This paper presents flexible NdFeB-PDMS composite magnets with tunable magnetic and mechanical properties optimized for applications in corrosive marine environments. The magnetic and mechanical properties were studied for different NdFeB powder concentrations and the performance of the magnetic composites for different exposure times to sea water investigated systematically. The remanence and saturation magnetizations could be tailored by the powder concentration, whereby up to 70 %wt concentration could be employed without compromising the integrity of the magnets. The elastic modulus of the composite magnets was about $10^5$ times lower than the one of a bulk permanent magnet. This ensures a high bending flexibility, which allows the magnets to be attached to curved surfaces as illustrated for a giant clam, crab and turtle. At the same time, the weight of the composite magnets is reduced by a factor of about 10, which poses less burden to animals’ natural free movement. Without a protective layer, the composite magnets lose more than 50 % of their magnetization after 51 days in seawater. However, the durability of the composite magnets has been improved considerably by using polymer coatings. Parylene C was the most effective for this, providing
corrosion resistance, flexibility and enhanced biocompatibility. Parylene C films of 2 µm and 4 µm thicknesses provided excellent protection of the magnetic composite in corrosive aqueous environments for 65 and 82 days, respectively. By combining the composite magnets with tunnel magnetoresistance sensors, a magnetic animal monitoring system was established that was used to track the behavior of giant clam, crab and turtle.

1. Introduction

Understanding the behavior of free-living marine organisms is pivotal for many conservation efforts (REF) and examining how change, such as overfishing and climate variability, affects marine ecosystems [1]. For this, many researchers have turned to animal-attached tag technology [2] where study animals carry archival ‘smart’ tags that record a suite of parameters to quantify particular aspects of their behavioral ecology or physiology [2]. This approach, though powerful, is challenging [3-8], not least because the marine environment is corrosive and tag-carrying animals may expose their devices to extremes in pressure and temperature [9]. Almost two decades ago, researchers suggested that magnetic sensing systems could be attractive for monitoring some aspects of animal behavioral ecology. Not only are magnetic fields well tolerated by marine animals [8], but also the magnetic properties exhibited by magnets in water are well defined [10]. In particular though, the approach advocated the use of a magnet attached to the study animal on a moving element, such as a limb, that changed position with respect to another animal body part, such as on the animal trunk, on which a magnetic field sensor was mounted. In this case, movement of the limb with respect to the body was apparent via changes in the magnetic field intensity recorded by the sensing system [10]. The specifics of the early measuring systems consisted of a magnetic monitoring system composed of a small neodymium magnet coupled with a Hall-effect magnetic field sensor. Indeed, such systems provided critical data in areas as diverse as the feeding behavior [10], limb movements [11], respiration [12], defecation and heart rates [13] of a number of marine vertebrates. Rare earth and ferrite magnets
have also latterly been utilized in systems exploring spawning of fish\textsuperscript{[14]} and foraging activities of marine homeotherms\textsuperscript{[15-18]}. A little discussed problem in these studies, however, is the effect of the stability of the attachment of the magnet on the quality of the signal. In particular, small magnets (ideal for minimizing the detrimental effects of tags\textsuperscript{[19]} attached to flexible surfaces, such as on animal skin, fur or feathers, can produce large changes in magnetometer response as a result of system mechanical instability. This is particularly the case in tri-axial magnetometers, which are beginning to be used in studies of animal behavior\textsuperscript{[20]}, because they are sensitive to both magnet angle and distance between magnet and sensor\textsuperscript{[20]}. In order to provide a more versatile solution for magnetic-based underwater monitoring systems, we propose the use of composite magnets. Mixing magnetic fillers into a soft and flexible carrier matrix has been recently proposed for a new generation of magnetic composite materials\textsuperscript{[8,21,22]} and exploited in biomedical\textsuperscript{[23-26]}, robotics\textsuperscript{[27-31]}, and automotive\textsuperscript{[32-34]} fields. The formability, multi-directional deflection, low weight and tailored magnetic properties of such flexible composite magnets allow for prescribed magnets to be constructed so that their attachment to animals is mechanically stable. Since they can mirror the body contours and have much less intrusive attachment along the body of animals, the drag force\textsuperscript{[19]} and the likelihood that animals will be disturbed by the physical presence of the system are, thereby, reduced\textsuperscript{[35]}. By merging NdFeB magnetic powder with PDMS, we generate a material that can be permanently magnetized, offering both the advantages of hard-magnetic materials, as well as the compliance, flexibility and minimal weight of a polymer. PDMS offers low–cost, rapid and simple fabrication with a high degree of freedom with respect to the shapes, chemical resistance and biocompatibility of the system\textsuperscript{[36-38]}. While progress has been made in the area of magnetic nanoparticles\textsuperscript{[39]}, NdFeB micro powder is still an attractive choice, due to the high energy product, large coercive field and remanent induction\textsuperscript{[40,41]}. Isotropic NdFeB powder is also inexpensive, due to the comparatively large abundance of Nd and Fe, and has good thermal
aging characteristics [40-42]. As a result of this, NdFeB-based composites have been proposed for applications such as soft MEMs [43,44] microfluidic pressure sensitive valves [45], micromanipulation tools [46], microrobots [27] or energy harvesting [65].

