

Developing a Rubber based Nanocomposite

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ABSTRACT

Polymer compounds such as Natural Rubber (NR), which consists of compounds such as isoprene, are capable of being processed for the manufacture of a range of rubber based products for a large variety of applications. The properties of a natural rubber compound are susceptible to enhancements in their properties through the incorporation of nanofillers into its matrix. This study addresses the preparation of a natural rubber based nanocomposite that utilizes graphene as a nanofiller for the facilitation of the required enhancement in the rubber compounds properties. The nanocomposite specimens used in the study were prepared by means of acid-coagulation. The acid-coagulation formulation utilized was adapted from methodologies employed in commercial applications. The enhancement in the rubber properties due to the incorporation of the nanofiller was validated by means of mechanical testing. Prior to the testing, the applicable standard for tensile property testing was identified to be ASTM D412. Through the acclaimed standard, a mould to facilitate the preparation of the required specimens was 3D printed from PETG. The primary aim of the study was to determine the effect of large concentrations of graphene (beyond 2.5wt %). The results from the mechanical testing of the acid-coagulated samples exhibited enhancements in the elongation at break and tensile strength between unfilled NR and the graphene filled NR nanocomposite. With the incorporation of 5wt% of graphene, the elongation at break of the rubber increased to 687%, showing a 25% increase. The tensile strength of the rubber increased to 4.07 MPa, showing an enhancement of 102% in comparison to the pristine rubber compound.

KEYWORDS: *Natural Rubber, Graphene, Acid-Coagulation, Tensile strength, Elongation at break.*

1 INTRODUCTION

Natural rubber (cis-1, 4-poly (Isoprene)) is a polymer that is procured from the latex of the Hevea Brasiliensis tree along with other non-polymer by products. The NR can be isolated and made into sheet through the process of coagulation. Coagulation is primarily influenced by the type of coagulating agent utilized. The most commonly used category of coagulating agent is an acid, primarily, Formic acid. Formic acid is a caustic Carboxylic acid that is colorless, pungent and is highly advocated for use as a coagulant due to its generation of a favorable level of dry rubber in the coagulated compound (Oktriyedi, Dahlan, Irfannuddin, & Ngudiantoro, 2021). In the process of acid-coagulation, the addition of the easily ionized Formic acid into the latex allows for the latex to coagulate into a solid. When the Formic acid ionizes, the produced hydrogen ions react with the negative charges on the surface of the polymer membrane, allowing for the formation of neutrally charged rubber particles. Thereafter, on the collision between the neutrally charged particles, the outer membrane of the polymer particles fragment apart allowing the polymer molecules to agglomerate and coagulate to form a solid compound (Veerendra, 2020). The generated natural rubber presents a large range of applications, in the manufacture of tires, gloves and other engineering products (Erman, Mark, & Roland, 2013). However, owing to its deficient strength and low modulus, the applications of natural rubber have been restricted. In order to overcome the barriers presented, studies focused on the preparation of natural rubber-based nanocomposites through the assimilation of a suitable nanofiller phase into the matrix of the natural rubber to obtain improvements in the mechanical properties of the rubber beyond those offered by the unfilled rubber (Wang, Liu, Wu, Wang, & Zhang, 2010). Studies carried out on graphene nanoparticles have shown that the incorporation of a miniscule amount of graphene can result in great enhancements to the properties of the rubber compound. This is a result of the greater aspect ratio of graphene (Sur, 2012) along with its inherently high

mechanical properties (Liu, et al., 2021). Additionally, graphene can be functionalized to further elevate the properties and reactivity of the nanofiller. This is demonstrated in a study by Jose and Susamma (Jose & Susamma, 2021), where the incorporation of 0.5phr of graphene modified with dodecyl amine led to the tensile strength of the rubber compound increasing by 74%.

