







MODIFICATION OF SURFACTANT CHEMICAL STRUCTURE FOR GRAPHENE/BIOPOLYMER CONDUCTIVE NANOCOMPOSITES

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ABSTRACT

This research aimed to modify and examine the role of new graphene-compatible surfactants and the mechanism in the stabilisation of graphene incorporated into biopolymer matrix namely natural rubber latex (NRL) and cellulose for the preparation of conductive nanocomposites. The surfactants were systematically designed and synthesised to have enhanced compatibility with graphene as compared to commercially available common surfactants. The modifications are centred on variation of surfactant chain degree as well as aromatic numbers on surfactant tail, aromatisation on surfactant headgroup, ion exchange of hydrophilic headgroup, and metal incorporation on surfactant headgroup. The graphene-compatible surfactants have been investigated by a range of techniques including proton nuclear magnetic resonance (¹H NMR) spectroscopy, air - water (a/w) surface tension measurement, and zeta potential measurement. The performance of the synthesised surfactants for the dispersion of graphene in biopolymer was studied by field emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy, and atomic force microscopy (AFM). The electrical conductivities of the nanocomposites were also measured using four point probe measurement. The aggregated structures of surfactants in aqueous phase and in graphene dispersion were examined using small-angle neutron scattering (SANS) analysis. Research finding showed that aromatisation is a crucial factor influencing surfactant compatibility with graphene surfaces where the intensity is enhanced with increasing the number of aromatic groups on surfactant molecular structure. The synthesised surfactants exhibit more uniform dispersion of graphene compared to commercial surfactants used in this study. The highest electrical conductivity achieved for nanocomposite with NRL was $1.08 \times 10^{-2} \text{ S cm}^{-1}$ while for cellulose was $2.71 \times 10^{-5} \text{ S cm}^{-1}$. Analysis using SANS showed that the most efficient surfactants for both nanocomposites exhibited micelle shape similar with graphene which are stacked-disk and layered structure. In conclusion, the presence of higher aromatic groups in the surfactant structure gives rise to relative graphene-compatibility and thus the nanocomposites final properties. In implication, the results obtained are beneficial for the development efficient surfactants for carbon nanomaterial and lowdimensional nanomaterial based technology.



PENGUBAHSUAIAN STRUKTUR KIMIA SURFAKTAN UNTUK KOMPOSIT NANO KONDUKTIF GRAFENA/BIOPOLIMER

ABSTRAK

Kajian ini bertujuan untuk mengubah suai dan mengkaji peranan surfaktan baharu yang serasi dengan grafena dan mekanisme dalam penstabilan grafena yang dimasukkan ke dalam matriks biopolimer iaitu lateks getah asli (NRL) dan selulosa untuk penyediaan komposit nano konduktif. Surfaktan telah direka dan disintesis secara sistematik untuk meningkatkan keserasian dengan grafena berbanding dengan surfaktan umum yang tersedia secara komersil. Pengubahsuaian tertumpu pada variasi darjah rantai surfaktan dan juga bilangan aromatik pada ekor surfaktan, pengaromatikan pada kumpulan kepala surfaktan, pertukaran ion pada kumpulan kepala hidrofili, dan pemasukan logam pada kumpulan kepala surfaktan. Surfaktan yang serasi dengan grafena telah dikaji dengan pelbagai teknik termasuk spektroskopi resonans magnet nukleus proton (¹H NMR), pengukuran tegangan permukaan udara – air (a/w) dan pengukuran potensi zeta. Keupayaan surfaktan yang disintesis bagi 05-4506 penyerakan grafena dalam biopolimer dikaji oleh mikroskopi pengimbas pancaran medan elektron (FESEM), mikroskopi penghantaran elektron resolusi tinggi (HRTEM), spektroskopi Raman, dan mikroskopi daya atom (AFM). Kekonduksian elektrik komposit nano juga telah diukur menggunakan pengukuran kuar empat titik. Struktur gabungan surfaktan dalam fasa akua dan dalam serakan grafena telah dikaji menggunakan analisis serakan neutron sudut kecil (SANS). Dapatan kajian menunjukkan bahawa pengaromatikan adalah faktor penting yang mempengaruhi keserasian surfaktan dengan permukaan grafena di mana intensiti ditingkatkan dengan menambah bilangan kumpulan aromatik pada struktur molekul surfaktan. Surfaktan yang disintesis ini memperlihatkan serakan grafena yang lebih seragam dibandingkan dengan surfaktan komersil yang digunakan dalam kajian ini. Kekonduksian elektrik tertinggi dicapai bagi komposit nano dengan NRL adalah $1.08 \times 10^{-2} \text{ S cm}^{-1}$ manakala bagi selulosa adalah $2.71 \times 10^{-5} \text{ S cm}^{-1}$. Analisis menggunakan SANS menunjukkan bahawa surfaktan yang paling cekap untuk kedua-dua komposit nano memperlihatkan bentuk misel serupa dengan grafena iaitu cakera-tindanan dan struktur berlapis. Kesimpulannya, kehadiran kumpulan aromatik yang lebih tinggi dalam struktur surfaktan meningkatkan keserasian grafena secara relatif dan juga sifat akhir komposit nano. Implikasinya, dapatan yang diperoleh adalah bermanfaat untuk pembinaan surfaktan yang cekap untuk teknologi berasaskan bahan nano karbon dan bahan nano berdimensi rendah.







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LIST OF ABBREVIATIONS

	¹ H NMR	Proton Nuclear Magnetic Resonance
	AES	Auger electron microscopy
	AFM	Atomic force microscopy
	AGU	Anhydroglucopyranose
	AOT	Aerosol-OT
	BMIM-BF ₄	1-butyl-3-methyl-imidazolium tetrafuoroborate
	BMIM-Cl	1-butyl-3-methyl-imidazolium chloride
	BMIM-DBS	1-butyl-3-methyl-imidazolium
05-4500	6832 (Distaka.upsi.edu.my	Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jali Shah
\bigcirc	BMIM-DS	1-butyl-3-methyl-imidazolium dodecylsulfate
	CAPB	Cocamidopropyl betaine
	CF	Cellulose fibre
	cmc	Critical micelle concentration
	CNTs	Carbon nanotubes
	СРР	Critical packing parameter
	СТАВ	Cetyltrimethylammonium bromide
	CVD	Chemical vapour deposition
	DBS-AN	Anilinium dodecylbenzenesulfonate
	DC3Ph2	Sodium 1,4-dioxo-1,4-bis(3-phenylpropoxy)butane- 2-sulfonate
	DDAB	Dodecylethyldimethylammonium bromide