For the application of a magnetic composite in marine applications, the susceptibility of the composite to oxidation, biofouling and any corrosive reactions is critically important. In this paper, we report on the development of flexible magnetic NdFeB-PDMS composite magnets with widely tunable properties and study the effects of a seawater environment on the performance of the magnets. We also propose a solution that avoids deterioration of the magnetic properties when the composite is exposed to seawater over extended periods of time, while maintaining the mechanical flexibility. The composite magnets were tested by combining them with magnetic sensors and attaching them to animals. The magnetic animal monitoring system was then used to detect animal movement via a wireless readout system.

2. Fabrication and Characterization

2.1. Fabrication of composite magnets

The fabrication of the composite magnets comprises four steps; molding, particle alignment, curing and demolding (Figure 1). The fabrication process includes an optional optimization step to obtain a higher remanent magnetization than previously reported [47-49], by particle alignment using a magnetic field, prior to curing.

The preparation of PDMS (Dow Corning Corp. Slygard® 184) includes mixing the elastomer and the curing agent at a 10:1 weight ratio. Composite materials were prepared by dispersing NdFeB microparticles (Molycorp MQP-16-7FP, 5 μm average diameter) into the PDMS, and mixing them thoroughly by mechanical stirring. Concentrations of 10 %wt, 50 %wt and 70 %wt were prepared to study the effects on the mechanical flexibility and magnetic properties. The composites were patterned by pouring them into poly(methyl methacrylate) molds fabricated using a CO₂ laser cutter (Universal Laser Systems Inc.PLS 6.75). Air bubbles
were eliminated by vacuum desiccation. A flat top surface of magnets was obtained by utilizing a casting blade/micrometer adjustable applicator (SH1117/100, Sheen). For the optional alignment of the magnetic fillers along a preferential direction, the composite was subjected to a unidirectional magnetic field of 1.5 T generated by an electromagnet. Finally, the composite was cured at 90 °C for one hour.

Figure 1. Schematic diagram of the composite magnet fabrication process. The NdFeB-PDMS material mixture is formed inside a PMMA mold. It is then cured and released from the mold. For optimized results, the magnetic particles are aligned prior to curing with a magnetic field.

Although it has been found that varying the Nd content can decrease the oxidation rate of NdFeB alloys [49], the goal of this study was to develop a more effective solution that does not compromise the magnetic properties while maintaining the flexibility of the composite magnets. To this end, different protective coatings were tested, including Parylene C, UV resin, epoxy, acrylic and parafilm. The magnetic composites were encapsulated in the following ways:
1.) The Parylene C (poly(dichloro-p-xylylene)) coating was applied using the PDS 2010 Parylene Deposition System (SCS). With a Parylene granule of 2 mg, a coating layer thickness of 1 µm was obtained. Further details of this process can be found elsewhere [50].

