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Abstract

Electrodes fabricated from electronically active polymers offer some benefits over those fabricated with common metals, including an appreciable resistance to corrosion and lower density. These benefits, and potentially others, manifest the advantages of using conductive polymers in lieu of metals for the mass production of ignition systems. In this work, spark gap igniters were fabricated using a potentially low-cost, roll-

to-roll compatible process utilizing the doped conductive polymer polyaniline as the electrode material. Subsequently, nanothermite was printed on the spark gap igniters between the organic leads and ignited using a high voltage source to demonstrate the effectiveness of the device. All of the igniters successfully fired with a mean spark over voltage of 3.14 kV. In addition, all of the igniters with deposited nanothermite successfully ignited the material. Accordingly, this work outlines the materials and processes required to develop organic-based spark gap igniters and establishes a baseline for future work related to the metal-free ignition of energetic materials.

1 Introduction

Since the 1930s, metallic igniters have been used in systems ranging from pulsed power thrusters **1** to explosive initiators **2, 3**. Metallic igniters have low resistance, on the order of 5 Ω or less, but feature a number of drawbacks including high susceptibility to corrosion and comparatively high density. Conductive polymer igniters provide an alternative to these traditional ignition systems, as they can be fabricated using a potentially low-cost, easily scalable manufacturing process. However, to the best of the authors' knowledge, a demonstration of printed organic electronic spark gap igniters has not occurred to date.

In prior work, conjugated polymers have shown promising electrical conductivity, flexibility, and comparatively low densities **4**. Conductive polymers are also able to be processed from solution, which allows for their use in low-cost printing **5**, doctor blading, and related manufacturing processes. Furthermore, these materials have the added feature of possessing easily tailored electrochemical properties **6**, facilitating their use in a variety of applications including sensors **7**, light-emitting diodes (LEDs) **8**, and photovoltaic and thermoelectric devices **9**.

Material systems consisting of the conductive polymer polyaniline (PANI) have been shown to have conductivity on the order of 100 S/cm when mixed with m-cresol **10** and have exhibited useful properties, such as appreciable corrosion resistance and flexibility **11**. These material systems have been thermally inkjet printed to create thin conductive films with high resolution **12** and have been successfully used in applications such as ammonia gas sensing **13**. The most conductive state of polyaniline is its emeraldine salt form, specifically when it is doped with a protonic acid, such as camphorsulfonic acid (CSA) **14**. When combined with a solvent, such as m-cresol, polyaniline films have demonstrated properties similar to metal films at high temperatures **15**.

In general, spark gap ignition systems have been successfully triggered on the sub-microsecond scale **16**, which is critical in events such as a vehicle accident or explosive ignition. In addition, the low current required to create a voltage breakdown across a spark gap allows for the use of small capacitors for ignition, minimizing the total space needed for the entire ignition system. A spark gap igniter fabricated using PANI presents the opportunity for a lightweight, metal-free alternative to traditional ignition systems. This work demonstrates the effectiveness of a spark gap igniter fabricated with a PANI solution using doctor blading; each spark gap igniter successfully fired, and an additional subset successfully ignited nanothermite. Furthermore, the manufacturing technique demonstrated in this work can be implemented on a large scale (e. g., using roll-to-roll manufacturing), presenting a new and potentially economical method for fabricating igniters.

2 Experimental Methods

2.1 Ink Formulation

To create a solution viable for coating using a doctor blade, polyaniline powder (3M) was doped with camphorsulfonic acid (99 %, Sigma-Aldrich) by crushing the two constituents into a fine powder with a mortar and pestle at a ratio of 10 to 6 repeat units of aniline to each camphorsulfonic acid molecule. The solvent m-cresol was chosen for use here due to its low viscosity and previously mentioned ability to render high conductivity solutions. This solvent (99 %, Fisher Scientific) was added to the conductive powder, and the

solution was mixed in a resonant mixer (LabRAM, Resodyn Acoustic Mixers, Inc.) at 80 % intensity for 8 min, overturned, then mixed at 80 % intensity for an additional 8 min. An 8 wt% solids loading was found through testing to be the highest solids loading suitable to ensure homogeneous sample fabrication with the doctor blading technique.

2.2 Sample Fabrication

Spark gap igniter samples were fabricated using a doctor blade fabrication technique. Negative molds of the spark gap geometries were cut from 0.19 mm thick cling vinyl (Cricut Explore One) and adhered to an inkjet printing transparency substrate (Mitsubishi Imaging, Inc.) which provided improved geometric control for polar solvents, allowing the substrate to be kept at room temperature throughout the duration of the manufacturing process.