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	DDAF	Dodecylethyldimethylammonium trichloromonobromoferrate
	DFT	Density functional theory
	DLS	Dynamic light scattering
	DRC	Dry Rubber Content
	DS-AN	Anilinium dodecylsulfate
	DTAB	Dodecyltrimethylammonium bromide
	DTAF	Dodecyltrimethylammonium trichloromonobromoferrate
	EDL	Electrical double layer
	EPA	Environmental Protection Agency
	FAOSTAT	Food and Agricultural Organization Statistic
	FESEM	Field emission scanning electron microscopy
05-450	6°FGN 💮 pustaka.upsi.edu.my	Functionalised graphene hah
	FLG	Few layer graphene
	FTIR	Fourier transform infrared
	GCP	Graphene/cellulose paper
	GNPs	Graphene nanoplatelets
	GNS	Graphene nanosheets
	GO	Graphene oxide
	HMIH	1-hexyl-3-methylimidazolium hexafluorophosphate
	HRTEM	High-resolution transmission electron microscopy
	ILs	Ionic liquids
	MC	Microcrystalline cellulose
	MLG	Multilayer graphene





	MWCNTs	Multi-walled carbon nanotubes	
NDI-1 N,N napl		N,N'-bis-[2-(ethanoic acid sodium)]-1,4,5,8- naphthalene diimide	
	NDI-2	N,N'-bis-[2-(ethanesulfonic acid sodium)]-1,4,5,8- naphthalene diimide	
	NR	Natural rubber	
	NRL	Natural rubber latex	
	РММА	Poly(methyl methacrylate)	
	PS	Polystyrene	
	PSS	Poly(sodium 4-styrenesulfonate)	
	PVP	Polyvinyl pyrrolidone	
	RGO	Reduced graphene oxide	
05-450	SAILs	Anionic surfactant ionic liquids	
	Stans pustaka.upsi.edu.my	Small-angle neutron scattering Pustaka TBainun	
	SBR	Styrene butadiene rubber	
	SC	Sodium cholate	
	SDBS	Sodium dodecylbenzenesulfonate	
	SDS	Sodium dodecylsulfate	
	SEM	Scanning electron microscopy	
	SLD	Scattering-length density	
	SWCNT	Single walled carbon nanotube	
TC3Ph3Sodium 1,5-dioxo-1,5-bis(3-phenylpropo phenylpropoxy)carbonyl) pentane-2-sulf		Sodium 1,5-dioxo-1,5-bis(3-phenylpropoxy)-3-((3-phenylpropoxy)carbonyl) pentane-2-sulfonate	
	TC3Ph3-AN	Anilinium1,5-dioxo-1,5-bis(3-phenylpropoxy)-3-((3-phenylpropoxy)carbonyl) pentane-2-sulfonate	
	TCE	Thermal conductivity enhancement	







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	TEM	Transmission electron microscopy
	TLC	Thin layer chromatography
	TMS	Tetramethylsiloxane
	TRGO	Thermally reduced graphite oxide
	TSC	Total solid content
	VOCs	Volatile organic compounds
	a/w	Air-water
	A_{cmc}	Limiting area per molecule at cmc
	a_o	Area occupied by surfactant molecule
	C_{I}	Surface concentration at bulk phase
	D	Distance between bilayer in lamellar
05-4500	D-band ⁸³² pustaka.upsi.edu.my <i>G</i> -band	Disorder band Perpustakaan Tuanku Bainun Graphitic band Abdul Jalil Shah
	h	Distances of two particles
	I(Q)	Scattering intensity
	I_D/I_G	Ratio of defect and graphitic band intensity
	L	Thickness of bilayer in lamellar
	l_o	Length of hydrophobic tail
	Μ	Number of bilayer in lamellar
	P(Q)	Form factor
	R_a	Polar radius for ellipsoidal micelle
	R_b	Equatorial radius for ellipsoidal micelle
	R _{cylinder}	Radius of cylindrical micelle
	R _{disk}	Radius of stacked disk micelle





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R_{f}	Retention factor
R_{sphere}	Radius of spherical micelle
S(Q)	Structure factor
V(h)	Potential energy
V_A	van der Waals interaction
Vo	Volume of hydrophobic tail
V_R	EDL interaction
V_T	Potential barrier
V_{vdW}	van der Waals potential
X	Aspect ratio
Γ	Adsorption isotherm
Устс	Surface tension at cmc
O5-4506 ⁶ ζ ² -potential ^{ustaka.upsi.edu.my}	Perpustakaan Tuanku Bainun Zeta-potential in Abdul Jalil Shah
heta	Surface coverage
λ	Wavelength
ho	SLD
σ	Electrical conductivity
τ	Surfactant monolayer thickness

 Γ_m Surface concentration of monolayer







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- В Small-Angle Neutron Scattering Data of DC3Ph2 and TC3Ph3 (Section 4.1)
- С Surfactant Coverage Index (ϕ) Calculation (Section 4.5)
- D List of Publications and Conference







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CHAPTER 1

INTRODUCTION



1.1 Rationale

Driven by the prosperous economical aspect given by graphene-based industry that has been applied in some countries e.g. South Korea, Malaysia has also take the current "graphene-fever" and incorporated it as one of the national aspiration in "National Graphene Action Plan 2020". The aim is to encourage academician and industrial sector on the development of graphene-related research. As a direct response, this research was focused on the incorporation of graphene to the largest market potential of renewable polymers produced in Malaysia and Indonesia. While graphene promised array of extraordinary properties, one major problem to application realisation of this materials is the difficulty to form stable dispersions in most solvents due to the propensity of graphene sheets to coming together and form







stacking (D. Li, Muller, Gilje, Kaner, & Wallace, 2008). Methods to overcome this based on the use of surfactants as dispersing agent are generally favoured and results in improved dispersion stability (Coleman, 2009; Lotya, King, Khan, De, & Coleman, 2010); however the dispersion mechanism has not been clearly determined. Too many commercial surfactants such as sodium dodecylsulfate (SDS) and sodium dodecylbenzylsulfonate (SDBS) have been hailed as being graphene compatible surfactants, but research into the design of graphene-compatible compounds, henceforth "graphene-philic compounds", are yet to be appearing in scientific articles. Therefore, this research was conducted to evaluate the ability of each custom-made surfactants and surfactant ionic liquids as well as the commercial surfactants (for comparison purposes) to provide enhanced graphene dispersion inside the polymer matrix to make conductive nanocomposites via latex technology.

