BIODEGRADABLE ELECTRICAL INTERCONNECTS FOR TRANSIENT IMPLANTABLE SYSTEMS

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ABSTRACT

This study presents the development and characterization of biodegradable electrical interconnects comprising biodegradable conductive polymer composites for use in transient implantable systems. The biodegradable conductive polymer composites were developed using iron (Fe) microparticles as the conductive filler and polycaprolactone (PCL) as the insulating matrix. The electrical resistivity and the mechanical and electrochemical properties of the composites were investigated during physiological degradation. The electrical percolation threshold was found at 17% iron volume fraction, but higher volume fractions exhibited more stable electrical resistivity throughout the time course of degradation. An electrical lifetime of over 20 days was achieved with 40% Fe composites, where the average resistivity was 0.3 Ω·cm. Adhesion tests under physiological aging conditions were also performed. Biodegradable electrical interconnects based on 40%vf Fe-PCL composites were successfully micropattened in daisy-chain structures to illustrate process compatibility of these materials.

INTRODUCTION

There has been growing interest in the development and study of biodegradable medical devices in the medical and health industry. Since these devices comprise biodegradable materials, which can gradually decompose and be expelled from the body, patients do not need a second surgery to remove the devices from their bodies after healing. In addition, biodegradable devices overcome the negative effects associated with permanent implants, such as fibrous encapsulation and stress-shielding at the implant-tissue interface [1]. For these reasons, biodegradable implantable devices have been proposed for the monitoring and treatment of short-term ailments [2]. Biodegradable analogues of passive RF pressure sensors have been demonstrated, where degradation lifetime can be tailored based on the material composition and sensor design. For example, the degradation rate of zinc/iron inductors used in sensors can be controlled by altering the exposed area ratio of these two metals [3]. To date, biodegradable devices have been limited to either passive designs or active devices with short (i.e., minutes to hours) functional lifetime [4]. To achieve active biodegradable devices with clinically-relevant functional lifetimes, research must not only address the sensor and power source [5], but also the circuitry and electrical interconnects.

Non-degradable polymer-metal composites have been studied previously for interconnect materials because of their low process temperature, light weight, and environmental friendliness. Generally, these interconnect materials are developed using metal (e.g., silver, gold, and nickel) as the conductive filler and polymer (e.g., epoxy, silicone, polyimide) as the insulating matrix [6]. With appropriate materials modification, conductive polymer composites are interesting options for biodegradable system interconnects.

The behavior of such composite interconnects can be studied by use of percolation theory. Percolation theory is a statistical model that describes how randomly positioned sites are connected in a disordered system. Above a critical concentration of positioned sites, called the percolation threshold, a connected path is formed through the system [7]. Percolation theory has been used to interpret the electrical percolation of composite materials consisting of conductive filler in an insulating matrix. Composites behave as insulators and as conductors when the concentration of conductive filler is far below and above the percolation threshold, respectively. Further, composites show an appreciable change in electrical resistivity when the concentration crosses the percolation threshold.

We present the development of electrical interconnects comprising biodegradable conductive polymer composites for transient implantable systems. The electrical, mechanical, and electrochemical properties of the composites are investigated during physiological degradation. The percolation point of these composites is identified during this characterization, and favored compositions with reasonably stable properties are selected for subsequent testing. Finally, biodegradable electrical interconnects based on these favored compositions are micropatterned to demonstrate their compatibility with MEMS processing.

METHODS

Fabrication

Biodegradable conductive polymer composites were developed using Fe microparticles as the conductive filler and PCL as the insulating matrix, and micropatterned onto polylactic acid (PLA) substrates by screen printing to form electrical interconnects. (Fig. 1) First, the Fe powder (<10 µm, ≥99.9% trace, Sigma Aldrich) was serially washed with dichloromethane (≥99.8%, Sigma Aldrich) and 1,4-dioxane (99.5%, Acros Organics) in triplicate. PCL (average M_n 80,000, Sigma Aldrich) pellets were solubilized in dioxane to a concentration of 200 mg/mL. Oleic acid (90%, Sigma Aldrich) was then added to the serially-washed Fe as a surfactant to facilitate the homogeneous suspension of Fe in the PCL solution. Finally, PCL solution was added to the Fe and oleic acid mixture to reach the desired volume fraction.

