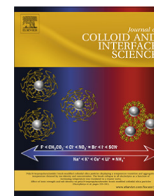




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Regular Article

Rational design of aromatic surfactants for graphene/natural rubber latex nanocomposites with enhanced electrical conductivity



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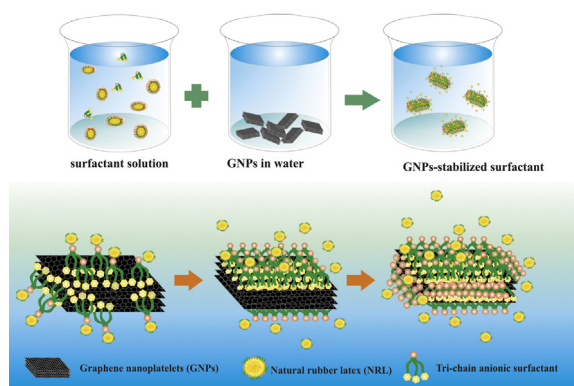
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GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Graphene nanoplatelets (GNPs) can be dispersed in natural rubber matrices using surfactants. The stability and properties of these composites can be optimized by the choice of surfactants employed as stabilizers. Surfactants can be designed and synthesized to have enhanced compatibility with GNPs as compared to commercially available common surfactants. Including aromatic groups in the hydrophobic chain termini improves graphene compatibility of surfactants, which is expected to increase with the number of aromatic moieties per surfactant molecule. Hence, it is of interest to study the relationship between molecular structure, dispersion stability and electrical conductivity enhancement for single-, double-, and triple-chain anionic graphene-compatible surfactants.

Experiments: Graphene-philic surfactants, bearing two and three chains phenylated at their chain termini, were synthesized and characterized by proton nuclear magnetic resonance (¹H NMR) spectroscopy. These were used to formulate and stabilize dispersion of GNPs in natural rubber latex matrices, and the

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Nomenclature

^1H NMR	proton nuclear magnetic resonance	TCE	thermal conductivity enhancement
AFM	atomic force microscopy	TSC	total solid content
CNTs	carbon nanotubes	VOCs	volatile organic compounds
Cmc	critical micelle concentration	A_{cmc}	limiting headgroup areas at the cmc
DRC	dry rubber content	γ	surface tension
FESEM	field emission scanning electron microscopy	γ_{cmc}	limiting surface tension at cmc
GNs	graphene nanosheets	$I_{\text{D}}/I_{\text{G}}$	intensity ratio of disorder-induced d-band and the G-band
GNPs	graphene nanoplatelets	Γ	limiting surface excess
HRTEM	high-resolution transmission electron microscopy	Γ_{m}	limiting values of surface concentration of monolayers
MWCNTs	multi-walled carbon nanotubes	R_{a}	polar axis ratio of ellipsoidal micelle
NR	natural rubber	R_{b}	equatorial axis ratio of ellipsoidal micelle
NRL	natural rubber latex	R_{disk}	stacked disk radius
PS	polystyrene	R_{sphere}	spherical micelle radius
PSS	poly(sodium-4-styrenesulfonate)	θ	surface coverages
SANS	small-angle neutron scattering	X	aspect ratio of ellipsoidal micelle
SDBS	sodium dodecylbenzenesulfonate	ζ -potential	zeta potential
SDS	sodium dodecylsulfate		
SLD	scattering-length density		

properties of systems comprising the new phenyl-surfactants were compared with commercially available surfactants, sodium dodecylsulfate (SDS) and sodium dodecylbenzenesulfonate (SDBS). Raman spectroscopy, field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), and high-resolution transmission electron microscopy (HRTEM) were used to study structural properties of the materials. Electrical conductivity measurements and Zeta potential measurements were used to assess the relationships between surfactant architecture and nanocomposite properties. Small-angle neutron scattering (SANS) was used to study self-assembly structure of surfactants.

Findings: Of these different surfactants, the tri-chain aromatic surfactant TC3Ph3 (sodium 1,5-dioxo-1,5-bis(3-phenylpropoxy)-3-((3-phenylpropoxy)carbonyl) pentane-2-sulfonate) was shown to be highly graphene-compatible (nanocomposite electrical conductivity = $2.22 \times 10^{-5} \text{ S cm}^{-1}$), demonstrating enhanced electrical conductivity over nine orders of magnitude higher than neat natural rubber-latex matrix ($1.51 \times 10^{-14} \text{ S cm}^{-1}$). Varying the number of aromatic moieties in the surfactants appears to cause significant differences to the final properties of the nanocomposites.

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1. 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 physico-chemical properties. The wide range of potential applications of graphene call for an increased demand for graphene and derivatives, such as graphene nanoplatelets (GNPs). GNP is a multilayer graphene consisting of ~ 10 – 30 sheets of graphene with inherited monolayer graphene properties [1a,b]. As such, GNPs are much easier to obtain than graphene nanosheets (GNs) which have single-, bi- or few layers (no more than ten), and so have potential for large scale production of graphene-based materials [1a,b]. Now, the challenge is to explore which materials graphene can potentially add significant value.

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 of importance 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 inter-sheet 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].

The advantages offered by surfactant-stabilized graphene dispersions, with the chemical anchoring offered by a hydrophilic NR matrix to fabricate nanocomposites, can be accomplished using a latex-based method to generate natural rubber latexes (NRLs). This technique was initially used for the dispersion of carbon nanotubes (CNTs) in polymer matrices [7,8]. A key feature distinguishing this latex-based approach from other nanocomposite preparation methods (e.g. solvent mixing) is the use of surfactants. These added surfactants are physico-chemically adsorbed at graphene-polymer interfaces and reduce the surface energy

(interfacial tension) by balancing lyophobic and lyophilic interactions. To date, there are only a limited number of studies concerning graphene/polymer nanocomposites obtained by this straightforward latex technique; and these report only commercially available surfactants, such as the anionic sodium dodecylsulfate (SDS), sodium dodecylbenzenesulfonate (SDBS) and the non-ionic Triton-X100 for example [9,10]. Although these surfactants are said to offer improved graphene dispersion stability, undoubtedly certain optimal surfactant structures will offer greater graphene-compatibility, and surfactant concentration may also affect the efficiency of the nanofiller. Thus, when employing surfactants as dispersants for graphene, it is critical to select appropriate surfactant structures bearing “graphene-philic” moieties. For enhanced dispersion stability, the interaction between surfactants and graphenes must be strong enough to cover the graphene surfaces with surfactant shells/layers which prevent close approach of the graphene sheets, and thereby prevent aggregation. It was hypothesized that surfactants bearing multiple aromatic moieties would lead to enhanced interactions with graphenes via π - π interactions, and higher dispersion stabilities [11]. A recent paper showed that graphene compatibility can be enhanced by incorporating multiple aromatic groups, and also alkyl chain branching of the surfactants [9]. It is a logical step to suggest that increasing the number of aromatic rings in surfactant molecules could enhance further still graphene-surfactant dispersion stability.

Previously, a custom made aromatic analogue of the common anionic AOT surfactant has been reported to have very significant CNT-compatibility [5,12]. Furthermore, introduction of a third surfactant chain TC3Ph3 (previously known as TcPh), being the tri-chain version of di-chain aromatic surfactant DC3Ph2 (known as DCPh) was shown to further enhance the dispersion stability. In that work, the synthesized surfactants were used to stabilize CNT dispersions in NRL to form conductive nanocomposites [5,12]. Even though they are used at relatively low concentrations (0.016–0.032 M), in particular the tri-chain surfactant TC3Ph3, exhibited remarkable CNT-compatibility. Although there was only a small change in surfactant structure, a notably improved conductivity enhancement was observed (~ 2 orders of magnitude). This is markedly higher than found for the commercial surfactants SDS and SDBS when used under similar conditions. Clearly, these new custom-made CNT-compatible surfactants appear to have advantages over the common commercial surfactants used in major recent studies [7,8,10].