1.2 It is the Graphene Era: Prospects vs. Challenges of Applications into **Polymer Nanocomposites**

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Since the discovery of graphene in 2004 by Geim and his colleagues in University of Manchester, it has flooded worldwide research interests. Many forecasted graphene as future materials and are presumed to hold higher prospect than the former carbon nanotubes (CNTs). This is due to its outstanding properties such as good optical transparency; estimated to be ~97.7% (Nair et al., 2008), large surface area (theoretical value of 2630 m²) (Y. Zhu et al., 2010), exceptional thermal conductivity of 5000 W m⁻¹ K⁻¹ (Balandin et al., 2008) and also high electron mobility and electrical conductivity (Bolotin et al., 2008). The media has also added to the hype, by enthusing over the way that this new family of carbon can be readily synthesised from

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cheap graphite and will transform many industrial aspects. Those exciting properties, especially high electrical conductivity are reported to be potentially replacing traditional conductive fillers e.g. carbon black for its ability to give orders magnitude enhancement of insulating polymer such as natural rubber (NR) and cellulose at relatively low loading (Y.-R. Kang, Li, Hou, Wen, & Su, 2012; Tkalya et al., 2014; Tkalya, Ghislandi, de With, & Koning, 2012; Weng et al., 2011).

With the worldwide still-growing interest and continuing experimental efforts in maximising the application of graphene in many research fields, Malaysia also taking big strides towards graphene-related research by establishing it as one of the national aspiration of "National Graphene Action Plan 2020". The ideas stem from Malaysia's aspiration to be a high-income nation by 2020 and beyond with improved 05-4506 jobs and rich high value-innovative products by incorporating graphene in industrial bases sector. Provided with the wide possible variety applications of graphene in industry, these may contribute to the raking up of more than RM 250 million on the national income and to help create 9,000 new jobs for the industries by 2020. Among a large array of possible implementation of graphene in industry, there are five priority areas; one of them is rubber additives and polymer nanocomposites.

In line with the spirit of the Environmental Protection Agency (EPA) in developing sustainable material, rubber additives and polymer nanocomposites is particularly interesting considering that Malaysia is blessed with abundant source of natural rubber and cellulose fibre which now widely studied for the development of conductive nanocomposites. If executed correctly and can be translated into commercial market, this will add value to the existing rubber and crop industries and





lift the gross national income. Thus, as an attempt to leverage the value of the final products, research on developing conductive graphene-biopolymer composite, required to be optimised and the problems that may hinder the application realisation needs to be addressed.

Natural rubber is one of the must studied natural polymers for producing carbon nanomaterial-filled composites ever since carbon black once steal the limelight in research field before the discoveries of more advance carbon materials. Natural rubber (NR) is a biohydrocarbon polymer widely consumed in industrial activities especially for tire manufacturing or medical use (gloves). According to data released by Statistics Division of Food and Agricultural Organization (FAOSTAT), Malaysia share as one of the world's leading suppliers of NR (673,513 tonnes in 2016) after 05-4506 Indonesia (3,157,780 tonnes in 2016) and Thailand (4,476,636 tonnes in 2016) (FAOSTAT, 2018). Economically, given the current availability and cheap price of NR (estimated at RM 1.00/kg) compared to synthetic polymer as polystyrene (estimated 650.00/kg using scientific supplier), development of at RM nanocomposites using this material is expected to infiltrate potential market (Malaysia Rubber Board, 2018). However, theses polymer suffers for the lack of conducting network in the rubber internal structure resulting low electrical properties. When such nanofiller as graphene are incorporated in NR matrix, the nanocomposites are targeted to deliver conductive materials as copper to fabricate wire components (Mohamed et al., 2014; Mohamed et al., 2015; Sadasivuni, Ponnamma, Thomas, & Grohens, 2014). In most cases, industrial parts are demanding for material with improved performance while lowering the unit price. For a long term growth of conductive materials, a







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cheaper material as graphene nanocomposites wiring technologies would be economically preferable than transition metal.

An increasing demand for sustainable and versatile electric products component have driven the research interest on renewable polymer-based composite, particularly, cellulose-based materials. Growing numbers of scientific publications therefore mainly focused on the development of electrically conductive or electrochemically active cellulose paper as energy storage devices (Y.-R. Kang et al., 2012; Weng et al., 2011; Ye et al., 2016). Wide varieties of cellulose were used, ranging from microcrystalline to nanofibrillated cellulose (Carrasco et al., 2014; Cataldi et al., 2015; Feng, Zhang, Shen, Yoshino, & Feng, 2012; B. Wang, Lou, Wang, & Hao, 2012; F. Wang, Drzal, Qin, & Huang, 2015). Cellulose, which is the most abundant natural polymer on earth, is mostly known as the main composition on paper production. It may be extracted from plant (woods), animals, or some bacteria (Rojas, 2016).

One of the most sought out fibrous materials source after a decrease of the woods sources for papermaking is Kenaf (Hibiscus cannabicus L.) tree (Abdul Khalil, Alwani, & Omar, 2007; Abdul Khalil et al., 2014). Aside from the feasibility to be processed into pulps, it can be used as building materials or biocomposites. It has many advantages to name as being inexpensive and requires little care since it can grow in a wide range of climatic conditions. There are two distinct fibres that made up Malaysian Kenaf; bast and core with a composition respectively are 35% and 65% (Abdul Khalil, Ireana Yusra, Bhat, & Jawaid, 2010). Data released from the Ministry of Plantation Industries and Commodities revealed that the total production of dried



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stem Kenaf in Malaysia on 2016 was estimated to be 11,518 tonnes (Ramli, 2017). Given the abundance and relatively low capital investment of Kenaf, it is such an advantage to explore the most promising application of Kenaf-based materials for improved value.

During recent years, polymer reinforced carbon nanomaterials has dominated various publications. However, a similar question has continuously prompted between scientists, "where can we find such cost-conscious material to produce nanocomposite?" With the rise of graphene, there is currently a growing interest in processing graphene/polymer nanocomposites, both from the point of view of fundamental properties determination and the development of new applications. Yet, graphene have problems of their own, to do with their poor solubility and tendency to re-agglomerate during material processing. In addition, preparing such composites was extremely difficult because the strong intersheet interactions prevent them from dispersing in water or polymer solution (Green & Hersam, 2009a; Texter, 2014).

