DEVELOPMENT OF CARBON NANOTUBE (CNT)-PHILIC SURFACTANT DESIGN FOR LATEX TECHNOLOGY

ARGO KHOIRUL ANAS

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ABSTRACT

The aim of this study is to investigate the roles played by the chemical nature of the CNT-philic surfactant for dispersing MWCNTs in polymer matrix. In this respect, the performance of single-, double-, and triple- chain anionic sulphosuccinate surfactants for the dispersion of MWNCTs in natural rubber latex (NR-latex) via latex technology was studied using a range of techniques, including field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and Raman spectroscopy. The conductivities of the nanocomposites were also measured using four point probe instruments. The results show MWCNTs were efficiently dispersed in NR-latex with an aid of hyper- and benzene ring- branched triple-chain sulphosuccinate anionic surfactants, namely, sodium 1,4-bis (neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-sulphonate (TC14) and sodium 1,5-dioxo-1,5-bis (3-phenylpropoxy)-3-((3-phenylpropoxy)carbonyl)pentane-2-sulphonate (TCPh), respectively. Importantly, compared to commercially available surfactants sodium dodecyl sulphate (SDS) and sodium dodecylbenzenesulphonate (SDBS), the use of TC14 and TCPh surfactants exhibits more homogeneously dispersion of MWCNTs. This indicates the performance of TC14 and TCPh as dispersants is better than both of commercially available surfactants. This study generates a fundamental understanding of the molecular structure requirements for surfactants to disperse MWCNTs via latex technology approach.

PEMBINAAN REKA BENTUK SURFAKTAN NANOTIUB KARBON (CNT)-FILIK BAGI TEKNOLOGI LATEKS

ABSTRAK

Tujuan kajian ini adalah untuk menyiasat peranan ciri kimia surfaktan CNT-filik bagi menyerakkan MWCNTs di dalam matrik polimer. Dalam hal ini, keupayaan surfaktan anionik sulfosuksinik rantaian tunggal-, dua-, dan tiga- bagi penyerakan MWNCTs dalam getah semulajadi (NR-latex) melalui teknologi lateks telah dikaji menggunakan pelbagai teknik, termasuk mikroskopi pengimbas pancaran medan elektron (FESEM), mikroskopi transmisi elektron (TEM), dan spektroskopi Raman. Kekonduksian nanokomposit juga telah dikaji menggunakan instrumen prob empat titik. Hasil kajian menunjukkan, MWCNTs terserak dengan efisien di dalam NR-latex dengan bantuan surfaktan anionik sulfosuksinik yang mempunyai rantaian bercabang tiga berlebihan dan bergelang benzena, yang dinamakan, natrium 1,4-bis (neopentiloksi)-3-(neopentiloksikarbonil)-1,4-dioksobutana-2-sulfonat (TC14) dan natrium 1,5-diokso-1,5-bis (3-fenilpropoksi)-3-((3-fenilpropoksi)karbonil) pentana-2-sulfonat (TCPh). Pentingnya lagi, dibandingkan dengan surfaktan komersial seperti natrium dodesilsulfat (SDS) dan natrium dodesilbenzenasulfonat (SDBS), penggunaan TC14 dan TCPh memberikan hasil penyerakan MWCNTs yang lebih homogen. Ini menunjukkan keupayaan TC14 dan TCPh sebagai penyerak adalah lebih baik berbanding kedua surfaktan komersial tersebut. Kajian ini memberi kefahaman asas tentang struktur molekul yang diperlukan oleh surfaktan bagi menyerakkan MWCNTs melalui pendekatan teknologi lateks.

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LIST OF ABBREVIATIONS

$(CD_3)_2CO$	Acetone-d_6
^{1}H-NMR	Proton Nuclear Magnetic Resonance Spectroscopy
AOT	Aerosol-OT/Sodium bis(2-ethylhexyl) sulphosuccinate
C	Carbon
CalTech	California Institute of Technology
$CDCl_3$	Chloroform-d
C_H	Chiral Vector
CH_3	Methyl
cmc	Critical Micelle Concentration
CNTs	Carbon Nanotubes
CO_2	Carbon Dioxide
CTAB	Cetyl Trimethyl Ammonium Bromide
CVD	Chemical Vapour Decomposition
D-band	Disorder Band
DRC	Dry Rubber Content
FESEM	Field Emission Scanning Electron Microscopy
G-band	Graphite Band
H	Hydrogen
H_2SO_4	Sulphuric Acid
HCl	Hydrochloric Acid
HNO_3	Nitric Acid
HRTEM	High Resolution Transmission Electron Microscopy
i	Integer
I_D/I_G	Intensity ratio of the D- and G- bands