Screen printing was performed using 10-mil-thick polyester shim as the stencils. First, the polyester shim was micromachined with a CO_2 laser. The patterned shim was then laminated onto PLA substrates using polyvinyl alcohol (PVA) as the adhesive. The PLA substrates had been previously metallized with Fe traces 100 nm in thickness by sputter deposition through a shadow mask and laser micromachined (532 nm wavelength, 100 µJ pulse energy, 1 ns pulse width, and 10 W maximum power) to pattern the Fe traces.

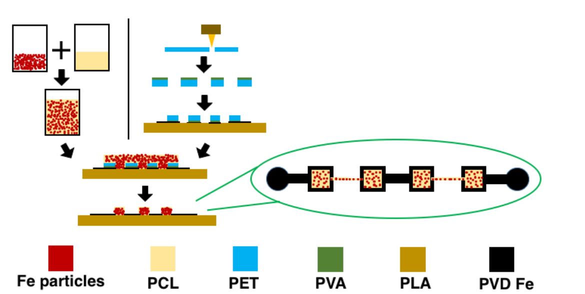


Figure 1: Fabrication scheme and daisy chain structures of Fe-PCL biodegradable electrical interconnects.

Specifically, 25% of the Fe surface area of each pad was ablated to expose the underlying PLA to promote adhesion of the composites. Finally, the Fe-PCL composite was applied and screen printed onto the pre-patterned Fe-PLA substrate. In this manner, electrically-continuous daisy chain structures were micropatterned on the PLA.

Electrical and Mechanical Characterization

As electrical conductivity and mechanical robustness are key design requirements for interconnects, the effect of physiological degradation on the electrical resistivity and elastic modulus of Fe-PCL composites was investigated. Composite films with different volume fractions of Fe were prepared and immersed in simulated body fluid (SBF) at 37ºC in an incubator to simulate physiological degradation. At intermittent time points, the resistivity of the films was measured using electrical probe testing. In addition, physiologically conditioned Fe-PCL composite films were mechanically strained to 1% tensile strain at 1 Hz for 100 cycles in a uniaxial mechanical testing system (Bose Electroforce 3200) to monitor the elastic modulus of the composite with respect to degradation time. As biodegradable electrical interconnects may also be exposed to occasional mechanical strain due to physiological loading and local micromotion, the electrical resistivity of mechanically and physiologically conditioned Fe-PCL films was also monitored.

The functional lifetime of electrical interconnects may also be limited by its adhesion strength. While this is not desirable, physiological degradation may further exacerbate the effect. In order to overcome this design challenge, it was important to enhance the adhesion strength of Fe-PCL composites on biodegradable substrates and to ensure that the adhesion persists throughout physiological degradation. Towards these goals, as well as to demonstrate the processing compatibility of biodegradable Fe-PCL interconnects on similarly biodegradable substrates, Fe-PCL electrical interconnects were screen printed onto micropatterned Fe-PLA substrates. Specifically, iron traces were micropatterned onto a 250-µm-thick PLA substrate by sputter deposition through a shadow mask to form a grid of 10mm x 10mm squares of 100 nm thickness. Next, the sputtered Fe was ablated with an array of 250-µm-wide square holes to expose 25% of the underlying PLA and Fe-PCL composite (40%vf of Fe) was screen printed onto the micropatterned Fe using the fabrication procedure described earlier. Samples was then diced into individual coupons comprising three test samples per coupon and immersed in SBF at 37ºC for physiological conditioning. At periodic time points, samples were retrieved for optical microscopy and adhesion testing in accordance with ASTM D3359-09 guidelines [8]. Briefly, two intersecting cuts were made through the Fe-PCL composite in each sample using a razor blade; the intersection point was aligned with the center of each square pattern and the intersection angle ranged between 30º and 45º. For each test, 75-mm-long strip of Scotch permanent tape was adhered onto the cut Fe-PCL composite with the tape running in the same direction as the smaller intersecting angle. Good contact was ensured before proceeding. Within 90 ± 30 s of application, the tape was pulled off rapidly at a peel angle as close to 180º as possible. Finally, the cut area was inspected for removal of composites from the substrate and adhesion was rated based on the ASTM scale. The scale ranges from 0 to 5, which correspond to complete removal of the adhesive material (i.e., poorest adhesion) and negligible loss of adhesive material, respectively.

