Analysis of Poly(dimethylsiloxane) Printability for Security Printing Applications

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Abstract

Security printing prevents forgery, tampering, and counterfeiting of a wide variety of documents and consumer goods. In this research, a polymer-based 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, is easily incorporated into poly(dimethylsiloxane) (PDMS), an elastomeric polymer. In this study, PDMS-based ink for security printing applications is studied by tuning the initial polymer viscosity with a solvent. Additionally, the film quality is explored through both optical and mechanical techniques. Printing conditions and an appropriate mechanophore-polymer system are determined to be appropriate for printing with an aerosol-jet micro printer. The responsiveness of mechanochromic ink is shown through fluorescence of the printed area.

Background

A mechanophore is a compound whose reaction can be triggered by a mechanical force. One particularly useful mechanophore is spiropyran, which is known for its color changing and fluorescent properties. Spiropyran transforms to merocyanine when a stress is applied to the system, causing a reversible color change to occur as seen in Figure 1. Covalently linking spiropyran into an elastomeric poly(dimethylsiloxane) (PDMS) network allows for covalent bond activation under macroscopic deformation.[3] During formulation, PDMS is crosslinked into polymer chains that chemically bond to one another. This process occurs when the crosslinking agent (or curing agent) is added during formulation. This particular polymer-mechanophore system has the possibility to be printed onto legitimate products with detection following a force on the printed area, and is an interesting system for the security printing industry. In addition, spiropyran can be transformed to merocyanine with heat and UV light. Unfortunately, PDMS is a highly viscous polymer and is difficult to print through traditional methods. The approach being taken to solve this problem is to dilute the polymer with a solvent (toluene) before curing to make the polymer printable with an ordinary household printer.

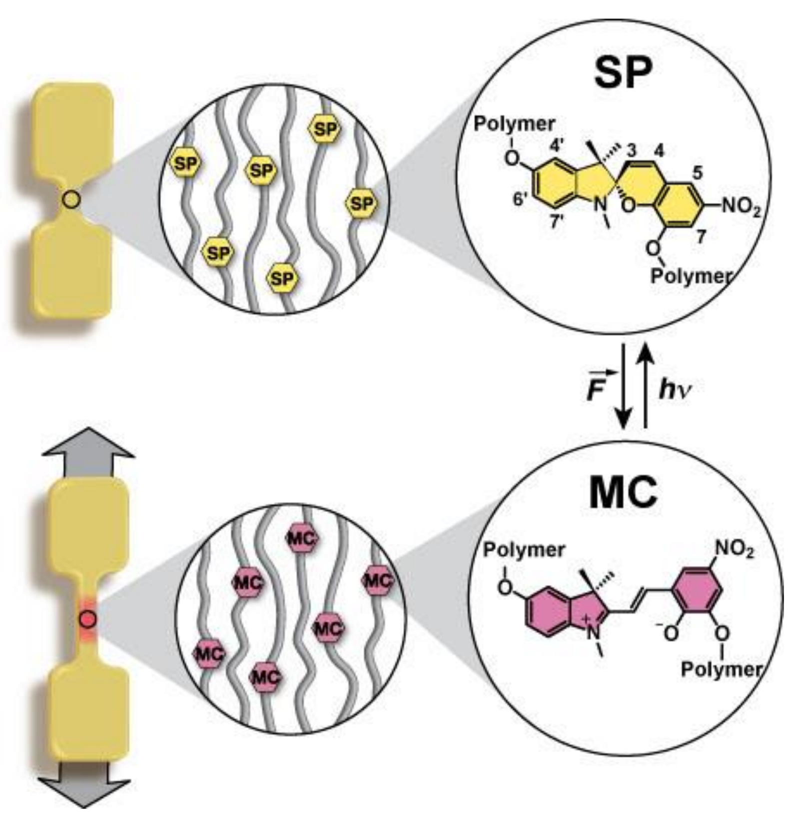
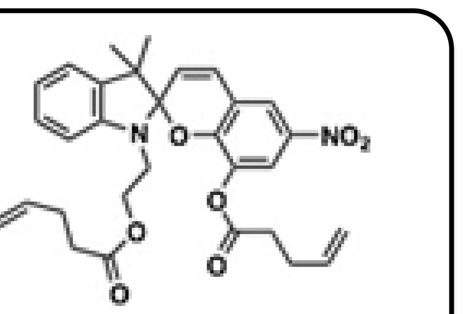