LDS	Lithium Dodecyl Sulphate
MWCNTs	Multi-Wall Carbon Nanotubes
N	Nitrogen
NR-latex	Natural Rubber latex
PANI	Poly(aniline)
PS	Poly(styrene)
PTFE	Poly(tetrafluoroethylene)
S	Sulphur
SDBS	Sodium Dodecyl Benzenesulphonate
SDS	Sodium Dodecyl Sulphate
STEM	Scanning Transmission Electron Microscopy
Surfactant	Surface Active Agent
SWCNTs	Single-Wall Carbon Nanotubes
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
TLC	Thin Layer Chromatography
TMS	Tetramethylsilane
TSC	Total Solid Content
γ_{cmc}	Surface tension at the cmc

CHAPTER 1

INTRODUCTION

1.1 Carbon Nanotubes and Its Applications

Nanotechnology is one of invention field that opens up a new perspective in observing, manipulating, measuring, and manufacturing of material deep into nanoscale dimension, roughly in range of 1 to 100 nm (Mongillo, 2007; Ratner & Ratner, 2002). Historically, the idea and concept of nanotechnology was first introduced by physicist Richard Feynman, in a talk entitled "There's Plenty of Room at the Bottom" at an Annual Meeting of American Physical Society in California Institute of Technology (CalTech) on 1959 (Ramsden, 2011). The term of "nanotechnology" was then coined by Japanese researcher namely Norio Taniguchi in 1974, at International Conference on Production Engineering. In the 1980's, Eric Drexler was further explored the existence of nanotechnology (Drexler, 1986). His book "Engines of Creation: The Coming Era of Nanotechnology and Nanosystem" (published 1986) is considered as the first book on nanotechnology and successfully created a number of advantages in developing nanomaterial properties.

Structures of nanomaterial have been reported to have unique chemical, physical, and biological properties (Weiss, Takhistov, & McClements, 2006). Based on this reason, the great potential of nanotechnology has been already attracted a number of research communities, especially for improving material performances. In this respect, nanotechnology involves integrated multidisciplinary field including physics, biology, chemistry, electronic, engineering, *etc.* Nanofibres, nanosilica, nanoclay and carbon nanotubes (CNTs) are the current examples of nanomaterial that have been successfully developed by implementing nanotechnology.

Since its discovered and fully characterised by Sumio Iijima in 1991 (Iijima, 1991), an intensive research activity on investigating the incredible properties and performance of carbon nanotubes is significantly increased. The first CNTs observed were multi-wall carbon nanotubes (MWCNTs), which are arranged by rolling up of two or more concentric cylinders of graphite sheet (Figure 1.1a). In contrast, single-wall carbon nanotubes (SWCNTs) consist of single graphite sheet which rolled up into a hollow cylinder (Figure 1.1b). They exhibit outstanding electrical, mechanical, and thermal properties compared to traditional fillers, such as micro-particle carbon black (Tilstra *et al.*, 2008), and have therefore already attracted interest in numerous industries for possible applications including electronic wires, hydrogen storage, field emission devices, electrochemical devices, supercapasitor and transistor (Baughman, Zakhidov, & de Heer, 2002; Jarosz *et al.*, 2011). In addition, these various outstanding properties also promisingly enabled their use as an ideal nanofillers for polymeric reinforcement to produce nanocomposites (Guo, Zhu, Lin, & Zhang, 2008).

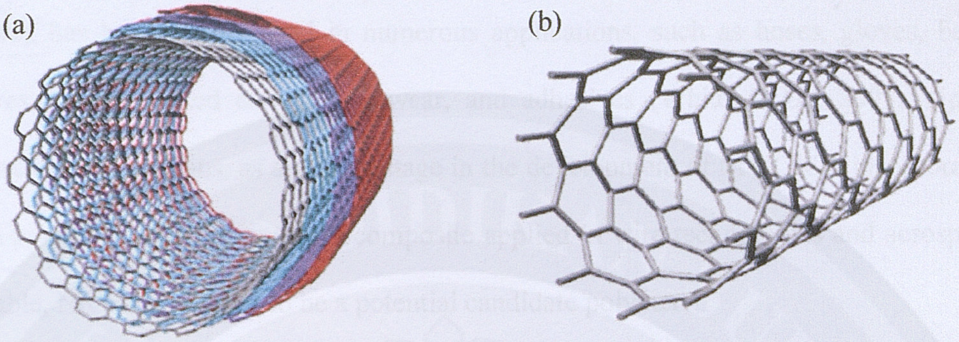

Figure 1.1 The schematic of: (a) multi-wall carbon nanotubes (MWCNTs) and (b) single-wall carbon nanotubes (SWCNTs) (Zhang, Bai, & Yan, 2010)