The challenge was to find a process that yielded a uniform dispersion of graphene in a polymer matrix as well as the control properties of the filler-matrix interface. If such materials are to be commercialised, there is also a need to provide a simple yet effective method for dispersing graphene in polymer matrix. One possible way to afford a dispersible graphene is by covalent treatment which leads to the disruption of sp^2 -conjugated network. In the context of conductive nanocomposites design, these effects are unfavourable because it gives a detrimental effect to the electrical properties. The answers could lay on the so-called latex technology which





employing surfactants as a third agent to tailoring the interfacial interaction between graphene and polymer matrix (Tkalya, Ghislandi, Alekseev, Koning, & Loos, 2010; Tkalya et al., 2012).

1.3 Latex Technology – The Role of Surfactants

The principle of latex technology by using surfactant to assist incorporation of filler on polymers was started back in the 1980's when used to improve the dispersibility of clay minerals in polymer matrices. The idea was put forth by Lagaly to make clay/polymer nanocomposite (Lagaly, 1999). When dispersed into polymer matrices, it is difficult to achieve fully exfoliated clay-polymer nanocomposites because of the propensity to agglomerate into tactoids, rather than forming individualised monolayers. A complete exfoliation (or nearly so), can be achieved by the use of either organic compounds or surfactants (Fornes, Yoon, Hunter, Keskkula, & Paul, 2002; LeBaron, Wang, & Pinnavaia, 1999; R. K. Shah, Hunter, & Paul, 2005). A similar strategy has been used after the discovery of carbon nanotubes by Sumio Ijima in 1991. Surfactants again used to enhance compatibility between polymer host and CNTs for the development of electrically conductive nanocomposite (Grossiord et al., 2008; Regev, ElKati, Loos, & Koning, 2004; J. Yu et al., 2007).

Even after decades of utilisation, there is no general consensus on the definition of "latex technology". Some confusion about the meaning of this term has ensued with surfactant-free systems also being considered (Fan, Zhang, Tjiu, & Liu, 2013; Pham, Dang, Hur, Kim, & Chung, 2012; D. Wang et al., 2013; Zhan, Lavorgna,







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Buonocore, & Xia, 2012). To avoid arbitrary distinctions with other latex-based methods (Fan et al., 2013; Pham et al., 2012; Zhan et al., 2011), the term "latex technology" will be applied throughout this study to refer the fabrication of composites with colloidal systems comprising aqueous dispersions of nanofiller and polymer matrices stabilised by surfactants which non-covalently bind to the filler surfaces.

The first paper on the preparation of graphene/polymer nanocomposites via latex technology (see Figure 1.1) was written by Tkalya et al. (2010). They revealed that graphene/polymer nanocomposites prepared through this technique exhibited relatively good dispersion quality and gave a pronounced enhancement of electrical conductivity compared to those prepared using other techniques. The versatility of 154506 latex technology to offer low percolation threshold and relatively high conductivity then immediately triggered others to work in this area with much success (Aguilar-Bolados, Brasero, Lopez-Manchado, & Yazdani-Pedram, 2014; Ghislandi, Tkalya, Marinho, Koning, & de With, 2013; Matos, Galembeck, & Zarbin, 2014; Tkalya et al., 2010). The avoidance of volatile and organic compounds (VOCs) in this technique poses a positive step towards the more environmentally friendly handling of graphene.

To achieve graphene dispersibility for latex technology processing, surfactants which are active at graphene surfaces are needed. The duality characteristics of surfactants which allow altering the surface energy and aggregated to form micelles are important to facilitate the formation of stable colloidal systems. At the graphenewater interface, the surfactant tails are attached – driven by hydrophobic interactions helping to separate the graphene sheets to prevent agglomeration via electrostatic or





steric stabilisation (Lotya et al., 2009; Mohamed et al., 2016; R. J. Smith, Lotya, & Coleman, 2010). Unfortunately, relatively few commercial surfactants exhibit any significant compatibility with graphene, and the systematic design of graphene-compatible surfactants is only in its infancy.



Figure 1.1. Schematic Illustration of Graphene/Polymer Nanocomposite Preparation using Latex Technology (Tkalya et al., 2010)

Studies have noted that surfactants able to mediate filler-polymer interactions and improve the filler-to-matrix transfer properties (Matos et al., 2014; Regev et al., 2004; Shahil & Balandin, 2012; Yoonessi & Gaier, 2010; J. Yu et al., 2007), although different conclusions were reached. Juhué & Lang (1993, 1994) declared that the final properties of the resulting polymer films are influenced by the nature of the polymer, particle size and distribution, particle morphology and the amount of surfactant. With





regard to nanofiller properties, Zuberi, Sherman, & Cho (2011) as well as Lisunova and co-workers presumed that the presence of a surfactant layer atop the nanofiller surface would hinder the electron mobility between the nanofiller conductive network to give higher resistivity values (Lisunova, Lebovka, Melezhyk, & Boiko, 2006). Recently, Tkalya et al. (2010) also showed this, by using high surfactant levels (up to 10-fold excess) to obtain stable graphene dispersions. The presence of excess surfactant in the final composites was acknowledged to affect the ability of graphene to fully enhance the electrical conductivity of the resulting nanocomposites. Therefore, there is an imperative to search for new types of surfactant which can efficiently provide a good dispersion quality at low loading.

O 05-4506 1.4 Graphene-Compatible Compounds

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1.4.1 **Ionic Surfactants**

For decades, ionic surfactants have been widely accepted as the preferable choice for carbon family/water dispersion (Díez-Pascual et al., 2018; Islam, Rojas, Bergey, Johnson, & Yodh, 2003; Matarredona et al., 2003; Moore et al., 2003; Strano et al., 2003). Owing to the extensive compatibility between ionic surfactants and carbon materials, this type of surfactants has massively employed for investigation in dispersion. graphene SDS (sodium dodecyl sulfate), **SDBS** (sodium dodecylbenzenesulfonate) and CTAB (cetyltrimethylammonium bromide) are the most frequently used surfactant to decrease the agglomerative tendency of CNTs (L.







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Jiang, Gao, & Sun, 2003; Rausch, Zhuang, & Mäder, 2010), and in graphene recently (Lotya et al., 2009). Also investigated later was the use of sodium cholate (SC) surfactant (Lotya et al., 2010). All the selected surfactants exhibited graphene-compatibility and has been widely invoked in studying graphene dispersion in water as well as to stabilise colloidal system consisting of graphene and polymer matrices.