2.) Clear epoxy adhesive (ALTECO F-05) was applied using disposable polyethylene pipets and then cured for 4 minutes at room temperature.

3.) Flexible photopolymer resin (FLFLGR01, Formlabs) was applied with disposable polyethylene pipets. It was then exposed to ultraviolet light in a CL-1000 UV Crosslinker for 15 minutes to cure.

4.) Acrylic (VCF Films) and 5.) Parafilm “M” (American National Can TM) were applied using outgassing effects created by vacuum soldering.

### 2.2. Characterization of composite magnets

The optical microscopy image in Figure 2a shows the cross section of a composite magnet that was magnetized after curing with NdFeB concentration of 50 %wt, revealing a relatively homogeneous distribution of the magnetic powder in the polymer matrix. Figure 2b shows an image of a composite magnet that was magnetized before curing, revealing that the different processing methods have no effect on the particle distribution, as there is no apparent difference in the particle arrangement.

This was achieved by mixing the powder thoroughly via mechanical stirring and without any additional measure to reduce agglomeration, such as using surfactants [51],[52] or hydroxypropyl cellulose (HPC)[53].

The composite magnets showed a high mechanical flexibility (Figure 2c), enabling their attachment to marine animals with minimal impact on their behavior. This feature allows the magnets not only to conform to the body curvature of marine animals, but also to follow their body movements. The numbers of species that can be explored and the possible applications...
are also increased, due to the high formability of NdFeB/PDMS composite magnets (Figure 2d).

Compared to a typical commercial permanent magnet (©K&J Magnetics, NdFeB grade N52, V=0.13cm³, 1.27g), composite magnets of the same volume with 50 %wt and 10 %wt were 3 times and 13 times lower in weight, respectively. This is a crucial aspect, since the low weight of the composite magnets poses less burden to marine animals, particularly in species, where overall body density is finely balanced with that of seawater.

![Figure 2 a) Optical microscopy image of the cross-section of a regular magnetic composite sample (magnetized after curing) and b) optimized composite sample (magnetized before curing) c) Flexible NdFeB-PDMS magnetic composite ribbon bent by hand. d) Examples of different shapes and sizes of composite magnets.](image)

The magnetic properties were characterized for cylindrical composite magnets with 1 cm in length and 0.2 cm in diameter at room temperature using a vibrating sample magnetometer. Composite magnets with NdFeB concentrations of 10 %wt, 50 %wt and 70 %wt were investigated, and samples with 50 %wt were studied with and without NdFeB particle
alignment. The magnetization curves revealed that the composite magnets have the same coercivity ($H_c$) of (5.4±0.1) kOe, independent of the concentration (Figure 3), while the remanent and saturation magnetizations had a positive linear relationship with the concentration (Figure 4a). According to the manufacturer’s specification, the value of $H_i$ of NdFeB particles is (4.7-5.5) kOe \cite{54}, which indicates that the magnetic properties of the particles were not affected by the fabrication process. It also shows that the magnetostatic interaction between the particles at these concentrations did not lead to a considerable agglomeration.

![Figure 3. Magnetization curves of magnetic composite magnets with a cylindrical shape. The percentage values indicate the NdFeB powder concentration. The NdFeB powder particles were either aligned (optimized) or not aligned (regular) before curing.](image)

The optimization step, in which a magnetic field is applied prior curing, improved the values of saturation and remanence magnetizations of the composite magnets (Figure 3 red and blue loops, respectively). The remanent magnetization, which is the most relevant parameter for the intended application, increased by 16 %, due to the alignment of the particles’ anisotropy axis with the applied magnetic field. In addition, the magnetic properties were reproducible for
different samples from the same magnetic composite batch, confirming the homogenous dispersion of the NdFeB powder inside of the PDMS.

