

Investigating the Mechanochromic Properties of Elastomers

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Introduction

This project aims to investigate the mechanochromic luminescence properties of different dyes and polymer blends - that is the change in intensity and/or colour change of a luminescent material when a mechanical force is applied, such as stretching which we will be using in our project. There are three important concepts essential in explaining this phenomenon, namely luminescence in polymers, deformation of polymers, and the changes in arrangement of the dye upon the application of a mechanical force.

Concepts

1. Luminescence in polymers

Luminescence properties can be conferred to a non-luminescent polymer matrix by physically dispersing a luminescent dye into the polymeric matrix. When photons strike the material, the electrons in the dye absorb the energy of the photons. The increase in energy causes the electrons to move to a higher energy state. However, the electrons are very unstable at this higher energy state. As such, the electrons promptly return to its stable ground energy level and in the process releasing energy in the form of photons.

2. Deformation of polymers

Polymer chains are entangled in the solid state. When a force is applied to the polymer, the tangled polymer chains are straightened, causing the polymer to macroscopically change dimensions. As a result, the intermolecular distances of the dye also changes [1].

3. Arrangement of dye in polymers

When a mechanical force is applied on the polymer, it will result in the structural modifications of the molecular assemblies of dyes dispersed in the polymeric matrix. The emission wavelength of the dyes is dependent on their intermolecular distances. When dyes are close, their interaction between the conjugated molecular orbitals change their ground and excited state energy levels. This change in arrangement of the dyes (Fig.1) results in the change in wavelength of the electromagnetic waves emitted.

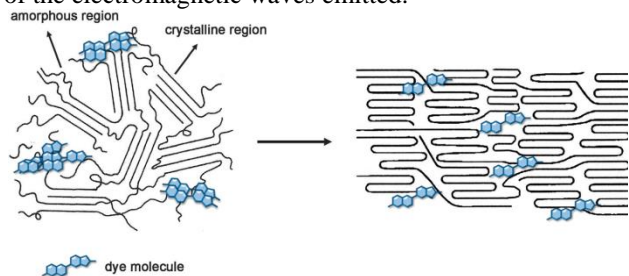


Figure 1: Mechanical stimuli leading to colour change [2,3]

Polymers which are characterised by optical responsiveness to mechanical stimuli are known as mechanochromic polymer blends. Mechanochromic polymers have evoked major interest with significant progress being made in engineering applications and mass market consumer products for healthcare in the recent years [4]. Some examples include chromogenic materials made up of either a functional dye covalently linked to the polymer chains or physically dispersed in the continuous macromolecular matrix. Such a polymer blend can also be applied to surfaces that are prone to straining, e.g. fabric material for sport to detect the amount of force one is exerting [5].

Our project aims to investigate the mechanochromic properties of 1-Ethynylpyrene when incorporated into the Polydimethylsiloxane (PDMS) elastomer and obtain a polymer-dye system capable of exhibiting observable changes in luminescence upon mechanical stress. By applying these knowledge and the results from experiments, we aim to explore relevant and useful applications for our mechanochromic polymer blends in the current world.

1-Ethynylpyrene in Polydimethylsiloxane (PDMS) network

Introduction and Hypothesis

Pyrene (Appendix 1) is an aggregachromic dye. It exhibits different luminescence in its aggregated and monomer states. When deposited into the PDMS network, the dye concentration could be tuned to engineer aggregated or monomeric states. A functionalized pyrene dye that's capable of chemically cross-linking with PDMS through hydrosilylation was used [6]. Upon application of mechanical force to the polymer-dye system, the chain slippage and reorganization promote the break-up of non-covalent interactions among chromophore molecules and their mixing within the polymer matrix, causing the dye to assume its monomer state.

Blending of 1-Ethynylpyrene

Silicone elastomer base (1.0 g), elastomer curing agent (0.10 g) and 1-Ethynylpyrene (0.010 g) was added onto the teflon dish. The resulting mixture was stirred until the dye was uniformly spread. The teflon dish was then covered with aluminum foil before holes were poked using a needle to allow for evaporation. The teflon dish was left in the oven at 80°C for 16 hours. This procedure created a PDMS polymer with 1% dye concentration. The experiment was repeated

for different concentrations of dye by varying the mass of the dye added¹.

Investigation on Dye Concentrations

Polymer films of 4 different dye concentrations casted on the teflon dish, namely 0.3%, 0.5%, 0.75%, and 1.00%, was obtained and a dogbone strip was cut from it. The luminescence and dimensions of the polymer strips were measured with the aid of a photoluminescence spectrometer. However, the 0.30 % and 0.50% dye concentration samples had more significant monomer peaks even before stretching. Therefore, we concluded that further stretching will not bring about a significant change in colour of luminescence. The other 2 strips were each stretched by the same percentage of its original length and the luminescence of the stretched strips was measured. The results obtained (Graph 1 of Appendix 4) were used to calculate the **ratio of luminescence**² in each of the 4 samples (Table 1).