The use of anionic surfactant SDS (Compound 1, Table 1.1) in preparation of poly(methyl methacrylate) PMMA reinforced functionalised graphene (FGN) nanocomposite was reported by S. Jiang and co-workers (S. Jiang et al., 2013). Nanocomposites are prepared by two different methods namely, latex technology plus melt blending (composite 1) and direct melt blending (composite 2). Unlike composite 1, composite 2 suffers severe agglomeration thus cannot attain the same dispersion level and reinforcing effectiveness as SDS stabilised FGN/PMMA nanocomposite. They showed that initial treatment by the use of surfactant as stabilising agent can effectively enhance the thermal and mechanical properties of the final product. The remarkable improvement of FGN/PMMA nanocomposite properties was assumed to the presence of SDS on graphene surfaces which enables strong interfacial interaction between SDS coated FGN sheets and PMMA matrices. This enhanced particle-to-matrix load transfer between FGN to PMMA.

More recently, a work by Aguilar-Bolados et al. (2014) had shown that graphene with surfactant coatings are distributed uniformly and arranged interstitial latex particles as observed under transmission electron microscopy (TEM). As a result, compared with the neat natural rubber, addition of 1 wt% SDS in thermally reduced graphite oxide (TRGO) and polymer matrices system leads to a significant





elastic modulus enhancement relative to the NR matrix. In addition, the conductivity of NR/TRGO stabilised SDS nanocomposites was 6 orders of magnitude higher than NR alone ($\sim 10^{-12}$ S cm⁻¹), close to the 10^{-6} S cm⁻¹. Although exciting, they focused on the effect of nanofiller loading to the final composite properties. Thus, it is hard to highlight the significant role of surfactant as polymeric reinforcing agent.

Table 1.1

Graphene-Philic Surfactants Referred in the Text





Table 1.1 (Continued)



Studies pointed out that the hydrophobic interactions cause significant attraction between alkyl tails and graphene surfaces in water (Meyer, Rosenberg, & Israelachvili, 2006). The low solubility of alkanes in water suggest the dodecyl tails of SDS interact and wrap onto the graphene surfaces, preventing water to reach the sheet surface and hence impending aggregation. Using Auger Electron Spectroscopy (AES) and Fourier Transform Infrared (FTIR) L. Jiang and co-workers proved the presence of surfactant tails adhered to the nanotube surfaces (L. Jiang et al., 2003). The ideal scenario is that the alkyl tails would cover the graphene surfaces such that all the graphene sheets were completely separated into monolayer sheets: practically,



however, this is nearly unattainable. Recent studies noted there are regions where surfactant adsorption does not occur. SDS does not adsorb onto regions containing other functionalities e.g. oxygen as in graphene oxide (GO) and the reduced form, reduced graphene oxide (RGO). In this case, the exfoliated state may not produce exclusively monolayer sheets, but instead few layer graphene (FLG) or even stacked graphene may exist (Glover, Adamson, & Schniepp, 2012; Hsieh, Punckt, Korkut, & Aksay, 2013).

Practical result have also achieved in using SDBS surfactant to produce polymer reinforced graphene nanocomposite. SDBS (compound 2 Table 1.1) has earned great interest in the field of nanocomposites because of its dispersive efficiency (Lotya et al., 2009; Parviz et al., 2012). One unique property that characterised SDBS from its cousin SDS is the presences of phenyl ring. This aromatic ring is likely to improve the intermolecular interaction between graphene and target molecules through the π - π interaction, hydrophobic and Coulombic interaction with the electron-rich of graphene surface. The synergistic effect of these moieties enables strong interactions of the surfactant molecule with both graphene sheets and water molecules, hence improves the dispersion of graphene in water and thus in polymer host (Lotya et al., 2009; Parviz et al., 2012; L. Zhang et al., 2014).

Despite the excellent history in CNT dispersion and polymer nanocomposite, there is not much work reported the dispersion of graphene in polymer matrix stabilised by SDBS. Ghislandi, Tkalya, Marinho, et al. (2013) reported works on SDBS for stabilising graphene and polypropylene (PP) system. This surfactant appears to be effective in isolating the agglomerated structure into individualised







graphene sheets. Without the presence of surfactant, the graphene sheets find themselves highly wrinkled or folded into a fluffy structure (see Figure 1.2d) due to the strong van der Waals interaction. Observation using scanning electron microscopy (SEM) gives evident to the homogeneous dispersion of graphene-coated SDBS in polymer matrix. The uniform dispersion of filler in polymer matrices (Figure 1.2f) is the reason of the low nanofiller loading (0.3 wt%) needed to form a conductive network inside polymer matrix by graphene/polypropylene composite (Ghislandi, Tkalya, Marinho, et al., 2013).



Figure 1.2. SEM Images of MWCNTs and Graphene Organised Respectively: (a and d) as Powder Compacts, (b and e) as Paper Films and (c and f) inside PP Polymer

d) as Powder Compacts, (b and e) as Paper Films and (c and f) inside PP Polymer Composites (f) Partially Wrapped Graphene Platelets inside the PP Polymer Matrix (f) (Ghislandi, Tkalya, Marinho, et al., 2013)

Further investigation utilising different anionic type has been made using sodium cholate (SC, compound 3 Table 1.1) surfactant by Shahil and Balandin (2012) to make multilayer graphene (MLG)/epoxy resin nanocomposites. High aqueous dispersion of graphene in SC solution (5 wt%) leads to a strong thermal conductivity

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enhancement of the composite final properties; from the initial value of ~5.8 to 14 W/mK. Tkalya and groups (2014) also reported study on SC surfactant but with different polymer and surfactant concentrations. Interestingly, the chosen surfactant concentrations for producing graphene via liquid-phase exfoliation were 0.1 and 1.0 mg/ml which is far below the critical micelle concentration (cmc) of SC itself (~5 mg/ml).

Initial dispersion study using this surfactant has reported that in the applied concentrations range, surfactant provided higher dispersion ability and stability than concentrations close to the cmc (Lotya et al., 2010). The discrepancy though remains unresolved. Instead, they prepared all subsequent dispersion in 0.1 mg/ml SC solution and thus on this study. A similar observation was perceived by L. Jiang et al. (2003) and Bystrzejewski et al. (2010) for the case of CNT dispersions using SDS and SDBS. They noted that it was possible to obtain stable and highly concentrated nanotube dispersions at surfactant concentrations below cmc, although the authors did not conclude on the mechanism. This study reveals somewhat surprising yet interesting fact that graphene with high dispersion and exfoliation degree gives an adverse reinforcing effect to the composite final conductivity. They suggested that the presence of certain amount micro-scale aggregates in relatively low dispersion stability of graphene can be somewhat beneficial to the higher electrical conductivity achieved by the produced composite.