![Graph a) Remanent and saturation magnetizations of composite magnets as a function of the NdFeB powder concentration; b) Young's modulus, E, and Yield strength of composite magnets as a function of NdFeB powder concentration.](image)

In order to study the mechanical properties of the composite magnets, a tensile test was performed using an electromechanical pull tester (Instron 5900-Series). Figure 4b shows the Young's modulus and Yield strengths of magnetic composite samples with different NdFeB concentrations taken from the stress/strain diagrams. The Young's modulus increased with increasing amounts of NdFeB powder, due to the reduced volume of the polymer bearing the stress in the powder network. A similar result has been reported for NdFeB/epoxy composites [55, 56]. The Young’s modulus of NdFeB magnets is 150 GPa [57], which is nearly $10^5$ higher than the one of the composite magnets. A similar trend can be observed for the yield strength, which increases with the filler content.

3. Results and Discussion

3.1. Magnetic properties of composite magnets in sea water
NdFeB powder is known for its poor resistance to corrosion, ostensibly limiting its use in underwater applications \[58, 59\]. In seawater, a deterioration of the magnetic properties occurs, due to the oxidizing environment, following an inverse parabolic rate law. Biofouling is another process that creates adverse effects on immersed magnetic materials, further limiting their utilization and accelerating the corrosion \[60\].

Therefore, the magnetic properties of NdFeB-PDMS composite magnets deployed in seawater were investigated for different lengths of time. To this end, cylindrical composite magnets were made with 50 %wt of magnetic powder and deployed at the Al Fahal reef in the Central Red Sea (geographic coordinates: 22.25285°N, 38.96123°E, average salinity: ~35 %, average temperature ~22°C). The results showed that both the remanence and the saturation magnetization followed the same trend, deteriorating quickly (Figure 5), with the greatest changes happening during the first 3 days. This is the case for both composite magnets made with optimized and regular fabrication processes. During the first 3 days, between 30 % and 38 % of the magnetization was lost and this figure increased to 60 % after 51 days.

Biofouling on the composite magnets was evaluated using both accumulation of matter in terms of the surface area covered and weight of the biofoulants. Using ImageJ software \[61, 62\], the area of the composite magnets surface covered by biofoulants after 51 days was found to be 13.2 % (inset in Figure 5). The biomass of the biofoulants was 10.2 mg/cm², as determined by gently scraping the surface of the magnets until no fouling was visible and weighing the fouling materials removed. This measurement represents the upper limit of what would be expected given that biofouling on sedentary substrates is likely greater than when the material is attached to mobile organisms. In addition, a visual assessment found that other materials, such as PMMA and metals (deployed at the same time as composite magnets) had more biofouling. Given the rapid decline in remanent magnetization, which occurred much faster than visible biofouling, corrosion is likely the primary factor limiting the longevity of the magnets.
Figure 5. Saturation and remanent magnetizations of cylindrical composite magnets with 50% wt NdFeB powder in sea water. The NdFeB powder particles were either aligned (optimized) or not aligned (regular) before curing. The inset shows a stereoscope image of a composite magnet after 51 days in sea water, revealing biofouling on its surface.

3.2. Polymer coatings for corrosion protection

The capability of the polymer coatings to preserve the composite magnet properties was evaluated over a period of 21 days. Coatings slow down the corrosion compared to the unprotected composite magnets (Figure 6). However, all polymers had limited success in protecting the magnetic properties, except for Parylene C, in which case the remanent magnetization of composite magnet remained stable over 21 days.
Based on this, Parylene C was used in further investigations and samples of magnetic composites were coated with thicknesses of 2 µm and 4 µm thickness. The parylene C coatings preserved magnetization for nearly 65 days for 2 µm and 82 days for 4 µm coatings (Figure 7). This may be explained by the low water and gas permeability of Parylene C \[^{39,63}\]. Parylene C also exhibits a high biocompatibility, is optically transparent and flexible (\(~4\) GPa of Young’s modulus) \[^{64-67}\], which are additional features making it suitable for marine animal monitoring applications.