Dye Concentration	Original Ratio ³ (O)	Stretched Ratio ⁴ (S)	Change in Ratio (O-S)
0.30 %	0.76	-	-
0.50 %	0.58	-	-
0.75 %	5.87	4.58	1.29
1.00 %	6.41	0.44	5.97

Table 1: Ratios of Luminescence (dogbone film)

Discussion of results

Samples with different dye concentrations were experimented on to determine the optimal concentration which would give rise to the largest change in the luminescence ratios. By normalising the monomer peaks and excimer peaks (Graph 1 of Appendix 5), it was observed that the 1.00 % dye concentration sample experienced the largest change in luminescence as represented by the largest drop of the excimer peak when stretched. Therefore, we decided to settle on using 1.00 % dye concentration in our next experiment to investigate the relationship

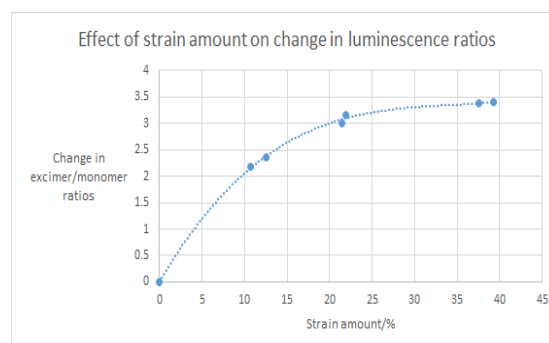
¹ The calculations for the dye concentration can be found in Appendix 2

² The method of calculating ratio of luminescence can be found in Appendix 2

between the amount of strain and the change in luminescence.

Investigating the Relationship between Strain Amount and Change in Luminescence

Three polymer films of 1.00 % dye concentration casted on the teflon dish was obtained and a dog-bone shaped strip was cut from it. The luminescence and dimensions of the first polymer strip (Appendix 3) was measured with the aid of a photoluminescence spectrometer. A small stretching force was applied on the strip and the new luminescence and dimensions of the stretched strip were measured. The steps are repeated again for the same polymer strip to gather more data points. The same is done for the other two polymer strips and the data obtained (Graph 2 of Appendix 5) were used to plot a graph of the ratio of intensity of the excimer and monomer peaks over the strain amount. We quantified strain amount and the ratio of intensity of the two peaks using formulas (Appendix 2). The excimer peak is **around** 500 nm whereas the monomer peak is **around** 395 nm.



Graph 1: Effect of strain amount on change in luminescence ratios

Discussion of results

From the graph, we could see that the ratio of intensity drops as the strain amount increases. This showed that the dye became more monomeric in nature as the polymer was stretched which conforms to our hypothesis. The change in luminescence was significant enough for it to be observable. Now that a polymer-dye system which exhibits significant change in luminescence had been successfully obtained, we decided to move on to investigate certain potential applications of our mechanochromic polymer blend.

³ The Original Ratio is the ratio of luminescence of the sample before stretching

⁴ The Stretched Ratio is the ratio of luminescence of the sample after stretching

Applications

1. Incorporating in Fabric

Silicone elastomer base (1.0 g), elastomer curing agent (0.10 g) and 1-Ethynylpyrene (0.010 g) was added onto the teflon dish. The resulting mixture was stirred until the dye is uniformly spread. A piece of 100 % cotton fabric was cut and drop-casted with the mixture using a syringe. The cotton was then placed on a piece of fluorosilane coated polyethylene terephthalate (PET) which we left in the oven at 80°C for 16 h. This procedure creates a fabric incorporated with a 1 % dye concentration polymer blend.

Optimisation of Conditions

We aim to create a piece of fabric which changes its luminescence much like the polymer films we created. However, when we used the same conditions in making the polymer previously as shown in the steps stated above, the dye assumed a largely monomeric state (Graph 3 of Appendix 5). A possible reason was that the structure of the fabric was preventing the dye from aggregating. To solve this problem, we came up with two possible solutions. The first was to simply increase the dye concentration which had been shown to increase the dye aggregation in our previous experiment. The second was to create a thicker coating that fills the gaps inside the fabric so as to encourage the aggregation of the dye. This could be done by increasing the amount of mixture and dipping the fabric in it. It was found that increasing the dye concentration was more successful in encouraging aggregation (Graph 4 of Appendix 5). Therefore, the experiment was repeated while varying the concentration of the dye used to obtain a piece of fabric which would exhibit a large change in luminescence when stretched.