Compared to extensive works using anionic surfactants, literature on graphene dispersion or exfoliation using cationic surfactants remained scarce. This is ironic considering the earliest study on surfactant aggregation on graphite surface used





cationic surfactant namely cetyltrimethylammonium bromide (see Table 1.1) as a model (Manne, Cleveland, Gaub, Stucky, & Hansma, 1994). It was noted that the electrostatic interactions of CTAB tail and graphene surface prevented neighbouring graphene sheets re-stacking for agglomeration (Manne et al., 1994; Paruchuri, Nguyen, & Miller, 2004).

Using strategy popularised by Coleman groups (Lotya et al., 2009), Griffith and Notley (2012) have studied the effect of CTAB concentration (0.1 – 0.9 mM) on the yield of graphene exfoliated from graphite. The highest graphene dispersion achieved at a surfactant concentration of 0.7 mM; slightly below its cmc (around 0.9 – 1.0 mM) with the surface tension of CTAB solution approximately 40 mN m⁻¹. Later, Z. Wang et al. (2013) also suggested that CTAB helps to match the surface energy between graphene and water for dispersion – claiming a stable dispersion of 15 days. However, the studies were limited to the measurement of CTAB surface tension, rather than surfactant-stabilised dispersions of graphene (Z. Wang et al., 2013).

Among a number of studies trying to disperse graphene in polymer matrix, Kim and co-workers applied CTAB at its cmc (0.9 mM) to prepare nanocomposite of styrene butadiene rubber (SBR) and graphene. The results revealed that CTABstabilised MLG is far more effectively dispersed in the SBR matrix than the raw MLG (J. S. Kim, Hong, Park, & Shim, 2010; J. S. Kim, Yun, Kim, & Shim, 2011). The zeta (ζ)-potential was used to characterise the dispersion state of the system. It has been suggested that adsorption of CTAB onto MLG surface impart a positive charged on MLG sheet, hence enables them to strongly interact via electrostatic forces with the negatively-charged SBR particles (Figure 1.3).





Figure 1.3. The Zeta Potential vs. pH for (a) SBR Latex, (b) MLGS-COOH in Water, and (c) MLGS+CTAB in Water (J.S. Kim et al., 2010)

As a result, a uniform homogeneous dispersion of filler in the SBR matrix leads to a notable thermal and electrical properties enhancement of the nanocomposite. The stabilisation of colloidal graphene/NR latex system by CTAB was also reported by Matos et al. (2014). TEM elemental mapping of nitrogen revealed that CTAB adhered at the edge of RGO sheets to give a positively charged and is responsible for the enhanced interfacial interaction of RGO and NR matrix. The ability of surfactants to alter interfacial energy is one of the driving forces for the migration towards the interface during film formation (Zhao, Dobler, Pith, Holl, & Lambla, 1989). It is this characteristic that was proposed to be an important factor for the interaction between filler and polymer matrix.





1.4.2 Surfactant Ionic Liquids

Ionic liquids (ILs), defined as low melting liquid salts, has been widely considered environmentally benign compound in material processing. This is because of low vapour pressure, low toxicity, recycling ability, and tuneable design for specific synthetic or chemical applications (Docherty & Kulpa Jr, 2005; Greaves & Drummond, 2008; Lu, Yan, & Texter, 2009; Weingärtner, 2008). The most common ILs dominating scientific research is 1-butyl-3-methyl-immidazolum halides (BMIM-X; general structure is given in Table 1.1). It was the ability of the long chain analogues of these BMIM-based ILs to self-assemble in aqueous solution and forming micelles that leads a coined term of "surfactants ionic liquids" for this novel compounds (P. Brown, Butts, Eastoe, Fermin, et al., 2012; El Seoud, Pires, Abdel-05-4506 Moghny, & Bastos, 2007; Galgano & El Seoud, 2010, 2011).

Until today, studies on surfactant ionic liquids are mostly centred on the synthesis, characterisation, or applications in traditional emulsions (Galgano & El Seoud, 2011; Jiao et al., 2012; G. Singh, Singh, & Kang, 2016). It was until McCoy group used cationic surfactant ionic liquids namely dodecyltrimethylammonium trichloromonobromoferrate (DTAF, Table 1.1) to make magnetic graphene oxide that showed the possible compatibility of surfactant ionic liquids for graphene family (McCoy, Brown, Eastoe, & Tabor, 2015). In the followings, it will be shown that the widely used ILs to mediate the graphite exfoliation either as a pure ILs, or a mixture with water and/or polymer is those based on imidazolium counterion. Thus, the attentions in this section are limited to those involving the aforementioned compound.





It is therefore can be used as a map to draw the relationship with the particular surfactants ionic liquids that were used in this thesis.

Among the earliest investigation on the use of imidazolium-based ILs for carbon nanomaterial exfoliation was conducted by Fukushima and co-workers (Fukushima & Aida, 2007; Fukushima et al., 2003). They successfully untangled nanotube bundles by grinding nanotubes in a series of fluorinated-bearing imidazolium ILs by which the resulting nanotube gels was called "bucky gels of ionic liquids". It was postulated that the imidazolium-nanotube π -networks was responsible for the individualised nanotube forming conductive network structure. The resulting gel medium containing nanotube network allowed further application for fabrication of electroconductive polymer/nanotube composite materials. A wide variety of research groups have since used imidazolium-based ionic liquids for de-bundling carbon nanotubes (Di Crescenzo et al., 2009; Price, Hudson, & Tour, 2005; Shim & Kim, 2009; J. Wang, Chu, & Li, 2008).

Following a detailed exposition by Fukushima groups in opening a greener alternative route for exfoliating nanotubes, particularly imidazolium-based monomers (Fukushima & Aida, 2007), N. Liu and co-workers demonstrated a one-step electrochemical exfoliation of graphite in a system consisting of a range of imidazolium-ILs and water (N. Liu et al., 2008). To the resulting dispersion, polystyrene was added by simple blending to produce graphene/polystyrene composite. A remarkable electrical conductivity enhancement was reported, reaching to 13.84 S m⁻¹ from ~ 10^{-14} S m⁻¹ (intrinsic electrical conductivity of neat polystyrene) with just addition of 4.19 vol% graphene. Similar method involving mixture of water





and ionic liquids later was used by Lu and his group to produce graphene and fluorescent carbon nanoribbons (Lu, Yang et al., 2009). A detailed mechanism on how the exfoliation took place in the presence of ILs (BMIM-Cl and BMIM-BF4; see structure in Table 1.1) was given, underlining the role of ILs to intercalate between graphene sheets, giving a further distance for the adjacent graphene sheet to aggregate. The interactions of ILs with graphene surface are credited to cation- π and/or π - π interaction. Instead of following the previous steps, Nuvoli et al. (2011) ground graphite with 1-hexyl-3-methylimidazolium hexafluorophosphate (HMIH) and used long-hour (24 h) bath ultrasonications to form readily dispersed graphene in HMIH (see Table 1.1). They claimed a highest graphene concentration reported in literature was achieved, giving a value of 5.33 mg mL⁻¹ according to gravimetric analysis. Analysis was brief, noting on the physical characterisation of resulting nanosheets. Work on mixing ILs with other solvents was also existed in literature (Y. Chen, Zhang, Zhang, Yu, & Ma, 2011; Najafabadi & Gyenge, 2014), however it is not the main interest in this study and will not be discussed further.

