Blend of Styrene Butadiene Rubber/Natural Rubber with Graphene Inclusion (BR/NR/GE): A review

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Rubbers are used in different environmental conditions. Due to their intrinsic nature of being highly elastic and their relatively low strength, rubbers cannot efficiently resist some of the stresses applied to them. In order to improve the electrical conductivity, stiffness and thermal strength of natural and synthetic rubber blends, graphene can be used as a suitable candidate as additive/filler. The study will review the influence of the blending techniques employed, miscibility, and how graphene can be incorporated into the styrene-butadiene rubber (SBR)/natural rubber (NR) blends.

Keywords: natural rubber, synthetic rubber, graphene, additive/filler

Mengel van stireenbutadieenrubber/natuurlike rubber met grafeeninsluiting (BR/NR/GE): 'n Oorsig Rubber word in verskillende omgewingstoestande gebruik. Omdat hulle intrinsiek hoogs elasties is maar oor relatief lae sterkte beskik, kan rubber nie sommige van die spannings wat daarop uitgeoefen word, doeltreffend weerstaan nie. Ten einde die elektriese geleidingsvermoë, styfheid en termiese sterkte van natuurlike en sintetiese rubbermengels te verbeter, kan grafeen 'n geskikte kandidaat wees om as bymiddel/vulstof gebruik te word. Hierdie studie bied 'n oorsig van die invloed van die mengeltegnieke wat gebruik word, van mengbaarheid, en van hoe grafeen in mengels van stireenbutadieenrubber (SBR)/natuurlike rubber (NR) geïnkorporeer kan word.

Sleutelwoorde: natuurlike rubber, sintetiese rubber, grafeen, bymiddel/vulstof

Introduction and background

A polymer blend is defined as a mixture of two or more polymers. Polymer blends are fabricated in order to create or produce a novel polymer composite with physical properties different from the starting materials. Combinations of polymers can be manufactured in order to produce polymer blends with varying properties, which differ from those of the individual components. In 1846 Alexander Parkes, a metallurgist, invented the first polymer blend. The mixture was made of three polymers, namely: cellulose nitrate, natural rubber, and gutta-percha. This blend: by Alexander Parkes, gained traction after being used successfully in electrical insulation, protection of wounds, and in photography (White, 1998).

There are a number of reasons for the manufacture of polymer blends, some of which are mentioned above. In order to manufacture polymer blends, certain factors need to be considered. Likewise, the dispersity of the additive in the matrix. Many researchers have found that additives easily agglomerate when incorporated into a polymer matrix. Therefore, in order to circumvent agglomeration, additives, e.g., graphene are functionalised before being incorporated into a matrix.

In order to fabricate a rubber composite, a standard process called vulcanisation is used to crosslink the rubber matrix. Goodyear discovered the vulcanisation process in 1839. Goodyear heated natural rubber mixed with sulfur in a temperature range of between 130 to 180 °C and observed a chemical reaction. The mixture is hardened as a result of the addition of sulfur, forming a crosslink with natural rubber (Ileda, 2014). However, the mixture of rubber and sulfur has some form of network inhomogeneity. The development of new ways in which rubbers can be vulcanised without showing network inhomogeneity, is crucial.

Mansilla, et al., (2016) found that elastomeric blends recorded improved properties when compared to compounds made with pure elastomers. The elastomeric blends, in most cases, are reinforced with particles in order to enhance their properties. Fillers that are usually used in the rubber industries are carbon black, silicate, and carbon nanotubes. However, some of the listed fillers are not environmentally friendly, while some do not improve the structural and non-structural functions of elastomers.

This study will review styrene-butadiene/natural rubber blends, as opposed to rubber blends in general. The review will focus more on the application of styrene-butadiene/natural rubber blends, the significance of the fabrication methods, the different additives that are typically used in the rubber industry, and the emerging additives that can change the rubber industry for the better.