The purpose of this new paper is to investigate whether a similar strategy can be applied to obtain graphene-compatible surfactants. To reveal any specific effects using these custom made surfactants, comparisons of physico-chemical properties were also made with single chain commercial surfactants; SDS and SDBS (Table 1). The effect of surfactant concentration on electrical conductivity enhancement of the resulting nanocomposites is also considered. The results show that the new DC3Ph2 and TC3Ph3 are viable surfactants for stabilizing dispersions of GNPs in NRL matrices. These findings advance understanding of optimizing graphene-compatibility by modifying surfactant chain architecture. In particular, it is shown here that the number of aromatic moieties per surfactant molecule is an important parameter for improving properties of these nanocomposites.

2. Materials and methods

2.1. Materials

The matrix polymer, NRL was supplied from the Malaysian Institute of Nuclear Technology Research, with the total solid content (TSC) and dry rubber content (DRC) being 54% and 56%,

respectively. Methods to determine the TSC and DRC can be found elsewhere [13]. GNP powder (UG Pro 880, average thickness 0.98–3.54 nm) were obtained from UGENT Tech Pte Ltd and dried in an oven for 6 h at 70 °C prior to use. SDS (99%, System) and SDBS (technical grade, Sigma Aldrich) were used as received. The surfactants DC3Ph2 and TC3Ph3 were custom-made and synthesized as detailed previously [5]. Details regarding surfactant characterization can be found in [supplementary material](#).

2.2. Preparation of graphene dispersion

The GNP dispersions were prepared using surfactants, and a Branson 5510 sonicator, with 135 W of 42 kHz ultrasound. Surfactant concentrations were varied from 0 to 0.032 M. For comparable studies, the filler loading was fixed at 2 wt%, relative to the TSC of the NRL. A known amount of GNP was initially dispersed in a 10 mL surfactant solution and stirred for 1 h. The resulting dispersions were then subjected to sonication for 2 h.

Here, the amount of filler in the composite was calculated based on the dry mass of NRL (TSC). For instance, to prepare composites starting from 2.5 g of NRL, we consider 1.35 g of dry rubber (solid content of 54%). Therefore, the amount of filler added to the surfactant solutions corresponds to 2 wt% of 1.35 g dry rubber, giving the amount of 27.0 mg GNP powder.

2.3. Nanocomposite preparation

The NRL (2.5 g) was subsequently added to the 10 mL graphene-stabilized surfactant dispersions and stirred for 1 h. The mixtures were then sonicated (Branson 5510 sonicator) for 2 h and cast into a mould. Nanocomposites were obtained after drying in an oven at 70 °C overnight.

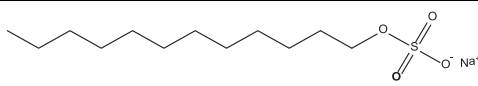
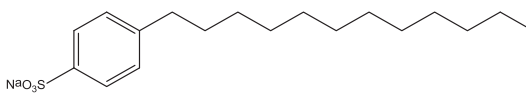
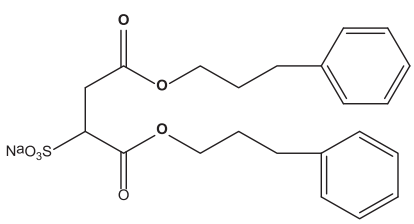
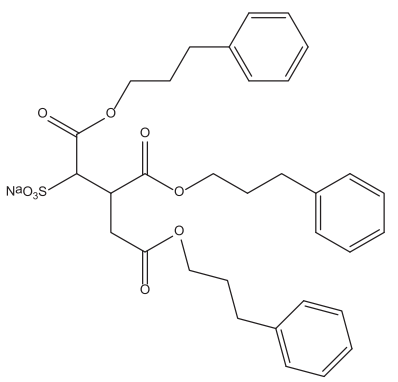
2.4. Electrical conductivity measurements

Electrical conductivities of the nanocomposites were determined using a standard four-point probe method. All samples were cut into 15 mm \times 15 mm and measured for the surface (in-plane) direction. For each sample, conductivity data represent the averages of three consecutive measurements. All conductivity measurements were performed at room temperature (25 °C) with a programmable Keithley 2636A electrometer.

2.5. Characterization of morphology

A variety of experimental tools were used to characterize the morphology of GNP dispersions and the subsequent GNP/NRL nanocomposites. The dispersion of GNP flakes in the NRL matrix was studied using Raman spectroscopy, field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), and high-resolution transmission electron microscopy (HRTEM). To avoid charging the nanocomposites were coated with platinum (Pt) prior to SEM (Hitachi SU8020) imaging. To visualize the embedded microstructure of nanocomposites using HRTEM (JEOL 2100F), the samples were ultramicrotomed with a diamond knife to give sections with nominal thickness ~ 80 nm. Raman spectroscopy was used to evaluate the graphitic structure of GNPs. The Raman spectra were collected using a Renishaw InVia micro Raman system spectrophotometer with a 514 nm argon-ion laser source. Five regions were measured for each nanocomposite. AFM imaging was performed using a JPK Nanowizard III in tapping mode. The cantilever used was antimony-doped silicon with a nominal force constant of 50 N/m and a resonant frequency 353 kHz (HQ:NSC 15/AL BS from MikroMasch). Imaging was performed using a line rate of 0.8 Hz, an integral gain between 10 and 50 Hz, a

Table 1
Chemical structures of surfactants used in this work.

Surfactant	Structure	Chemical Name
SDS		Sodium dodecylsulfate
SDBS		Sodium dodecylbenzenesulfonate
DC3Ph2		Sodium 1,4-dioxo-1,4-bis(3-phenylpropoxy)butane-2-sulfonate
TC3Ph3		Sodium 1,5-dioxo-1,5-bis(3-phenylpropoxy)-3-((3-phenylpropoxy)carbonyl)pentane-2-sulfonate

proportional gain of 0.001 Hz, and a drive amplitude of 0.025 V. All imaging was performed in air and approximately 20°C.

2.6. Zeta potential measurements

Zeta potential measurements were performed by ELSZ-1000 Zeta-potential and Particle size Analyzer (Photal OTSUKA ELECTRONICS) with Smoluchowski equation as zeta potential conversion equation and 1 peak Lorentz fitting. Measurements were carried out with a flow cell at sampling time 400 μ s, cumulative number 7, measuring angle 15°, temperature 25 °C, pin hole size 50 μ m, cell constant 70.000 cm^{-1} . Properties of aqueous mixtures (refractive index 1.3328, viscosity 0.8878 cP, and permittivity 78.3 Fm^{-1}) were used for calculation of zeta potential. Zeta potential values were finally obtained as average values of 10 runs for each sample.

2.7. Small-angle neutron scattering (SANS)

Small-Angle Neutron Scattering (SANS) studies were carried out on the time-of-flight LOQ instrument at ISIS, UK. The accessible Q range was 0.007–0.23 \AA^{-1} , arising from incident neutron wavelengths of $\lambda = 2.2$ –10 \AA . Absolute intensities for $I(Q)$ (cm^{-1}) were determined to within 5% by measuring the scattering from a partially deuterated polymer standard. Neutrons are scattered by short-range interactions with sample nuclei, the ‘scattering power’ of different components being defined by a scattering-length density (SLD), ρ (cm^{-2}). The samples were prepared in 2 mm path-length quartz cells and held in a thermostatted automatic sample changer at 25 °C. Data have been fitted using the SASView interactive fitting program, fixing scattering length density differences as calculated and fitting for micellar volume fraction and appropriate

structural parameters as required by the different scattering laws (see [supplementary material](#)).

3. Results and discussion

3.1. Electrical conductivity of GNP/NRL composites

The development of latex technology as an economically scalable method to achieve uniform graphene dispersions has largely benefited from the extensive studies done with CNT/polymer nanocomposites [7,8,14]. Most studies have relied on improved physical properties of the nanocomposites to demonstrate how well the graphene is dispersed in the polymer matrices [1,15]. In the development of semi-conductive polymer nanocomposites the aims are usually a low percolation threshold with significant enhancement value [16,17]. For nanocomposites with insulating matrices to become electrically conductive, the filler concentration of must exceed the percolation threshold, where at certain loading fraction a system-spanning conductive network of filler particles is formed, leading to an abrupt rise in electrical conductivity [18]. Interestingly, latex-based filler-polymer composites are usually expected to have lower percolation thresholds than similar composites prepared using either solvent mixing or melt blending [17,19,20].