Figure 1. Spiropyran and Merocyanine Transformation[6]

Procedure

Materials

- Sylgard 184 Silicone Elastomer Base, Ellsworth Adhesives
- Sylgard 184 Silicone Elastomer Curing Agent, Ellsworth Adhesives
- Toluene
- Functionalized spiropyran (SP-b)-pen



(SP-b)-pen, supplied by UIUC

Formulation

PDMS was formulated using a 10:1 base to crosslinking agent ratio. After the polymer was weighed out, toluene is then added to a previously specified weight percent.

Viscosity Tests

Immediately after the polymer-solvent mixture was created, a small amount was placed on the rheometer and a viscosity test was run in order to determine the initial viscosity of the mixture.

Spin Casting

The same sample was then spin casted as a pre-printing test. After spin casting was completed, the glass slide was cured. At the end of the curing period, the dry film was qualitatively analyzed.

Printing

If the viscosity of the polymer was under 10 cP and the results of the spin casting were optimistic, the same toluene and PDMS mixture was recreated, printed, and cured. After the printed ink was cured, the sample was analyzed.

Viscosity Tests

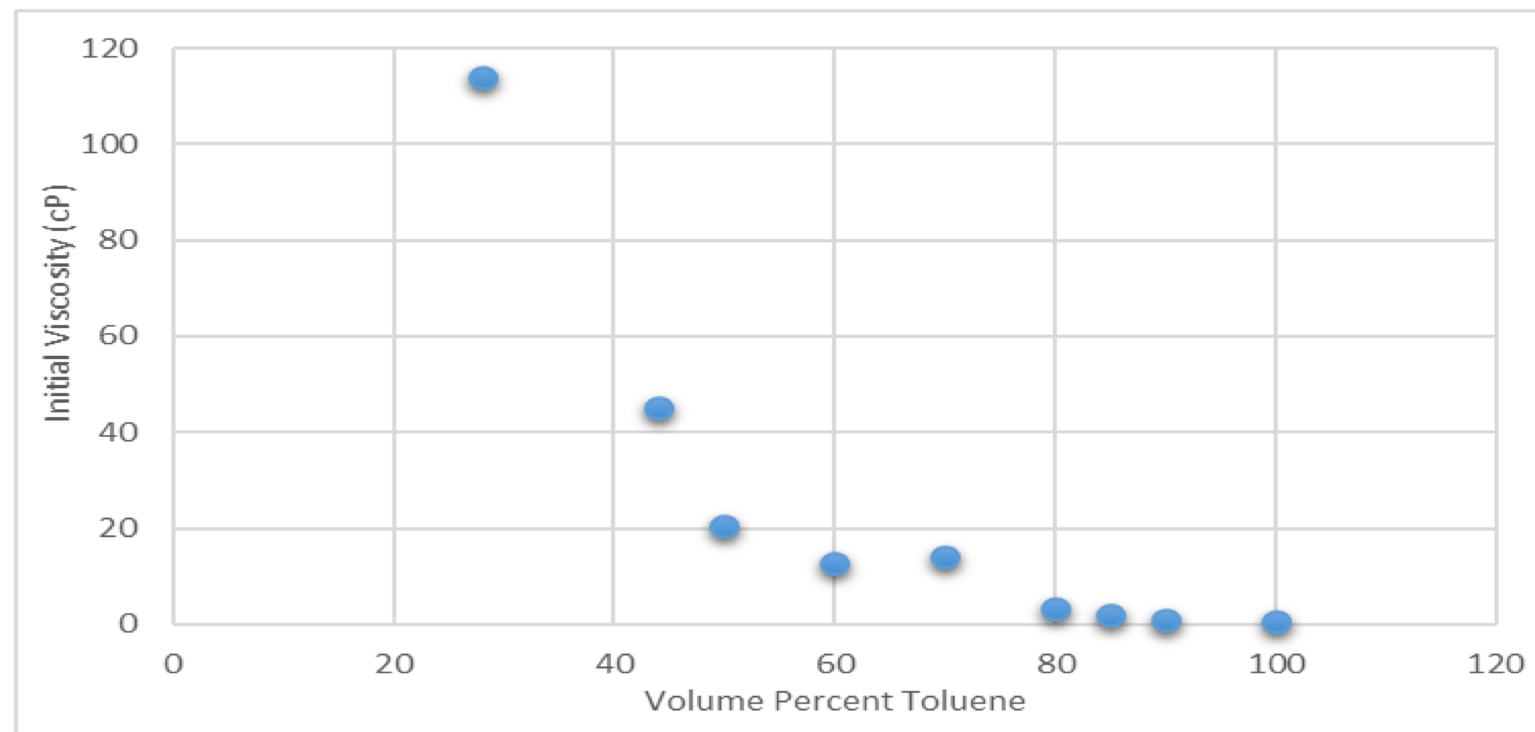


Figure 2. Initial Viscosity vs. Volume Percent Toluene Measurements

Printability

Figure 3. SEM Image of Plain Printer Paper

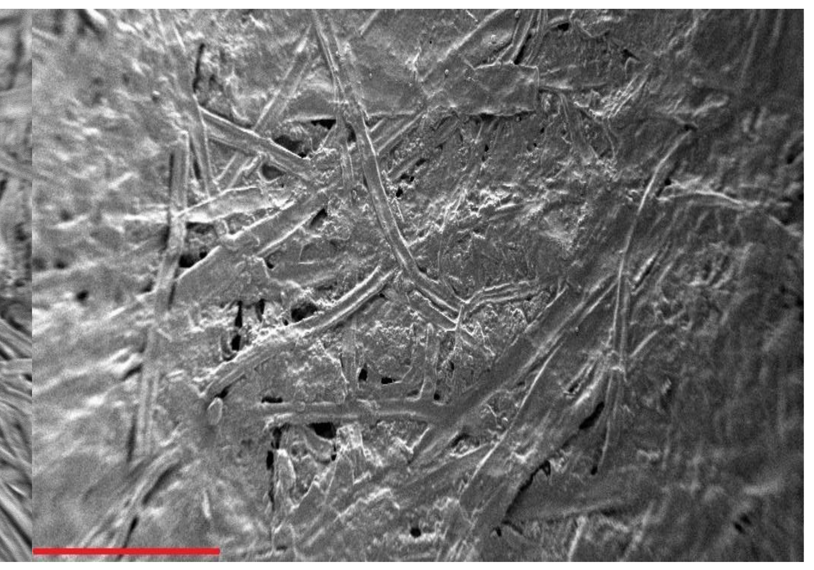


Figure 4. SEM Image of 85% Toluene – Oven Cured Printed onto Printer Paper

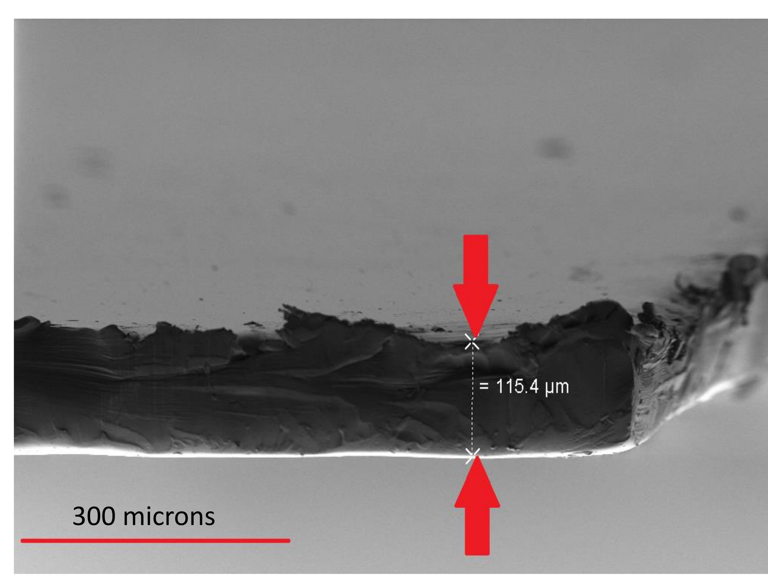


Figure 5. Cross-Sectional Area of Plain Kapton Film

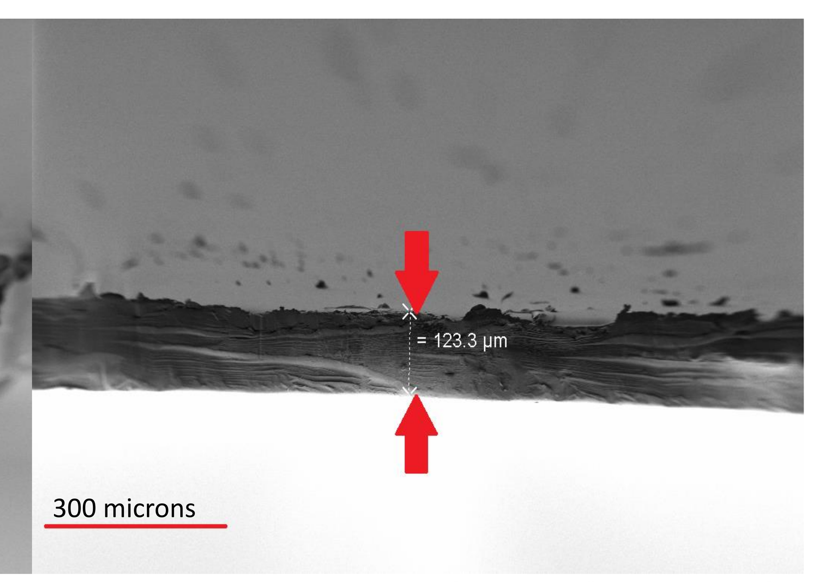


Figure 6. Cross-Sectional Area of Kapton Film with Two Coats of Printed 85% Toluene-PDMS Mixture

