Development of UV-Protection Roofing Tile from N-GQDs for Rubber Drying Chambers

Siriya Mektavepong and Wallapha Phatrabuddhikul

Princess Chulabhorn Science High School Pathumthani,
51 Moo 6, Bo Ngoen, Lat Lum Kaeo, Pathum Thani, 12140
Email: siriya911@gmail.com

Abstract
Improved methods of processing latex into rubber sheets will improve the incomes of small rubber producers. There are two ways in which latex can be processed into rubber sheets: fumigation and solar incubation. The fumigation method is expensive and produces pollution, but solar incubation can cause dark, sticky rubber sheets due to UV radiation, which reduces their value. (Aguele, 2015) A low-cost and environmentally-friendly solution to this problem was investigated here. A UV-protective roofing panel made using Nitrogen-doped Graphene Quantum Dots (N-GQDs) was developed and tested. N-GQDs were made using the hydrothermal process for 2 and 4 hours (T2 and T4) and the solvothermal process for 4, 6, and 8 hours (TS4, TS6, and TS8). It was found that all types of N-GQDs absorbed light in the UV range, withT4 showing the greatest absorption. T4 had the greatest Fluorescent Intensity (FL) value, emitting blue light, while for the solvothermal method TS6 had the highest FL value, emitting red light. T4 and TS6 were chosen for further testing, and were applied to a clear roofing tile. After installing the roof on the chamber, the temperature inside was higher than outside. The UV protection efficiency of the roof was measured at 93.27%. The average temperature was 45°C, which is the temperature needed for drying rubber sheets. Due to the roof's capability to absorb UV radiation and heat the chamber, our N-GQDs roof has a great ability to produce higher-quality rubber sheets.

Keywords**:** rubber sheet, drying chamber, N-GQDs roof, UV-protection

I. INTRODUCTION

Thailand is a major rubber producer. Thai rubber plantation farmers still prefer to convert fresh latex to raw rubber sheets because most Thai rubber plantations are small plantations with low productivity. Most of the rubber is processed into raw rubber sheets by the individual farmers to be sold to merchants or fumigation factories. (Kampan, 2017)

The processing of raw rubber latex into rubber sheets can be done in two ways: by fumigating raw rubber sheets or by drying raw rubber sheets. For the fumigation of raw rubber sheets, the cost of firewood is high, and heat loss is typically high. The second method, drying by solar incubation, can be considered a clean energy alternative that is not toxic to the environment and has unlimited renewable power. (Aguele et al., 2015) However, existing incubators often encounter problems with the formation of sticky and dark rubber sheets due to exposure to UV radiation, which reduces the value. One solution to the problem of UV damage is to use polycarbonate roofing tiles, but polycarbonate degrades, leading to long-term plastic waste issues. (Bacon et al., 2013)

Graphene quantum dots (GQDs) are particles having low biotoxicity and also have fluorescence properties. GQD particles absorb most radiation in the UVB range, and emit light covering the entire visible light spectrum, including the red part of the spectrum (Sk et al., 2014). The efficiency of GQDs can be improved by coating them with nitrogen, called Nitrogen-doped Graphene Quantum Dots (N-GQDs), which was found to increase the fluorescence quantum yield, or fluorescence efficiency, by up to 94% (Qu et al., 2014). The efficiency of GQD particles as a fluorescent agent capable of absorbing UV radiation makes them effective as a particle for UV protection. (Purcell-Milton & Gun'ko, 2012)

Two low-cost methods for synthesizing N-GQDs are hydrothermal and solvothermal which use different solvents. The hydrothermal method uses water as a solvent and the solvothermal method uses acid as a solvent. (Gu et al., 2016)

Here, we develop and test the effectiveness of N-GQD-coated UV-protective roofing for rubber sheet drying plants to produce high-quality rubber sheets according to ASTMD882 standards, which is the standard for testing physical properties of the polymer. The N-GQDs roofing dryer also uses clean energy that is not toxic to the environment and is a renewable energy. This allows farmers to reduce their energy costs while producing higher quality rubber. For this reason, UV-protective N-GQD-coated roofing tiles may help to increase the country's potential in rubber sheet exports as well as the income of rubber farmers.

