PREPARATION OF MULTIWALL CARBON NANOTUBES / POLYMER NANOCOMPOSITES STABILIZED BY 1-BUTYL-3-METHYL-IMIDAZOLIUM (BMIM)-SURFACTANTS

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ABSTRACT

This aims to prepare multiwall carbon nanotubes / polymer nanocomposite stabilized by 1-butyl-3-methyl-imidazolium (BMIM)-surfactant. Dispersibility of MWCNTs in cellulose and natural rubber latex polymer matrix was studied and prepared via latex technology approaches by addition of 1-butyl-3-methyl-imidazolium (BMIM)-surfactant. The ability of BMIM-surfactants for dispersing MWCNTs in polymer was characterized using a range of techniques including field emission scanning electron microscopy (FESEM), thermogravimetric analysis (TGA) and small angle neutron scattering (SANS). And for-point probe measurements. Research finding showed that MWCNTs were more efficiently dispersed in cellulose utilizing 1-butyl-3-methyl-imidazolium-dodecyl benzene sulfonate (BMIM-DBS) than commercially available surfactant sodium dodecylbenzenesulfonate (SDBS). In conclusion, surfactant counterion gives an importance effect to improve the dispersibility of MWCNTs in cellulose. In implication, the results will provide the significant interest in improving properties of cellulose based nanocomposites.

PENYEDIAAN NANOTIUB KARBON BERDINDING GANDA / POLIMER NANOKOMPOSIT DISTABILKAN OLEH 1-BUTIL-3-METIL-IMIDAZOLIUM (BMIM)-SURFAKTAN

ABSTRAK

Kajian ini bertujuan menyediakan nanotiub karbon berdinding ganda / polimer nanokomposit yang distabilkan oleh 1-butil-3-metil-imidazolium surfaktan. Penyerakan MWCNTs dalam matriks polimer selulosa dan getah semulajadi dikaji melalui pendekatan teknologi lateks dengan penambahan 1-butil-3-metil-imidazolium (BMIM)-surfaktan. Kebolehan BMIM-surfaaktan untuk menyebarkan MWCNTs dalam polimer dicirikan dengan menggunakan pelbagai teknik termasuk mikroskopi pengimbas pancaran medan elektron (FESEM), analisis termogravimetri (TGA), serakan neutron sudut kecil (SANS) dan pengukuran prop empat titik. Dapatan kajian menunjukkan bahawa MWCNTs disebarkan secara lebih efisien dalam selulosa menggunakan 1-butil-3-metil-imidazolium-dodesilbenzenasulfonat (BMIM-DBS) berbanding surfaktan komersil natrium dodesilbenzenasulfonat ((SDBS). Kesimpulannya, ion balas surfaktan memberi kesan penting kepada peningkatan penyebaran MWCNT dalam selulosa. Implikasinya, dapat kajian memberi tarikan yang signifikan dalam meningkatkan ciri-ciri nanokomposit berasaskan selulosa.

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Ag	Silver
Au	Gold
BMIM	1-Butyl-3-Methyl-imidazolium Ion
BNC	Bacterial Nanocrystalline Cellulose
C_{60}	Fullerene
$CDCl_3$	Chloroform-D
$(CD_3)_2CO$	Acetone-D_6
CH_4	Methane
C_2H_2	Ethyne
C_2H_6	Ethane
C_2H_4	Ethene
$CH_3(CH_2)11(OCH_2CH_2)7OCH_2CH_3)$	Polyoxyethylene 8 lauryl
CMC	Critical Micelle Concentration
CNCs	Cellulose Nanocrystals
CNR	Continuously Rao
CNTs	Carbon Nanotubes
(– COOH)	Carboxylic Acid
Co	Cobalt
CO	Carbon Monoxide
CTVB	Cetyltri- methylammounium 4-vinylbenzoate
CTE	Coefficient of Thermal Expansion