Although numerous methods of nanocomposite preparation exist, the most widespread method for nanocomposite preparation is the method of latex mixing (Bu, Wang, Zhang, Lavorgna, & Xia, 2017). The principal behind latex mixing comprises of blending the rubber latex with a suspension of the graphene nanofiller for the generation of a homogeneous dispersion. The dispersion can subsequently be coagulated or vulcanized for the generation of the final nanocomposite sample. The method of latex mixing provides advantages such as allowing a greater attainable degree of nanofiller dispersion and being environmentally friendly due to the requirement for an organic solvent (Bu, Wang, Zhang, Lavorgna, & Xia, 2017). However, due to the requirement of high-speed equipment for the dispersion of graphene within the latex, costs may escalate in the case of mass production of the dispersion (Bu, Wang, Zhang, Lavorgna, & Xia, 2017).

This paper utilizes a standard rubber curing method for the preparation of the rubber compounds with and without the incorporation of a nanofiller. This is done in order to observe the improvements in the mechanical properties of the natural rubber as a result of the graphene nanofiller assimilation. Additionally, the paper attempts the determination of the optimum concentration of graphene that leads to a maximum yield in the attained mechanical properties. This was accomplished through the testing of a large range of incorporated graphene concentrations (an expanded range was used, mainly beyond 2.5wt %, since a small range would be insufficient to provide clarity on the point of percolation). The range tested enabled the identification of the graphene loading beyond which the tested mechanical properties showed no further improvement. The range utilized for the testing was established through a literature survey that was carried out to determine the standard testing loadings. In addition, paper also addresses the use of standards such as ASTM D412 and ASTM D1415 for the manufacture of a mould to facilitate the specimen preparation. Since the subject of using nanoparticles for the reinforcement of rubber is a relatively new field of study, this paper aims to contribute to advancements in the field.

2 EXPERIMENTAL PROCEDURE

2.1 Materials

Natural Rubber latex used for the study was centrifuged NR latex that was purchased from Almar Trading Co., (PTE) LTD. The composition and properties of the NR latex used are shown in Table 1.

Table 1. Composition and properties of NR latex

Quality Parameter	Unit	Value
Total solid content	% wt	61.50
Dry rubber content	% wt	60.00
Non-rubber content	% wt	1.5
Ammonia content	% wt	0.8 (max)
Mechanical stability time	sec	800-1000
Volatile fatty acid number		0.025
KOH number		0.53
pH value		10.20

The graphene suspension used as the nanofiller was obtained from CeyGrene (Pvt) Ltd. The graphene was obtained as a suspension through the liquid phase exfoliation of vein graphite. The composition of the graphene suspension is given in Table 2.

Table 2. Composition of Graphene suspension

Chemical	%Weight
Distilled water	<80
Graphitic carbon	>15
Proprietary additive (PVP)	<5

For the facilitation of the acid-coagulation methodology, Formic acid was used as the main coagulant. The required formic acid was purchased from Glorchem Enterprise.

2.2 Mould design for specimen preparation

Design of the mould to be used for the preparation of the nanocomposite specimens was carried out by initially identifying the associated standards. The standards required to be utilized for the specimen dimensions were identified through a study that was carried out.

Through the study, it was identified that for the tensile testing of rubber, the ASTM D412 standards was used. This allowed for the determination of the elongation at break and the tensile strength of the rubber specimens. The standard specimen shape stipulated by ASTM D412 was a dog-bone/ dumbbell shape as shown in Figure 1.

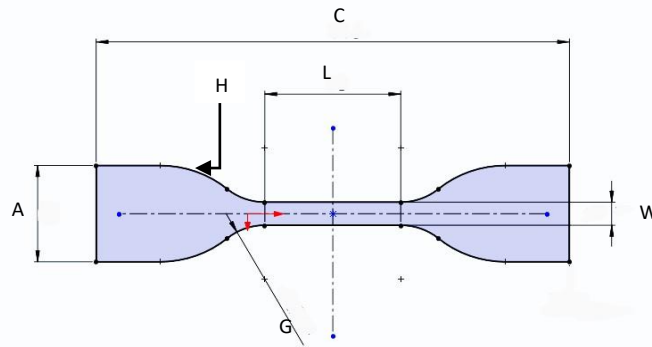


Figure 1. Design schematic for tensile specimen

ASTM D412 reports of six alternate dimension combinations for the specimen. The most generally preferred and used combination was that of “Die C”. Based on the specification for “Die C”, the dimensions of A, C, G, H, L and W are shown in Table 3.