Using a mixture of BMIM-Cl and cellulose, Peng and co-workers showed that such system can be used as a facile and straightforward route to prepare free-standing graphene/cellulose paper (H. Peng, Meng, Niu, & Lu, 2012). Given that cellulose is notoriously insoluble or indispersible in water or organic solvents, cellulose was first mixed with BMIM-Cl to ensure a homogeneous suspension. This was followed by mixing the BMIM-Cl/cellulose with GO-treated BMIM-Cl. Here, BMIM-Cl acted as stabiliser for both cellulose and graphene in water although at last BMIM-Cl was removed by washing with ultrapure water. The reported electrical property was 3.2 S m⁻¹. A subsequent study used a similar treatment of mixing GO with different





imidazolium-based ILs (Y.-K. Yang et al., 2012). The difference is on the polymer used to fabricate the composite and that instead of removing; they kept the ILs and labelled the product as IL-functionalised graphene. Polymer nanocomposites obtained from this approach boasted a very remarkable enhancement up to 13 order of magnitude electrical conductivity enhancement.

1.5 Tuning Polymer Properties by Graphene and the Potential Applications of Graphene/Biopolymer Nanocomposites

There is high industrial demand for composite materials, especially in the fields of transportation and electronic devices. The applications of latex technology as a simple, environmentally friendly and reliable alternative method to produce polymer reason produce composites thus already hit significant interest. Clearly, economical aspects are of primary importance to ramp up the large production of any materials offered on the commercial market. Today, researchers have been seeking ways to readily synthesise graphene in a large quantities using relatively cheap and abundant bulk graphite (Dreyer, Murali, Zhu, Ruoff, & Bielawski, 2011; Park et al., 2011; Park & Ruoff, 2009); at current market prices the raw cost of graphite powder is about 100 USD/kg using a scientific supplier. There have been some promising results, and thus utilisation of graphene for polymeric reinforcement may be a possible way to reduce the production cost of polymer nanocomposites. The efficient CNTs also still expensive until today, and the use of graphene potentially allows for comparable physical property enhancement at a fraction of the cost (Shahil & Balandin, 2012; Tkalya et al., 2010).









In general, potential applications of composite filled with graphene based on latex technology have demonstrated very exciting results. It offers an improved electrical conductivity at low filler content, high thermal conductivity, chemical and bacterial resistance and even gas barrier properties (see Table 1.2). All of these results would meet industrial needs for advancing the development of high performance light weight polymer composites (low graphene content) for aircraft components, thermally conductive support for thermal management (electronic devices) and engineering applications such as antistatic and electromagnetic interference (Agate, Joyce, Lucia, & Pal, 2018; Shahil & Balandin, 2012; Syurik et al., 2012; Yoonessi & Gaier, 2010).

These nanocomposites can also find applications involving solvent, gas and bacterial resistance in biomedical applications, pipelines for petroleum industry and hygiene products (George et al., 2018; Matos et al., 2014). Despite the hype, we should consider that it is too early to tell that graphene nanocomposites particularly those with latex technology will vastly reform the current-lab-scale production to industrial level. There are practical barriers that should be overcome and it requires to the collaboration of scientists and engineers to optimise the varied and exciting commercial uses of these conventional materials.







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Table 1.2

Potential Applications of Graphene/Biopolymer Nanocomposites

Composite ^a	Stabilisers ^b	Properties enhancement	References			
Natural Rubber						
FLG/NR	Curcumin	Mechanical properties	(George et al., 2018)			
RGO/NR CTAB - Storage module - Solvent/chemic - Microorganism - Electrical cond		 Storage modulus Solvent/chemical resistance Microorganism resistance Electrical conductivity 	(Matos et al., 2014)			
RGO/NR	O/NR PVP - Thermal conductivity - Solvent resistance		(X. Zhang et al., 2016)			
Potential ap composite wi	plications: Ac ring. taka.upsi.edu.my	Coustic insulation, food packag Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah	ing, hygiene product, PustakaTBainun			
		Cellulose				
G/MC	BMIM-Cl	Charge-discharge capacityStable cycling performancePhotothermal property	(Ye et al., 2016)			
RGO/Cell	BMIM-Cl	Mechanical flexibility	(H. Peng et al., 2012)			
GNS/CF	-	- Electrical conductivity	(YR. Kang et al., 2012)			

(Continue)

^aFLG: few-layer graphene; G: graphene; GNS: graphene nanosheets; NR: natural rubber; RGO: reduced graphene oxide; MC: microcrystalline cellulose; CF: cellulose fibre; Cell: Cellulose paper. ^bCTAB: cetyltrimethylammonium bromide; PVP: polyvinyl pyrrolidone; BMIM-Cl: 1-buthyl-3methyl-imidazolium chloride



Composite ^a	Stabilisers^b	Properties enhancement	References
GNS/CF	-	- Charge-discharge performance	(YR. Kang et al., 2012)
GNS/Cell	-	- Electrical conductivity	(Weng et al., 2011)
		- Mechanical flexibility	
		- Gravimetric capacitance	

Table 1.2 (Continued)

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Potential applications: Flexible supercapacitor, flexible electrodes, biomedical scaffolds on tissue engineering, medical devices, photothermal devices.

^aFLG: few-layer graphene; G: graphene; GNS: graphene nanosheets; NR: natural rubber; RGO: reduced graphene oxide; MC: microcrystalline cellulose; CF: cellulose fibre; Cell: Cellulose paper. ^bCTAB: cetyltrimethylammonium bromide; PVP: polyvinyl pyrrolidone; BMIM-Cl: 1-buthyl-3methyl-imidazolium chloride



1.6.1 Aim

The works on this thesis were carried out with the aim to design and study the role of new graphene-compatible surfactants and the possible mechanism in the stabilisation of graphene incorporated into biopolymer matrix for the preparation of conductive nanocomposites.