II. METHODS

Synthesis and spectroscopy of the N-GQDs

Hydrothermal N-GQDs were synthesized by adding 2.1 g of citric acid and 1.8 g of urea to 50 ml of deionized water and stirring until the solution fully dissolved, then heating at 160 ºC for 2 and 4 hours. (T2 and T4, respectively). A UV/VIS spectrophotometer was then used to observe the wavelengths absorbed by T2 and T4. Finally, the spectrum emitted by a Fluorescence Intensity (FL) spectrophotometer using excitation wavelengths ranging from 250 to 375 nm was observed.

Solvothermal N-GQDs were synthesized by adding 2.1 g of citric acid and 1.8 g of urea in 50 ml of 7.4 M sulfuric acid and stirring until the solution fully dissolved, then heating at 210 ºC for 4, 6, and 8 hours. (TS4, TS6, and TS8, respectively). The UV/VIS spectrophotometer was then used again, and the FL spectrophotometer was used for wavelengths ranging from 250 to 425 nm.

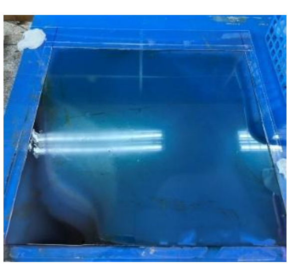

Figure 1. The roofing tile in the acrylic mold

Figure 2. The drying chamber

Making and testing of N-GQDs roofing tiles

T4, which absorbs light at the widest spectrum and has the highest FL, and TS6, which emits the highest wavelength and has the greatest FL, were chosen for further testing. 125 ml of each solution was mixed with 10 g of polyvinyl alcohol (PVA), then heated at 60 ºC with constant stirring for 2 hours. The solution was then poured into 10 x 10 cm and 50 x 50 cm acrylic molds (Figure 1) and allowed to cool until it formed a solid sheet. The sheet formed from PVA containing T4 is called P-UV and TS6 is called P-IR. The 10 x 10 cm sheets were cut into 5 pieces of 2 x 10 cm and tested with an ASTMD882 standard Tensile Tester.

UV-protection and heating efficiency of N-GQDs roofing tiles

One sheet each of 50 x 50 cm P-UV (on top) and 50 x 50 cm P-IR were layered to form a roof structure which was placed in direct sunlight. A UV meter was used to measure UV intensity at 12:00 pm directly above and below the roof at 5 points on the roof for 7 days. A drying chamber with dimensions 0.5 x 0.5 x 0.5 m was built with the same 2-layer P-UV/P-IR roof design, and placed outside, as shown in Figure 2. Temperature measurements inside and outside the chamber were made for 7 days at 8:00, 12:00, and 16:00.

III. RESULTS AND DISCUSSION

The spectroscopy of N-GQDs for different hydrothermal synthesis periods

Figure 3 shows that T2 and T4 both absorbed light in the UV range, but T4 had the wider absorbance range which is an important consideration for rubber production. Because the bandgap size, or energy band, of N-GQDs, is approximately 4 eV (Chuang, 2000), the particles do not absorb light with lower energies than the energy band. The energy of UV light

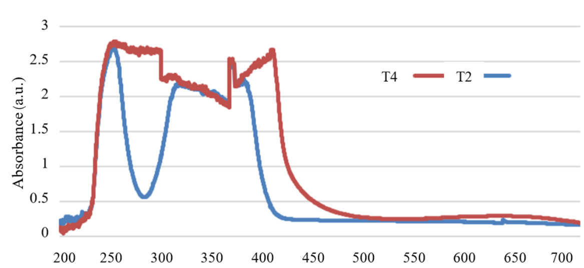

Figure 3. The absorbance spectrum of T2 and T4 solutions

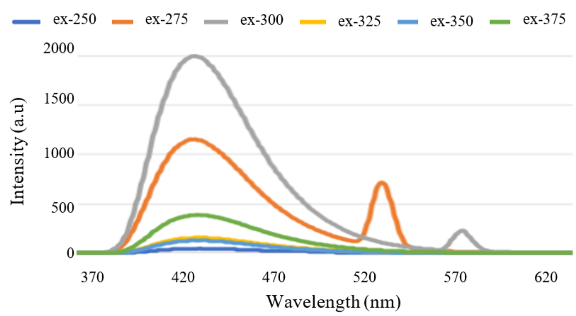

Figure 4. The emission spectrum of T4 solution

is 3–124 eV, allowing the N-GQD particles to absorb light in the UV range (Gu et al., 2016). However, the reason behind why is T4 can absorb light at wider range unclear.