Figure 6. Remanent magnetization of composite magnets coated with different polymers and deployed in the Red Sea.
Figure 7. Remanence magnetization of magnetic composites coated with 2 µm and 4 µm of Parylene C and deployed in the Red Sea.

3.3. Marine animals monitoring

Much basic knowledge about the behavior of free-living marine organisms can be obtained by examining animal movement, both translocational and otherwise. The versatility of the composite magnets should catalyze the development of more compelling and flexible underwater magnetic monitoring systems based on magnetic field sensors in combination with the developed corrosion-resistant and bendable composite magnets. By way of demonstration, our application had the stray field of the composite magnet measured by a magnetic tunnel junction sensor (TMR2305, Multi Dimension, Inc), finding the resulting signal (read via an in-house wireless communication module\cite{68,69}) was a function of the distance between the sensor and the composite magnet. With regard to location, the composite magnets were attached to animals using waterproof velcro (VLC02, Velcro® Brand Marine Grade Hook and Loop) and pure epoxy compound (Subcoat S, Veneziani Yachting). In case of a giant clam, *Tridacna gigas*, an important component of coral reefs ecosystems in the Red Sea, the sensor was mounted on one valve margin and the magnet on the opposite valve margin, which provides multiple response variables related to mantle opening (Figure 8a). In case of crabs (*Libinia emarginata*), the sensor was mounted on the carapace and the magnet on the third leg (merus...
section), in order to monitor the physical activity level of the crab (Figure 8b). Finally, in case of tortoises (*Aldabrachelys gigantea*), the sensor was mounted on the carapace (marginal scutes), and the magnet on the front right leg in order to monitor the animal’s physical activity (Figure 8c). The magnetic monitoring system operated reliably over distances of up to 10 cm between the sensor and the composite magnet, which was the maximum required for those three animals. No sign of deterioration of the magnets was found during the experiments, which lasted up to 24 hours. The signal derived from the animal monitoring experiments enables extraction pivotal information such as levels of activity over time (e.g. day time versus night) or as a function of proximity to predators etc.

Figure 8. Marine and terrestrial animal monitoring experiments utilizing composite magnets and commercially available magnetic sensors. a) giant clam, b) crab and c) giant tortoise. The bottom images show the sensor signal over time.

4. Conclusion

NdFeB-PDMS composite magnets were studied for underwater marine monitoring applications. The fabrication process involves minimal complexity and is highly versatile with respect to the shape of the magnets. The remanent magnetization can be enhanced by 16 % with an additional step, during which the magnetic particles are aligned by a magnetic field. The influence of the filler concentration on magnetic and mechanical properties was determined and
showed that they can be tailored within a wide range. The composite magnets have a large bending flexibility with a Young’s Modulus of $\sim 10^5$ times lower than the one of a bulk permanent magnet, in case of 10 %wt particle concentration. This means that they can readily conform to the curved surface of marine animals, as demonstrated by mounting composite magnets to a giant clam, crabs and turtles. The weight of the composite magnets can also be considerably reduced, by a factor of 13 in the case of 10 %wt particle concentration, compared to a bulk magnet. The proposed fabrication is cost-effective, due to the rapid production of reusable polymer molds by a CO$_2$-laser system. The performance of the flexible magnetic composites was tested in sea water, where they quickly showed a reduction in the remanent magnetization, due to corrosion and biofouling. A coating study revealed that Paralyne C is the most suitable and efficient polymer for protecting the composite from deterioration, providing corrosion resistance, flexibility and biocompatibility. The magnetic properties of the composite magnets were maintained for nearly three months while being deployed in the particularly harsh environment, with high salinity, temperature and growth rates of fouling communities, of the Red Sea. The composite magnets were tested in combination with magnetic sensors on three different animals underwater and on land using a reliable wireless monitoring system. The results show the suitability of the composite magnets for marine applications. Their low weight, mechanical flexibility and deformability provide the features necessary to tackle new applications and study species with a wide range in body size and morphology, which is not possible with rigid permeant magnets.

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