

Properties Enhancement of Water-Borne Polyurethane by Introducing Dopamine modified Graphene Oxide

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Abstract—This project aims to study the effects of incorporating Dopamine-modified Graphene Oxide (DGO) into Waterborne Polyurethane (WPU). It is hypothesized that Dopamine, a free radical scavenger and a biomimetic inspired from mussel adhesive proteins, when combined with Graphene Oxide, made from oxidizing graphene sheets using a modified Hummers' Method, will provide, when incorporated into WPU, the WPU with anti-UV properties as well as mild electrical conductivity for additional uses and improved mechanical properties.

I. INTRODUCTION

Polyurethane (PU) is commonly and widely used as a coating material for buildings, transportation and some scientific machines. However, PU shows poor UV resistance which means that long-term exposure to UV radiation will cause photodegradation of the PU which will lead to brittleness, stickiness and loss in adhesiveness. The PU may even fall off from the substrates¹. This can be harmful, since exposure of metal parts of the machine to the natural elements may cause corrosion².

To make the PU coating have anti-UV properties, we will use polydopamine, an anti-UV adhesive biomimetic polymer inspired from mussel adhesive proteins, and graphene oxides to not only protect the coating against UV radiation, but also to enhance its electrical conductivity for additional practical uses.

II. THEORETICAL BACKGROUND

Graphene, a single-atom sheet of sp²-bonded carbon atoms has strong mechanical, thermal and electrical properties³. Graphene is derived by oxidising graphite to graphene oxide to separate the layers due to sp²-sp³ bonds between carbon atoms and their neighbouring atoms and then reducing the Graphene Oxide back to Graphene. However, these single layers tend to aggregate or restack due to strong pi-pi stacking and hydrophilic interactions between the sheet⁴ and some of the -COOH groups in graphene oxide is necessary to form hydrogen bonds with polydopamine. Hence, complete reduction is not advisable and Graphene Oxide will be reduced to reduced Graphene Oxide (rGO) instead. As rGO is similar to graphene, it also has a tendency to restack. Hence, we believe that to achieve the optimum electrical conductivity and homogeneity of the material, about 1% by mass of rGO should be added to PU.

Polydopamine (PDA) has been reported to be able to act as a free-radical scavenger as its chemical structure is similar to that of eumelanins, which are well known natural pigments for the protection of human body against UV by

quenching reactive radicals⁵. PDA can also adhere well as it mimics mussel adhesive proteins⁶ which have shown to have very strong adhesiveness⁷.

Therefore, we hypothesize that the introduction of PDA coating GO with phenolic hydroxyl into the composites will enhance the anti-oxidant properties under UV condition. Moreover, the GO will significantly improve the mechanical properties and electrical conductivity of the waterborne PU. We will be using a waterborne PU as PU, which is usually dissolved in acetone to maximise the adhesiveness of the PU to the object it is applied on⁸, may be harmful to the environment^{9, 10}. Hence, we will be experimenting with water as a solvent for PDA since it is abundant and harmless to the environment.

III. METHODOLOGY

We used a simple 3-step method to synthesize our compounds as shown in the flowchart below (chart 1) and the detailed explanation of each step can be seen below the flowchart.

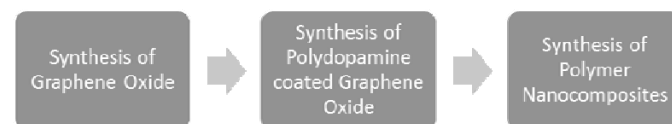


Chart : 3-Step Process of Synthesizing PU/DGO Compounds

A. Synthesis of Graphene Oxide

Graphite is a natural, layered allotrope of carbon where each graphite layer is 0.4nm away from each other. The detailed process is as follows:

1. Graphene Oxide was prepared using a modified version of the Hummers method where we used H₂SO₄ and KMnO₄ to oxidise the graphite layers, increasing the distance between graphite layers.
2. Graphene Oxide was then sonicated to separate oxidised graphite layers since the increased distance between Graphite layers after oxidation significantly weakens the Van der Waal's forces between the layers.