CVD	Chemical Vapour Deposition
DC	Direct Current
DNA	Deoxyribonucleic acid
DTAB	Dodecyltrimethylammonium bromide
DP	Degree of Polymerization
Fe	Iron
FESEM	Field Emission Scanning Electron Microscopy
HLB	Hydrophyle-Lyphophyle Balance
^{1}H-NMR	Proton Nuclear Magnetic Resonance Spectroscopy
HNO_3	Nitric Acid
H_2SO_4	Sulphuric Acid
MCC	Microcrystalline Cellulose
MWNTs	Multi Wall Carbon Nanotubes
NaDDBS	Dodecyl-Benzene Sodium Sulfonate
NFC	Nanofibrillated Cellulose
NRL	Natural Rubber Latex
Ni	Nickel
(– OH)	Hydroxyl
PSS	Poly(styrene sulfate)
Pt	Platinum
SANS	Small Angle Neutron Scattering
SDBS	Sodium Dodecylbenzenesulfonate
SDS	Sodium Dodecyl Sulphate

SWCNTs	Single Wall Carbon Nanotubes
TGA	Thermogravimetric analysis
TMS	Tetramethylsiloxane
UV	Ultraviolet

CHAPTER 1

INTRODUCTION

1.1 Background of study

Dimensionality shows a significant role in defining the characteristics of matter. The key factor in controlling the structure at the nanolevel and the development and introduction of novel properties is the nanostructure of a material. Therefore, nanotechnology is an extremely favourable field of the 21st century. It uses to complete restructure the technological applications in the fields of inorganic, semiconductors, as well as energy storage, biotechnology and organic materials (Okpala, 2013). In this sense, nanotechnology defines as the controlled handling of materials with at least one dimension less than 100 nm.

Nanotechnology challenges to combine chemistry, biology, materials science and physics to generate novel material properties, which can be employed to improve facile procedures for the creation of new biomedical products, high performance materials, electronic devices and custom articles. The manufacturing of nanotechnology is estimated to raise comprehensive technological growth. This technology also promotes the quality of life and social advances in many areas of life. The meaning of nano-composite material has widen considerably over the years to cover a wide variation of systems, for example, two-dimensional, three-dimensional, one-dimensional and amorphous materials, made of sharply diverse mixed and components at the nanometer scale.

As cited in Okpala (2013), Azonano (2009) reported that nanocomposites are “materials with a nanoscales structure that improve the macroscopic characteristics of products.” Nanocomposites can dramatically enhance properties such as electrical conductivity decreased gas, mechanical properties including strength, modulus, dimensional stability, flame retardancy, hydrocarbon permeability and water, thermal stability and chemical resistance. Azonano (2009) highlighted that nanocomposites normally are polymer, clay, carbon, or a combination of materials with nanoparticle building blocks.

Nowadays, researchers are interested in nanocomposite inorganic/organic materials, which are new technologies. These are the challenging and fast growing area of research. Considerable struggles are met in attempts to achieve control of the nanoscale structures by means new synthetic approaches. The characteristics of nanocomposite materials are based on the properties of their morphology, on their individual parents and interfacial properties. The very rapidly growing area in the field is producing several interesting novel materials with unique characteristics. These could be further developed by mixing characteristics from the parent constituents into a single material. It was cautioned that there are probability of other characteristics, which are unknown in the parent basic materials.

The nanocomposites are a matrix to which nanoparticles have been added to develop a specific property of the materials. Nanocomposites can also be described as nanomaterials which mix one or more individual parts to produce the finest characteristics of every one of the component. Nanocomposites are to maximize the processing procedures for inexpensive production costs.

Presently, there are four methods of processing used to manufacture polymer nanocomposites (Pegel, et al., 2008; Mu, Walker, Torkelson, & Winey, 2008; Moniruzzaman, & Winey, 2006; Kim, Han, & Hong, 2008). There are many processing techniques that can be used to synthesise the nanocomposites. Some of the techniques are; solution method, direct mixing, melt blending, and in situ polymerization (Miao, & Hamad, 2016). Among these processing methods, melt-blending procedure is regarded as the smoothest and the most efficient technique in an industrial perspectives. This method from the industrial point of view is preferred because it is less expensive compared to other methods. Thereby making it likely to produce high performance nanocomposites of polymer at a very low processing costs, and it makes commercial scale-up possible (Kim, Han, Kim, & Kim, 2009; Kim, Park, & Kim, 2009; Kim, Park, & Kim, 2006)