Styrene-butadiene/natural rubber blends

Natural rubber is extracted from the *Hevea brasiliensis* tree, a plant, native to the tropical Americas, in the form of latex (Cornish, 2014). Conventional natural rubbers are elastic and flexible. These properties enable natural rubbers to return to their original shape after an applied stress/tension is removed. In the science and engineering fraternity, natural rubber is known as *cis*-1,4 polyisoprene (Puskas, et al., (2014). Figure 1 shows the chemical structure of *cis*-1,4 polyisoprene.
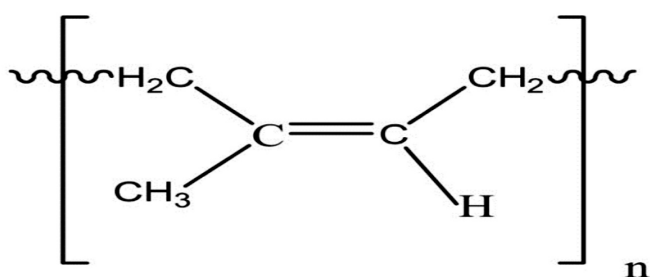

Figure 1: Chemical structure of cis-1,4 polyisoprene, a natural rubber (Ferreira, et al., 2009)

Due to the natural rubber's good properties, such as: high tensile strength, elasticity, flexibility, resistance to fatigue, and antiviral permeation, natural rubber has been extensively employed as the polymer matrix in the fabrication of tyres, gloves, condoms, etc. Natural rubber is biodegradable, and this property makes it the only elastomer that is environmentally friendly, in terms of biodegradability (Matos, et al., 2014). In

1844, Charles Goodyear accidentally mixed sulfur with natural rubber, thereby, causing natural rubber to become resilient, while retaining its elasticity (Puskas, et al., 2014). Chemically, sulfur crosslinks with small chains of natural rubber. The whole process is called vulcanisation, whereby natural rubber goes through the process of curing at a temperature of 150 °C. In order to make natural rubber competitive, but also to be able to meet mechanical requirements, vulcanisation packages are used to improve the properties of the natural rubber. In the curing of natural rubber (vulcanisation), there are the main ingredients that make curing efficient and economical; these ingredients are a sulfur accelerator, metal oxide, and fatty acid. Zinc oxide is a metal oxide, which is another standard additive that is added to natural rubber in order to improve the resistance of natural rubber against heat and ultraviolet degradation. There are more than 50 accelerators that are currently in use on a commercial scale. Accelerators in the typical vulcanisation system, are added in order to increase the speed of vulcanisation, but also to enable vulcanisation to proceed at lower temperatures, than the usual vulcanization temperature.

Styrene-butadiene rubber (SBR) is a synthetic rubber that is made by the co-polymerisation of styrene and butadiene monomers (Figure 3). SBR is comprised of between 10–25% of styrene and between 60–70% of butadiene monomers. This rubber was synthesised because some countries, during World War II, were not able to import natural rubber from tropical countries, hence, the aim was to synthesise a rubber as a substitute for natural rubber. The SBR nanocomposites are used to fabricate products, such as tyres, footwear, belts, and other industrial products. The key benefits of using SBR as a polymer matrix, are properties, such as: abrasion resistance, impact strength, and high tensile strength. SBR is often vulcanised by using the same agents that are used for vulcanising natural rubber. SBR performance is poor without reinforcement; hence, silica is the conventional reinforcement that is used to enhance the mechanical properties of SBR.
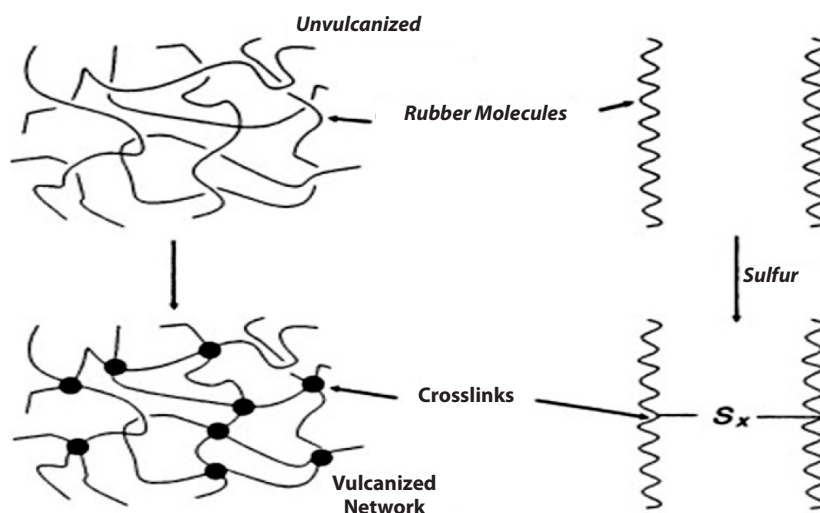

