Development of a Mechano-Responsive Ink for Security Printing

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Abstract

Security printing is an emerging field to prevent forgery, tampering, and counterfeiting of a wide variety of documents and consumer goods. In this work, mechanochromic ink for security printing is suggested as a viable option for a reversible, easily detectable way of determining the legitimacy of a document or product. Generally, mechanochromic polymers change color and exhibit fluorescence in response to a mechanical force due to the presence of mechanophore molecules covalently linked within the polymer structure. A well-known mechanophore, spiropyran (SP), is easily incorporated into poly(dimethylsiloxane) (PDMS), an elastomeric polymer. In this study, SP-PDMS ink for security printing applications is studied by tuning the initial viscosity with a solvent. Additionally, the printed film quality is determined through both optical and mechanical techniques. Printing conditions were determined for printing with a Nordson Engineered Fluid Dispensing (EFD) Printer. The responsiveness of the mechanochromic ink to mechanical loading is explored through visible color change.

Introduction

Counterfeiting is a global issue that wreaks havoc on global health, safety and financial well-being of individuals, governments, and corporations. Security printing involves developing anti-counterfeiting, print solutions for high value/high impact documents and products. A mechanoresponsive ink represents a new covert security feature that could be used to help prevent counterfeiting. Currently, thermal- and photo-responsive inks are available, but inks that exhibit a response to mechanical stimuli have yet to be developed.

Mechanoresponsive inks could be utilized in the security printing field for their response to physical stimuli, for example, a printed symbol on a product that changes color (mechanochromic) on being scratched. The response of a mechanoresponsive ink could be tuned to specific applications by altering the chemistry of the ink, providing a unique and tailored solution to multiple applications. However, challenges in developing such inks involve identifying a suitable mechanophore, a molecule activated by physical stimuli, a compatible matrix, and capable methods for printing the developed ink.

The work presented here investigated the use of a bis-alkene functionalized spiropyran, a well-known mechanophore, covalently linked into a polydimethylsiloxane (PDMS) matrix. In addition to its mechanochromic properties, spiropyran is also photo- and thermo-chromic, adding to the multifunctionality of a covert ink containing spiropyran. The preliminary effort investigated the development of a PDMS and toluene-based ink to be printed with an automated pneumatic dispensing system - a Nordson EFD (Engineered Fluid Dispenser). The specific curing and printing parameters were tuned to print films of low viscosity uncured PDMS mixed with toluene. A solution of spiropyran dissolved in toluene and mixed with PDMS was used to print a QR code, demonstrating proof-of-concept for this system as a security-end product.

Background

There are many examples of the use of mechanical force to induce chemical change within the field of polymer mechanochemistry [1-6]. In a mechanochemical reaction, mechanical energy is used in lieu of typical energy sources to overcome the chemical activation barrier and initiate a chemical reaction [1]. Special molecules that can undergo a reaction through a mechanical pathway are known collectively as mechanophores. A number of mechanophores are known and studied [7-19], but one mechanophore, spiropyran, is of particular interest for this work.

Spiropyran is a colorless, non-fluorescent molecule that exhibits photo-chromic, thermo-chromic, and mechano-chromic properties. When spiropyran is exposed to UV light or mechanical force, it undergoes a ring-opening reaction along the spiro- bond to form the colored, fluorescent merocyanine form of the molecule (see Figure 1) [20].

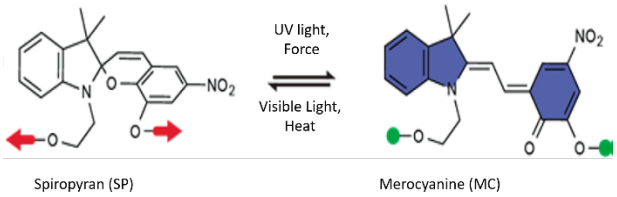


Figure 1: *Spiropyran to merocyanine reaction [21].*

Spiropyran is a popular mechanophore because of its easily detectable color change and compatibility with many polymer matrices. The mechanochemical behavior of spiropyran has been extensively studied within many polymer systems [20,22-27].

Ink Formulation and Printing

Ink Formulation

The PDMS ink used here was based on the formulation used by Gossweiler et al. [21]. Two forms of the ink were produced, an active ink containing spiropyran (SP-PDMS) and an inactive ink, not containing spiropyran (PDMS). Active ink was produced using a mixture of Slygard 184 (Dow Corning) PDMS elastomer and a solution of spiropyran dissolved in toluene. The spiropyran molecule used was functionalized such that covalent bonding with the PDMS matrix was possible. The functionalized spiropyran was

supplied by the University of Illinois at Urbana-Champaign. Slygard 184 curing agent was added to the base in a ratio of 1:10, and a 75 mg/ml solution of spiropyran dissolved in toluene was added. The total amount of spiropyran added was between 0.5-0.7 wt%. The ink was then mixed in a Thinky centrifugal mixer for 2 minutes at 2000 RPM, and then an additional 30 seconds at 2200 RPM. Inactive inks were produced in the same manner, however without the addition of spiropyran.

