

REARRANGEMENT BEHAVIOUR OF GRAPHENE DURING FILM FORMATION

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ABSTRACT

This work was carried out to explore the reinforcement mechanism of graphene in natural rubber (NR) latex. The proposed interaction between NR and graphene was presented to enhance better understanding of this mechanism during latex film formation, relating it to a measurable property namely, conductivity which is attributed to the graphene sp^2 π electron clouds. For all types of NR latexes *i.e.* HA (conventional), DPNR (deproteinized) and ENR (epoxidized), measurement of their surface resistivity showed the coagulant-dipped films to be all insulative regardless of the graphene dosage. In contrast, for their respective cast films, the top sides (facing the air during film drying) were insulative while the bottom sides (facing the glass mold) became static dissipative or conductive with increasing graphene dosage. This observation shows that during evaporation of latex from liquid to solid film, given enough time and fluidity, the incorporated graphene could rearrange within the latex matrix to form connecting networks essential for conductivity. Dipped film undergoes immediate solid film formation which locks the graphene *in situ* without much connected networks. However, cast film solidifies slowly, allowing the graphene to connect and form conductive network. The bottom side of cast films also consistently showed lower resistivity values than the top side. This suggests that during the slow drying process, the heavier graphene likely move to the bottom, causing the bottom side to end up with layers of connected graphene, while leaving the top side with haphazardly non-connected “floating” lighter weight graphene. Latex with lower total solid content was found to facilitate better graphene mobility and alignment towards static dissipative or conductivity film property. Conductive nature of NR latex cast films could be achieved simply by increasing the graphene dosage. HA and ENR have stronger tendency than DPNR to attain static dissipative or conductive range quicker, suggesting the role of innate proteins in this phenomenon.

INTRODUCTION

Over recent years there has been increased interest in the fundamental technological applications of graphene. Many labs are intensively exploring how to combine graphene with other materials, because doping even small amounts of graphene into host materials can have dramatic effects on physicochemical properties. The wide ranges of potential applications of graphene indicate for an increased demand for graphene. Graphene is composed of sp^2 -bonded carbon atoms arranged in a two-dimensional honeycomb lattice. The lattice can be seen as consisting of two interpenetrated triangular sub-lattices, for which the atoms of one sub-lattice are at the center of the triangles defined by the other with a carbon-to-carbon inter-atomic length, a_{C-C} , of 1.42 Å. The unit cell comprises two carbon atoms and is invariant under a rotation of 120° around any atom. Each atom has

one s orbital and two in-plane p orbitals contributing to the mechanical stability of the carbon sheet. The remaining p orbital, perpendicularly oriented to the molecular plane, hybridizes to form the π^* (conduction) and π (valence) bands, which dominate the planar conduction phenomena [1].

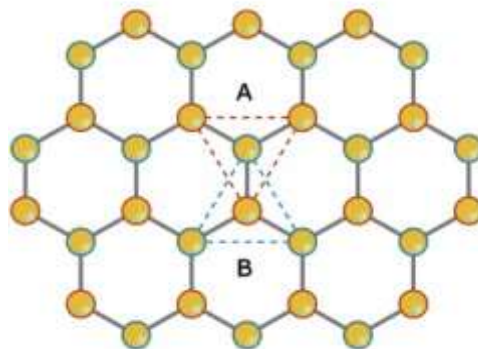


Figure 1: Atomic and electronic structures of graphene. Graphene lattice consists of two interpenetrating triangular sub-lattices, each with different colors. The atoms at the sites of one sub-lattice, (i.e. A) are at the centers of the triangles defined by the other lattice (i.e. B), with a carbon-to-carbon inter-atomic length of 1.42 Å.

For all its potential, graphene (whether single layer or multilayer) still suffers major drawbacks, especially in terms of stability when dispersed in solvents [2]. In this regard, it is obviously important to obtain graphene dispersions using low-cost and environmentally friendly techniques. Interest in aqueous graphene dispersions has been driven by the desire to minimize or eliminate VOCs (volatile organic compounds) in these formulations. One of the popular routes to prepare aqueous graphene dispersions is using surfactant-assisted sonication. Surfactant-stabilized graphene systems rely on repulsive intersheet interactions, provided by electrostatic or steric barriers, to overcome the natural destabilizing attractive inter-graphene interactions [3]. It is of special interest to formulate scalable graphene dispersions for practical for high volume manufacturing applications.