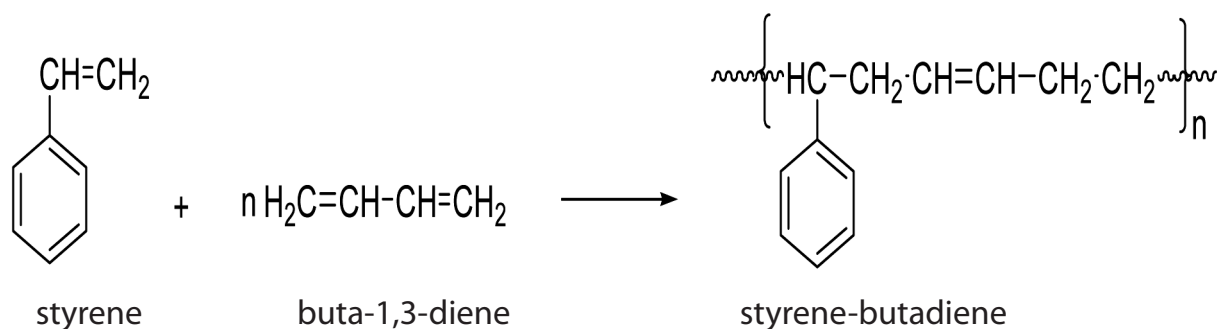**Figure 2:** Crosslinking of rubber networks (Coran, 2003)

Figure 3: The resultant chemical structure of styrene-butadiene rubber, a synthetic rubber

Natural rubber possesses good mechanical and dynamic properties. However, it has drawbacks, such as: low weathering, lack of oil resistance, and weak abrasion resistance, which make it necessary to be blended with styrene-butadiene rubber in orderto improve some of the properties. The NR/SBR blends are used in a wide range of applications, such as in the defence, automobile, aerospace, construction, medical care, and food industries.

Graphene as a filler to reinforce rubbers

The conventional filler that is used to reinforce NR/SBR blends is carbon black. However, the precursor of carbon black is crude oil, and the preparation processes generate excessive wastes (Kang, et al, 2017). Consequently, it is vital to research new fillers that can be incorporated into the rubber matrix without disadvantaging the environment. Graphene, as a filler in SBR/NR blends, shows significant potential, making it suitable to replace carbon black and add new properties to rubber blend composites.

Graphene is an allotrope of carbon in the form of a single layer of atoms in a two-dimensional honeycomb lattice, in which one atom occupies each vertex. Graphene is identified as a good candidate filler of many polymers to achieve their multi-

functionality, given the immense properties, such as high surface area, high gas performance barrier, good mechanical properties, and excellent electrical and thermal conductivity (Zhang, et al., 2019). Graphene is found in many forms; the format relies on the number of carbon layers that graphene has. In the market, there is graphene between 1–3 layers of carbon, and multi-layer graphene, also known as graphene nanoplatelets, between 2–10 layers of carbon (Mason, 2020).