In nanocomposite, nanoparticles (carbon nanotubes, clay and metal) act as fillers in a matrix, usually polymer matrix. Among all, one of the most exciting applications is carbon nanotubes (CNTs)/polymer nanocomposites. The appropriate combination of high aspect ratio, very low density, small size and extreme mechanical properties make CNTs suitable candidates and ideal reinforcing fillers of polymer materials. A huge part of the CNTs/polymer based composites exploit CNTs as a conductive filler dispersed in an insulating matrix. The applications spectrum of CNTs from electronics to aerospace sectors; for example, electromagnetic interference (EMI), electrostatic dissipation (Hyperion Catalysis International), shielding (Kim, et al., 2002) transparent conductive coatings (Wu, et al., 2004) and multilayer printed circuits (Shibayama & Nakasuga 2004). The objectives are to enhance inexpensive, easy-to-process and light “conductive plastics”, for future usages that semiconductors and/or metals are still favored. The key matters for generating technically motivating CNT/polymer nanocomposites are the comprehensive and proficient dispersal of separate single-walled carbon nanotubes (SWCNTs) into the polymer matrix, in addition to the force of the characteristics of the filler-matrix interface. If fine dispersed, the probable filler matrix interface area is enormous, and a suitable control of the interfacial interaction is vital for achieving optimal characteristics.

It was noted that CNTs are possibly the greatest substances with a tensile strength higher than steel (Zhang, et al., 2007). The first observation of discharge method using CNTs was reported by Iijima, (1991). Subsequently, other techniques have been used, for example, catalytic chemical vapor deposition of hydrocarbons (Scott, Arepalli, Nikolaev, & Smalley, 2001; Andrews et al., 1999) and laser vaporization (Scott, Arepalli, Nikolaev, & Smalley, 2001). Bonds of carbon covalent are among natures strongest bonds. The bonds are based on proper alignment of these bonds focused on nanotubes axis, would form an extremely resilient material.

It has been highlighted that the structures of nanotubes are tough and strong which could be bent and stretched into shapes without disastrous lack of structure in nanotube (Falvo et al., 1998). The nanotubes mechanical properties, for example, young's modulus and tensile strength are equal to that of diamond (Nadler, Werner, Mahrholz, Riedel, & Hufenbach, 2009). These designated structures, utilized as probable reinforcing materials are supported by the unique mechanical strength. Predictably, a better overall performance could be given to the polymer matrix by CNTs because of their exceptional and attractive physical properties and mechanical.

To reinforce polymers, using nanofillers is very important across varying fields; from completely industrial to scientific usages because of significant developments of the comprehensive characteristics accomplished at lower filler loadings. Consequently, polymer nanocomposites is regarded as a unique class of materials. It was reported that the dominant aims for using CNTs as nanoreinforcing fillers are: (a) strong interfacial connection among the nanotubes and polymer matrix (b) consistent diffusion of the nanotubes in the polymer matrix, which could be applied to fabricate of polymer nanocomposites comprising CNTs.

Generally, CNTs turn to bundle with each other and to make agglomerations because of the form of van der Waals appeals among the separate tubes (Ebbesen, 1997; Dresselhaus, & Avouris, 2001). There are restricted efficient load transfer to polymers due to weak interfacial bonding between polymer matrix and CNTs. Hence, the role of polymer nanocomposites participation is restricted (Gong, Liu, Baskara, Voise, & Young, 2000). It was found that CNTs functionalization is recognized as an efficient technique to carry out the uniform diffusion of CNTs and their compatibility with the polymers. The functionalization of CNTs could proceed to the improvement of the interfacial bond in-between polymer matrix and CNTs. Therefore enhancing physical characteristics of polymer nanocomposites containing CNTs (Sun, Fu, Lin, & Huang, 2002; Bellayer, et al., 2005).

Cellulose is gaining a lot of popularity from the experts of conductive nanocomposites fabrication (Klemm, Heublein, Fink, & Bohn, 2005; Kim, Yun, & Ounaies, 2006). Due to its compatibility potential, mechanical stability under atmospheric conditions and ability to absorb liquid, cellulose has become a renewable source-based biodegradable polymer and medium for presenting and transmitting information (Turner, Spear, Holbrey, & Rogers, 2004; Swatloski, Spear, Holbrey, & Rogers, 2002). Cellulose is also deemed to be biosource, light-weight and biologically compatible (Tanaka, Sano, Imai, & Akiyama, 2010; Yun & Kim, 2010). Therefore, scientists are increasingly paying attention to this natural polymer, considering it as an inexhaustible source of raw material to replace petrochemically derived compounds in many cases (Klemm, Heublein, Fink, & Bohn, 2005). However, cellulose is difficult to process in solution or as a melt because of its large proportion of intra and intermolecular hydrogen bonds. Room-temperature ionic liquids (RTILs), which are considered as desirable green solvents, have been recently reported to be effective and promising cellulose solvents (Zhang, Wang, Zhang, Wu, Zhang, & He, 2007). Because of advantages like excellent dissolving capability, negligible vapor pressure, recyclability and variation of its structure, this class of new cellulose solvents has attracted considerable attention and has been used to prepare different regenerated cellulose materials and cellulose derivatives.