Table 3. Die C specification for tensile specimen (ASTM International, 2009)

A	25 mm
C	115 mm
G	14 mm
H	25 mm
L	33 mm
W	6 mm

The specimen thickness was designated to be 2 mm according to the ASTM D412 standard.

Additionally, it was determined that the dimensions for a hardness testing specimen was dictated by the ASTM D1415 standard. According to this standard, the hardness specimen required its lateral dimensions to be greater than 20 mm. The specimen thickness was to be sustained between 8 – 10 mm (minimum value for thickness was 2 mm). The specimen was designed with lateral dimensions as shown in Figure 2, while the specimen thickness was set to be 10 mm.

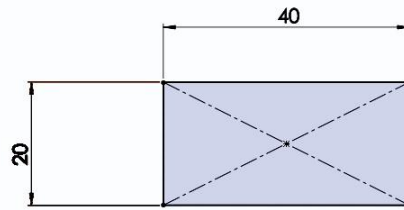


Figure 2. Design schematic for hardness specimen

The final mould was designed to hold five cavities for the tensile specimens (for the determination of average tensile strength) and a single cavity for the hardness specimen. The material used for the mould was Polyethylene terephthalate glycol (PETG) owing to its good chemical resistance against the coagulating agent (formic acid).

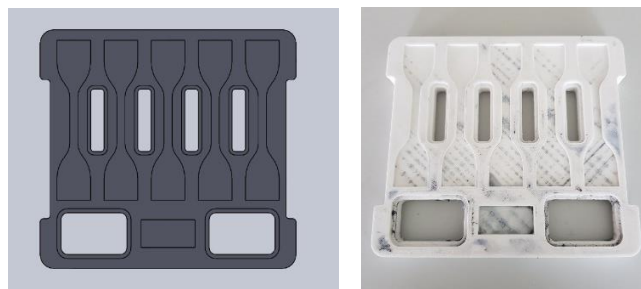


Figure 3. (a) SolidWorks mould design; (b) PETG printed mould

2.3 Coagulation methodology for specimen preparation

The applied coagulation methodology was derived from the methodology utilized in the rubber processing plant of Agalwatte Plantations PLC. For the study, 0.18g of formic acid was diluted with 14.4g of water. Prior to the addition of the diluted acid into the latex, the graphene suspension was incorporated and dispersed within the NR latex to obtain an NR-graphene mixture. The concentrations of graphene tested ranged from 0 to 20 wt% in NR. The dispersion of the graphene was facilitated by stirring for five minutes with a mixer. The diluted Formic acid was thereafter mechanically stirred into 40g of the NR-graphene mixture. Mixing was carried out in a glass beaker until the Formic acid was homogenized within the latex. The mixture was thereafter poured into the prepared mould and was left to coagulate for a period of 24 hours. A summary of the formulations tested are shown in Table 4.

Table 4. Summary of formulations tested

Test No.	Graphene (%wt)	Latex used (g)	Formic acid (g)	Water (g)
1	0	40	0.18	14.4
2	2.5			
3	5			
4	10			
5	20			

2.4 Mechanical property testing

The initially determined mechanical test to be carried out were:

- Tensile testing
- Hardness testing

However, due to issues with the hardness of the specimen prepared (as seen in results), only the tensile properties were tested for. The tensile properties tested were: the tensile strength and elongation at break. The prepared coagulation specimens were sent to the Industrial Technology Institute (ITI) for the tensile property testing.

3 RESULTS AND DISCUSSION

3.1 Coagulated samples

The samples prepared through the coagulation methodology are illustrated below.