A convenient way to convey the ability of each graphene-philic surfactant for dispersing GNPs into the NRL matrix is at a fixed graphene loading fraction, thereby facilitating direct comparison of the overall nanocomposite electrical conductivities. Here, conductivity is studied in terms of surfactant concentration with fixed GNP loading fraction (Fig. 1, Table 2). The percolation test was conducted using SDBS surfactant, giving a value at 0.2–0.6 wt% for this standard system. This value is in a similar range with the extensive

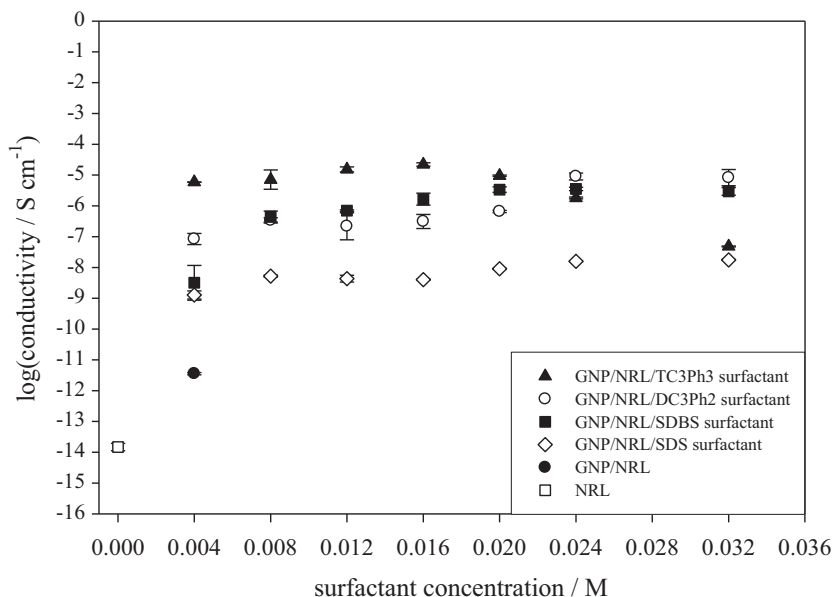


Fig. 1. Electrical conductivities of the NRL matrices and GNP/NRL composites containing phenyl-functionalized surfactants. The error bars are given for three experimental measurements.

data collected for various surfactants using latex dispersion technology [9], and also the solvent mixing route [17,21].

Without surfactant stabilizers, when dispersed in a NRL matrix ($1.51 \times 10^{-14} \text{ S cm}^{-1}$), GNPs enhanced the electrical properties ~ 2 orders of magnitude, giving an overall conductivity of $3.56 \times 10^{-12} \text{ S cm}^{-1}$. The widely used surfactant, SDS (0.032 M), indeed leads to a notable increase in electrical conductivity to $1.76 \times 10^{-8} \text{ S cm}^{-1}$. As evidenced by Fig. 1, changing to SDBS – which may be considered as SDS with one aromatic ring near to the headgroup, offers approximately an increase of 2 orders of magnitude in electrical conductivity over equivalent systems stabilized with SDS. The results and trends show a good agreement with previous work using multi-walled carbon nanotubes (MWCNTs) [5]. The double chain DC3Ph2 (previously known as AOTPh [5]) moderately increases the nanocomposite electrical conductivity up to $9.36 \times 10^{-6} \text{ S cm}^{-1}$. Further modification of the surfactant chain to be tri-chain surfactant TC3Ph3 (previously known as TCPH [5]) raised the electrical conductivity to $2.22 \times 10^{-5} \text{ S cm}^{-1}$ at 0.016 M surfactant concentration. Attempts to increase the surfactant concentration (0.020–0.032 M) to disperse greater quantities of graphene in NRL matrix did not result in higher electrical conductivities of the nanocomposites.

Recent work by Wang et al. reported that graphene exfoliation increased with ionic surfactant concentration [24]. It was further stated that the graphene concentration decreased after reaching an optimum surfactant concentration. The phenomenon was explained using DLVO theory, that for a given interparticle separation higher surfactant concentration will act to lower the potential barrier experienced between neighboring graphene sheets, leading to aggregation. Interestingly, the results presented here support this: there is a maximum concentration for each surfactant to produce nanocomposites with optimum electrical conductivity.

In the field of thermal interfacial materials, the efficiency of any filler is characterized by its thermal conductivity enhancement (TCE), which is calculated on the basis of the thermal conductivity of the composite compared to the thermal conductivity of the pure polymer matrix [25]. A similar concept is applied here to quantify the surfactant and/or filler as well as dispersion technique efficiency. The electrical conductivity enhancement can be defined as;

$$\text{Enhancement} = \frac{\text{conductivity of nanocomposite}}{\text{conductivity of polymer}} \quad (1)$$

Fig. 2 shows the conductivity enhancement of graphene/polymer nanocomposites using various techniques and nanofiller loadings (wt%). It can be seen that there is remarkable enhancement with the new nanocomposites introduced here at ~ 2 wt% loading fraction, especially for TC3Ph3 surfactant. Although the enhancement is not as high as graphene-polystyrene (PS) stabilized by poly(sodium-4-styrenesulfonate) (PSS) surfactant [26,27], TC3Ph3 is certainly more efficient since PSS was used at very high levels (~ 10 -fold excess). Moreover, it can be seen that nanocomposites prepared using latex technology offer greater electrical conductivity enhancement than those made via solution mixing and polymerization [6,21,26,28,29]. Clearly, these recently developed surfactants appear to have some advantages over the PSS mentioned above, given the ability to stabilize dispersions at lower levels, thus giving greater effective enhancements, and being water-based systems, they are certainly more economical and environmentally friendly. Previous studies focused on the final conductivity of the nanocomposites [17,26,27,30], whereas the electrical conductivity enhancement value, which is one of the most simple ways to assess the dispersant and/or filler efficiency, has only received attention from a few groups.

The results above strongly point to the influence of extra surfactant chains on the graphene-compatibility, and also the number of aromatic rings per surfactant molecule. This has been hinted at by others in previous literature; that the presence and number of aromatic rings per stabilizer molecule will strengthen π - π interactions between graphenes and surfactants [31–35]. Clearly, the surfactant chain structure and especially the extent of aromatic character are important factors for graphene-compatibility.***

3.2. Incorporation of GNP in the NRL: Morphology

FESEM images give insight into the dispersion state of nanofillers inside the polymer matrix. Fig. 3 shows FESEM images of GNP (a and a') and NRL (b and b'). The image of exfoliated GNPs inside the polymer matrix is distinguishable by the appearance

Table 2
Electrical conductivity of the GNP/NR-Latex nanocomposites stabilized by surfactants.

Surfactant	cmc (M)	γ_{cmc} (mN m ⁻¹)	Surfactant concentration (M)						
			0.004	0.008	0.012	0.015	0.020	0.024	0.032
Electrical conductivity of nanocomposites (S cm ⁻¹)									
TC3Ph3	0.0005	38.9	5.90×10^{-6}	8.55×10^{-6}	1.54×10^{-5}	2.22×10^{-5}	9.53×10^{-6}	1.81×10^{-6}	1.00×10^{-6}
DC3Ph2	0.0036	34.9	8.82×10^{-8}	3.42×10^{-7}	3.12×10^{-7}	3.39×10^{-7}	6.56×10^{-7}	9.19×10^{-6}	9.36×10^{-6}
SDBS	0.0015 ^a	36.5 ^a	5.61×10^{-9}	4.75×10^{-7}	7.03×10^{-7}	1.76×10^{-6}	3.42×10^{-6}	3.55×10^{-6}	3.04×10^{-6}
SDS	0.0080 ^b	34.7 ^b	1.32×10^{-9}	5.25×10^{-9}	4.44×10^{-9}	4.05×10^{-9}	9.06×10^{-9}	1.59×10^{-8}	1.76×10^{-8}

^a Data collected by Biswal and Paria [22].

^b Data collected by Sa and Kornev [23].