Figure 4 shows that when T4 was stimulated at a 300 nm wavelength, it had the highest FL value, with a peak wavelength of 438 nm showing that the roofing tile containing T4 best protects against UVB light. The synthesis time of N-GQDs directly affects the particle size (Papaioannou et al., 2019). In other words, a longer synthesis time will result in a decrease in the size of the particle. If the particles are too large, the properties of N-GQDs such as fluorescence are also reduced. (Gu et al., 2016)

The spectroscopy of N-GQDs for different solvothermal synthesis periods

Figure 5 shows that all three solutions had the greatest absorbance in the UV range. Solvothermal synthesis uses sulfuric acid as the solvent. This gives a sulfur coating to the N-GQD particles, which increases the energy band gap (Shi et al., 2022) and decreases the wavelength that the particles absorb.

Figure 6 shows that TS6 had a peak FL value at a wavelength of 525 nm and continuing to the red-light range for longer excitation wavelengths tested. Comparing the TS6 emission spectrum results to the results for the TS4 and TS8 (not included) showed

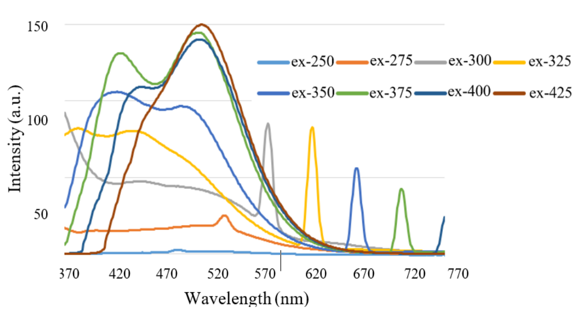

Figure 6. shows the emission spectrum of TS6 solutions

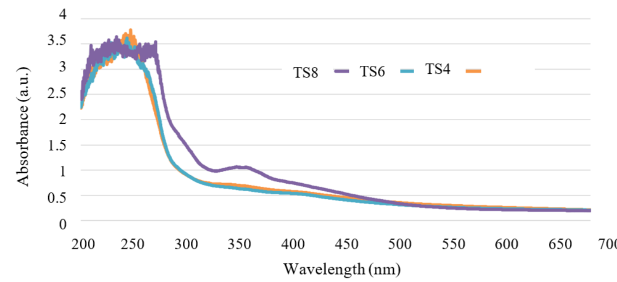

Figure 5. Absorbance spectrum of TS4, TS6, and TS8 solutions

that the synthesis time of 6 hours was the condition for which the FL was the highest, which means that this is the most appropriate condition to use for developing rubber-drying roofing tiles. In addition, TS6 emitted light at higher wavelengths than the hydrothermal synthesis. This is because the presence of sulfur coating causes the nanoparticle size increase which causes the light emission wavelength spectrum of solvothermal synthesized particles to be higher than that of hydrothermally synthesized particles. (Liu et al., 2013)

The Properties of N-GQDs roofing tile

As shown in figure 7, P-IR had the lowest strength and elongation at break, while PVA had the highest. P-UV can be stretched the most at 141% and the least is P-IR at 124%. The tensile strength of P-IR, P-UV, and PVA were 40, 61, and 71.5, respectively.

P-IR roofing sheets contain a mixture of sulfuric acid-based N-GQD. In 2000, it was reported that acetic acid content affects the structure of the PVA sheet, resulting in a decrease in the thickness of the PVA sheet and an increase in porosity due to the H_3O^+ concentration. As a result, the sulfuric acid-containing P-IR is less resilient than the P-UV roof due to the concentration of H_3O^+ ions, resulting in the sheet being more porous. (Chuang, 2000) Similarly, P-UV still shows a stress-strain curve comparable to PVA (control sample) but slightly lower. While the