The literature has not reported any significant information on SBR/NR blends, reinforced with graphene; thus, this study reviews rubber blends reinforced with graphene. Graphene is reported to be a significant filler to be studied in the rubber industry. The limitations that are associated with graphene, are such that it agglomerates when incorporated into rubber blends. In order to overcome the agglomeration of graphene into the rubber matrix, graphene can be functionalised. Graphene is functionalised as a result of its modification for good dispersity, which often, has an impact on the mechanical properties of the resulting rubber composites. Figure 4 shows the influence of graphene on the mechanical properties of polyurethane (PU) rubber. The mechanical properties of PU, increase with increment of various loadings of graphene.
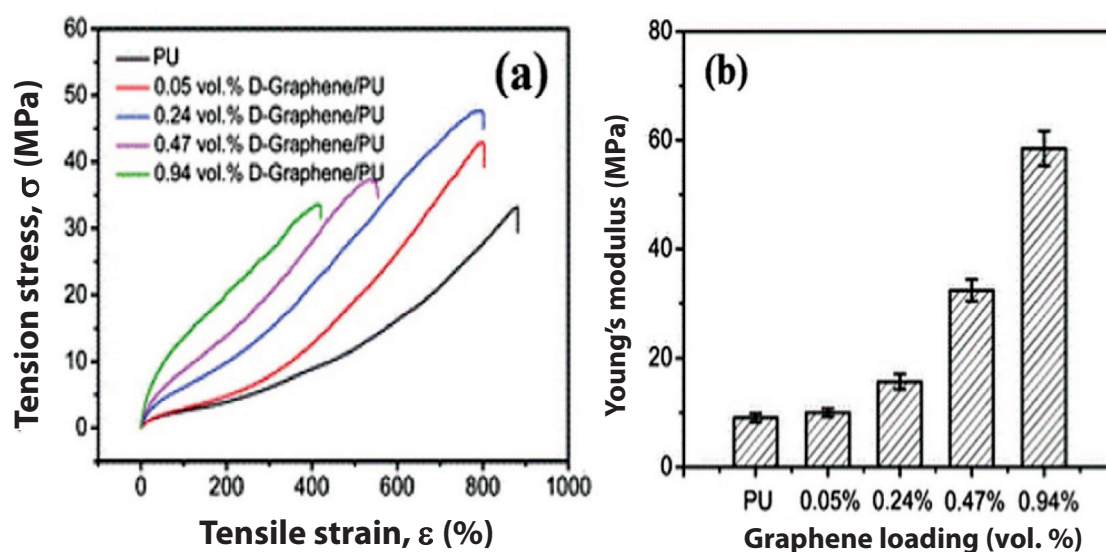

Figure 4: (a) Characteristics stress-strain curves for the PU/Graphene (b) Young's modulus of PU/graphene (Papageorgiou, et al., 2017)

The Hummers' method is a standard method used to functionalise graphene. Natural graphite is often used as a precursor to synthesise graphene oxide in the Hummers modified method. Strong oxidants, such as: concentrated sulfuric acid, potassium nitrate acid and potassium permanganate are used to oxidise graphite (Sohail, et al., 2017). Graphene oxide can be produced in an oxidation reaction, by producing functional groups on the basal plane (hydroxyl and epoxy groups) and edges (carboxyl acid groups). These functional groups that are found in the basal plane and the edges of graphene oxide, are hydrophilic, since they contain oxygen groups that enable the graphene oxide to be soluble in water (Shang, et al., 2019).

Oxygenated graphene, poorly conducts electricity and has poor thermal stability. Hydrogen hydrazine can be added to graphene oxide/rubber latex solution to deoxygenate or reduce the oxygen groups in order to restore both the electrical conductivity and thermal stability of the resulting composites (Su, et al., 2010). However, the use of hydrogen hydrazine to restore electrical conductivity and thermal stability, deteriorates the properties of the polymer matrix, especially, if thin film nanocomposites are to be fabricated (Lim, et al., 2019).

Kang, et al., (2017) adopted the Fourier-transform infrared spectroscopy (FTIR) to monitor the chemical changes from pristine graphite, graphene oxide to reduced graphene oxide. FTIR was used to evaluate the presence of the envisaged functional groups. The authors found that after the addition of hydrazine hydrate, the C=O absorption peak of graphene oxide disappeared from the FTIR spectra. Hydrazine hydrate successfully, reduced the oxygen groups on the surface of graphene oxide. Kang, et al., (2017) employed the X-ray diffraction technique to analyse the interlayer spacing patterns

of the above-mentioned samples. The interlayer *d*-spacing of graphene oxide is greater than that of graphite. This is because the oxidation reaction expanded the distance between the graphene sheets.