The 8 wt% solids solution was sonicated (1800 Ultrasonic Cleaner, Branson Ultrasonics) for 1 h prior to use, then pipetted on the edge of the molds. A plastic card was used as a squeegee to evenly distribute the solution into the molds. The cling vinyl was left on the substrate overnight to maximize geometric control during solvent evaporation. Subsequently, the cling vinyl was removed, and the samples were cured in an oven (APT.line ED, Binder, Inc.) at 85 °C for 1 h to remove the remaining solvent. This process is graphically represented in Figure 1. The resulting devices represent conductive polymer spark gap igniters printed on a flexible substrate, as shown in Figure 2a. A group of 10 of the substrates was weighed before and after sample deposition, revealing an average mass of 6.19 mg and a standard deviation of 0.99 mg of conductive ink per sample. Side view images (Krüss Drop Shape Analyzer - DSA 100) show a sample thickness of approximately 100 μm , as shown in Figure 2b.

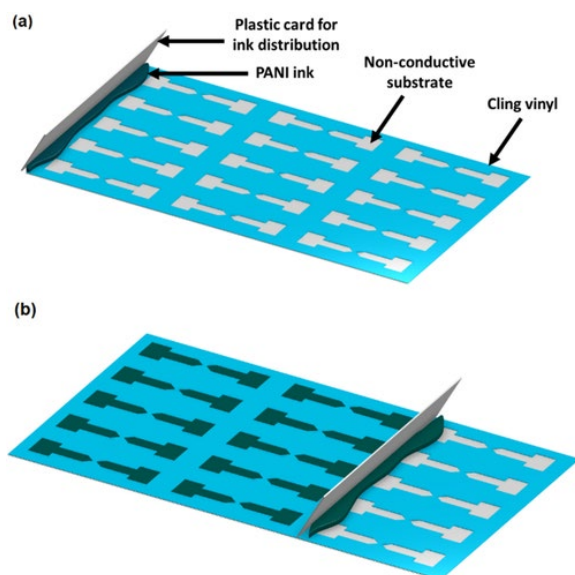


Figure 1 (a) The first sequence in a doctor blade fabrication technique. Note that the blue material represents the cling vinyl and the gray material underneath the cling vinyl represents the non-conductive substrate. (b) A sequence in the doctor blade process that displays the material being evenly distributed into the cling vinyl.

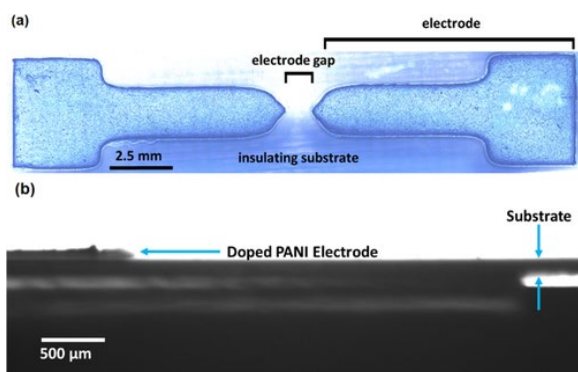


Figure 2 (a) Doctor blade fabricated PANI spark gap igniter on a flexible substrate and (b) a cross-sectional image of a representative PANI sample on a Mitsubishi Imaging transparency substrate.

Prior work has shown that nanothermite is suitable for use in small-scale igniters **17**. Al-Bi₂O₃ nanothermite was chosen as a candidate for testing the conductive polymer igniter's ability to ignite energetic material due to its destructive capabilities and ease of fabrication, as demonstrated in prior work **18**. The Al-Bi₂O₃ nanothermite was deposited on top of eight spark gap igniters using a BioFluidix PipeJet P9 system with a 500 μm nozzle. Nano-aluminum (82 % active aluminum, NovaCentrix, 80 nm) and nano-bismuth oxide (Nanophase Technologies Corporation, 38 nm) were mixed in a solution of Solsperse (Lubrizol) and dimethylformamide (DMF, Sigma-Aldrich) in a resonant mixer (LabRAM, Resodyn Acoustic Mixers, Inc.). The ink was mixed at an 80 % intensity for 8 min, overturned, then mixed at 80 % intensity for an additional 8 min. The solution was re-suspended for 30 min before printing using a sonicating bath (1800 Ultrasonic Cleaner, Branson Ultrasonics), then deposited on the selected eight igniters.

2.3 Test Setup

The spark gap igniters were tested with a high voltage power supply (Stanford Research Systems, PS365) with a voltage maximum of 5.2 kV and a current maximum of 50 μA. The samples were fastened to a plastic plate using alligator clips to prevent the sample from bending during testing. An oscilloscope (Agilent, DSO6014A) was connected to the power supply to record the voltage at the spark over event.