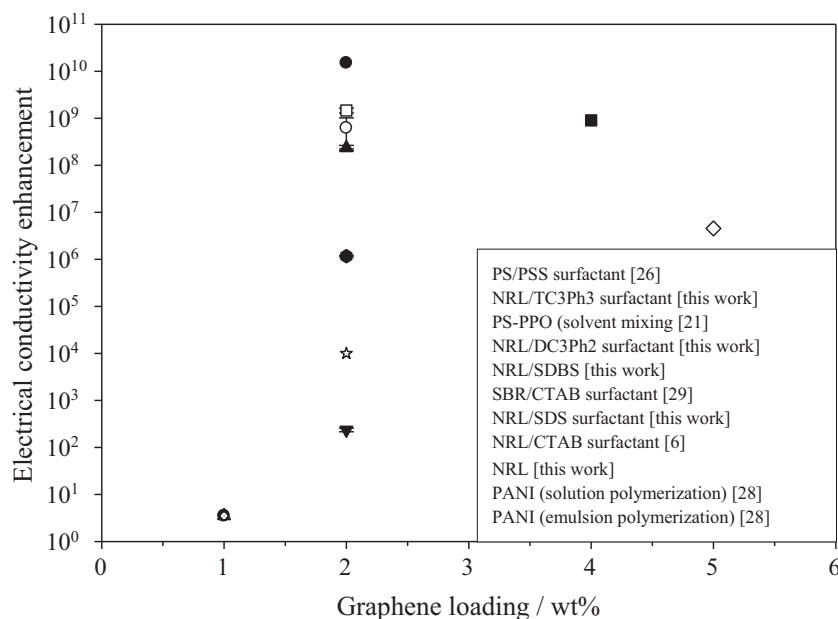


Fig. 2. Electrical conductivity enhancements with graphene/polymer nanocomposites. Characteristic error bars of three experimental measurements are shown for certain samples.

of bright flakes against a dark polymer matrix. As can be seen, the GNPs are present as flakes of different size and shapes, whereas the NRL appears as dark regions. The nature of such contrast can be explained by different secondary electrons generated in GNP and NRL, as explained elsewhere [8,30].

Without surfactant, aggregated structures of GNP in the NRL matrix are observed, as indicated by the diamond arrows (\blacklozenge). The agglomerated GNP structure appears as bulk pieces of filler at higher magnification instead of platelets (c') [30]. After introducing SDS and SDBS, the GNP aggregation seems to slightly decrease, giving more separated individual GNP flakes – represented by the stealth arrow (\rightarrow). Notably, the dispersion and stabilization of GNPs was notably increased with the aromatic surfactants DC3Ph2 and TC3Ph3, and it is even possible to see the presence of individual GNP flakes at higher magnification (f' and g'). Recalling the electrical conductivity measurements, it becomes apparent that there is a correlation between the extent of GNP dispersion and electrical properties of the nanocomposites. This again emphasizes the importance of designing and selecting optimized “graphene-philic” surfactants as stabilizers.

One of clearest ways to further characterize the morphology of nanofillers inside NRL matrices is with high resolution transmission electron microscopy (HRTEM). Fig. 4 (a-c) shows representative micrographs of ultramicrotomed thin section nanocomposites stabilized by the triple-chained TC3Ph3 surfactant. TEM micrographs reveal the presence of GNP particles as multilayer graphene sheets (Fig. 4a). Despite not achieving a high degree of exfoliation as

compared to other studies [36,37], the treatments with surfactant facilitate good dispersion of GNPs into the NRL matrix. The surfactant layers are thought to act as barriers between nearby GNPs from stacking as tactoids. It is important to mention that the GNPs are adhering to the latex particles (see Fig. 4b-c). The results suggest that TC3Ph3 surfactant provides good “bridging” between those two incompatible materials, GNPs and latex particles: this has also been found with other systems [6,38].

The prepared nanocomposites were also characterized by AFM, which is widely used to complement other microscopic techniques used to characterize composite materials [1,39,40]. AFM allows for easy sample preparation and the natural samples can be studied, since neither conductive coatings nor staining are required [39,40]. AFM tapping mode was chosen as the most appropriate imaging method to prevent damage to the probe or sample during imaging of the surface. (Interested readers can refer to appropriate literature [40]). Representative AFM images of GNP/TC3Ph3/NRL in tapping mode are shown in Fig. 5.

The GNP surface height image (Fig. 5a) shows a textured surface, but otherwise no indication of a dispersed material. The oscillatory noise present throughout is thought to be caused by feedback in the system due to the elastic response of the surface; however, despite this, the phase image (Fig. 5b) clearly shows thoroughly dispersed components throughout in the NRL. Therefore, the enhanced electrical properties can be considered to have

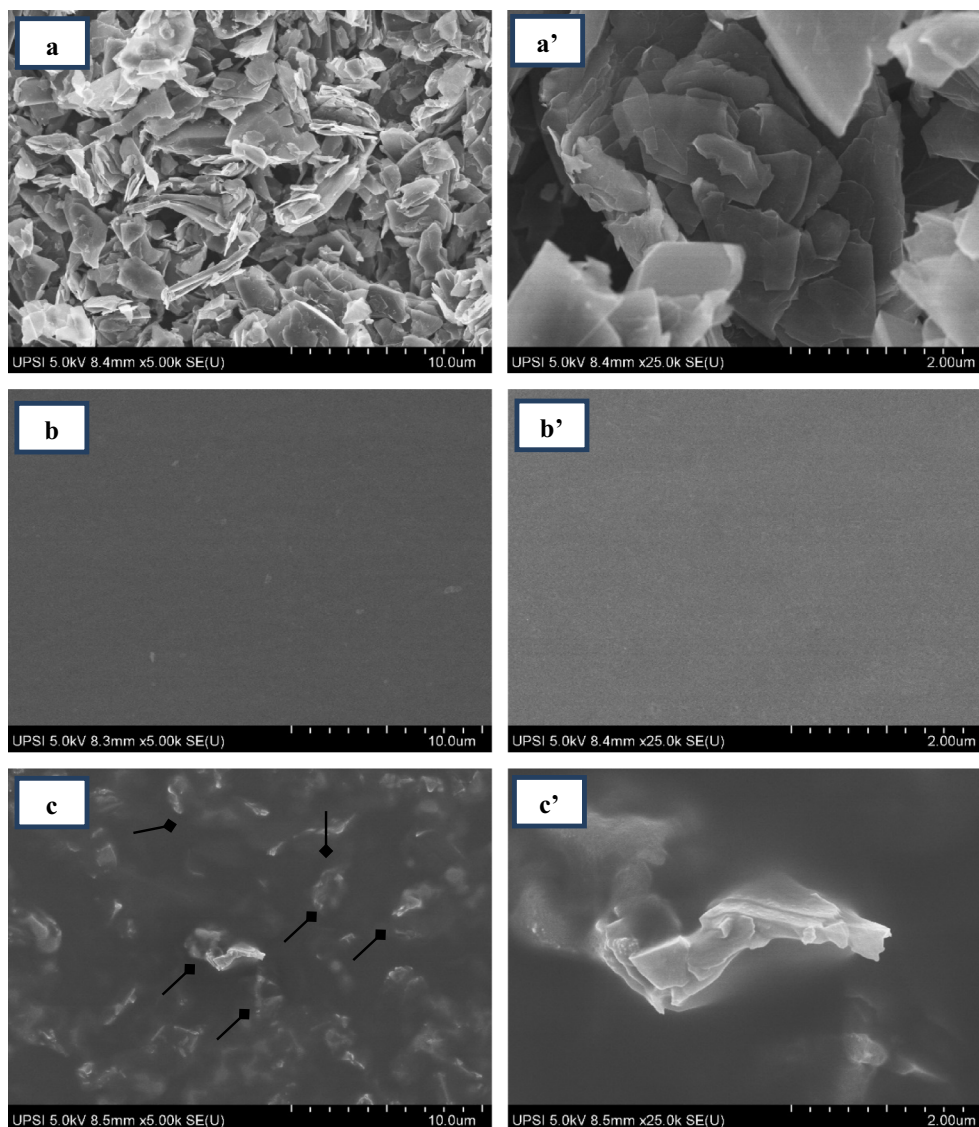


Fig. 3. FESEM images of GNP (a and a'), NRL (b and b'), GNP/NRL: without surfactant (c and c'), with SDS (d and d'), with SDBS (e and e'), with DC3Ph2 (f and f') and with TC3Ph3 (g and g').

arisen from the interfacial interactions of GNP nanoparticles in the NRL.