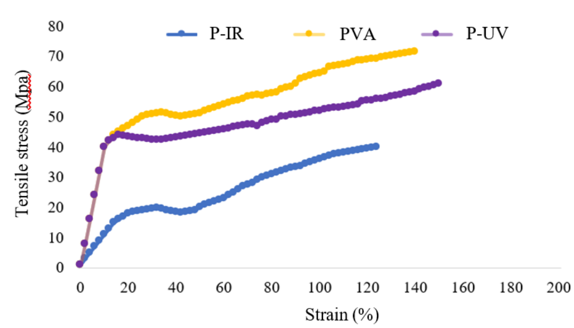

Figure 7. Stress-strain curves for P-IR, P-UV, and PVA

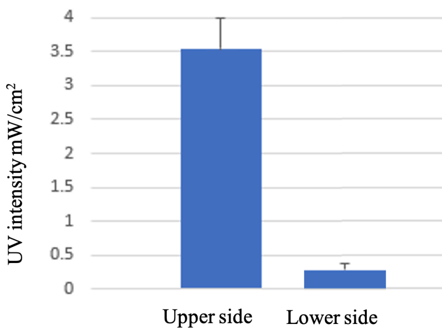

Figure 8. The average intensity of UV light above and below the P-UV/P-IR roofing assembly.

addition of T4 and TS6 did reduce the strength of the sheets, they are still usable for the intended application.

UV-protection and heating efficiency of N-GQDs roofing tiles

Figure 8 shows the average UV levels measured above and below the P-IR/P-UV roof assembly at noon. As can be seen, the average UV measured at the upper and lower side of N-GQDs is 3.54 mW/cm^2 and 0.25 mW/cm^2, respectively, giving an average UV protection effectiveness of 93% over the 7 days of testing.

Figure 9 shows that the temperature inside the chamber which use both P-UV and P-IR was higher than the temperature outside the chamber. The day with the highest indoor temperature was December 5th at 12:00, when it was 50.8 ºC. The average temperature difference between the inside and outside of the chamber at 8:00 was 5.2ºC, at 12:00 was 9.1ºC, and at 16:00 was 7.1ºC.

IV. CONCLUSION

From our study, we found that after synthesis, T4 had the highest absorbance in the UVA, UVB, and UVC ranges. In addition, TS6 had the highest FL in the range of red light. When the polymer was molded, we found that the P-UV roof from T4 retained more strength than the P-IR roof from TS6. After studying heat storage efficiency, we found that the temperature inside the solar drying chamber was higher than the temperature outside. The average UV protection efficiency of N-GQDs roof was 93.3%. Lastly, the average temperature inside the solar drying chamber was 43ºC, which is the most suitable temperature for

Date	8:00		12:00		16:00	
	Temperature inside (ºC)	Temperature outside (ºC)	Temperature inside (ºC)	Temperature outside (ºC)	Temperature inside (ºC)	Temperature outside (ºC)
1st Day	39.3	33.9	47.3	38.5	42.5	36.3
2nd Day	39.8	34.6	47.9	39.1	43.1	36.4
3rd Day	40.2	35.0	48.2	38.8	43.8	36.9
4th Day	38.3	34.0	50.8	39.1	42.6	36.5
5th Day	38.9	34.6	47.0	38.0	44.8	37.0
6th Day	38.6	32.1	45.7	37.5	45.1	37.4
7th Day	39.7	34.5	48.0	39.7	44.8	36.5
Average	39.3	34.1	47.8	38.7	43.8	36.7

Figure 9. shows the indoor and outdoor temperatures recorded in 3 time periods for 7 days

drying rubber sheets. Finally, we can conclude that our innovation, N-GQDs roofs can defend against UV rays while increasing the temperature in the chamber. The P-IR/P-UV roof tile on a rubber drying chamber can significantly enhance the efficiency of the drying process. The improved efficiency results in a higher yield of high-quality rubber sheets, which translates to higher income for rubber farmers and improved economic conditions in Thailand's rubber industry. While the findings suggest that N-GQDs roofing material is effective in reducing UV radiation and increasing temperature in a drying chamber, the study did not directly test the effect of the roofing material on the drying of rubber sheets. Further research is needed to investigate the efficacy of N-GQDs roofing material in actual rubber sheet drying. Furthermore, it is important to note that the present study only focused on comparing the efficiency of the N-GQDs roof with a PVA roof. Further research can be conducted to evaluate the efficiency of the N-GQDs roof compared to other roofing materials, such as plastic. Overall, the present study provides a promising avenue for enhancing the efficiency and economic viability of the rubber industry in Thailand.