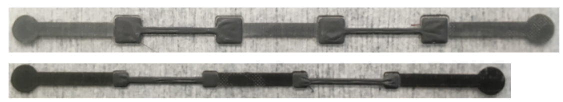
Electrochemical Properties Characterization

The degradation behavior of Fe-PCL composite films (40%vf Fe) were evaluated by linear sweep voltammetry (LSV) (Gamry Reference 600). The test was performed at 37ºC in SBF using a three-electrode configuration, where the working, counter and reference electrodes were the Fe-PCL composite, a platinum mesh, and a saturated silver/silver chloride electrode, respectively. The measurement scanned a 500 mV window centered about the open circuit potential at a scan rate of 2.5 mV/s after open circuit potential stabilization. The corrosion potential and corrosion rate were determined by linear fitting the results based on Tafel equations [9].

RESULTS AND DISCUSSION

Optical Images

Figure 2 shows the micropatterned biodegradable daisy chain structures comprising Fe-PCL composites interconnects bridging sputter-deposited Fe traces. The interconnect width and thickness were 350 µm and 250 µm, respectively, which agree with the microscale dimensions of MEMS devices. Together, the micropatterned daisy chain structures demonstrate the compatibility of Fe-PCL composite interconnects with standard MEMS processing techniques. Fig. 2B shows the backside view of a daisy chain structure to visualize the laser machined Fe traces featuring 25% areal exposure of the underlying PLA substrate. The ablated regions with PLA exposure are in direct contact with the overlying screen-printed Fe-PCL composite to promote adhesion.



(*A*)

(B)

Figure 2: Optical images of micropatterned biodegradable daisy chain structures comprising Fe-PCL conductive polymer composites as interconnects bridging sputter-deposited Fe traces. (A) Zoomed out. (B) Backside view of bridged pad structures in a daisy chain.

Electrical Resistivity

Figure 3 shows the electrical resistivity of Fe-PCL composite films as a function of volume fraction, parameterized by duration of physiological degradation. The electrical resistivity decreased by orders of magnitude between 5% and 20% volume fractions of Fe with a percolation threshold at approximately 17%vf, above which the electrical resistivity did not appreciably change. However, with physiological degradation, the resistivity of the composites at higher volume fraction of Fe (i.e. $\geq$40%) exhibited enhanced stability, potentially attributable to the smaller percentage of iron being lost at higher volume fractions as degradation proceeds (since the initial amount of iron at higher volume fractions is higher). Another potential explanation is that Fe corrosion products, such as oxides formed during degradation, present an electrical barrier to conduction.

Figure 4 shows the electrical resistivity of composites with varying volume fractions of Fe throughout the time course of degradation. The electrical resistivity of the films decreased by roughly 3 orders of magnitude after immersion in SBF. This is possibly due to electrolyte permeation into PCL, based on previous

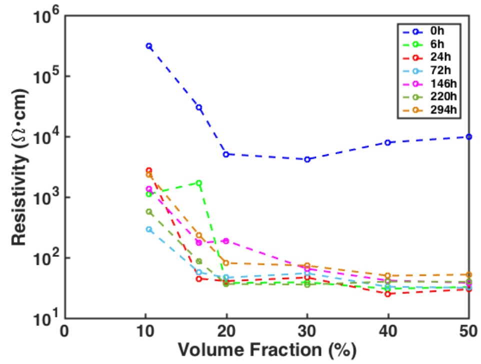


Figure 3: Electrical resistivity of Fe-PCL biodegradable conductive polymer composite films at varying volume fractions of Fe, parameterized by degradation time.

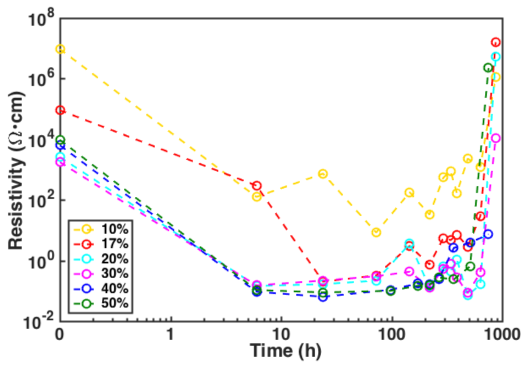


Figure 4: Electrical resistivity of Fe-PCL biodegradable conductive polymer composite films parametermized by volume fraction of Fe as a function of degradation time.