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1.6.2 Objectives

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The objectives of this research were:

- 1. To synthesise and characterise aromatic bearing surfactants and novel surfactant ionic-liquids for graphene/polymer nanocomposites prepared by latex technology.
- 2. To prepare graphene/polymer nanocomposites stabilised by aromatic surfactants and surfactant ionic-liquids.
- 3. To study the electrical properties and morphology of graphene/polymer nanocomposites stabilised by graphene-compatible compounds.
- 4. To study the interfacial behaviour between graphene and surfactant through airwater surface tension measurement for predicting graphene-compatibility
- 05-4506852 To study the colloidal stability of graphene dispersion aided by aromatic bearing surfactants and surfactant ionic liquids
 - 6. To investigate the self-assembly structure of aromatic surfactants and surfactant ionic liquids in aqueous phase as well as graphene/surfactant/water system
 - 7. To investigate the stabilisation mechanism involved in the surfactant-based graphene dispersion.





1.7 Scope of Study

As an attempt to fill the knowledge gap, this study focuses on systematically developing surfactant and surfactant ionic liquids for the preparation of nanocomposites with natural rubber latex and kenaf-bast nanofibrillated cellulose as polymer host. Two nanocomposites preparation were used: (i) dispersion of graphene nanoplatelets (GNPs) in natural rubber latex matrix with the help of surfactants and (ii) one-pot electrochemical exfoliation of graphite in surfactant–cellulose mixture.

Here, the anionic surfactants were analogue of the widely-popular surfactant in colloid science, Aerosol-OT (AOT; sodium bis(2-ethylhexyl) sulfosuccinate) which generated using standard chemistry (Nave, Eastoe, & Penfold, 2000), but with important modifications. The basic strategy utilises the introduction of certain of 4506 structural changes in surfactant chemical structure to enhance the graphenecompatibility via four complementary approaches which are varying the surfactant chain degree as well as aromatic numbers on surfactant tail, aromatisation on surfactant headgroup, ion-exchange on hydrophilic headgroup, and metal incorporation on surfactant headgroup.

Proton Nuclear Magnetic Resonance (¹H NMR) Spectroscopy was used for probing the molecular structure of the synthesised surfactants in this study. Air-water (a/w) surface tension measurements were used to investigate the interfacial properties of the surfactants in water and graphene dispersion. Surface tension measurements were carried out using Wilhelmy Plate method in Hirosaki University, Japan. Zeta (ζ)potential measurement was used to examine the colloidal stability of surfactantstabilised graphene dispersion. The aggregation properties of surfactants and ionic





liquids in aqueous phase as well as in the graphene-dispersion system were studied using small-angle neutron scattering (SANS) at Science and Technology Facilities Council, ISIS Neutron and Muon Sources in UK under experiment number RB1710004 and XB1890152.

The electrical conductivities of the resulting nanocomposites were measured through four-point probe method. Meanwhile, field emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM), atomic force microscopy (AFM) and Raman spectroscopy were employed to study the morphology of the resulting nanocomposites.



Significance of Study



It has been 14 years since the discovery of graphene. While there has been a vast literature on graphene synthesis, dispersion, or nanocomposites preparation the interest has not yet been slow down. During the past years, it has been recognised that translating nanotube-mediated surfactant dispersion into graphene-stabilised surfactant dispersion gives a significant impact yet simple in step toward the resulting polymer nanocomposites (Mohamed et al., 2016; Tkalya et al., 2012). As a result, an increasing number of research groups used latex technology for nanocomposites fabrication: although many do not explicitly stated in the text.







Currently, two routes were utilised to obtain surfactant-stabilised graphene dispersions: (i) from graphite as starting material (reduction of graphene oxide in the presence of surfactant and liquid-phase exfoliation) or (ii) dispersing the synthesised graphene in surfactant solutions through ultrasonications (bath or tip ultrasonicator) where the duration vary from minutes to hours. The benefits of employing surfactants in dispersing graphene into polymer matrices are clear. However, the colloidal aspect of surfactants stabilisation, how the surfactants arranged on graphene surfaces or the optimum surfactant for stable dispersion has been relegated. Some mentioning an excess amount but others simply used certain concentration without further explanation. Furthermore, advances have been hindered by a lack of reliable predictive models for designing graphene-philic molecules because studies have been restricted to dispersing graphene using commercially available surfactants (Green & Hersam, 2009a,b; S. Lin, Shih, Strano, & Blankschtein, 2011; Seo, Green, Antaris, & Hersam, 2011; Shih, Lin, Strano, & Blankschtein, 2015).

The works here has aimed to set a guideline to select appropriate surfactants for the development of graphene/biopolymer nanocomposites, and to compare together recent findings to guide future research directions. Questions related to the role of surfactant and the stabilisation mechanism was addressed and discussed. The knowledge gained from this study may help for the rational design of graphenecompatible surfactants. This should open the door to optimisation of latex technology for industrial chemistry processes, as an economic and environmentally favourable approach.





1.9 **Thesis Outline**

Thesis is organised in five chapters. Chapter 1 is introduction underlining the background and aim of the study. This section provides general overview about potential and limitations of incorporating graphene to polymer matrix for practical applications and industry. Chapter 2 is literature review that covers scientific knowledge related to the subjects mentioned in the preceding section. This chapter contains the theory about surfactants, ionic liquids, polymers, graphene, as well as colloidal stability mechanism related to the dispersion of solid material in surfactant solutions. Chapter 3 is experimental section which gives all the details of the synthesis method and characterisation used in this study. ¹H NMR characterisation of the synthesised surfactants was also discussed in this chapter. Preparation and 05-4506 characterisation of nanocomposites can be found in Chapter 3. Pustaka Bainun

Chapter 4 is composed of 5 sections. The first section (Section 4.1) describes study on varying aromatic numbers on surfactant chain toward dispersion stability of natural rubber composite. This is followed by study on the addition of aromatic group on surfactant headgroup and its effect on the electrical conductivity enhancement of nanocomposites in second section (Section 4.2). The third section (Section 4.3) covers effort in using anionic surfactant ionic liquids as an exfoliant and stabilising agent in producing cellulose conductive paper through one-pot electrochemical exfoliation. Further approach by incorporation of metal on cationic surfactant ionic liquids for the fabrication of cellulose conductive paper is provided in the fourth section (Section 4.4). The fifth section (Section 4.5) discusses the use of air-water surface tension measurement as a tool to study the interfacial behaviour of graphene and surfactants







in aqueous phase. Chapter 5 provides the conclusions of the research findings and recommendations of the future work.





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