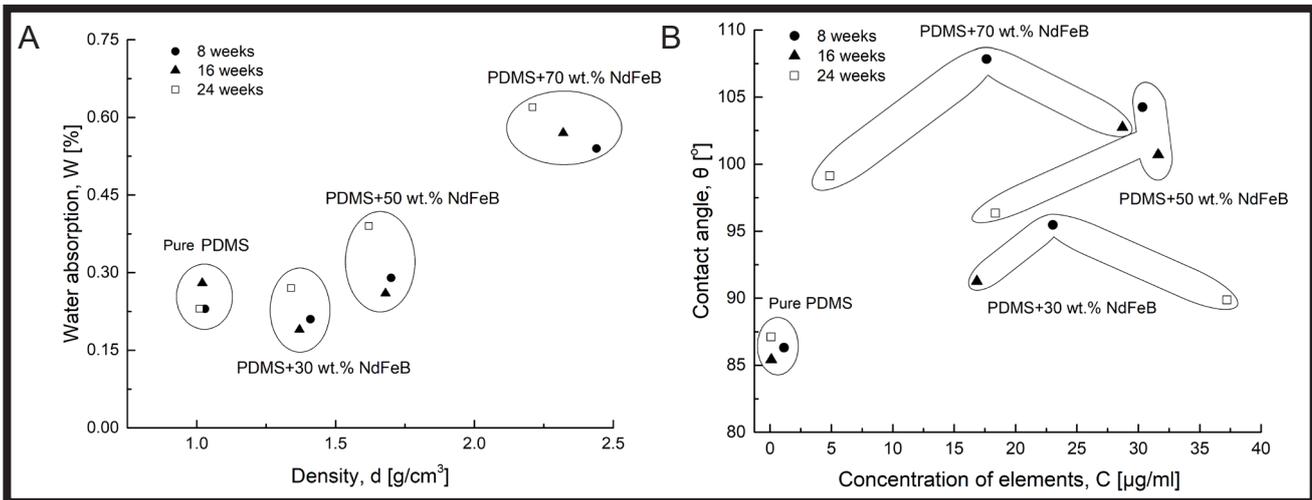


FIG. 5. The correlation between chosen parameters. (A) The water absorption (W) vs density (d) for the examined materials. (B) The contact angle of surface of materials (θ) vs the concentration of elements in solution (C).

The results of water absorption by the materials as a function of density are presented in FIG. 5A. The analysis of the data shows that the composites density is highly dependent on the percentage of composite filler. The presented results indicate that with the incubation time, the density decreased for each composite, which might result from the ions release to the solution and changes in the internal structure of the composite. The water absorption was less than 1% of weight of the sample for the examined composites. It was observed that for more dense materials the water absorption was higher and for the composites the water absorption increased with the incubation time.

It was expected that the contact angle value would change due to the elements diffusion to the contact solution. The relationship between those properties are shown in the graph (FIG. 5B). At first, it can be noticed that the samples wettability depends on the filler concentration in a composite. For the higher percentage of the metal filler, the more hydrophobic surface was obtained. Another relationship is connected with the incubation time. Longer incubation resulted in a lower contact angle for all the examined materials. It may be observed that there is no significant difference in a contact angle results between 16 and 24 weeks of incubation. Presumably, the impact of the solution reduces with time. The contact angle for pure PDMS leads to a conclusion that it is less hydrophobic than the PDMS-based composites. The changes between non-incubated composites and the materials after 24-week incubation is of a few degrees, for 30-0 and 30-24 it is around 8.5°, for 50-0 and 50-24 it is around 16.5°, for 70-0 and 70-24 it is around 23.5°. The contact angle obtained for pure PDMS is of a lower range than the data reported in the literature (107-116°). This can be caused by different manufacturing methods and the surface treatment [35-37].

Conclusions

The combination of the PDMS silicone and NdFeB micropowder can provide soft composite with advantageous properties. The presented data obtained for the examined materials show that the addition of metal powder results in the water contact angle and density increase.

The changes in a chemical composition of the conditioning solution are observed. The elements from the incubated samples are released into the solution, causing the increase in pH, redox potential and electrolytic conductivity values.

The ICP-MS analysis showed that the concentration of the elements is of a few µg/ml. That seems to be in a low range, but it is important from biomedical point of view. Potential applications can be considered after the reduction of elements release. The results show that an additional coating is needed. Special features of coating e.g. antibacterial properties or hydrophobic surface can improve composites characteristics.

The influence of the incubation solution on the material properties is noticeable. The density and water contact angle decrease, changing the ability of a material to work in a biological environment. For biomaterials the stability of the properties is crucial and has to be considered in fabrication. An additional coating for the composite surface can prevent from chemical decontamination of the environment the composite works in and from the changes in material properties.

The data presented in this work are preliminary investigations of this kind of biomaterials. Additional research is needed to evaluate the materials characteristics, especially biological properties and living cells behavior when in contact with a composite. At the same time, the research and experiments for surface coatings that meet the requirements should be carried out in order to increase the functionality of the material.

Acknowledgements

This scientific work was realized in the frame of works, No. WZ/WM-IIB/2/2020 and WI/WM-IIB/5/2021 and financed from research funds of the Ministry of Education and Science, Poland.

A special thanks to Prof. Barbara Leśniewska, DSc, PhD from Faculty of Chemistry, University of Białystok for performing ICP-MS tests.

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