Raman spectroscopy is a commonly used tool for the characterization of carbon materials since Raman scattering is strongly sensitive to the electronic structure of samples, and can give information about defects disorder, optical energy gaps, number of graphene layers, edge structure, amongst other properties [41,42]. Fig. 6 shows typical Raman spectra of GNPs with the characteristic peaks of graphite, namely the disorder band (D band) at $\sim 1353\text{ cm}^{-1}$ and the in-phase vibration of the graphite lattice (G band) at $\sim 1580\text{ cm}^{-1}$. It is obvious that after dispersing GNP using surfactant, the D band and G band are only slightly shifted, being at $\sim 1353 - 1358\text{ cm}^{-1}$ and $\sim 1581\text{ cm}^{-1}$, respectively.

Quantifying disorder in the GNPs was also attempted by analyzing the intensity ratio between the disorder-induced d-band and the G-band (I_D/I_G). Comparing the GNPs, it can be seen that the I_D/I_G ratios for the nanocomposites were markedly similar. A universal observation is that both the G and D bands do not undergo significant changes after surfactant treatment, indicating that the sp^2 network remains essentially intact. Raman spectra described above agree well with a previous study using MWCNTs, indicating

that the non-covalent functionalization of graphene sheets by the synthesized surfactants was successful [5,12].

3.3. Surfactant stabilization: relationship between number of aromatic groups and dispersion stability – zeta potentials and molecular interactions

In charged colloidal systems, and with ionic surfactants as stabilizers, repulsive surface interactions are related to zeta (ζ)-potential i.e. the electrical potential of the Stern layer [43–46]. Repulsive charge surface interactions are the underlying reasons for the successful dispersion of graphene using various types of surfactant [3,47–49]. In such surface-charge stabilized colloidal systems zeta potential measurements are useful to gain information about the origin of dispersion stability.

A range of surfactants have been investigated as stabilizers, and it was found the zeta potential varied with surfactant chemical structure/type. For each sample, ten separate measurements were performed here, since previous work by Hassan et al. suggested that at least six separate measurements should be performed to ensure reproducibility [50]. As a general guide, when ζ -potential

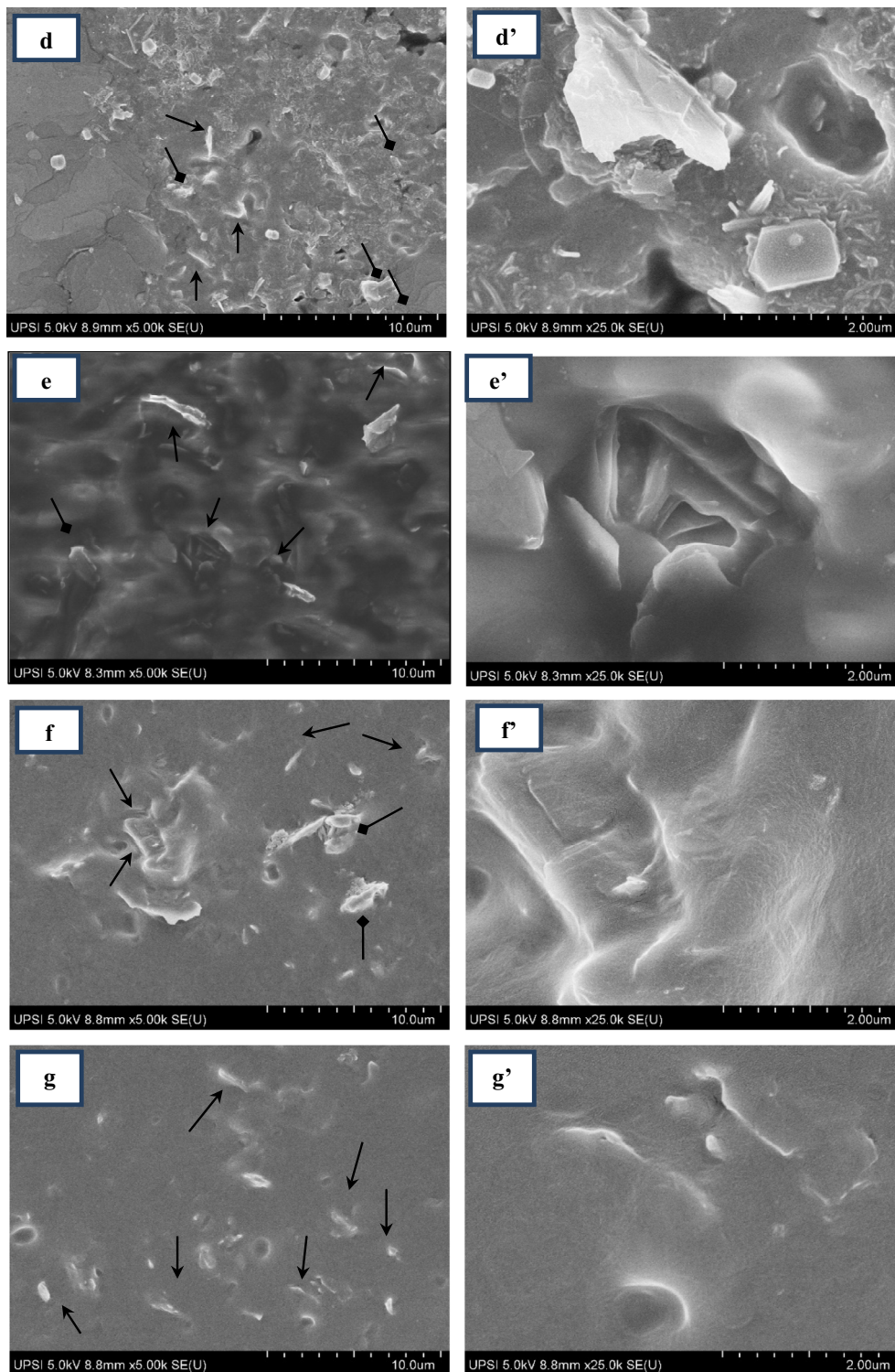


Fig. 3 (continued)

lies at 0–10 mV the system will be unstable, 10 – 30 mV considered as moderately stable, 30 – 60 mV has a good stability while over 60 mV will give an excellent stability [45,46]. Table 3 compares of electrical surface effects provided by surfactants used in this study. We observed ζ -potential for graphene dispersions stabilized by SDS and SDBS respectively are -43 mV and -40 mV, which is well beyond the accepted value for colloidal stability. The results

here are in line with the range of literature values for SDS and SDBS-stabilized graphene dispersions [3,48].

Comparing the results for these two surfactants, it can be seen that the presence of one aromatic ring with SDBS has only a weak impact on ζ -potential and colloid stabilization, considering that both are in similar range within experimental uncertainty. Moving to DC3Ph2 as dispersing agent gave rise to a notable increase in ζ -potential to -69 mV. Among the surfactants studied, TC3Ph3