Before printing, the ink was pre-cured in a vacuum oven at 5 in Hg vacuum pressure to increase viscosity to aid in printing. The length of time the ink was pre-cured for varied depending on the nozzle diameter used during printing and can be found in Table 1.

Printing

Printing Procedure

Using the ink formula described in the previous section, samples were printed using a pneumatic fluid dispensing system, a Nordson Engineered Fluid Dispensing (EFD) Printer. Samples were produced by printing a thin film of inactive PDMS on a glass slide, allowing the film to cure at room temperature overnight, and subsequently printing active SP-PDMS in the form of a quick response (QR) code on top of the inactive film. A schematic of the sample can be seen in Figure 2, below.

The printer required a number of parameters to be tuned in order to achieve satisfactory prints. These parameters included ink viscosity (a function of oven temperature and pre-curing duration), ink printing pressure, print-head speed, nozzle diameter, and dispensing height. The parameters varied depending on the substrate and the type of print desired, and were tuned in order to achieve a balance between the ink's self- adhesion and its adhesion to the substrate. These parameters are summarized in Table 1.

***Table 1**: Printing parameters for PDMS ink substrates and QR codes.*

	Substrate Film	QR Code
Pre-cure Temperature	45° C	45° C
Pre-cure Time	60 min	45 min
Print Pressure	60 psi	60 psi
Print Speed	15 mm/s	4 mm/s
Dispensing Height	0.5 mm	0.05 - 0.1 mm
Nozzle Diameter (ID)	0.51 mm	0.1 mm
Trace Width	1 mm	0.2 mm

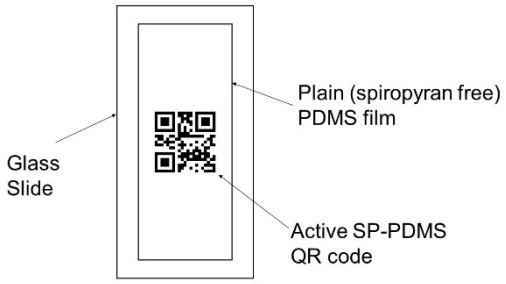


Figure 2: Schematic of printed sample for mechanical testing.

Printing Results

After curing the samples for no less than 5 days in ambient conditions, they were removed from their glass backings prior to mechanical testing. Representative printed samples can be seen in Figure 3, with inactive samples on the left, and UV-activated samples on the right. The inactive QR code blends in well with the plain substrate, with only slight embossing detectable.

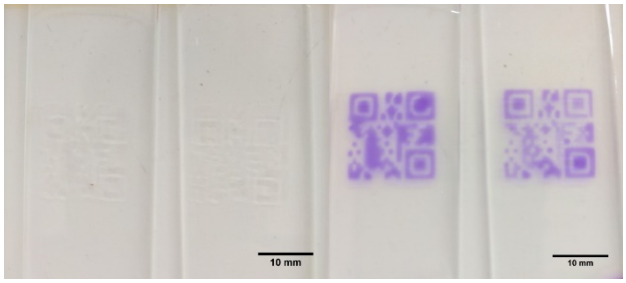


***Figure 3:** Inactive PDMS printed sample (left), UV activated PDMS-SP printed sample (right).*

Mechanochemical Characterization

The printed samples were tested in tension and evaluated with an in-situ optical imaging technique to visualize the mechanochemical response of this SP-PDMS system [22]. This imaging technique takes advantage of the fact that the merocyanine form is a purple color whereas the spiropyran form is near colorless. A schematic of the experiment is shown in Figure 4.