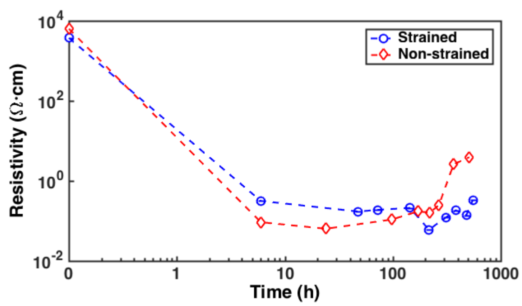


Figure 5: Electrical resistivity of Fe-PCL biodegradable conductive polymer composite films (40%vf of Fe) as a function of degradation time with and without intermittent strain.

measurements that showed the resistivity of PCL decreased by 2 orders of magnitude after immersion in SBF. The electrical resistivity of composite films with volume fractions of Fe above 17% stablized at approximately 0.1 Ω·cm within 6 hours after immersion in SBF, which indicates that the composites can behave functionally within a short period of time after immersion. Although the resistivity is higher than traditional interconnect materials, the Fe-PCL composites above the percolation threshold are still candidate materials for use in low current interconnects. In addition, the electrical resistivity of composite films with volume fractions of Fe above 17%vf remained stable within 500 hours of immersion in SBF and, thus, demonstrated a liftetime of over 20 days. After 500 hours, the resistivity of all films started to increase as corrosion proceeded. Because stability of conductivity over the functional lifetime of the interconnect is an important parameter, composites with 40%vf of Fe were selected for use in subsequent testing.

To assess the effects of intermittent strain on the interconnect conductivity, the electrical resistivity of 40%vf Fe-PCL composite films as a function of degradation time with and without intermittent cyclic tensile strain is compared (Fig. 5). The mechanical conditioning simulated the strains that an implanted chip may experience in the body. Each strained sample was subjected to 100 cycles of a 1% strain at a frequency of 1 Hz. The resistivity of the intermittently strained films decreased and stabilized to approximately 0.3 Ω·cm within 6 hours in SBF, similar to the electrical resistivity of films that had not undergone mechanical strain. In addition, the resistivity fluctuations of both films were commensurate, which indicates that the stability in resistivity of composites with 40%vf of Fe was not significantly affected by intermittent strain under physiological degradation.

Mechanical Properties

During the intermittent strain process described above, it was possible to assess the elastic modulus of the 40%vf composite material as a function of degradation time (Figure 6). The elastic modulus of the composite was 200 MPa prior to immersion in SBF. The elastic modulus was larger than that of bulk PCL (0.8 ± 0.1 MPa) because Fe microparticles increased the modulus. The elastic modulus increase stabilized at approximately 400 MPa after immersion in SBF. A possible explanation for this behavior is the formation of oxides during degradation resulting in an increased elastic modulus. However, the elastic modulus is still lower than that of metal and semiconductor interconnects (≈ 100 GPa), which suggests that the composites are more compliant and could provide more flexibility in interconnection. The elastic modulus fluctuated within 25% over 500 hours, indicating a relatively good stability in degradation.

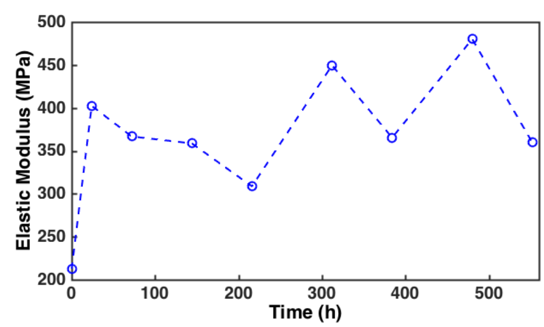


Figure 6: Elastic modulus of Fe-PCL biodegradable conductive polymer composite films (40%vf of Fe) as a function of degradation time under intermittent strain.