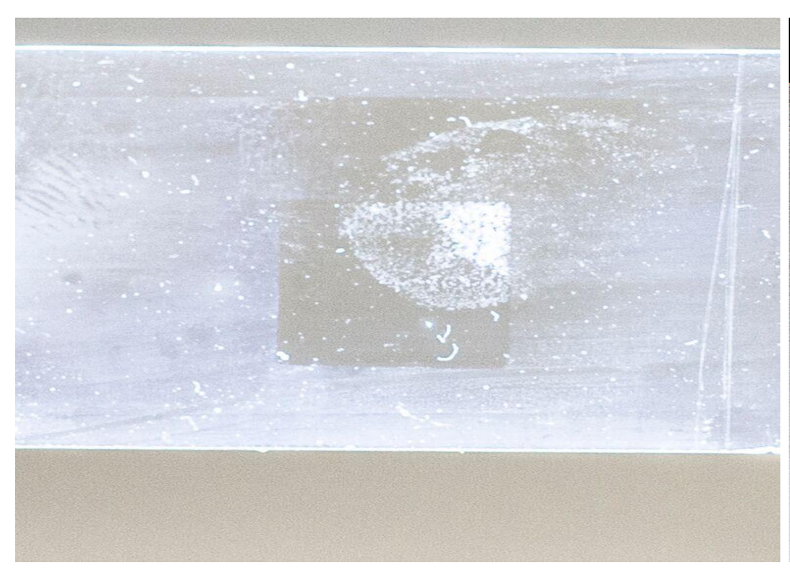


Figure 7. 85% Toluene – PDMS Mixture onto Glass and Oven Cured

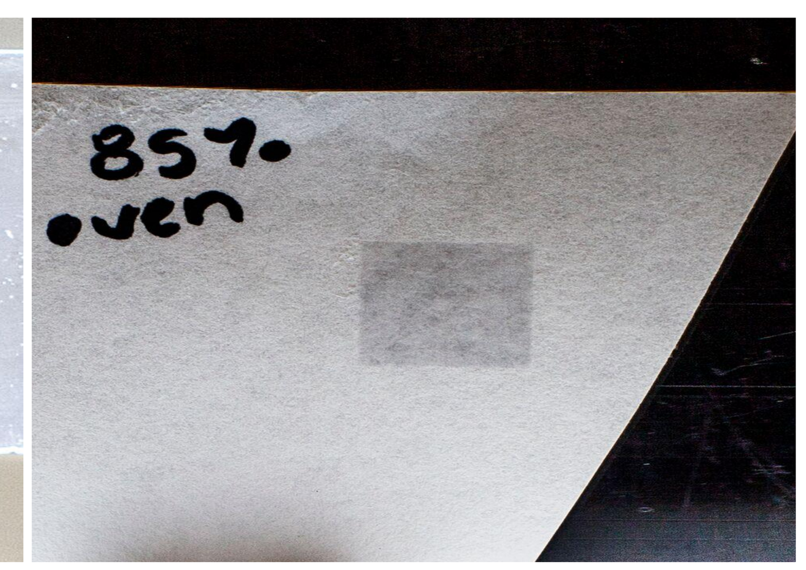


Figure 8. 85% Toluene – PDMS Mixture Printed Printed onto Plain Printer Paper and Oven Cured