Natural rubber (NR) is a low cost and easy to obtain polymer with great potential for carbon-based polymer nanocomposites [4]. Despite the fact that NR is widely used for tire manufacturing and in the medical applications, this hydrophilic polymer is generally less appropriate for electrical applications due to the absence of an internal conducting network. On the other hand, incorporating nanofillers such as graphene into NR matrices, is expected to generate electrically conductive nanocomposite materials. Therefore, over recent years, research on carbon nanomaterials and NR has been mainly dominated by development of enhanced electrically conductive nanocomposites [5,6]

Experiments so far could not conclude any distinct or marked improvement in the mechanical properties of graphene/NR latex composites using pristine graphene, graphene oxide or differently functionalized graphenes. In respect to this, it is very likely that the current approach of using conventional compounding route to integrate commercially available graphene into NR latex system is not sufficiently effective to transform the latex

into a mechanically enhanced material. Graphene by itself is known to be a highly electrically conductive material due to the hexagonal honeycomb layers which allow the π electrons to move around freely on its lateral planes. With this concept in mind, incorporation of graphene into NR latex which is an insulator by nature, ought to some extent transform the NR latex into a semi or fully conductive material. This approach may be beneficial for NR to be used as flexible conductive or ESD devices. As such, experiments were carried out to incorporate graphene into conventional NR latex and also specialty NR latexes to examine their resulting conductivity behaviour. Specialty NR latexes *e.g.* deproteinized (DPNR) and epoxidized (ENR) natural rubber latexes were selected for study because in composition, these specialty latexes are considered “cleaner” than conventional NR latex due to the treatments the former latexes have undergone, hence expected to have less or negligible non-rubber components. This study aims to investigate whether the conductive nature of the graphene/NR latex composites could be affected by the innate non-rubber components in NR latex.

EXPERIMENTAL

Graphene dispersions (10% stock in anionic surfactant) were used. The graphene flakes are about 100 nm in lateral size, with at least 20% of it being 1-3 layers, and the rest generally 5-6 layers thick. Graphene were compounded into pre-vulcanized NR latex (MR Grade, Getahindus) from 0.1phr up to maximum 6 phr. Compared to studies carried out before this, higher amount of graphene was selected for the current study to determine threshold of the graphene dosing that will trigger conductivity. Prior to use, the graphene dispersions were exfoliated one day earlier for a total of not less than 6 hours using a probe sonifier. On the day of experiment, the graphene dispersions were again exfoliated for at least 2 hours and then compounded immediately into the pre-vulcanized NR latex. The compounded latex was left to stir for overnight and diluted to 30% total solids content the next day for fabrication of thin films (straight cast and coagulant-dipped). The compounded latex was then left to stand for another day to allow the graphene to settle to the bottom. Following this, about 2/3 from the upper portion of latex was removed, the remaining latex was stirred and cast films were then prepared from this latex, denoted as “*settled latex*” in this study. This additional process was used to simulate “increased dosing” of graphene in a reduced volume of latex. All films were cured at 70 °C for 2 hours. Conductivity of films was measured using the TECMAN surface resistance meter (TM 385).

For experiments with specialty latexes, the DPNR and ENR latexes were compounded in the usual manner based on a sulphur vulcanization formulation. Compounded high ammoniated NR latex (HA) was used as control. Graphene dispersion was next added into these compounded latexes to a final concentration of 3.5phr. Compounds were diluted with water to varying TSC (total solids content) ranging from 50-30% to facilitate preparation of cast films with different thickness between 0.02-0.04 cm. The films were left to dry adequately at ambient condition followed by leaching in water and post-vulcanized at 100°C for 20 minutes. Conductivity of films was measured using the TECMAN surface resistance meter (TM 385).