The field of nanocomposite involves the study of two or more phase material where at least one of the dispersed phases has one dimension in the nanometer scale (Ajayan, Schadler, & Braun, 2003). The exciting properties of nanocomposite materials are come from their unique combinations of material structure that are unachievable by conventional composite. Generally, these combinations can generate different properties than those of each single component. In case of CNTs, incorporation of this nanofiller into polymer matrix was firstly reported by Ajayan, Stephan, Colliex, and Trauth (1994). This pioneer study become starting point of nanocomposite research, which then followed by other various study using different types of polymer.

Recently, De Rosa, Sarasini, Sarto, and Tamburrano (2008) noted the need in the aerospace industry for nanomaterials with not only superficial properties but also high-performance materials. Natural rubber latex (NR-latex) is one class of biosynthesised, hydrophilic polymer that performs various attractive properties, such as high resilience, good tear resistance, good tensile strength (Pichayakorn, Suksaeree, Boonme, Taweepreda, & Ritthidej, 2012). As a result of these notable features, NR-latex has been widely used in numerous applications, such as hoses, gloves, belts, tires, rubber-backed carpets, footwear, and adhesives (White & De, 2001; Yip & Cacioli, 2002). Thus, as a critical stage in the development of MWCNTs incorporated in polymers for obtaining nanocomposite applied in wire technologies and aerospace cable, NR-latex appears to be a potential candidate polymer.

In addition, the CNTs have been used to produce conductive materials used in aerospace-based technology (De Rosa *et al.*, 2008; Njuguna & Pielichowski, 2003). Conductive materials such as copper are conventionally conducted to fabricate wire components. Unfortunately, they have greater mass, which is not appropriate for aerospace conditions (De Rosa *et al.*, 2008). CNTs are around six times lighter than copper and are an order of magnitude more conductive. Hence, when incorporated into a polymer as the nanocomposites, they have great potential to replace traditional transition metals components (Zhong *et al.*, 2012).

However, due to CNTs' miniscule size, their outstanding properties can only be utilised if they are homogenously dispersed in polymer matrixes that provide good filler-matrix interface performance. In this respect, good dispersibility of CNTs is still a major challenge because of strong Van der Waals forces rendering agglomeration (Choi, Park, Kim, & Jhon, 2005). Furthermore, the CNTs are chemically inert and potentially entangled causes the individual tubes have a tendency to form aggregation. To overcome these hurdles, two various approaches are mostly used to provide homogenously dispersed of CNTs in polymer matrix including mechanical and chemical approach (Ma & Kim, 2011). The mechanical approach includes stirring, ultrasonication, extrusion, calendering, and ball milling. However, these processes are not completely ideal due to low efficiency and high time consuming. On the other hand, chemical approach consists of two strategies for treating CNTs surface: (1) covalent treatments and (2) non-covalent treatments, potentially shows good performance for CNTs dispersion.

In the first strategy, the treatment of the CNTs' surface improves the interfacial interaction between the CNTs and the polymer matrix via covalent bonding. It can be employed by using concentrated acid such as nitric acid (HNO_3) (Yu, Jin, Peng, Wang, & Yang, 2008), mixture of nitric acid/sulphuric acid (HNO_3/H_2SO_4) (Wang, Iqbal, & Mitra, 2005), and also mixture of nitric acid/sulphuric acid/hydrochloric acid ($HNO_3/H_2SO_4/HCl$) (Osorio, Silveira, Bueno, & Bergmann, 2008), as an oxidant agent to functionalise the CNTs surface. The excitation phenomenon from sp^2 to sp^3 hybridisation will be occurred in the formation of carbon atoms. Hence, the exited carbons will be easily reacts with other molecules or atoms to form reactive functional group such as hydroxyl or carboxyl. Unfortunately, the electrical properties of CNTs have been demonstrated to be substantially affected by the disruption of their π-system (Vaisman, Wagner, & Marom, 2006).