As biodegradable electrical interconnects must maintain adhesion onto similarly biodegradable substrates, the adhesion of Fe-PCL composites on Fe-PLA substrates was investigated with respect to degradation time (Fig. 7). From previous experiments, it was found that the composites showed poor adhesion on stainless steel substrates, where composites could be peeled off without effort (i.e., rating of 0 in adhesion tests). Further, it was hypothesized that the corrosion products formed during degradation could embrittle the Fe-PCL composite and deteriorate its adhesion. However, the design of the Fe traces presented in this study, which featured 25%

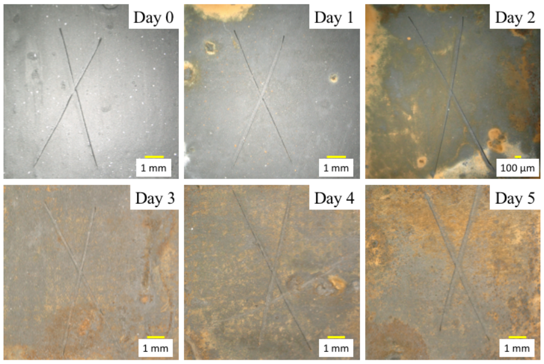


Figure 7: Optical images of physiologically conditioned Fe-PCL composites (40%vf of Fe) after adhesion tests were performed on PLA substrates with micropatterned Fe traces.

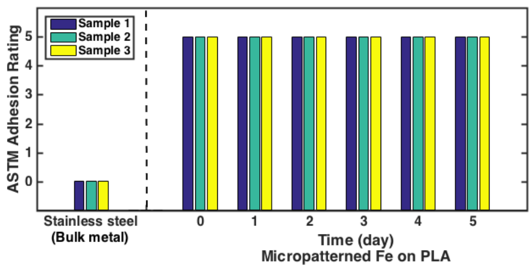


Figure 8: Adhesion test ratings of Fe-PCL composites on micropatterned Fe-PLA compared against stainless steel (i.e., bulk metal) control samples. Tests were performed on Fe-PCL composites after varying immersion times in SBF to simulate degradation conditions. Adhesion is rated between 0 to 5; higher ratings correspond to better adhesion.

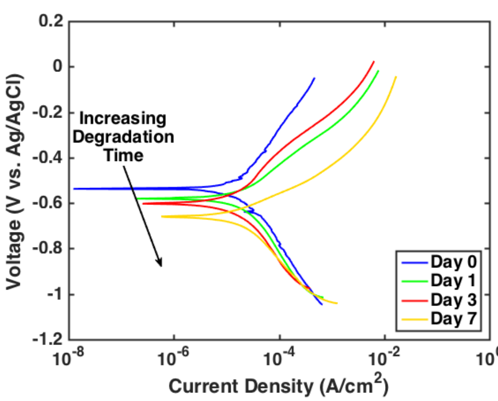


Figure 9: Polarization curves of Fe-PCL biodegradable conductive polymer composite films (40%vf of Fe) after physiological degradation.

areal exposure of the underlying PLA substrate, significantly improved its adhesion with Fe-PCL composites. Specifically, the composites scored the maximum adhesion rating (i.e., 5) and retained their adhesion strength throughout the time course of degradation (Fig. 8). The results not only confirmed that the design of the micropatterned Fe traces and Fe-PCL composites can successfully resolve previous adhesion challenges, but also support their use for biodegradable electrical interconnects in transient implantable applications.

Electrochemical Properties

Figure 9 shows the polarization curves of Fe-PCL biodegradable conductive polymer composite films with 40%vf of Fe throughout degradation. The corrosion potential of the composite films was -0.537 V vs. Ag/AgCl prior to degradation conditioning in SBF, which approximates the corrosion potential of bulk Fe. The corrosion potential decreased when the degradation time increased, indicating the increasing corrosion tendency of the films. Moreover, the corrosion current density increased as a function of time, implying an increased corrosion rate as degradation continued.

CONCLUSIONS

In this study, the suitability of Fe-PCL composites as potential candidates for biodegradable electrical interconnects was investigated. The electrical percolation threshold of Fe-PCL composites was found at 17%vf of Fe. Stability of resistivity over a reasonable functional lifetime was achieved by utilizing composites with 40%vf Fe, in excess of the percolation threshold; stability was maintained even under intermittent tensile strain. Short term adhesion testing indicated reasonable adhesive stability of these interconnect materials. These properties, together with the relatively low composite elastic modulus, suggests their potential application as interconnects. The biodegradable electrical interconnects were shown to be compatible with standard processing techniques through the formation of micropatterned daisy-chain structures.

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