RESULTS AND DISCUSSION

Figures 2 and 3 show the surface resistance values (ohm) obtained from NR/graphene composites with varying amounts of graphenes. Generally, the values in ohm denote the following properties;

$10^3 - 10^5$: conductive

$10^6 - 10^{11}$: static dissipative

10^{12} : insulative

Figure 3: Surface resistance of PV-NRL/graphene composites (0.1 to 4 phr)

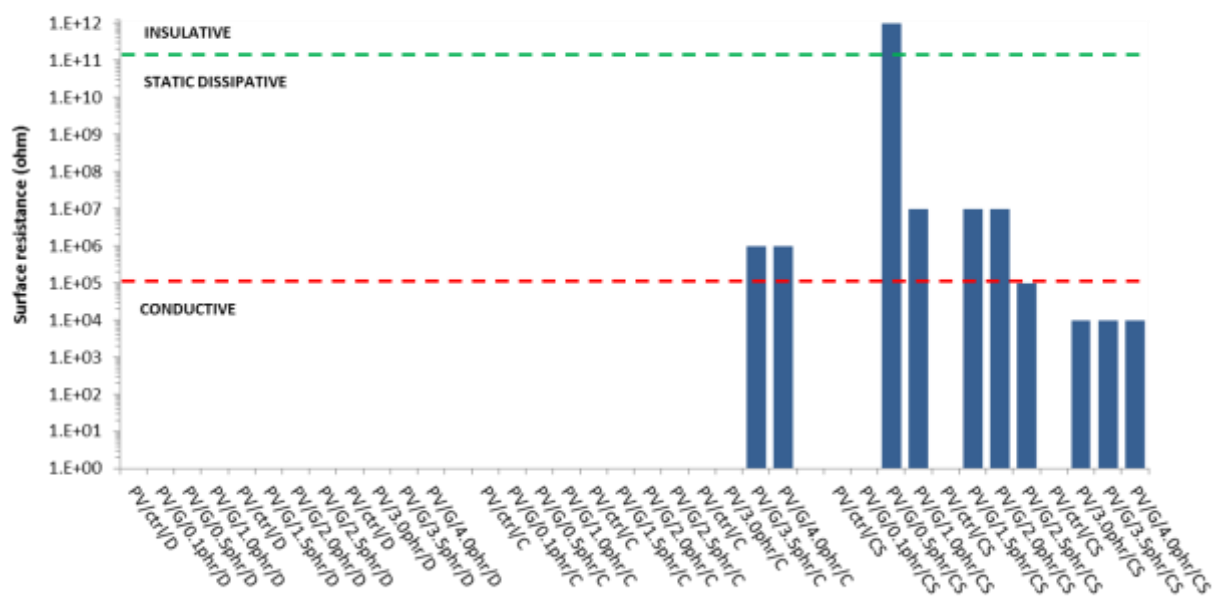
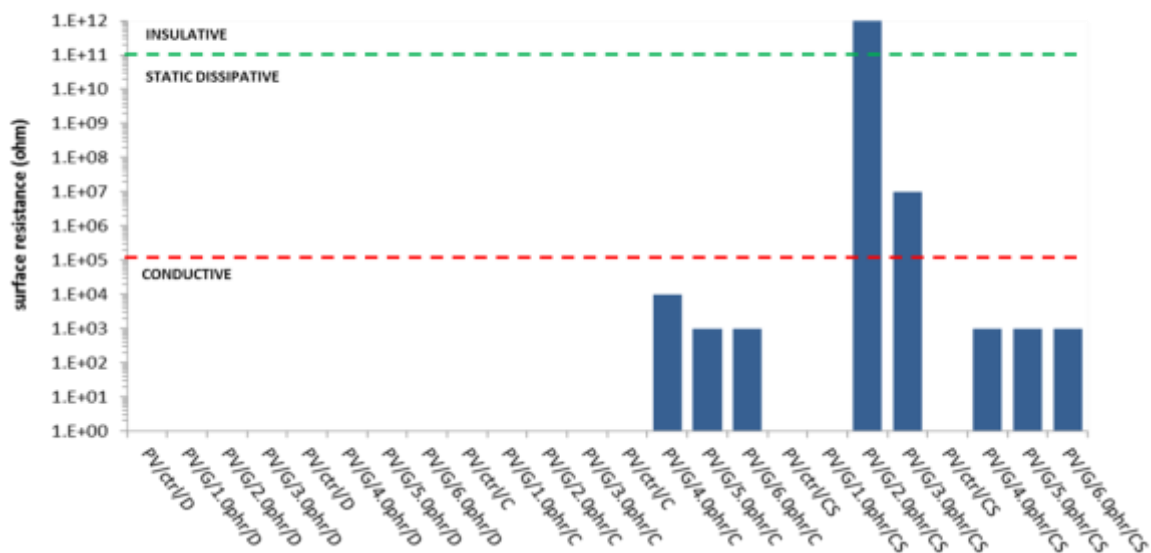