Incorporated Spiropyran

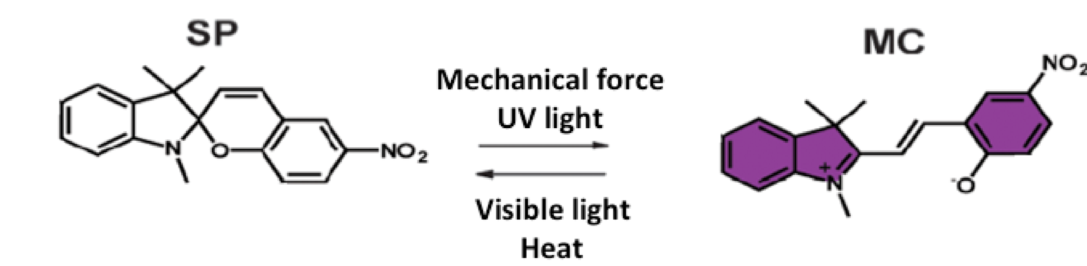
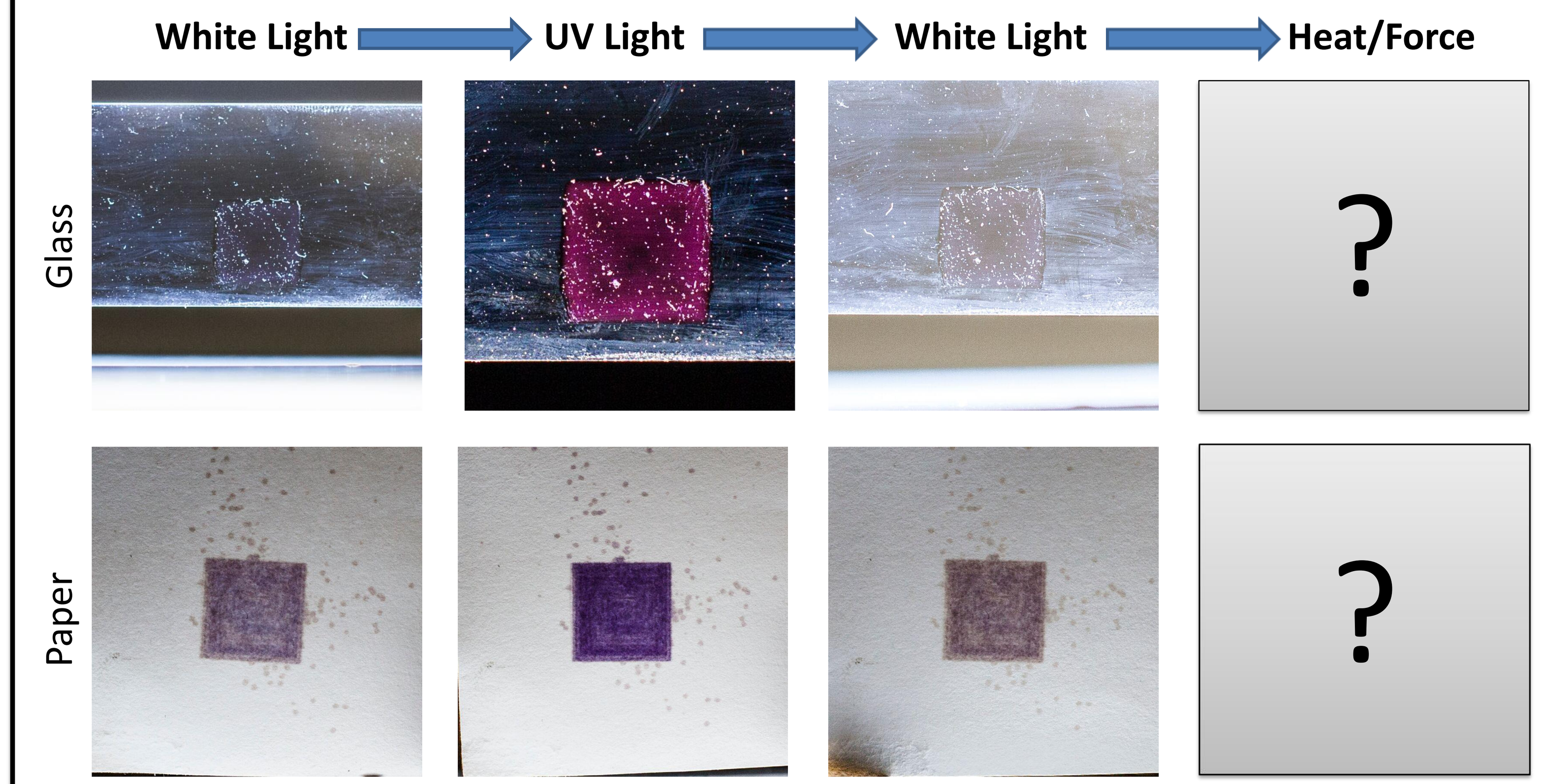


Figure 9. Reaction of Spiropyran to Colored and Fluorescent Mirocyanine[7]



Results

90:10 and 85:15 toluene:PDMS were found to be optically similar with optical microscopy and scanning electron microscopy. The 85:15 ratio printed more precise lines and had less over spray than its counterpart. When spiropyran is added it is speculated that it will have trouble finding PDMS due to the excessive amount of toluene in solution, so in 85% toluene it will have a better chance of finding the polymer than in 90% toluene. It was concluded that the 85:15 ratio of toluene to PDMS was the best system to embed and print with spiropyran. Spiropyran (0.5 wt% SP in PDMS) was successfully incorporated into the 85:15 system and printed.

Future Work

Examine the response of the films to heat. Investigate if spiropyran is covalently linked into the PDMS-toluene system by the printed film responsiveness to mechanical forces.

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