On the other hand, for non-covalent strategy, CNTs are incorporated into a polymer matrix with the help of a surfactant (so-called 'latex technology') that has the ability to both assist in dispersion and arrange the nanocomposite to be more useful in numerous applications (Preetha, Thomas, & Joseph, 2012). This is a safe method which has been frequently used for CNTs stabilisation is both organic and aqueous solvent. Geng, Liu, Li, Shi, and Kim (2008) reported that non-covalent treatment by surfactant has been successfully improved the CNTs-polymer interfacial interactions, so that enhanced the dispersion of CNTs in polymer matrix. This improvement of CNTs dispersion has a good effect on the properties of nanocomposite. Importantly, there is no disturbance on the π-system of CNTs because the surfactant-CNTs interaction is based on physical adsorption which effectively prevents CNTs from aggregation.

1.2 Latex Technology and Its Applications

The method of utilising a surfactant or latex technology generates a stable, mixed colloidal system that contains a suspension of CNTs in a polymer matrix. Latex technology is quietly new method which has been used for incorporating CNTs in polymer matrix via liquid phase. This method is applied using non-toxic solvent which make it environmental friendly, easily handling, reliable, and reproducible (Tkalya, Ghislandi, de With, & Koning, 2012). Yu *et al.* (2007) incorporated multiwall carbon nanotubes into polystyrene (PS) using latex technology to provide conductive nanocomposites. They reported the electrical conductivity of MWCNTs/PS nanocomposites is higher than pure PS matrix, about ten orders of magnitude. Their result suggested that latex technology can be adapted for preparing other nanocomposites with different type of CNTs or polymer.

The utilising of surfactant makes latex technology different with other CNTs dispersion techniques such as solution mixing, melt blending, and in situ polymerisation (Ma & Kim, 2011). In this respect, the surfactants will adsorb at the CNTs-polymer interface and reduce the interfacial tension by balancing lyophobic and lyophilic interactions. Importantly, the unique chemical structure of the surfactant enables the arrangement of a stable structure via lyophobic parts (called as 'tails') and lyophilic parts (called as 'head groups'), where the tails interact with the CNTs surface.

1.3 Surfactant and Its Applications

As a result, latex technology has triggered significant efforts to find a molecular structure that promotes efficient stabilisation of CNTs in polymer matrixes. Thus, the effect of some commercially available ionic surfactants, including sodium dodecyl sulphate (SDS) (Haldorai, Lyoo, & Shim, 2009), sodium dodecyl benzenesulphonate (SDBS) (Preetha *et al.*, 2012), and lithium dodecyl sulphate (LDS) (Chatterjee, Lorenzo, & Krishnamoorti, 2011), as well as non-ionic surfactants such as Triton X-100, Tween-20, Tween-40, Tween-60, and Tween-80 (Wenseleers *et al.*, 2004) have been studied. The results demonstrated that surfactants with long, highly branched and unsaturated carbon chains are better at dispersing CNTs in polymer matrixes. This result is correlated to the π-electronic affinity of the surfactant toward the CNTs benzene rings (Vaisman *et al.*, 2006).

The aforementioned studies showed the nature of the straight chained surfactants that are the most efficient at dispersing CNTs in polymer matrixes. However, applications are restricted because studies have concerned on limited range commercially available surfactants and based upon head group selection. Therefore, further systematic studies of surfactant architecture can help elucidate the general tendencies of surfactant analogues that assist the dispersion of CNTs in polymer matrixes. One of typical surfactant type that attracted attention in dispersion study is sulphosuccinate surfactants. It is mainly surprising that these surfactants have not yet been systematically studied because these surfactants, such as the commercially available Aerosol-OT (AOT, sodium bis(2-ethylhexyl) sulphosuccinate), have already been investigated to have multiple hydrophobic tails that adsorb onto CNTs and lead a temporary surface charge due to the interaction with the hydrophilic polymer (Bai *et al.*, 2012).

Up to now, a study on AOT-analogue surfactants for stabilising mixed colloidal system of water in continuous, supercritical carbon dioxide (CO_2) phase microemulsions (w/c) was studied by Eastoe, Yan, and Mohamed (2012). Importantly, this study demonstrated that the stability of this mixed colloidal system can be remarkably improved via the addition of a third, hyper branched hydrocarbon and methylated chain, *i.e.*, TC14 surfactant (sodium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-sulphonate) (Mohamed *et al.*, 2010). The introduction of this tri-chain surfactant is commonly believed to efficiently reduce the surface energy and packing requirements of a surfactant at the CO_2-water interface (Mohamed *et al.*, 2010). Importantly this feature also seems to be similar being obvious in arranging CNTs dispersibility in polymer matrix (Bai *et al.*, 2012; Clark, Subramanian, & Krishnamoorti, 2011; Rastogi *et al.*, 2008).