Zhang, et al., (2019) employed the Raman spectroscopy technique that is equipped with a 532 nm wavelength laser and a 50X objective lens to evaluate the exfoliation of graphite into GO. They prepared GO by using the Hummers' modified method. The *D* and *G* bands of GO were observed at wave numbers of 1356 cm⁻¹ and 1590 cm⁻¹, respectively. These results are attributed to the fact that the exfoliation was successful since they are the in-phase stretching vibration of the C-C bonds in the graphite lattice and the disorder in the graphite sheet.

Dong, et al., (2020) studied the functionalising capabilities between N-cyclohexyl-*2*-benzothiazolesulfenamide (CZ) and hydrazine hydrate (HH) that can be used to aid the de-agglomeration of graphene (G) and hence, have a uniformly dispersed graphene and good interfacial interaction with SBR/NR blends. The authors found that with HH-G incorporated into the polymer blend, the HH-G sheets were stacked with many layers in the rubber matrix, indicating the poor dispersion of HH-G, whilst CZ-G sheets were almost monodispersed in the rubber matrix. The authors conducted that the surface of the CZ-G was rough with the polymer matrix and the interface zone between CZ-G and the rubber phase being blurry, thereby, proving the good compatibility and strong interfacial interaction between CZ-G and rubber blends. The advantage of CZ is that it also forms a part of the vulcanisation fillers. Therefore, by using it as a functionaliser, it can lower the costs, but also the number of fillers that are expected to be incorporated into the polymer blends.
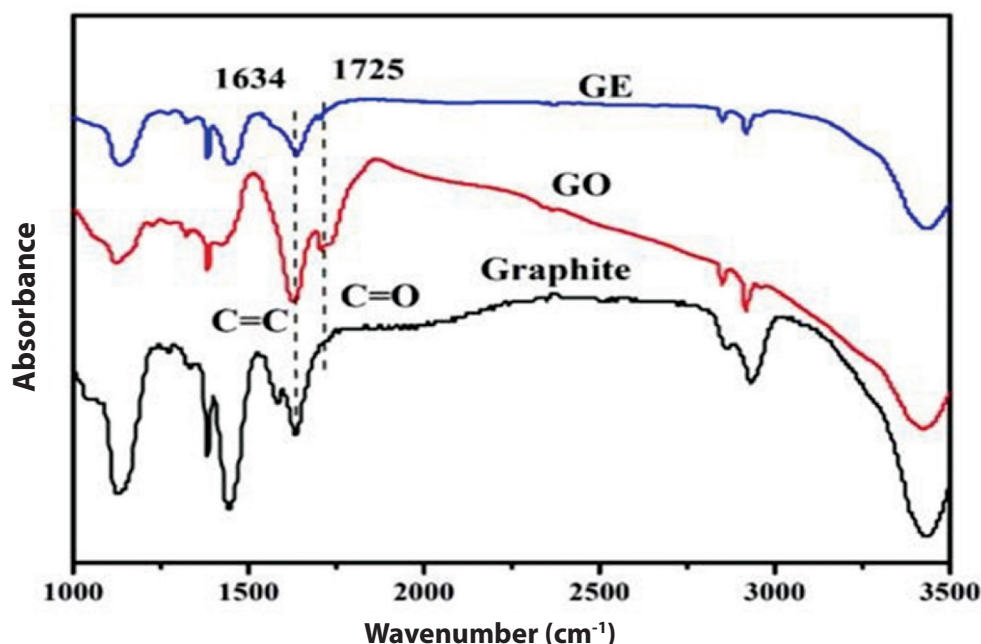

Figure 5: Fourier transform infrared to monitor the chemical change from pristine graphite, graphene oxide to reduced graphene oxide (Kang, et al., 2017)

Fabrication methods of NR/SBR blend

There are various methods that are used to fabricate rubber nanocomposites. Although, where nanoparticles are involved in reinforcing rubbers, solution mixing, latex blending, melt mixing and hot-melt extrusion are the main fabrication techniques employed to prepare rubber nanocomposites. Every fabrication method, has its advantages and disadvantages. A polymer blend is the physical mixture of two or more polymers without any chemical reaction between them, therefore, the fabrication technique of polymer blends is imperative, since it contributes immensely to the properties of the blends. It is crucial to choose a fabrication method that is in line with the required attributes, since the technique can affect the morphology and the interaction of the two polymers.