V. REFERENCES

1. Aguele, F., Idiaghe, J., & Apugo-Nwosu, T. (2015). A Study of Quality Improvement of Natural Rubber Products by Drying Methods. Journal of Materials Science and Chemical Engineering, 03(11), 7-12. https://doi.org/10.4236/msce.2015.311002

2. Bacon, M., Bradley, S., & Nann, T. (2013). Graphene Quantum Dots. Particle &Amp; Particle Systems Characterization, 31(4), 415-428. https://doi.org/10.1002/ppsc.201300252

3. Chuang, W. (2000). The effect of acetic acid on the structure and filtration properties of poly(vinyl alcohol) membranes. Journal of Membrane Science, 172(1-2), 241-251. https://doi.org/10.1016/s0376-7388(00)00336-7

4. Gu, J., Zhang, X., Pang, A., & Yang, J. (2016). Facile synthesis and photoluminescence characteristics of blue-emitting nitrogen-doped graphene quantum dots. Nanotechnology, 27(16), 165704. https://doi.org/10.1088/0957-4484/27/ 16/165704

5. Kampan, P. (2017). Sustainability and Competitiveness of Thailand's Natural Rubber Industry in Times of Global Economic Flux. Asian Social Science, 14(1), 169. https://doi.org/10.5539/ass.v14n1p169

6. Liu, F., Jang, M., Ha, H., Kim, J., Cho, Y., & Seo, T. (2013). Graphene Quantum Dots: Facile Synthetic Method for Pristine Graphene Quantum Dots and Graphene Oxide Quantum Dots: Origin of Blue and Green Luminescence (Adv. Mater. 27/2013). Advanced Materials, 25(27), 3748-3748. https://doi.org/10.1002/adma.201370175

7. Papaioannou, N., Titirici, M., & Sapelkin, A. (2019). Investigating the Effect of Reaction Time on Carbon Dot Formation, Structure, and Optical Properties. ACS Omega, 4(26), 21658-21665. https://doi.org/10.1021/acsomega.9b01798

8. Purcell-Milton, F., & Gun'ko, Y. (2012). Quantum dots for Luminescent Solar Concentrators. Journal Of Materials Chemistry, 22(33), 16687. https://doi.org/10.1039/c2jm32366d.

9. Qu, D., Zheng, M., Zhang, L., Zhao, H., Xie, Z., & Jing, X. et al. (2014). Formation mechanism and optimization of highly luminescent N-doped graphene quantum dots. Scientific Reports, 4(1). https://doi.org/10.1038/srep05294

10. Shi, H., Zhao, Q., Zhou, C., & Jia, N. (2022). Nitrogen and sulfur co-doped carbon quantum dots as fluorescence sensor for detection of lead ion. Chinese Journal of Analytical Chemistry, 50(2), 63-68. https://doi.org/10.1016/j.cjac.2021.09.010

11. Shi, R., Bi, J., Zhang, Z., Zhu, A., Chen, D., & Zhou, X. et al. (2008). The effect of citric acid on the structural properties and cytotoxicity of the polyvinyl alcohol/starch films when molding at high temperature. Carbohydrate Polymers, 74(4), 763-770. https://doi.org/10.1016/j.carbpol.2008.04.045

12. Sk, M., Ananthanarayanan, A., Huang, L., Lim, K., & Chen, P. (2014). Revealing the tunable photoluminescence properties of graphene quantum dots. J. Mater. Chem. C, 2(34), 6954-6960. https://doi.org/10.1039/c4tc01191k

ACKNOWLEDGEMENTS

We would like to express our deep and sincere gratitude to our supervisor, Mr. Khunthong Klaythong, and our special supervisor, Asst. Prof. Voranuch Thongpool, for guiding and encouraging us in this research. Thank you to Dr. Samorn Pato, school principal of Princess Chulabhorn Science High School, for giving us permission to conduct this research as well as allowing us to use the school's facilities.