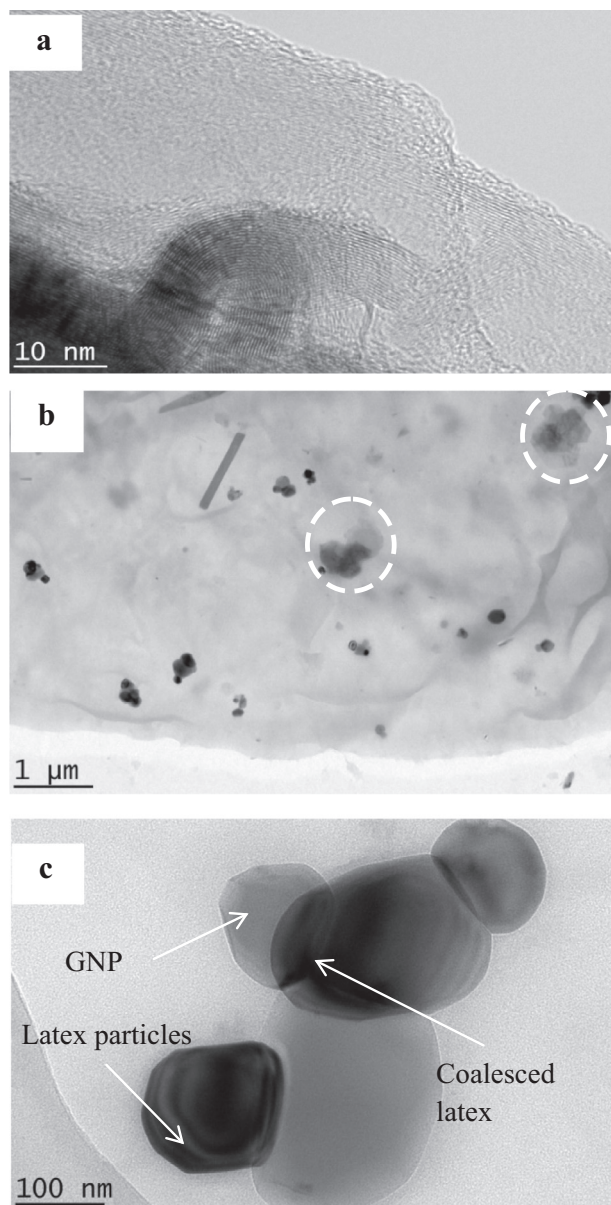


Fig. 4. TEM micrographs of GNP/NRL/TC3Ph3 nanocomposites.

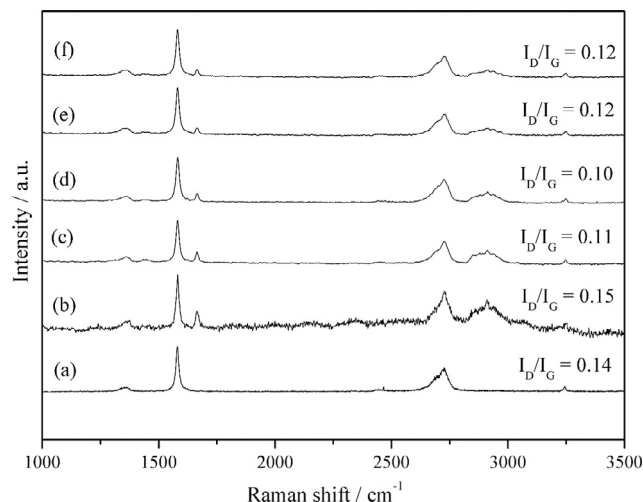


Fig. 6. Raman spectroscopy of graphene and nanocomposites. (a) GNP, (b) GNP/NRL, (c) GNP/NRL/SDS, (d) GNP/NRL/SDBS, (e) GNP/NRL/DC3Ph2, (f) GNP/NRL/TC3Ph3.

Table 3

ζ-potential data for graphene dispersions with different surfactants.

Surfactant	Number of aromatic ring(s)	ζ-potential / mV	Electrical conductivity enhancement
SDS	N/A	-43 ± 4	1.17×10^6
SDBS	1	-40 ± 8	2.36×10^8
DC3Ph2	2	-69 ± 7	6.21×10^8
TC3Ph3	3	-95 ± 6	1.47×10^9

resulted in a significant increase in ζ-potential to reach -95 mV, thereby conferring high dispersion stability. This increased dispersion ability may explain the origin of the significant enhancement in electrical conductivity caused by the TC3Ph3 surfactant.

Examining the effects of surfactant types on ζ-potential an interesting pattern emerges: higher ζ-potentials were observed on increasing the number of aromatic moieties in the surfactant molecules. (However, from the aliphatic SDS to the aromatic SDBS the effect remains subtle). Work on adsorption of aromatic compounds using CNTs previously suggested that π-π interactions between compounds and CNT-surfaces depend on the number, size and shape of the aromatic groups [11,31].

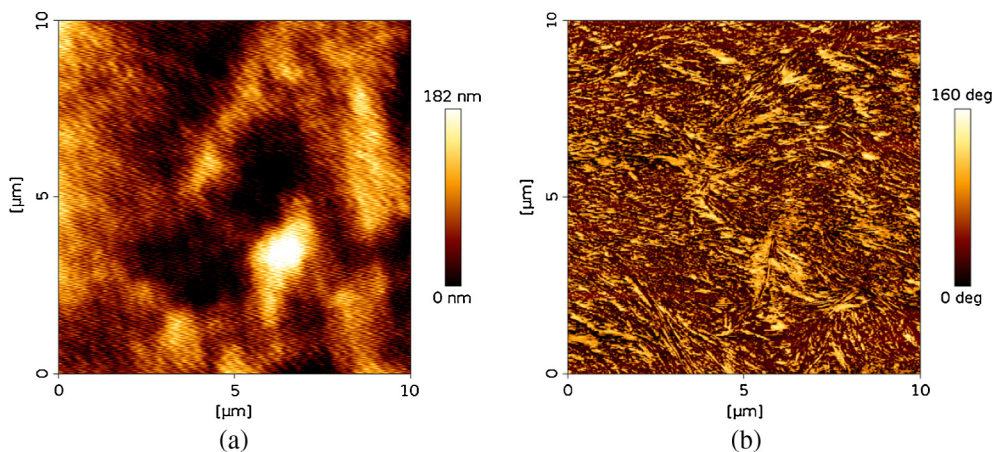


Fig. 5. AFM tapping mode images of GNP/NRL/TC3Ph3 surfactant composites [surf] = 0.016 M. (a) height image. (b) phase image.

Theoretical studies have identified that non-covalent interactions for π - π systems with aromatic-bearing compounds may be rather complex, and may result from a combination of electrostatic, hydrophobic, and van der Waals interactions [51,52]. Drawing parallels with those theoretical studies, stronger electrostatic interactions will also contribute to enhanced π - π interactions by improving the stability of graphene-coated surfactant complexes. This trend may be explained by stronger hydrophobic interactions between the surfactants and graphene surfaces, as corroborated by the variations of aqueous surfactant properties shown in Table 1. As can be seen the cmc (which is one measure of overall surfactant “hydrophobicity”) in general decreases with increasing surfactant aromatic content. This trend with increasing the number of aromatic rings mirrors the changes in stability and properties of the GNP-latex systems discussed above.

3.4. Surfactant self-assembly: a SANS study

Although visualization of the structure and nature of the GNP dispersions can be carried out using microscopy techniques e.g. AFM, TEM, SEM; these methods are not able to give reliable information on about how the surfactants organize on GNPs. Despite that surfactant dispersions of graphene-based materials are of great interest, a clear picture of surfactant aggregation/adsorption remains limited. Simulation work has offered insight into how some commercial surfactants aggregate on the graphene surfaces,

but many aspects still remain to be understood [53,54]. Experimentally, small-angle neutron scattering (SANS) can provide useful information on the self-assembly structure surfactants with graphenes [55]. In the absence of inter-micellar interactions the scattering intensity $I(Q)$ is proportional to the form factor, $P(Q)$, which reports information on particle size and shape. Full details of the scattering form factors and parameters of the models used in this study can be found in the [supplementary material](#).