Figure 4: Surface resistance of PV-NRL/graphene composites (1-6 phr)



Abbreviations (on x axis):

PV Pre-vulcanized natural rubber latex

G graphene

<i>phr</i>	<i>part per hundred of rubber (number preceding it denotes amount of graphene used)</i>
<i>ctrl</i>	<i>control film (without graphene)</i>
<i>D</i>	<i>dipped film</i>
<i>C</i>	<i>cast film</i>
<i>CS</i>	<i>cast film made from compounded latex which was allowed to settle overnight (refer experimental section for further description on this)</i>

Interestingly, none of the dipped composite film (symbolized as *D* in *Figures 3* and *4*) displayed any surface resistance reading. Under normal condition, this happens when a material is highly insulative and hence, beyond the measurement limit of the meter. This observation suggests the dipped films were essentially insulative regardless of the graphene dosage, even up to high level of 6 phr. In contrast, cast films of parallel graphene dosages (symbolized as *C*) already gave readings within the static dissipative or conductive range. One possible reason for this could be associated with the different nature of film formation for the dipped and cast films. For dipped films which use the aid of coagulant, a thin layer of latex is immediately gelled onto the glass former upon contact with the coagulant. This essentially locks the incorporated graphene within the latex matrix almost instantly, leaving not much opportunity for the graphene flakes to further orientate or align themselves. Cast films on the other hand, are prepared by pouring the latex onto a glass mold and the latex is allowed to dry slowly at room temperature without the aid of coagulant. During this slow drying period, both the latex particles as well as the incorporated graphene flakes have high mobility until up to a certain extent where the latex particles coalesce and the cast film becomes dried enough to cease mobility of the graphene. Before reaching this stage, the heavier graphene flakes have likely sediment while the lighter ones are still dispersed within the latex interstices. Given time, it is possible that this “*micro phase separation*” of graphene from the latex results in a thin deposit of closely connected graphene layers at the far side (*i.e.* bottom) of the cast NR films. Graphene is conductive by nature hence the continuous “*connectivity*” of these graphene flakes within the NR matrix will cause the insulating NR film to exhibit conductivity. Coagulant-assisted dipped films failed to show any conductivity simply because the graphene flakes are immediately locked haphazardly within the NR latex matrix. This “*immediate locking*” prevents the graphene flakes to orientate or connect with each other to form any conductive path.

This study also shows that in order to exhibit conductivity, graphene need to be used at relatively high dosage compared to other rubber chemicals involved in a conventional latex formulation for dipped products. This was initially deduced from the cast films made from “*settled latex*” as described earlier in the experimental section. In reality, “*settled latex*” simulates a condition whereby graphene content is increased simply by removing the upper portion of latex after the graphene are allowed to settle to the bottom of the container, and the latex is then stirred again before cast films are made out of it. From *Figure 3*, it can be seen that throughout the series of experiments carried out, only cast films prepared from the “*settled latex*” (symbolized as *CS*) showed signs of static dissipative or conductive at low “*apparent*” dosage of graphene. In subsequently experiments, this conjecture was confirmed by actual dosing of the latex with high amount of graphene and the cast films made were indeed found to be static dissipative or conductive. In general, results suggest that in order to enter the static dissipative region, at least 3.5 phr of graphene is needed,

and at 4 phr the composites could be made conductive. Nevertheless, these observations were found to be rather erratic whereby measurements at different parts of the films sometimes gave different results. It was also noticed that for cast films, the surface facing the glass mold (bottom) would almost always display stronger conductivity than the film surface facing the air (top). This supports the graphene "*micro phase separation*" explained earlier whereby during the slow drying process of the cast latex films at room temperature, the bottom film surface likely has a layer of connected graphene flakes while the top film surface comprised haphazardly non-connected "*floating*" lighter weight graphene, a phenomenon attributed to simple nature of sedimentation involving particulates of different sizes and weights.