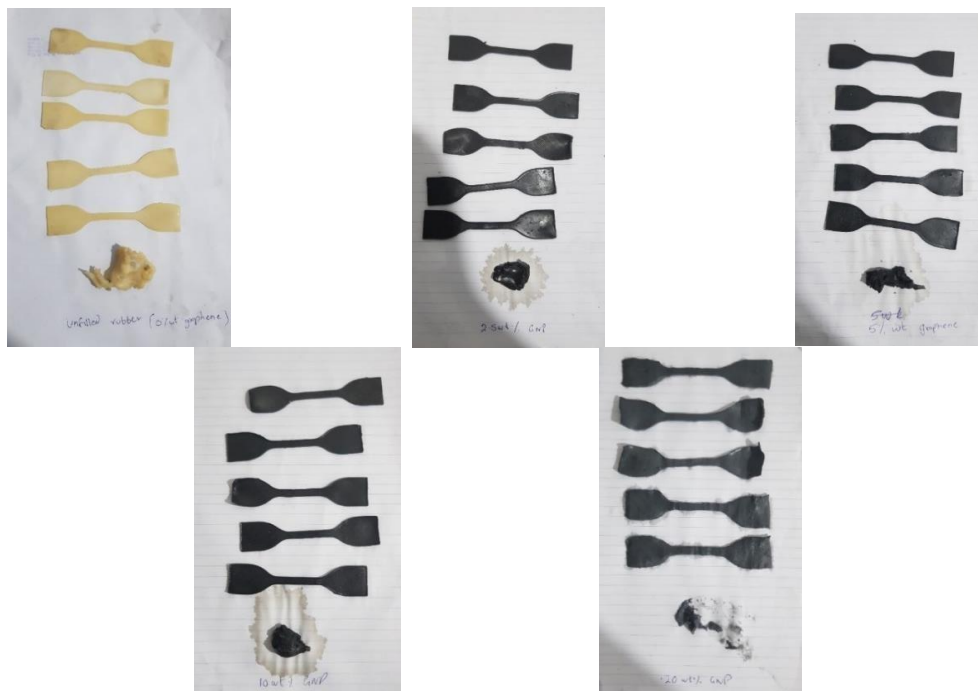


Figure 4. (a) unfilled sample; (b) 2.5wt% graphene; (c) 5wt% graphene; (d) 10wt% graphene; (e) 20wt% graphene

From the prepared samples, it can be identified that the hardness of the specimen for each sample shows a degree of disfigurement. This prevented the hardness of specimens from being used for mechanical testing. The observed disfigurement was attributed to a slight amount of pre-coagulation that took place on the addition of the Formic acid. This likely reduced the total rubber content in the latex, thereby leading to the hardness specimen being less structurally sound in comparison to the tensile samples. The pre-coagulation an issue for the tensile specimens owing to the lower thickness of tensile specimens.

3.2 Mechanical properties of NR-graphene nanocomposites

Through the test carried out by ITI, it was observed that for certain specimen fractures eventuated from the grips instead of the specimen gauge length. The data from these particulars, specimens were excluded from consideration since they would prove to be ineffectual in the determination of the mechanical properties. The data of force and elongation undergone by each of the tested specimens are as follows:

- Unfilled sample (0wt % graphene)

Table 5. Force and elongation for the unfilled sample

Specimen	Force (N)	Elongation (mm)
1	14.7	185.03
2	18.3	188.63
3	14.7	170

- 2.5wt % graphene sample (2.5wt % graphene)

Table 6. Force and elongation for 2.5wt % of the graphene sample

Specimen	Force (N)	Elongation (mm)
1	30	190
2	16.7	160
3	10.7	160
4	31.7	200

- 5wt % graphene sample (5wt % graphene)

Table 7. Force and elongation for 5wt % of the graphene sample

Specimen	Force (N)	Elongation (mm)
1	39.3	230
2	29	230
3	37	220

- 10wt % graphene sample (10wt % graphene)

Table 8. Force and elongation for 10wt % of the graphene sample

Specimen	Force (N)	Elongation (mm)
1	15	190
2	27	200
3	13	180
4	25.3	210
5	15.3	180

- 20wt % graphene sample (20wt % graphene)

Table 9. Force and elongation for 20wt % of the graphene sample

Specimen	Force (N)	Elongation (mm)
1	13.7	180
2	21	200
3	29.3	200
4	23	180

Based on the data for each sample, the tensile strength and elongation at break were determined to be:

- Unfilled sample (0wt % graphene)

Table 10. Tensile strength and elongation at break for the unfilled sample

Specimen	Tensile strength (MPa)	Elongation at break (%)
1	1.749	560.70
2	2.551	571.61
3	1.727	515.15

- 2.5wt % graphene sample (2.5wt % graphene)

Table 11. Tensile strength and elongation at break for 2.5wt % of the graphene sample

Specimen	Tensile strength (MPa)	Elongation at break (%)
1	3.450	575.76
2	2.092	484.85
3	1.346	484.85
4	3.658	606.06

- 5wt % graphene sample (5wt % graphene)

Table 12. Tensile strength and elongation at break for 5wt % of the graphene sample

Specimen	Tensile strength (MPa)	Elongation at break (%)
1	4.586	696.97
2	3.467	696.97
3	4.150	666.67

- 10wt % graphene sample (10wt % graphene)

Table 13. Tensile strength and elongation at break for 10wt % of the graphene sample

Specimen	Tensile strength (MPa)	Elongation at break (%)
1	1.860	575.76
2	3.400	606.06
3	1.649	545.45
4	2.993	636.36
5	1.872	545.45

- 20wt % of the graphene sample (20wt % graphene)

Table 14. Tensile strength and elongation at break for 20wt % of the graphene sample

Specimen	Tensile strength (MPa)	Elongation at break (%)
1	1.729	545.45
2	2.450	606.06
3	3.548	606.06
4	2.959	545.45

The mean mechanical properties of the NR-graphene nanocomposites prepared through latex mixing and acid-coagulation are shown in Table 15.

Table 15. Average tensile properties for each sample tested

Test No.	Formulation	Tensile strength (MPa)	Elongation at break (%)
1	40g NR latex	2.01	549
2	40g NR latex + 2.5wt% graphene	2.64	538
3	40g NR latex + 5wt% graphene	4.07	687
4	40g NR latex + 10wt% graphene	2.35	582
5	40g NR latex + 20wt% graphene	2.67	576

From the data observed in Table 15, it is apparent that the tensile properties of the NR notably increases on the addition of the graphene nanofiller in comparison to pristine NR. It can be identified that on the addition of 5wt% graphene, the tensile strength of NR is enhanced by almost 102% while the elongation at break exhibits an improvement by almost 25%.

The observed enhancements in the properties are likely attributed to the diffusion of the polymer particles between the particle-particle interfaces, in addition to the probable homogeneous dispersion of the nanofiller within the NR matrix.

However, once the loading of graphene is increased beyond 5wt%, a drop in the tensile properties after which no further improvement in properties seen at the 5wt%, loading can be observed. This is likely to be a result of aggregation of the graphene nanofiller at loadings greater than 5wt% Nanofiller aggregation results in an elevated difficulty for the interpenetration of the NR leading to relatively lacking tensile properties as seen in Figure 5.

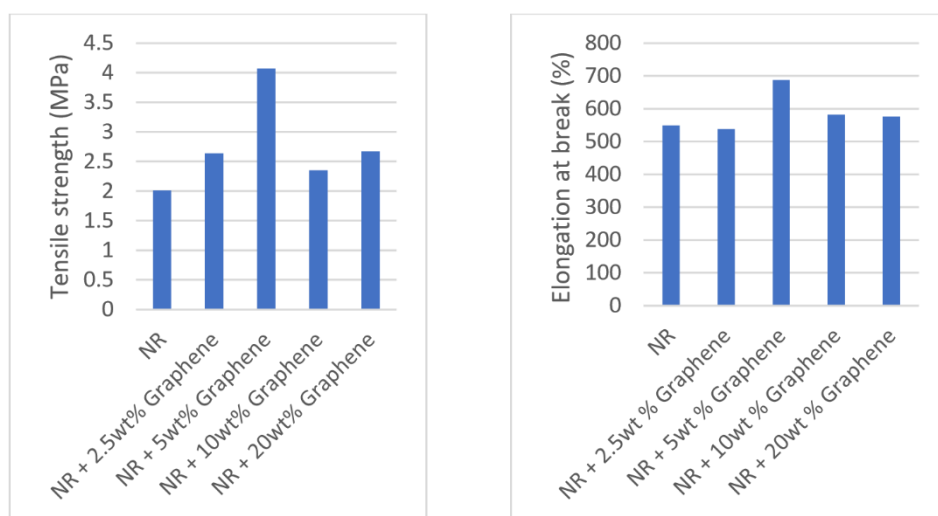


Figure 5. Graphical representation of tensile strength and elongation at break of the NR-graphene nanocomposites