Hence, a uniformed, yellow graphene oxide layer is obtained, which is further dispersed into water to form a colloid.

B. Preparation of dopamine-modified GO

1. 0.605g of Tris (hydroxymethyl) aminomethane is used to form a buffer solution at pH 8.5 and Graphene oxide colloid is added.
2. 1.1g of Dopamine Hydrochloride is added to 500ml of Graphene Oxide Colloid. At pH 8.5, Dopamine will polymerize most readily, coating the Graphene Oxide layers.
3. The solution is then left on constant magnetic stirring at room temperature for 2 hours. After mixing, filtration is performed on the solution and a gel-like filtered cake is obtained, which is then washed with water several times to get rid of unreacted dopamine.

Resultant gel-like filtered cake is then dispersed in 500ml of H₂O, resulting in a 0.5 wt. % DGO solution.

C. Preparation of Polymer Nanocomposites

1. Varying amounts of DGO at 0.0%, 0.5%, 1.0%, 2.0% and 4.0% concentration were added to 5g of Water-borne Polyurethane (WPU) to obtain different samples of DGO concentration on WPU.
2. DGO solution was dispersed via bath sonication into WPU solution.
3. Solution is then poured into a plastic petri dish and left to dry in a fan oven overnight maintained at a constant temperature of 70°C.

D. Subjecting of Samples under Ultraviolet Rays

The samples of 0.0%, 0.5%, 1.0%, 2.0%, and 4.0% were placed in a UV Chamber for a maximum of 240 hours and were taken out at 120 hour intervals for testing. The conditions of the UV Chamber are as below:

- Irradiance Control: 300nm – 400nm (simulating UVA which ranges from 315nm to 400nm)
- Irradiance: 60.0 W m⁻²
- Chamber Temperature: 50.0 °C
- Black Standard Temperature: 62.9 °C
- Relative Humidity: 50%
- Fan speed: 1000 rotations per minute

These conditions simulate the natural conditions in Singapore which are as follows: (Taken from World Health Organisation Website and National Environment Agency Singapore):

- Average UV Irradiance in Singapore in 2014 (Jan-Sept): 37.4 W m⁻²
- Average Humidity in Singapore: 80%
- Average Temperature in Singapore: High: 31°C; Low: 25°C

E. Characterization of Tensile Properties and Electrical Conductivity

The tensile properties were measured using an Instron 5567 machine according to ASTM D638 type V at a crosshead speed of 100 mm min⁻¹. The electrical conductivity of the PU/D-Graphene Oxide nano-composites were measured by a MCP-T610 low resistivity meter (Mitsubishi Chemical Analytech) with a standard four point probe.

IV. RESULTS AND DISCUSSION

A. Samples

Four samples of varying concentrations of 0.0%, 0.5%, 1.0%, 2.0% and 4.0%PU/DGO nano-composites were produced as shown below in Figure 1.1.

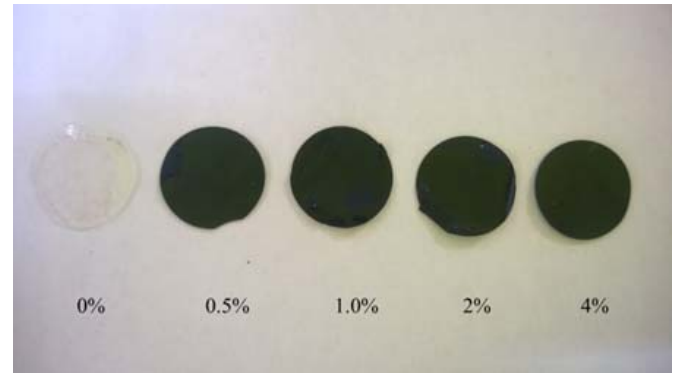


Figure 1.1: Samples produced.