Figure 4 shows the results for studies with DPNR and ENR specialty latexes. For this study, only cast films were prepared, and the graphene dosage was fixed at 3.5phr in view of the favorable conductivity behavior observed in the earlier experiments described above. Interestingly regardless of types of latexes or experimental conditions, results consistently showed that the top surfaces (*i.e.* surface facing the air) of all cast films were insulative. In contrast, some of the bottom surfaces (*i.e.* surface facing the glass mould) were either static dissipative or conductive. This suggests that while the wet latex films were being left to dry slowly at ambient condition, the graphene platelets have also started to sediment to the bottom. Slowness of the drying process allowed free mobility to the graphene to settle near to the bottom and formed connecting layers which consequently conferred some extent of conductivity to the dried films. When this happened, the bottom surface of cast films would expectedly have greater amount of graphene while the top surface would be nearly depleted of graphene as the slow drying process continued. Sedimentation of graphene would eventually cease when the cast films began to dry up, blocking any further mobility. This is the very reason dipped films failed to show any static dissipative or conductive properties compared to their cast counterparts when compounded with the same amount of graphene. Coagulant-dipped films undergo almost immediate ceasing of particle mobility upon contact with the coagulating agent, and in this manner it causes the graphene platelets to form randomly dispersed entities rather than connecting layers which facilitate conductivity.

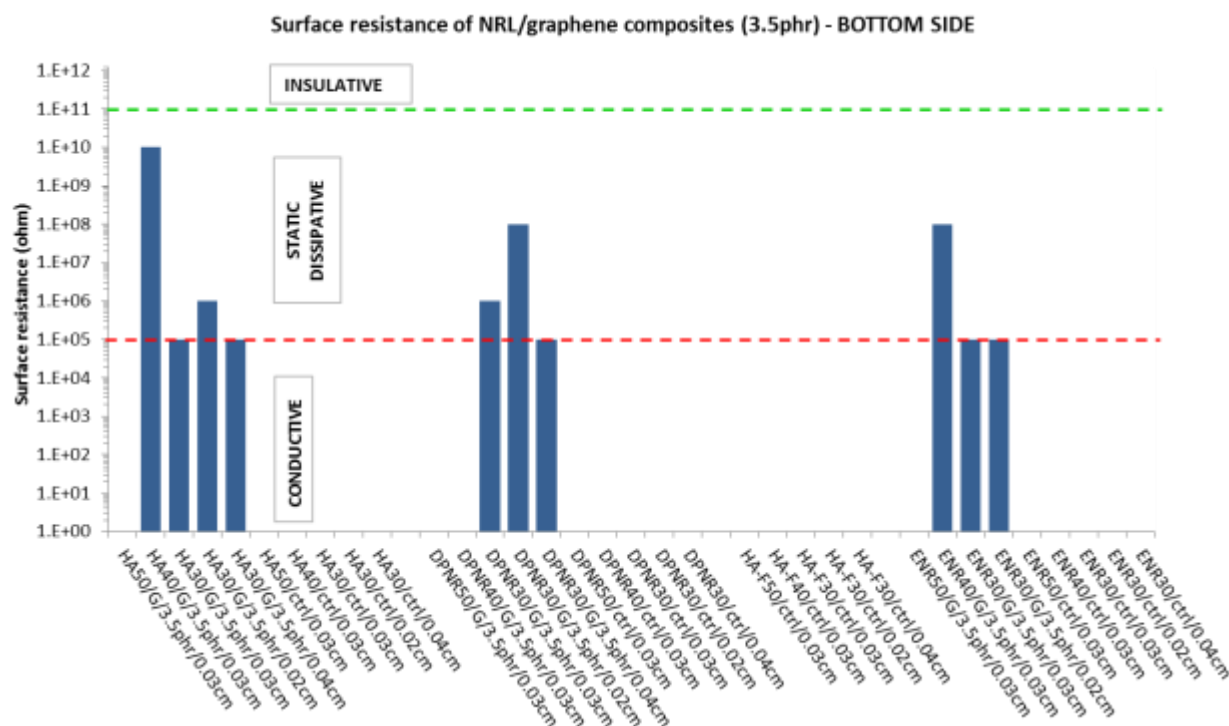


Figure 4: Surface resistance of NR latex cast films compounded with 3.5phr of graphene

Abbreviations (on x axis):

- HA High ammoniated natural rubber latex (compounded using generic thin film formulation)
- HA-F High ammoniated natural rubber latex (compounded using foam formulation)
- DPNR Deproteinized natural rubber latex (compounded using generic thin film formulation)
- ENR Epoxidized natural rubber latex (compounded using generic thin film formulation)
- G graphene
- phr part per hundred of rubber (number preceding it denotes amount of graphene used)
- Ctrl control film (without graphene)
- 50, 40, 30 total solids content at indicated percentage (%)
- 0.02, 0.03, 0.04cm film thickness (cm)