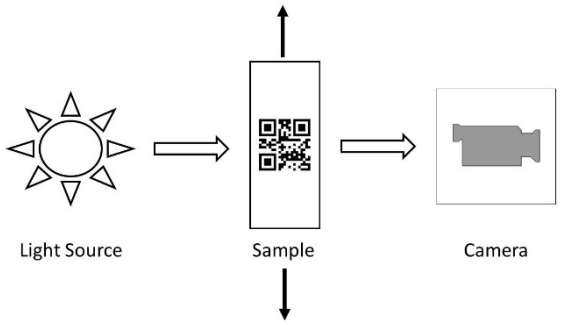


***Figure 4:** Schematic of experimental setup showing the loading scheme and imaging method.*

Mechanical Testing

Monotonic tension tests were performed using a Test Resources 100R1000 load frame. To determine a suitable displacement rate, inactive PDMS samples were tested at a range of displacement rates from 0.025 in/min to 1.0 in/min. Raw displacement and load data was recorded during the tests. Engineering stress and strain were then calculated from equations 1 and 2,

$$\sigma = F/A \tag{1}$$

$$\epsilon = \Delta L/L_0 \tag{2}$$

where σ is the engineering stress, F is the applied load, A is the cross-sectional area of the tested film, ε is the engineering strain, ΔL is the displacement, and L_0 is the original gauge length. Due to the fact that there is a non-negligible reduction in cross sectional area at higher strains, there is likely a discrepancy between the engineering stress reported and the true stress. For the purpose of our analysis, engineering stress was used.

Figure 5 shows the engineering stress vs. engineering strain response for the inactive PDMS film substrates at 4 different rates. For this PDMS, there was not significant displacement rate dependence, so a displacement rate of 0.1 in/min was selected for all further tests.

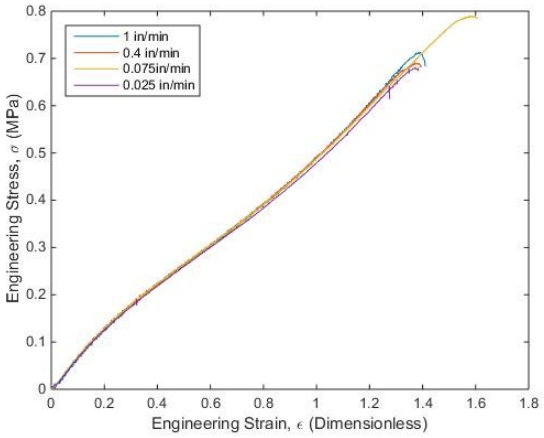


Figure 5: *Stress-strain response inactive PDMS printed films at various displacement rates.*

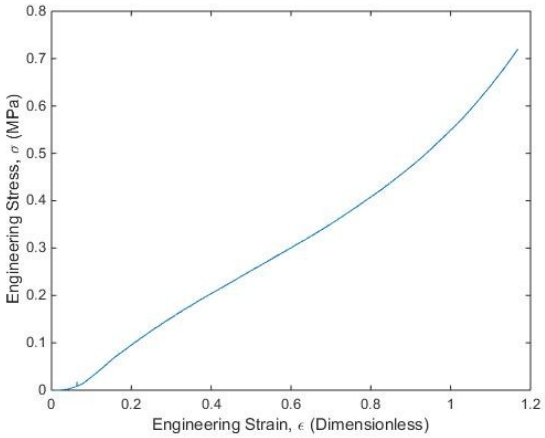
Optical Imaging

During tensile testing of the samples, photos were taken using a Basler acA1300-200uc camera at regular, known intervals.

Characterization Results

Initial mechanochemical characterization results were inconclusive as no chemical activation was observed through visual color. Figure 6 shows the engineering stress - engineering strain response of a representative sample as well as photos of the same sample at the initial and final positions. Notice the absence of visible color change between the photos in Figure 6b; this indicates a lack of detectable chemical transformation from spiropyran to merocyanine.

It was believed that the mechanical properties of the printed films were inadequate to achieve the stress-strain conditions needed to activate spiropyran. It has been shown by Johnson et al. that the temperature and duration that Sylgard 184 PDMS is cured has an effect on mechanical properties, with increased temperature and duration being related to increased mechanical strength [28].



(a) *Mechanical response of printed inactive (PDMS) film with active (SP-PDMS) QR code printed on the surface, tested in tension at 0.1 in/min.*

(b) Images of the sample in Figure 6a before testing (left) and at maximum strain (right).

Figure 6: *Mechanical/optical testing results for printed inactive (PDMS) film with active (SP-PDMS) QR code printed on the surface.*

Using this information, samples were post-cured in a vacuum oven. The mechanical characterization of these post-cured samples showed the largest increase in strength for samples cured for 40 hours at 65°C. Figure 7 shows the engineering stress - engineering strain behavior of the post- cured samples compared to those without the post-cure treatment. Samples cured at elevated temperatures for longer periods of time reached significantly higher stresses for a given displacement, especially in the strain-hardening region, when compared with samples with no, or shorter, post-cure treatment.