4 CONCLUSION

In the following study, latex mixing was utilized for the dispersion of the graphene nanoparticles within the NR matrix at distinct loadings varying from 2.5 – 20 wt%. The curing methodology used for the sample preparation was acid-coagulation. Afterwards, the tensile properties of the nanocomposite samples were tested for. Through the obtained results, it was observed that the incorporation of the graphene nanofiller led to enhancements in the properties of the coagulated specimens when compared to the unfilled sample. The enhancements were likely a result of the interfacial interaction between the NR and graphene along with the likely uniform dispersion of the nanofiller within the NR matrix. From the samples tested, it was observed that the highest tensile strength and elongation at break were extracted at a graphene loading of 5wt%. This enhancement demonstrated that the incorporation of graphene in the rubber matrix showed capability for the optimization of mechanical properties for future applications. Therefore, the improvements made to the tensile properties of the rubber encourage expansions in the field of application for the nanocomposite. Applications may include technical components in automobiles that require a higher degree of elasticity. They may also be implemented for the preparation of stronger latex gloves with better puncture resistance for use in healthcare and hygiene.

The results obtained in the study can be further optimized by refining the tested graphene loadings through the use of smaller incremental steps between 2.5wt % and 10wt %. This allows for the investigation of the rubber properties at much greater detail to refine the test results allowing a significantly precise optimum loading of graphene to be determined. The study can be further improved through modifications made to the specimen preparation procedure to ensure that the identified pre-coagulation can be minimized or eliminated. Additional considerations may include the testing of the other prevalent properties of rubber such as wear resistance, hysteresis, and dielectric properties.

5 ACKNOWLEDGEMENTS

The author expresses his gratitude to Mr. Chaminda Jayalath of Star Construction Pvt Ltd for his provision of laboratory facilities during the pandemic, thereby enabling the experimentation to be carried out.

REFERENCES

- ASTM International. (2009). *Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers - Tension*. Retrieved from UnivStrut: <http://www.univstrut.com/uploadfiles/pdf/3.pdf>
- Bu, Q., Wang, J., Zhang, K., Lavorgna, M., & Xia, H. (2017). *Graphene-Rubber Nanocomposites: Preparation, Structure, and Properties*.
- Erman, B., Mark, J. E., & Roland, C. (2013). *The Science and Technology of Rubber*. Oxford: Elsevier.
- Jose, J., & Susamma, A. (2021). Studies on natural rubber nanocomposites by incorporating amine functionalised graphene oxide. *Plastics, Rubber and Composites*.
- Liu, B., Pavlou, C., Wang, Z., Cang, Y., Galiotis, C., & Fytas, G. (2021). Determination of the elastic moduli of CVD graphene by probing graphene/polymer Bragg stacks. *2D Material*.
- Oktriyedi, F., Dahlan, M. H., Irfannuddin, & Ngudiantoro. (2021). Impact of latex coagulant various from rubber industry in South Sumatera. *AIP Conference Proceeding 2344*.
- Sur, U. K. (2012). Graphene: A Rising Star on the Horizon of Materials Science. *International Journal of Electrochemistry*.
- Veerendra. (2020, December 22). *Which acid is used for coagulating rubber from latex?* Retrieved from <https://www.aplustopper.com/acid-used-coagulating-rubber-latex/>
- Wang, Z., Liu, J., Wu, S., Wang, W., & Zhang, L. (2010). Novel percolation phenomena and mechanism of strengthening elastomers by nanofillers. *Physical Chemistry Chemical Physics*, 1-2.