When the cast films were prepared using latex at varying TSC ranging from 50% to 30%, results showed that for all types of latexes (HA, DPNR and ENR), as the TSC became lower, there was greater tendency for the cast films (bottom surface) to move from being insulative to become static dissipative or conductive. This again shows that some extent of sedimentation and alignment of graphene had taken place to form connecting graphene layers during slow drying of the wet latex films; obviously mobility of the graphene to the bottom side of the films was facilitated better when the latexes were more dilute (*i.e.* lower TSC).

When the films were prepared using the same TSC *i.e.* 30% but with varying thickness ranging from 0.02 - 0.04 cm, the cast films trended toward static dissipative and conductive

as the film thickness was increased. This is understandably attributed to the greater amount of latex being used to increase the film thickness, along which more graphene would have also been incorporated into the thicker films as a result. This observation simply confirmed that the conductive nature of NR latex cast films could be attained by increasing the amount of incorporated graphene.

Between the different NR latexes studied *i.e.* HA, DPNR and ENR, results generally indicated that HA and ENR have stronger tendency to attain static dissipative or conductive nature quicker than DPNR when dosed with graphene under the same experimental conditions. This observation suggests the innate proteins in the NR latex likely have some strong influence or roles in boosting the conductive force of NR latex in the presence of graphene.

It has been found by observation that the cast films, the top sides (facing the air during film drying) were insulative while the bottom sides (facing the glass mold) became static dissipative or conductive with increasing graphene dosage [7]. The film formation process speculated as the following sequences shown in Figure 5.