Post-cured active (SP-PDMS) samples were then tested and imaged as described in the previous sections. Figure 8a shows engineering stress - engineering strain curves for a representative post-cured sample and Figure 8b shows visible images of the same sample before and after mechanically testing. The post-cured samples did not show visible evidence of chemical activation with mechanical loading; however, the post-cured samples were still successfully activated with UV light (see Figure 8b).

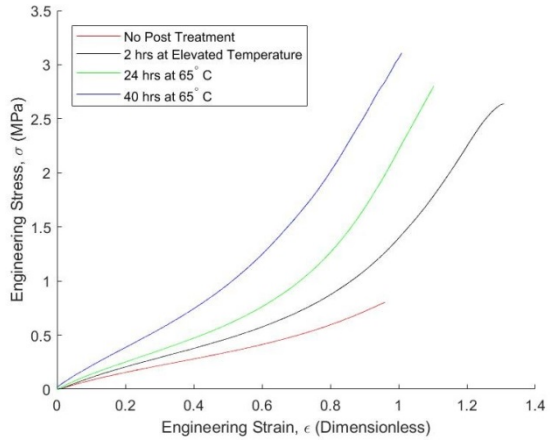
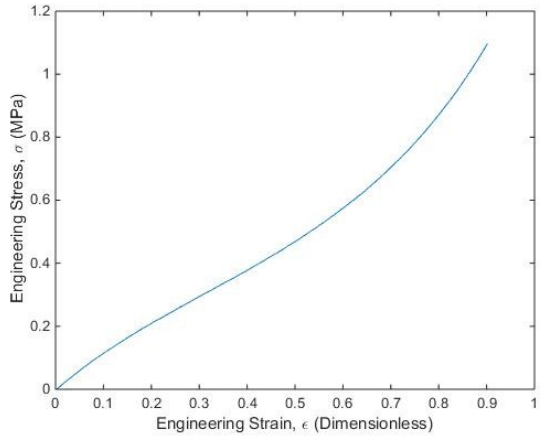
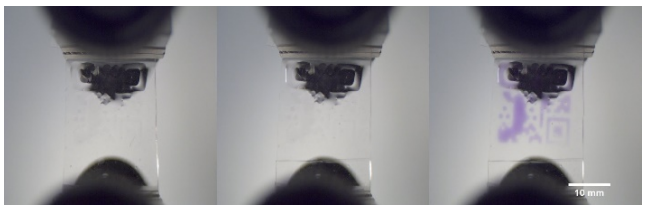


Figure 7: *Mechanical response for inactive (PDMS) samples with varied post-cure treatments.*



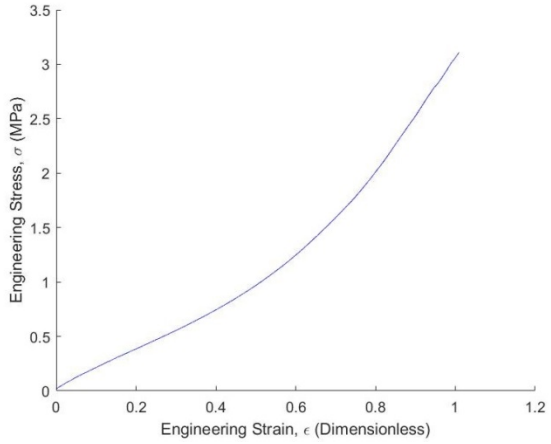
(a) Mechanical response of representative post-cured active (SP-PDMS) sample.



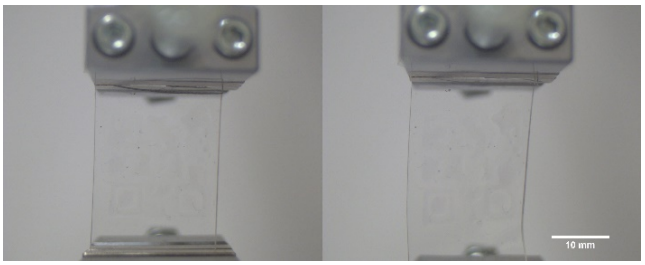
(b) Images of the post-cured active (SP-PDMS) *sample before testing (left), after failure (middle), after UV activation (right).*

Figure 8: *Mechanical/optical test of post-cured active (SP-PDMS) sample.*

The post-cured strengthened samples did not exhibit visible color change (chemical activation) due to mechanical loading in tension, and it was believed that a higher concentration of spiropyran may provide detectable activation. New samples were produced using 5x the concentration of spiropyran previously used. The new samples contained 2.5 wt% spiropyran and were post-cured at 65°C for 40 hours. The increased SP content active SP-PDMS samples were tested in the same manner described above. Figure 9a shows a representative engineering stress - engineering strain response for these samples and Figure 9b shows pre- and post-testing images. Again, no chemical activation was detected visibly.