1.4 Research Objectives

The aim of this research is to systematically study the roles played by the chemical nature of the CNT-philic surfactant (surfactant-like-CNT) in the stabilisation of MWCNTs incorporated in NR-latex.

Thus, the objectives of this research were:

1. To synthesise and characterise CNT-philic surfactants for latex technology.
2. To investigate morphology and electrical properties MWCNTs/NR-latex nanocomposite stabilised by CNT-philic surfactants.
3. To formulate the proposed mechanism of CNTs stabilisation by CNT-philic surfactant.

1.5 Scope of Study

In general, the concern of this study is directed towards the synthesising CNT-philic surfactants for latex technology, which is consequently important in preparation of conductive nanocomposites. The surfactant compounds were synthesised using standard method (Nave, Eastoe, & Penfold, 2000) with chain modification based using different alcohol precursors. The approach focused on two strategies: effect of hyper methylated- and benzene ring- branched. In this case, the incorporation of MWCNTs is facilitated by the surfactant tails interacting with the NR-latex matrix in an attempt to improve the electrical properties of the nanocomposites.

For the characterisations of surfactants, proton nuclear magnetic resonance spectroscopy (^{1}H-NMR) and CHNS elemental analysis were employed. Meanwhile, the nanocomposite samples were characterised by four point probe measurement, field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and Raman spectroscopy.

1.6 Significance of Study

Significantly, the result of this study is beneficial to enrich the fundamental understand of CNTs-dispersing effort. Here, we develop a systematic study of CNT-philic surfactant architecture by choosing a range of sulphosuccinate type surfactant introduced hyper methylated- and benzene ring- branched in their alkyl chains. The effects of the surfactant-stabilised MWCNTs/NR-latex nanocomposites on the composites' morphological and electrical properties are investigated by studying the behaviour of single-chain, double-chain, and triple-chain sulphosuccinate analogues that compared as a function of their tail structure. It is generates additional insight into the molecular requirements of the surfactant used to disperse MWCNTs into the NR-latex matrix via latex technology approach. Furthermore, this information can be used as extra guidelines in developing of the next generation of conductive CNTs-polymer based material, such as nanowire concept in aerospace technology.

CHAPTER 2

LITERATURE REVIEW

2.1 Carbon Nanotubes

2.1.1 Synthesis of CNTs

The development of carbon nanotubes is initiated by a high interest of several researchers in the field of carbon-based material before 1980s (Monthioux & Kuznetsov, 2006). It was then followed by Kroto, Heath, O'Brien, Curl, and Smalley (1985) that discovered a new molecular carbon structure known as fullerene, usually consists of 60 carbon atoms (see Figure 2.1). This discovery was inspired Iijima to investigate new cluster of carbon using similar method to that used for synthesising of fullerene, known as arc-discharge evaporation (Iijima, 1991). By applying high resolution transmission electron microscopy (HRTEM), he observed the appearance of carbon structure consists of needle-like tubes, which currently known as CNTs. The initial observation by Ijima in 1991 was multi-wall carbon nanotubes. It is continued by the discovery of single-wall carbon nanotubes in 1993, separately by Iijima group at the NEC (Iijima & Ichihashi, 1993) and Bethune group at the IBM (Bethune *et al.*, 1993).

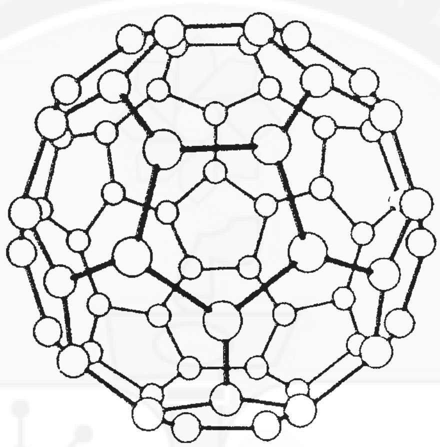

Figure 2.1 C_{60}: Buckminsterfullerene (Harris, 2009)

Recently, there are three dominant methods to synthesise CNTs including arc discharge, laser ablation, and chemical vapour decomposition (CVD) (see Figure 2.2). In arc discharge method, 20 V of voltage and 50 – 100 A of current were generated between two graphite electrodes under inert atmosphere of helium or argon. The distances between both of electrodes are adjustable, so that the arc discharge between cathode and anode can be occurred. After the arc discharge was completed, the CNTs can be collected from the cathode. This synthesise method appears very simple, however usually produces low yield of CNTs and needs careful control of experimental condition (Harris, 2009). The next method for synthesising CNTs is