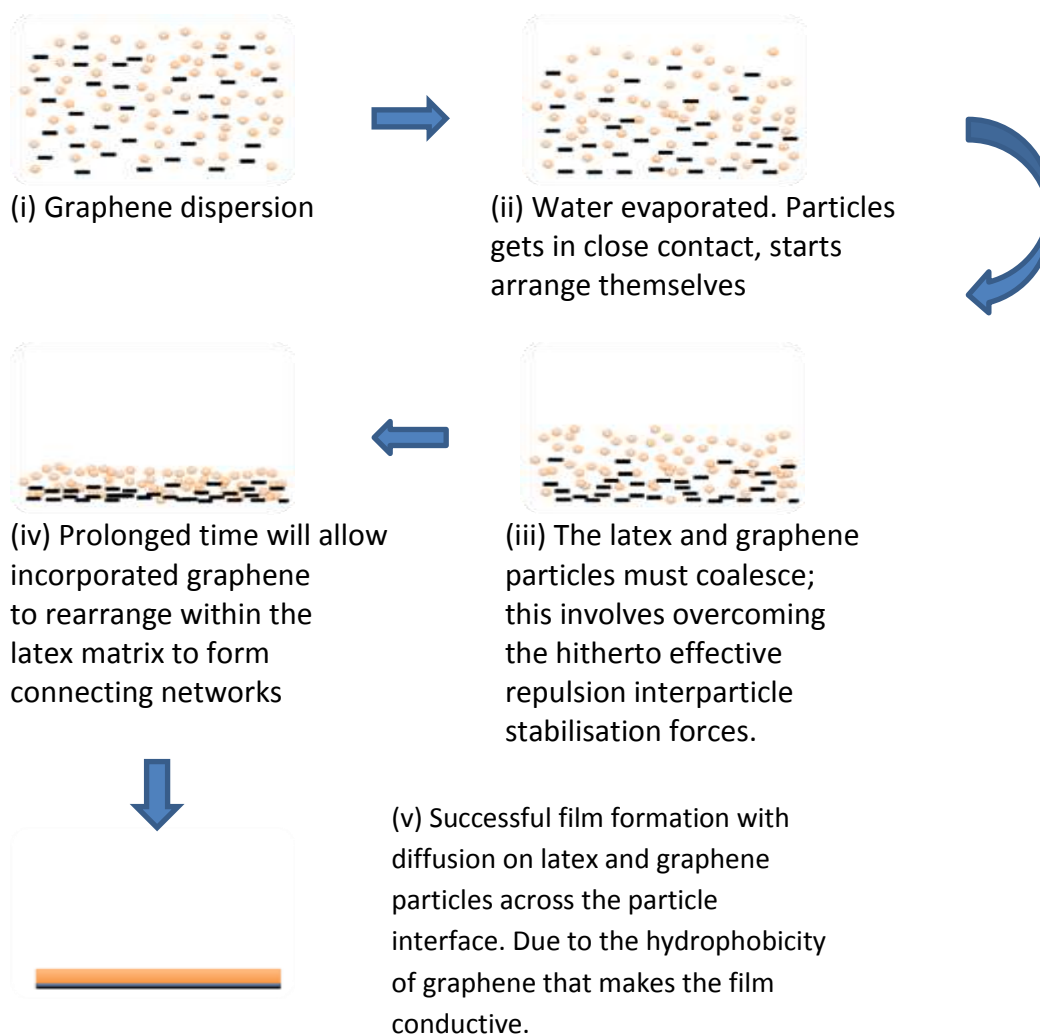


Figure 5: Schematic process of film formation of the conductive film.

During evaporation of latex from liquid to solid film, given enough time and fluidity, for the incorporation of graphene to rearrange within the latex matrix to form connecting networks which is crucial for conductivity. Meanwhile, for dipped film undergoes immediate solid film formation which locks the graphene in situ without creating much connected networks. However, cast film solidifies slowly, allowing the graphene to connect and form conductive network. The bottom side of cast films also consistently showed lower resistivity values than the top side. This suggests that during the slow drying process, the heavier graphene likely move to the bottom, causing the bottom side to end up with layers of connected graphene, while leaving the top side with haphazardly non-connected “floating” lighter weight graphene. Latex with lower total solid content was found to facilitate better graphene mobility and alignment towards static dissipative or conductivity film property. Conductive nature of NR latex cast films could be achieved simply by increasing the graphene dosage. HA and ENR have stronger tendency than DPNR to attain static dissipative or conductive range quicker, suggesting the role of innate proteins in this phenomenon.

CONCLUSIONS

For all types of NR latexes *i.e.* HA, DPNR and ENR, all the coagulant-dipped films were insulative regardless of the increasing graphene dosage. In contrast, for the cast films, only the top side was insulative while the bottom side was observed to be either static dissipative or conductive. Lower TSC of latex facilitated better graphene mobility and alignment to form connecting layers at bottom side of the cast films towards static dissipative or conductivity property. Conductive nature of NR latex cast films could be attained simply by increasing the amount of incorporated graphene. HA and ENR have stronger tendency than DPNR to attain static dissipative or conductive nature quicker, suggesting the role of innate proteins in this phenomenon.

REFERENCES

- [1] B.T. Kelly, Physics of graphite, Applied Science Publishers, London (1981)
- [2] J. Texter, Graphene Dispersions, Curr. Opin. Colloid Interface Sci 19 (2014), 163–174,
- [3] M. Lotya, Y. Hernandez, P.J. King, R.J. Smith, V. Nicolosi, L.S. Karlsson, F.M. Blighe, S. De, Z. Wang, I.T. McGovern, G.S. Duesberg, J.N. Coleman, Liquid Phase Production of Graphene by Exfoliation of Graphite in Surfactant/Water Solutions, J. Am. Chem. Soc 131 (2009) 3611–3620
- [4] A.A. Azira, M.M. Kamal and M. Rusop, Reinforcement of graphene in natural rubber nanocomposite, AIP Conference Proceeding 1733,020003 (2016)
- [5] A. Mohamed, A.K. Anas, S.A. Bakar, T. Ardyani, W.M.W. Zin, S. Ibrahim, M. Sagisaka, P. Brown, J. Eastoe, Enhanced Dispersion of Multiwall Carbon Nanotubes in Natural Rubber Latex Nanocomposites by Surfactants Bearing Phenyl Groups, J. Colloid Interface Sci 455 (2015)
- [6] C.F. Matos, F. Galembeck, A.J.G. Zarbin, Multifunctional and Environmentally Friendly Nanocomposites between Natural Rubber and Graphene or GrapheneOxide, Carbon 78 469-479 (2014)
- [7] T. Kim Song, A. A. Azira, M. Kok Lang, L. Hui Mei, R. Roslim, Solid State Phenomena, Vol. 264, pp. 17-20, 2017