It can be observed that the Dopamine-modified Graphene Oxide was well dispersed into the Waterborne Polyurethane. However, the control sample (0.0%) could not be extracted from the petri dish after exposure to UV conditions for 120 hours as seen in Figure 1.2 below.



Figure 1.2: PU nano-composites with 0% DGO after exposure to UV radiation for 120 hours.

The fact that the PU/DGO compounds were able to be extracted from the petri dish while the 0.0% PU compound was not shows that the presence of DGO significantly improves the anti-oxidant properties of PU. Here, UV-induced degradation is similar to thermo-oxidative oxidation and is induced by free radicals, which are produced by the

reaction of PU with oxygen with UV light as a catalyst. For the PU samples with various DGO concentrations, presence of polydopamine act as radical scavenger to stabilize free radicals, hence preventing degradation. That is why it exhibits anti-oxidant properties as proven by our findings.

B. Tensile Strength

The tensile properties, including tensile strain and tensile stress of all samples decrease with the increasing of the exposure time to UV radiation, as shown in Figure 1.3

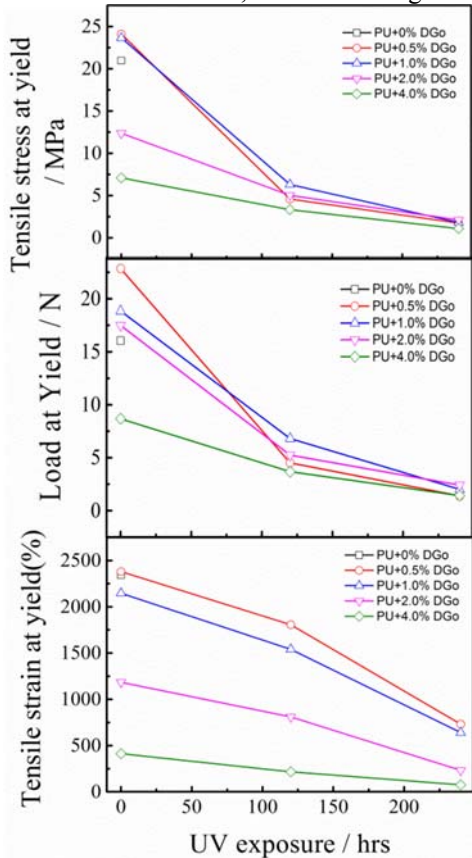


Figure 1.3: Tensile strain at yield, Load at yield, Tensile stress at yield of PU/DGO composites containing different content of DGO (0%, 0.5%, 1.0%, 2.0%, and 4.0%) after exposure to UV radiation for different amount of time.

From the graphs in Figure 1.3, it is evident that the initial tensile stress for 0.5% and 1.0% samples are higher than the control while the 2.0% and 4.0% samples have lower initial tensile stress compared to the control. This is so as Polymer nanocomposites typically exhibit optimal mechanical properties at a certain filler content. When stiff filler content is too high, the nanocomposite becomes more brittle and fails at lower strain. This known as ductile to brittle transition. With regards to the 2% and 4% samples, it is evident that their filler content is too high, causing the PU/DGO compounds to become more brittle than the control. The relation between initial tensile stress and concentration of DGO used can be seen in Figure 1.4.

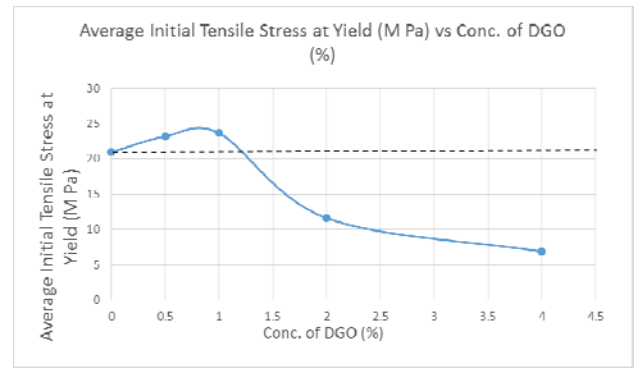


Fig 1.4: Average Initial Tensile Stress at Yield (MPa) against Conc. Of DGO (%)