SANS profiles of solutions for aromatic surfactants are shown in Fig. 7 (SDS is not included). For direct comparisons, measurements were conducted at the same surfactant concentration and temperature. The scattering profiles for the surfactant solutions were fitted to form factors describing either a charged spherical or a charged ellipsoidal particle model, with a charge repulsion $S(Q)$ structure factor peak following the Hayter-Penfold model [56]. Here, the scattering profiles of the SDBS solution was consistent with charged spherical micelles and a micellar radius (R_{sphere}) of 22.0 Å (Table 4). The fitted micellar dimensions are $R_{\text{sphere}} = 22.0$ Å (Table 4). At odds with the large number of SANS studies on SDS, SDBS has not been much explored. In an earlier study, Zhou et al. reported the formation of spherical micelle for various SDBS concentrations although they did not calculate the micellar radius [57]. The work presented here is in broad agreement with that of Cheng and Gulari which reported the formation of spherocylinder micelles with a radius of ~ 22 Å [58]. A simulation study by Palazzesi et al. also predicted a spherical-ellipsoidal formation

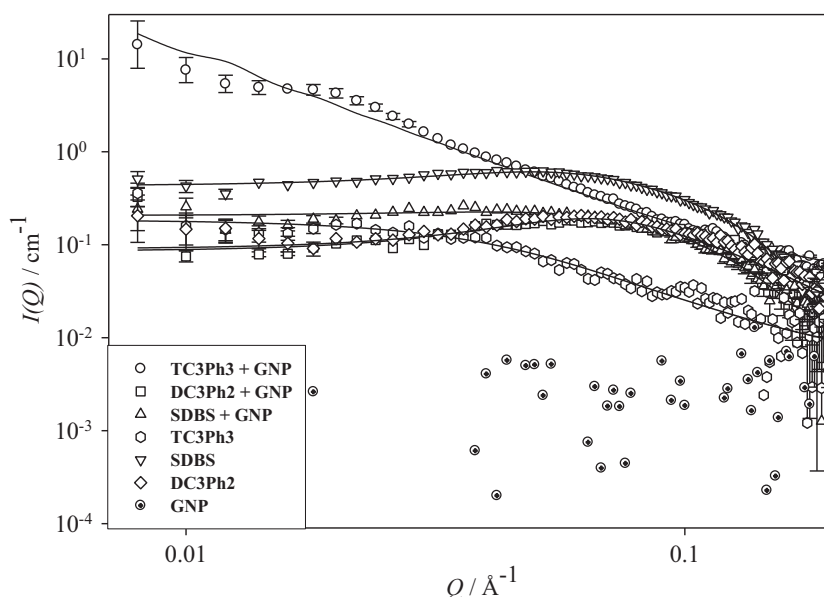


Fig. 7. SANS profiles for SDBS, DC3Ph2, TC3Ph3 surfactants solutions and GNP dispersions. [Surfactant] = 0.03 M and T = 25 °C. Lines are model fits for charged spherical and ellipsoidal micelles (with and effective Hayter-Penfold $S(Q)$), or stacked disk model (TC3Ph3 + GNP only). Characteristic error bars are shown for the lowest intensity samples.

Table 4
Model fit parameters for the SANS Data.^a

Sample	Model	$R_{\text{sphere}} \pm 2 \text{ \AA}$	$R_a^b \pm 2 \text{ \AA}$	$R_b^c \pm 2 \text{ \AA}$	$R_{\text{disk}} \pm 50 \text{ \AA}$	$X \pm 0.2$
SDBS	Sphere	22.0	–	–	–	–
DC3Ph2	Ellipsoid	–	5.0	24.0	–	4.8
TC3Ph3	Ellipsoid	–	5.0	32.0	–	6.4
SDBS + GNP	Sphere	22.0	–	–	–	–
DC3Ph2 + GNP	Ellipsoid	–	25.0	15.0	–	0.6
TC3Ph3 + GNP	Stacked Disk	–	–	–	286.0	–
GNP	N/A	–	–	–	–	–

^a [surf.] = 0.030 M except for GNP only. Charged micelles were fitted with interparticle structure factor $S(Q)$ for Hayter-Penfold model.

^b Radius polar.

^c Radius equatorial.

for SDBS with a mean micellar radius of 20 Å [59].

Moving to other surfactant structure, both of the di-chain and tri-chain compound; DC3Ph2 and TC3Ph3 scattering profiles were found to be well represented by charged ellipsoidal micelles and a $P(Q)$ with polar axis ratio R_a , equatorial axis ratio R_b , and aspect ratio X multiplied by an electrostatic repulsive $S(Q)$ (Hayter-Penfold model) [56]. An overview of the parameters obtained using the model is given in Table 4. The work presented here is in agreement to that found in the literature, reporting micelle formation for the di-chain surfactant (AOT) and highly-branched tri-chain surfactant (TC14 surfactant) [60,61]. The addition of the third surfactant chain would possibly make hydrocarbon chains expanded from the micellar center, forcing ellipsoidal micelles to fatten somewhat due to the extra phenyl rings. The equatorial dimension as seen by SANS thus increases by 8 Å.

Parallel SANS experiments with GNP dispersion were conducted and compared to those with the GNP-free surfactant solutions. A GNP dispersion in water without surfactant was also studied, showing no SANS and hence no evidence of colloidal structure/dispersion. When GNPs were dispersed with SDBS, the SANS data were still similar, analyses showing no significant changes in shape and size ($R_{\text{sphere}} = 22.0$ Å). The scattering intensities throughout the Q -range are slightly lower than those from the SDBS system, suggesting adsorption of SDBS on GNPs. This SANS behavior is analogous to the previous work on surfactant stabilization on CNT dispersions which is known to exhibit low Q scattering after surfactant adsorption [62–64]. Thus, the scattering from these spherical micelles is essentially unaffected, and indicates little perturbation to the spherical micelles of SDBS by GNP, suggesting weak graphene-SDBS interactions.

For GNP dispersed with DC3Ph2, aside from the intensity differences over $Q < 0.03$ Å⁻¹, the scattering is still similar to the native DC3Ph2 solution, as was found with SDBS systems. The data set could be adequately fitted to a charged ellipsoidal form factor model multiplied by the Hayter-Penfold $S(Q)$ (fit parameters in Table 4). Interestingly, the micellar radii undergo significant changes with the polar radius being 20 Å larger, and the equatorial radius shrinking for the GNP dispersion. These differences can be attributed to the presence of GNPs dispersed in the DC3Ph2

micelles. It is clear that GNP dispersions are present, but beyond that the results cannot be further interpreted.

Introduction of GNP in the TC3Ph3 solution resulted higher SANS intensities, very different from those from the pure TC3Ph3 solution. Looking at the data on a logarithmic scale, $I(Q)$ scales approximately as Q^{-2} , which is characteristic of 2-dimensional structures [55,65,66], and the fitted disk radius (R_{disk}) is 286 Å. These general observations are distinctly different from those for the single- and di-chain surfactants, and in the case of TC3Ph3 the aggregate structure changes from ellipsoidal micelles to tactoid-type for the GNP dispersions. The SANS for GNP/TC3Ph3 and GNP/DC3Ph2 dispersions at different surfactant concentrations were also studied, and are given in supplementary material together with the fitted curves and parameters.

It is well known that surfactants form various aggregate morphologies in the presence of carbon nanomaterials [9,10,53,54,67]. However, the impact to the shape and size of aggregates are less studied and understood. On varying the number of surfactant chains (tails), it appears that the micelle shape and size transformation becomes pronounced. Further points of interest are the ellipsoid-to-disk transition of the tri-chain surfactants, and its relationship to the effectiveness in dispersing GNPs; these will be further discussed in the next section.

3.5. Model for surfactant – graphene interactions

It is interesting to speculate on the plausible reasons for the observed micellar shape changes. Early studies on surfactant-aided CNT dispersions generated by ultrasound recognized the adsorption of hydrophobic surfactant tails on CNT surfaces [10,67]. The interactions between surfactant tails and CNT surfaces (or here graphene sheets) are therefore likely to be hydrophobic rather than Coulombic. Consequently, the affinity of surfactants for carbon surfaces is believed increase with the number of surfactant tails per molecule [5,9].