The latex blending is the blending of a polymer in the form of a latex, followed by drying or coagulation. In the process of blending, the fillers can be added without any hindrances and other processes, e.g., ultrasonication can be performed. It has been, reported that where latex-blending technique is employed, fillers disperse evenly. Furthermore, this technique minimises problems, e.g., the chemical changes caused by heat and friction. The disadvantage of latex blending is that it has not been widely explored in the industries. It is mostly used for research purposes.

The electrostatic adhesion mechanism has proven to be effective when a latex blending technique is employed to blend natural and synthetic rubbers. The ion migration from natural to synthetic rubber, enhances the adhesion and cohesion of the synthetic/natural rubbers in the blends (Linares, et al., 2010). Therefore, ion migration can modify the compatibility of the

polymer blends, which also contributes to the enhancement of the mechanical properties. Jose, et al., (2005) compared poly (vinyl chloride) (PVC) and natural rubber blends, prepared by latex blending and dry blending. The authors found that with latex blending, the aging resistance, oil resistance and processability of PVC/NR blends were found to have improved when compared to those that were prepared by dry blending.

Compatibility of SBR/NR blends

Rubber blends are classified into two types, namely: immiscible and miscible blends (Kaliyathan, et al., 2020). The immiscible rubber blends are also called heterogeneous blends. The immiscible blends, evaluated under a microscope, indicate a phase-segregated morphology. They are known to have poor adhesion of which, compatibiliser is necessary when such rubbers are to be blended. Moreover, on the other hand, miscible rubber blends are homogeneous and compatible. Compatible blends are reported to exhibit better mechanical properties when compared to incompatible blends; hence, compatible blends are easy and relatively cheap to fabricate/mould (Mohamed, 2005). There are no miscible natural rubber blends in the market due to the associated hydrophobic properties of natural rubber. The essential improvement of miscibility that can be achieved, where natural rubber is involved, is partial miscibility. Through that, the improved properties can be observed when compared to totally immiscible rubber blends (Cook, 2021).