(a) Mechanical response of a representative active (SP-PDMS) sample with 2.5 wt% spiropyran, post- cured for 40 hours at 65° C.

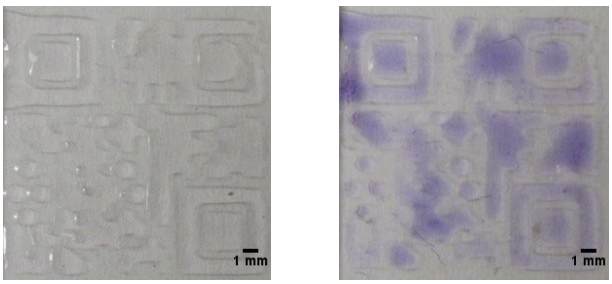


(b) Image of sample in Figure 9a before testing (left), and after testing (right).

Figure 9: *Mechanical/optical test of representative 2.5 wt% spiropyran SP-PDMS sample post-cured at 65 C for 40 hours.*

Mechanical Activation

Since attempts to quantify the mechanical-chemical relationship of this SP-PDMS system were unsuccessful, a qualitative demonstration of this system's mechanochemical properties are provided. The SP-PDMS printed QR code can be mechanically activated by applying a compressive impact load. Figure 10 shows an active SP-PDMS sample that has been mechanically activated through this method using several impact events with a hammer. The purple color is clearly visible; however, the color is not as vibrant as compared with a UV activated sample.



(a) SP-PDMS sample before impact. *(b) SP-PDMS sample after mechanical activation through impact.*

Figure 10*: Response of an active SP-PDMS sample to mechanical impact.*

Because the spiropyran to merocyanine reaction is reversible and repeatable, the SP-PDMS ink as printed can repeatedly be turned "on" and "off". The ink can be reverted from purple (merocyanine) back to clear (spiropyran) with the selective application of heat or visible light, and it can be turned purple (merocyanine) again with either mechanical impact or UV light. Figure 11 shows the pathways the printed SP-PDMS QR code can take to transform from a covert security feature to an overt security feature and back again.

***Figure 11**: Transformation pathways of a printed SP-PDMS QR code.*

Conclusions and Future Work

Procedures were identified to successfully print a small, covert security feature using the EFD and an SP-PDMS ink. The most important printing parameter was found to be the ink viscosity, which is a function of the temperature and duration of the pre-curing procedure. If the ink is not viscous enough, it will flow on the substrate, making small features difficult to print. However, if the ink is too viscous, it will either not dispense, or will dispense in an uneven fashion and produce wavy prints. The exact parameters differ depending on the printing objectives as well as the substrate. Successful printing for this work was performed on both glass and PDMS substrates. In addition, QR codes with very fine features were also successfully printed.

The QR codes produced in this study were not readable by commercial QR code readers due to some of the QR code features bleeding together. This was likely due to ink viscosity and QR code scale. Printing with a more viscous ink would lessen the bleeding issue. The distance between features was on the same order as the trace width used, so it was difficult to maintain the needed resolution. Printing on a larger scale allows for sharper features and produces a readable QR code, and was demonstrated through prior work with this SP-PDMS ink system by the authors.

Attempts to activate the SP-PDMS ink with mechanical force in a controlled and measured way were unsuccessful. Printed films failed before change in color was detectable, and strengthening samples by post-curing them at elevated temperatures was also unsuccessful in producing detectable mechanical activation. The increase of spiropyran concentration in the ink did not result in detectable mechanical activation through tension. The work presented by Gossweiler et al. has shown that the activation of spiropyran in this PDMS matrix is possible through a monotonic tension test, and further work is needed to identify why the films presented here did not activate with similar tests [21]. The SP-PDMS films presented here were substantially thinner than those in Gossweiler et al., and were printed rather than cast which may have an effect on the activation of the SP-PDMS films. Additional studies are needed in order to quantify the mechanical-chemical relationship of this printed SP-PDMS system.

The work presented here demonstrates that a SP-PDMS based ink is viable option for use as a mechanoresponsive security ink. It was shown that the ink can be activated either with UV light or with mechanical impact, and the ink can be reverted to its colorless form using visible light or heat. The multiple activation pathways add additional layers of security that can be used to authenticate documents or products. The printability of the ink has been demonstrated by printing films on glass and a small QR code on a PDMS substrate. Future work could refine the printing techniques to produce higher quality prints on a variety of substrates.

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