Three concentrations, namely 2 %, 3 %, and 5 % were chosen. For each of the fabric, the luminescence and dimensions were measured with the aid of a photoluminescence spectrometer. They were stretched by the same percentage of its original length and the luminescence of the stretched strip was measured. The data collected (Graph 5 of Appendix 5) was used to calculate the change in ratio of the luminescence⁵ in each of the 3 samples (Table 2).

From the table, we concluded that 3 % was optimal when incorporating the polymer-dye system into a fabric.

Sample	Original Ratio (O)	Stretched Ratio (S)	Change in Ratio (O-S)
2 %	1.26	0.76	0.50
3 %	2.87	1.93	0.94
5 %	3.13	2.79	0.34

Table 2: Ratios of Luminescence (fabric)

2. Coating of Low Density Polyethylene

Silicone elastomer base (1.0 g), elastomer curing agent (0.10 g) and 1-Ethynylpyrene (0.010 g) was added onto the teflon dish. The resulting mixture was stirred until the dye is uniformly spread. A piece of plastic from a plastic bag was cut and drop-casted with the mixture using a syringe. The plastic was then coated evenly with the help of a spincoater which ran at 600 rpm. The plastic was then placed on a piece of fluorosilane coated PET which we left in the oven at 80°C for 16 h. This procedure creates a plastic coated with a 1 % dye concentration polymer blend.

Optimisation of Conditions

We aim to create a piece of coated plastic which responds sensitively to stretching through a change in luminescence much like the polymer films we created. However, when the same conditions in making the polymer previously was used, the dye assumed a largely monomeric state (Graph 6 of Appendix 5). The same problem was found when experimenting with the fabric. Therefore, we likewise increased the concentration of the dye.

We chose three dye concentrations namely 1 %, 2 %, and 3 %. For each of the plastic, the luminescence and dimensions were measured (Appendix 2) with the aid of a photoluminescence spectrometer. They were stretched by the same percentage of its original length and the new luminescence of the stretched strip was measured. The data collected (Graph 7 of Appendix 5) is represented in the table below. It was found that 3% was the optimal dye concentration as both 1% and 2% produced more significant monomeric peaks as compared to excimer peaks.

⁵ The method of calculating ratio of luminescence can be found in Appendix 1

Sample	Original Ratio (O)	Stretched Ratio (S)	Change in Ratio (O-S)
1 %	0.69	-	-
2 %	0.41	-	-
3 %	1.98	1.42	0.56

Table 3: Ratios of Luminescence (plastic)

References

- [1] M. Rubinstein and R. H. Colby, *Polymer physics, Oxford University Press* **2003**
- [2] A. Pucci and G. Ruggeri, Mechanofluorochromism: An Overview, *J. Mater. Chem.* **2011**, *21*, 8282
- [3] F. Ciardelli, G. Ruggeri and A. Pucci, Dye-containing polymers: methods for preparation of mechanochromic materials, *Chem. Soc. Rev.* **2013**, *42*, 857
- [4] Y. Jiang, An outlook review: Mechanochromic materials and their potential for biological and healthcare applications, *Materials Science and Engineering C* **2014**, *45*, 682
- [5] J. L. Garaud, *Inorganic Polymers Chapter 16 "Silicones in Personal Care Applications"*

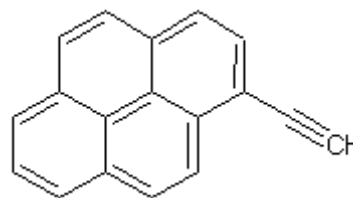
Conclusion

Increases in the change in the excimer/monomer ratios of 1-Ethynylpyrene was observed a mechanical stress was applied to the PDMS matrix increases. There were also observable changes in luminescence of 1-Ethynylpyrene when mechanical stress were applied to different matrixes (PDMS with fabric, PDMS with plastic) which brings us a step closer to discovering potential applications, for instance indicators and signs of breakage in clothing and plastic bags.

- [6] L. N. Lewis, K. G. Sy, G. L. Bryant, Jr., and P. E. Donahue, Platinum-Catalyzed Hydrosilylation of Alkynes, *Organometallics* **1991**, *10*, 3750

Appendix

Appendix 1



Appendix 2

Calculating Strain Percentage

$$\text{Strain} = \frac{L(\text{Current Data}) - L(\text{Original Data})}{L(\text{Original Data})}$$

Calculating Ratio of Luminescence

$$\text{Ratio of Luminescence} = \frac{\text{Intensity of Excimer peak}}{\text{Intensity of Monomer peak}}$$

Calculating the dye concentration for ethynylpyrene

$$\text{Concentration of dye in polymer} = \frac{\text{Mass of ethynylpyrene dye used}}{\text{Mass of silicone elastomer base used}}$$