However, despite the observation that 0.5% and 1.0% samples have higher initial tensile stress at yield, a T-Test of both 0.5% vs 0.0% (T-Stat of 1.188 < T Critical two-tail of 4.302) and 1.0% vs 0.0% (T-Stat of 0.895 < T Critical two-tail of 4.302) samples have shown that the differences between these two groups are insignificant. This suggests that the increase in initial tensile stress at yield for the samples is not due to the addition of DGO. However, more research can be done here as per observation, the initial tensile stress at yield does increase after addition of DGO. Hence, it does suggest that addition of DGO may increase the tensile strength of WPU.

A summary of the data obtained can be seen in the scatter plot with trend line in Figure 1.5. The trend line shows a clear downward trend in terms of tensile stress across days of UV exposure.

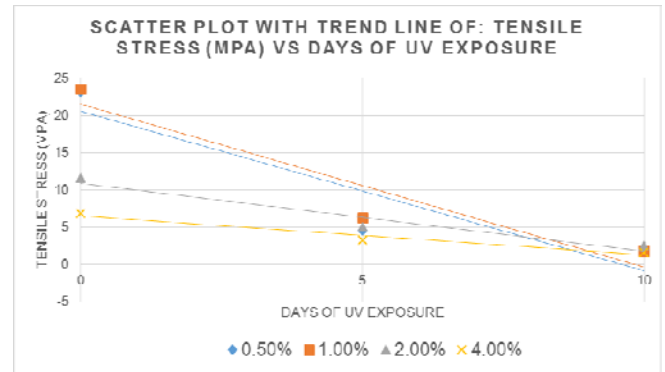


Figure 1.5: Scatter plot with Trend line of: Tensile Stress (MPa) vs Days of UV Exposure

However, using the values obtained, we conducted an Analysis of Variance Test without replication, and we found that the decrease in maximum tensile stress across days of UV exposure to be insignificant as the P-Value is 0.349847, higher than the alpha value of 0.05. Therefore, this proves that UV Exposure does not affect the tensile strength of the material significantly, showing that the DGO provides strong anti-UV properties to the material at all concentrations.

Therefore, from Fig 1.4 it can be concluded that presence of DGO does not increase the tensile strength of DGO,

however from Fig 1.5, presence of DGO prevents the decrease in tensile strength due to UV exposure.

C. Electrical Conductivity

After testing for electrical conductivity, the results show that PU composites with 0.0%, 0.5%, 1.0% and 2.0% DGO have low electrical conductivity, while the conductivity slightly increases with the content of DGO. Furthermore, when the DGO content of the nano-composite increases to 4.0%, it shows an electrical conductivity of 2.3 S m^{-1} , calculated by using the equation $\sigma = \frac{1}{\rho}$.

The composites only show considerable electrical conductivity at 4.0% and above concentration (as shown in Figure 1.6) of DGO in PU. This shows that the compounds are capable of conducting electricity at a 4.0% concentration with an electrical conductivity of 2.3 S m^{-1} , comparable to that of Germanium which has an electrical conductivity of 2.17 S m^{-1} at 20°C ¹¹.