In the current study, it is seen that the tri-chain surfactant TC3Ph3 does not behave like the other surfactants. A model is proposed (see Fig. 8) where the surfactant molecules interact with aromatic containing tails face-on, covering the graphene surfaces due to π - π interactions. This organization will maximize the “tail-

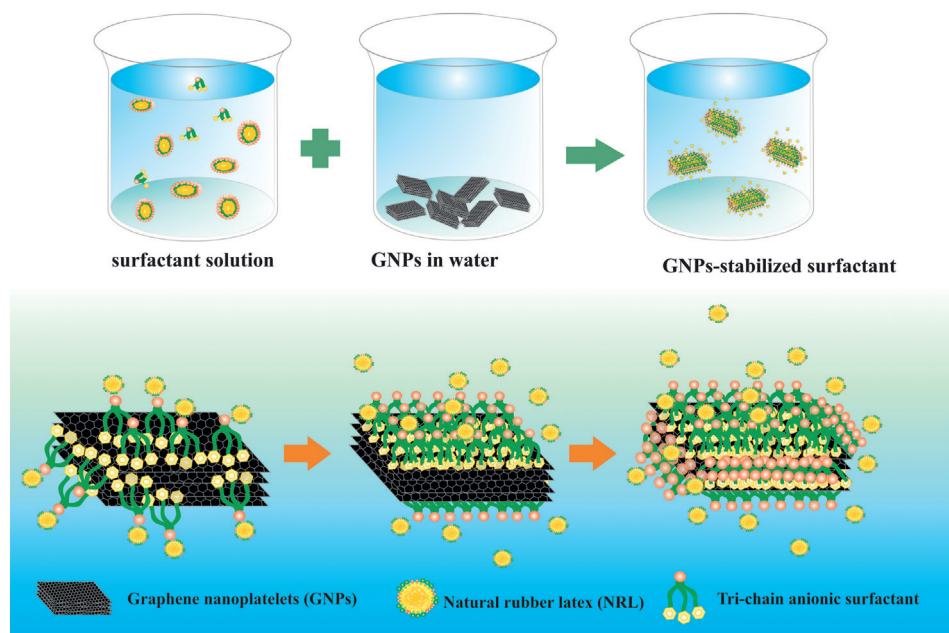


Fig. 8. Schematic of surfactant self-assembly in GNP/NRL systems.

to-graphene” interactions and consequently minimize the contact of water molecules with graphene surfaces that would lead to destabilization [53,67]. The hydrophilic surfactant parts will then arrange themselves facing away from the graphene surfaces and interact with the shell layer latex particles [68,69].

Furthermore, experimental evidence shows that there is an ellipsoid micelle-to-stacked disk transition for the GNP-stabilized TC3Ph3 system. Rather than GNPs being dispersed by micelles, the surfactant molecules might preferentially adsorb on graphene surfaces. This seems likely, given that GNPs were shown previously to be described by stacked-disk scattering with radii of 1250 Å and 2.08 μm [65,66]. As a result, the GNP-surfactant aggregates take the form of stacked disk micelles with the GNPs decorated by surfactant layers. This picture is consistent with the work of Matarredona et al. on the stabilization of nanotube dispersions using SDBS [70]. They also postulated that the SDBS molecules wrapped round the external walls of nanotubes to give apparently cylindrical micelles. A recent review of the collective work on simulation studies by Lin et al. [53] also shows that the surfactant tails will distribute as much as possible on both graphene surfaces, giving “sandwich-like” assembled structures, although for certain surfactants e.g. SDBS some regions might still remain exposed to the aqueous phase.

For graphene-surfactant dispersions in water, there will be a dynamic equilibrium between surfactant molecules in the bulk phase, at the air–water interface and those adsorbed on graphene surfaces. Considering surfactants cover GNP surfaces uniformly, then surfactant adsorption could be described with a Langmuir iso-

therm, which is generally used to model the equilibrium adsorption from an ideal bulk solution to an ideal monolayer [46].

One way to estimate the surface concentration for the monolayer adsorption on graphenes is to consider the limiting surface excess (Γ), which can be estimated reliably from aqueous surface tension data via the Gibbs equation (Eq 2). Here the Gibbs equation applied to the air – water interface has been used to gain insight into adsorption at the graphene aqueous interface, assuming adsorption at the two interfaces is essentially similar [23,64]. (The assumption is that surface densities on GNPs surfaces are similar to those at model air–water surfaces).

$$\Gamma = -\frac{1}{mRT} \frac{d\gamma}{\ln c} \quad (2)$$

To estimate adsorption on graphene surfaces, data from the air–water surfaces were used as inputs to a Langmuir isotherm (Eq 3) for assessing limiting values of surface concentration of monolayers, Γ_m (mol m⁻²) and surface coverages (θ). Where C_1 is the surfactant concentration in the bulk phase and a is a constant. Fig. 9 summarizes the different adsorption isotherms for DC3Ph2 and TC3Ph3 surfactants. Aqueous surface tension data and values for C_1 , Γ_m , Γ and θ along with other physical parameters derived from surface tension data are given in [supplementary material \(Table S5\)](#).

$$\Gamma = \frac{\Gamma_m C_1}{C_1 + a} \quad (3)$$

$$\theta = \frac{\Gamma}{\Gamma_m} \quad (4)$$

Interestingly, the concentration needed to achieve the same surface coverage (θ) is significantly lower for TC3Ph3 ($\theta = 1.00$, $C_1 = 0.002$ M) than for the di-chain surfactant (DC3Ph2; $\theta = 0.99$, $C_1 = 0.007$ M). In other words, TC3Ph3 does not require as high a bulk concentration surfactant to attain full coverage ($\theta = 1$). This order follows the graphene dispersion stabilities and electrical conductivities reported earlier in this paper.

4. Conclusions

The aim of this study was to explore structural modifications of highly efficient surfactants for stabilizing graphene dispersions in hydrophilic natural rubber polymer matrices. This has been achieved by investigating a range of anionic surfactants which can be readily synthesized from commercially available precursors. A clear correlation was observed between the number of aromatic moieties of a given surfactant and its performance in stabilizing GNPs – NRL, as gauged by the electrical conductivity of the nanocomposites and ζ -potentials of the particle surfaces. A similar trend in aromatic group numbers versus dispersion stability has been observed but for the aqueous graphene dispersions [34,35].

These results have important implications for the rational design of graphene-compatible surfactants. The advantages are that this latex technique is relatively straightforward to carry out, and measured electrical conductivity enhancements can be used to screen target compounds expected to exhibit enhanced compatibility/interaction with graphene surfaces. Despite the fact that the final nanocomposite conductivities are notably lower than the extensive graphene/polymer nanocomposites in literature [1,10,26,49], the enhancement is remarkably high given the relatively low surfactant levels compared to other works using this latex technology approach [6,9].

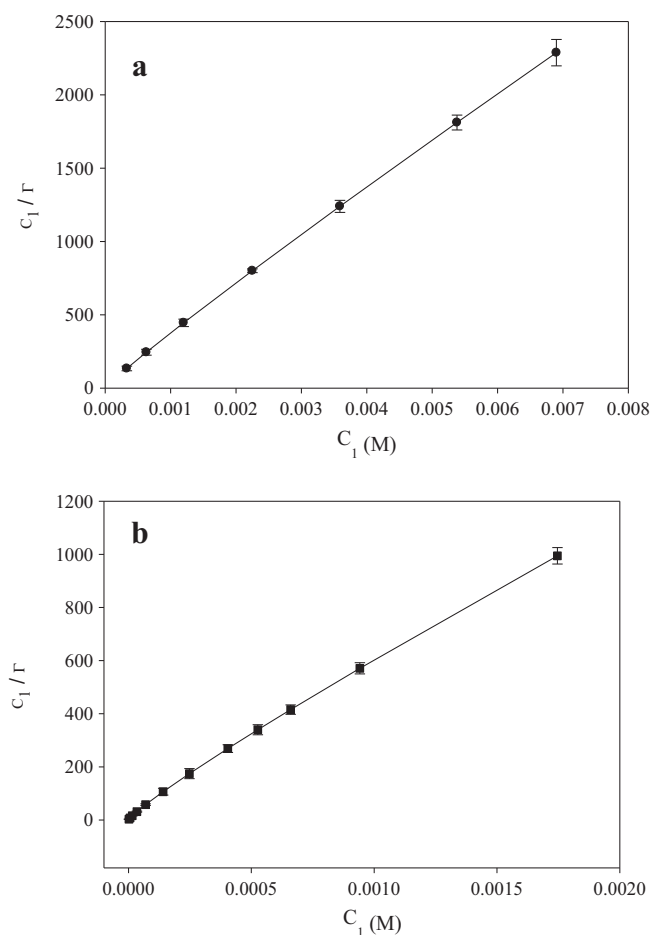


Fig. 9. Langmuir adsorption isotherms for (a) DC3Ph2 (b) TC3Ph3 surfactants. Characteristic error bars are shown to represent uncertainties for three experimental measurements.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.jcis.2018.01.041>.

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