3 Results and Discussion

Breakdown voltages for the spark gap igniters without nanothermite present are shown in Figure 3. Of the 26 samples tested, all successfully sparked over, with a mean voltage of 3.14 kV and a standard deviation of 0.31 kV. The conductivity of the printed samples was measured by first thermally evaporating gold contacts of thickness 100 nm and then using the van der Pauw measurement method **19** to ascertain that the conductivity of the samples was approximately 20 S/cm. The spark gap samples displayed no visible signs of degradation after sparking. A single spark gap igniter was fired 15 times to test the robustness of the igniter, and the device fired successfully each time. The gap width was calculated from the approximate distance measured in pixels from one lead of the spark gap to the other to provide a more accurate small-scale measurement. The distance in pixels was then converted to mm based on a calibration slide provided with the camera.

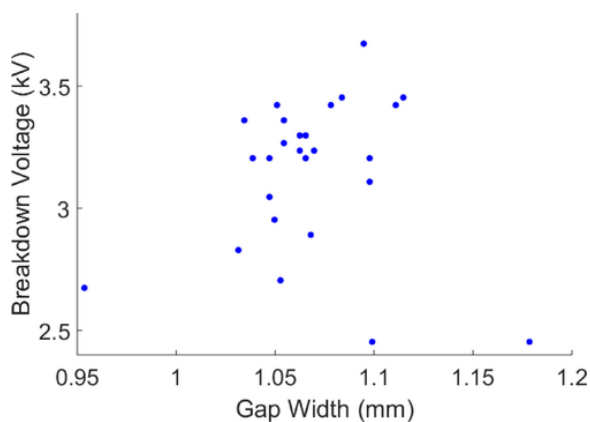


Figure 3 Recorded breakdown voltage for the PANI spark gap igniters compared to measured gap width.

The spark gap igniters with nanothermite present were tested in the same manner as those without nanothermite. All eight of the igniters successfully ignited the deposited nanothermite material with the reaction captured by a high-speed camera (Phantom V10) with a frame rate of 9000 fps and a 60 μ s exposure. Still, frames from a representative event are shown in Figure 4a. This sample ignited at a breakdown voltage of 4.41 kV, slightly higher than the breakdown voltage required for a spark gap without nanothermite, due to the added resistance of the nanothermite between the leads. Before and after images of the nanothermite on the PANI spark gap are shown in Figure 4b.

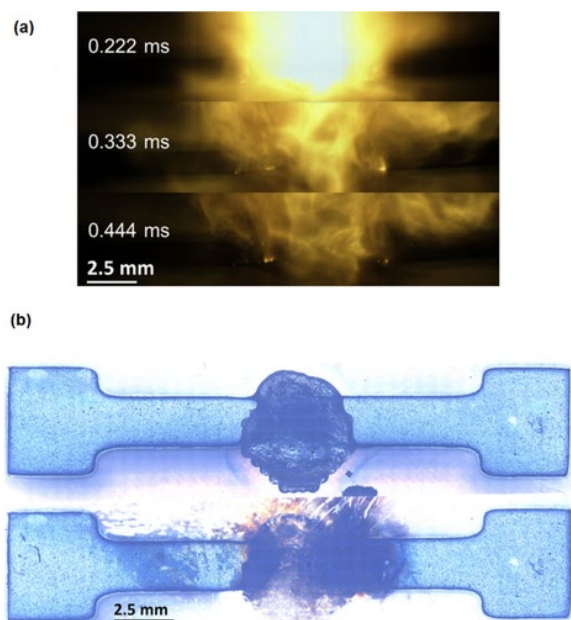


Figure 4 (a) High speed footage of ignited nanothermite printed on a PANI spark gap igniter and (b) a pre- and post- ignition sample.

4 Conclusions

This work has shown that a PANI conductive polymer ink can be made into functional spark gap igniters using doctor blade manufacturing. With the fabrication technique demonstrated here, the geometry of the PANI igniters can be tailored to fit existing circuits or initiation systems; the negative mold cutting technique allows for the freedom to change the gap width, creating the ability to tailor the spark gap size to fit the system in which it is used. Doctor blading has proven to be a successful avenue for producing polyaniline igniters and can now be exploited on a larger manufacturing scale for applications, such as airbag ignition.

Future work will span the integration of a metal-free energetic material with the PANI ink used in this study to create samples in a similar fashion. A fully integrated conductive, energetic ink would provide a bulk fill material with the potential of use in entire circuit geometries, creating a fully ignitable circuit. In addition, a small power source could adequately supply the high-voltage, low-current power needed to ignite the spark gap, introducing the possibility for use in small-scale applications. Furthermore, the resulting igniter would be completely organic, flexible, corrosion-resistant, reliable, and lightweight, and thus tailorable to fit the needs of many existing systems.

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