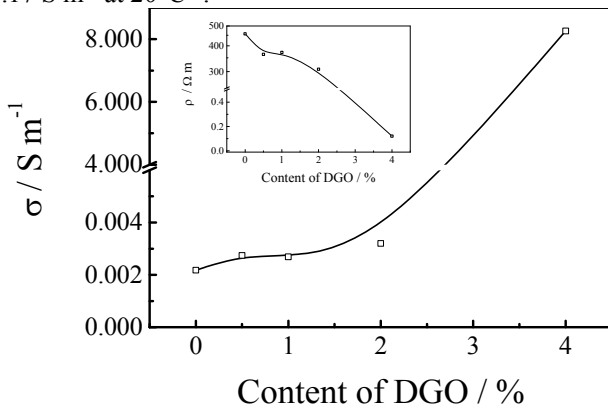


Figure 1.6: Graph of Content of DGO/% against $\sigma / \text{S m}^{-1}$

The results indicate that a certain content of DGO will improve the conductivity of non-conductive materials like PU. This is based on percolation theory, whereby when a network of conductive phase is almost formed, tunnelling of electrons can easily take place and electrical conductivity becomes much higher. The results also show that with a high-PU-low-DGO content, the compounds exhibit low electrical conductivity. However, it is expected that the conductivity of the filler will improve by annealing the filler¹², reducing the percolation threshold.

V. PRACTICAL APPLICATIONS

The project has a clear practical application as mentioned in the introduction whereby the PU/DGO compounds can now replace conventional PU as coatings for experimental equipment that are commonly exposed to UV radiation for a long period of time such as in the case of a Stevenson Screen where the new PU can be used as a varnish for the wood frame to protect both the equipment inside and the wood frame from UV-induced photodegradation. In the synthetic fibres of Spandex, indicated as the “polyurethane

elastic fibre”¹³ that is often used in sportswear, it is highly likely that the material will be exposed to UV frequently. We propose to replace the polyurethane used with our enhanced UV resistant PU to act as a UV-shielding layer that can better protect the athletic from the harmful effects of long term UV exposure during their sports activities.

The PU/DGO compounds may also exhibit anti-static properties after annealing and hence, can also act as a material to reduce static build-up in both the experimental equipment mentioned above and the spandex material used for sportswear.

In terms of feasibility, the synthesis process can be easily scaled up. Graphene Oxide is now commercially available. For the other chemicals, the cost usually depends on volume and the cost would not be high in terms of high volume purchase. In terms of its manufacturing process, the simple 3-step manufacturing process as mentioned above makes the compound easily reproducible in a mass scale. However, considering that the compounds have to be slow dried, the process would take a fairly long amount of time. This can be combated by stacking the production to ensure a continuous output towards the end of the production line.

VI. CONCLUSION

From the results obtained, this research shows us a very promising material that is both UV-resistant and can exhibit anti-static properties. The results have confirmed our hypotheses that incorporation of DGO does significantly improve both the anti-oxidant properties of PU as well as provide strong UV-resistance to the PU. The incorporation of DGO also allowed for the PU to exhibit electrical conductivity at a certain filler content. However, the results we obtained indicated that that electrical conductivity of the compounds are only shown at filler content of 4.0% and above and this is at the expense of reduced initial tensile stress at yield as the initial tensile stress at yield for 4.0% sample is below the control.

Therefore, for future research purposes, we propose to further study compounds with DGO concentrations varied at 0.5% to 1.0% as these show the most promising initial tensile stress at yield. We also propose to perform a Gel Permeation Chromatography (GPC) analysis of the before and after UV treatment to study the properties and effects that DGO would provide to PU as a prior Fourier Transform Infrared Spectroscopy (FTIR) analysis had shown that the difference was too small and hence, inconclusive. Also, to further confirm the observed results that polydopamine does enhance the WPU with anti-UV properties, we propose to incorporate GO modified with phenethylamine to the PU to act as a control to the rest of the samples. With regards to their low conductivity as shown from our research, we propose to anneal the polymer nanocomposites as we hypothesize that with the annealing of the filler, the

percolation threshold of the filler will decrease and achieve electrical conductivity. Due to the nature of the compounds being of low-DGO-high-PU content, we hypothesize that it is likely that at 0.5%-1.0% filler content, the PU/DGO compounds can exhibit anti-static functions and hence, future research can be directed here as well. Another possible future study can be done on the electrical conductivity of samples after UV exposure to ensure consistency in conductivity throughout exposure to UV.

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