Transmission electron microscopy (TEM), dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and atomic force microscopy (AFM) are techniques that are used to characterise the miscibility of polymer blends (Pichayakorn, et al., 2013). However, the TEM can characterise the blend morphology, but the sample preparation is time-consuming. DMA and DSC indirectly characterise the miscibility without giving information about the blend morphology. In contrast, AFM offers faster sample preparation and understandable information about the morphology of the blends (Jeon, et al, 2003). Klat, et al., (2018) studied the (AFM) technique by comparing the results of the phase morphologies of NR/SBR blends obtained, from AFM with TEM. The authors found that the AFM technique offers faster sample preparation and again, the phase morphology of the blends obtained from the TEM is similar to that obtained from AFM. Klat, et al., (2018) concluded that the AFM is one of the best techniques that can be used to characterise the miscibility of polymer blends. The miscibility of NR/SBR blends improves with increasing vinyl content. In Figure 6, the authors compared the topography maps of low vinyl (LV) and high vinyl (HV) contents of NR/SBR blends.
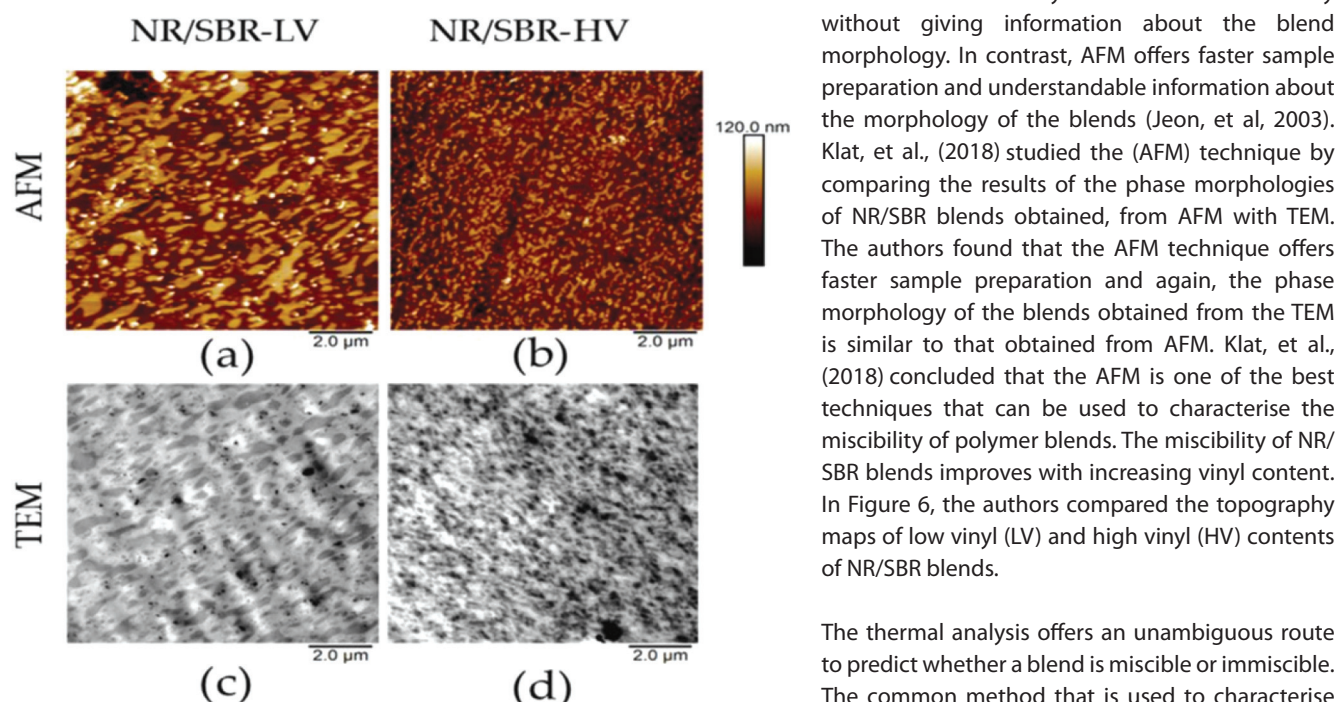
The thermal analysis offers an unambiguous route to predict whether a blend is miscible or immiscible. The common method that is used to characterise the glass transition temperature (T_g) of polymer blends is the DSC. The glass transition temperature

Figure 6: Comparison of atomic force microscopy (AFM) topography maps with TEM images: AFM topography maps of (a) NR/SBR–LV and (b) NR/SBR–HV and TEM images of (c) NR/SBR–LV and (d) NR/SBR–HV

can be used to evaluate the miscibility of polymer blends. Immiscible blends, often record a two-phase characteristic of the T_g, while the miscible polymer blends exhibit a single phase character on the DSC thermographs. Salgueiro, et al., (2007) studied the blends of SBR/NR by employing the Positron Annihilation Lifetime Spectroscopy (PALS) and the DSC techniques. The authors found that for pure elastomers (natural rubber and styrene-butadiene rubber), only one T_g each, was observed. Furthermore, in the SBR/NR blends, two T_gs were, shown, proving that SBR/NR blend is an immiscible blend, and a blending agent is an essential requirement to improve the compatibility of the two rubbers.

Table I: Glass transition temperatures (T_gs) for pure NR, pure SBR and the SBR/NR blend (Pichayakorn, et al., 2013)

	Compound		
	A	**B**	**C**
SBR	0	50	100
NR	100	50	0
T_g [K] (DSC)	213,1	214,5/226,4	229,6

Conclusion

The thermal analysis any polymer mixture, is a good measure of polymer blend miscibility. The AFM is one of the techniques that stands out amongst other techniques as one of the best, as it details the understandable results of the degree of miscibility of polymer blends. Latex blending is an excellent technique that can be used to incorporate graphene when compared to dry blending. Furthermore, the latex blending technique should be capacitated for it to be used to fabricate products or composites in the industries. The combination of NR/SBR/GE, shows a potential for the resulting product to be applied in wearable devices and sensitive strain sensors; however, more research is still needed on the modification of these blends.

Dates

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