As far as the cellulose solubility is concerned, imidazolium type of ionic liquids have shown the best performance (Swatloski, Spear, Holbrey, & Rogers, 2002). Therefore, imidazolium-based ionic liquid monomers are ideal candidates to combine with cellulose as they possess high affinity and compatibility characteristics. For this reason, (Murakami, Kaneko, & Kadokawa, 2007) 1-butyl-3-methylimidazolium chloride (BMIMCl) is one of the most effective ionic liquid solvents for breaking down the strong intra and inter-molecular interactions that are present in cellulose. Use of ionic liquids in new cellulose processing and materials technologies is a topic of burgeoning interest. The use of ionic liquids for cellulose dissolution stems from the unique properties of ionic liquids to interact with the strong hydrogen bonds of polysaccharides. The scientific discovery of the dissolution of cellulose in ionic liquids is being translated into new processing technologies, cellulose functionalization methods and new cellulose materials including blends, composites, fibers and ion gels. These materials could replace current analogs to overcome the environmental issues associated with petroleum-based products. Although there are many ionic liquids available with the ability to dissolve cellulose, the processing difficulties such as fractionation need to be overcome to support large-scale use. However, as a result of the chemical versatility of both cellulose and ionic liquids, new developments leading to the next generation of cellulosic materials are expected in the near future (Isik, Sardon, & Mecerreyes, 2014).

Carbon nanotubes (CNTs) are referred to as one of the most versatile additives of composites because it can develop thermal, mechanical and electrical characteristics of cellulose (Uchida & Kumar, 2005). Specifically, homogeneous distribution of CNTs in the cellulose matrix would contribute to improving its characteristics. However, the nonreactive surface and strong aggregation properties of CNTs due to van der Waals attract have restricted the effectiveness of CNTs with cellulose during the time of mixing (Fei, Lu, Hu, & Xin, 2006). It has been stated that chemical modification of CNT is the most successful dispersion technique, which forms carboxyl functional groups on the surfaces and the ends. This carboxyl functional group binds the CNTs with cellulose very tightly. However, the chemical modification would significantly transform their desirable properties. Consequently, CNTs dispersion in solvents is a requirement to utilize the unique multifunctional properties of CNTs while preparing CNT/cellulose composites (Fugetsu, et al., 2008).

Natural rubber latex (NRL), cis-1, 4-polyisoprene, is a high molecular weight polymeric material, sticky milky white or slightly yellowish opaque fluid. The major commercial source of NRL is the Para rubber tree, *Hevea brasiliensis*, a member of the spurge family *Euphorbiaceous* (Dusotoit-Coucaud, et, al, 2010). Natural rubber (NR) is considered as one of the most important bio-based polymers possessing excellent chemical and physical properties like an outstanding elasticity and flexibility. It is widely used in various areas such as tyres, sport shoes, sealing materials and dairy rubber items (Le, et al, 2014). For instance, about 70% of rubber consumed in tire industry is from NR. Recently, nanofillers have been added into tire tread compounds in order to impart them with some functionalities like gas barrier, flammability resistance, electrical conductivity, polymer blend compatibility (Le, et,. al, 2016).

Carbon nanotubes (CNTs) and graphene have been used to fabricate NRL nanocomposites to gain improvement in electrical and mechanical properties. The fillers are added to the rubber matrix according to the requirement of material properties. Several methods including solution casting, melt mixing, and in situ polymerization of monomers with presence of CNTs have been tried to prepare polymer nanocomposites (Elango, Gupta, Lih Jiun, & Golshahr, 2017; Chen, Tao, & Liu, 2006). Nevertheless, the main challenge in the processing of carbon nanotubes is the overcoming of the strong van der Waals attraction energy of ca. 500 eV/ mm of tube-tube contact, which makes them aggregate into bundles or ropes in the polymer matrix diminishing the inherent properties of the polymer itself (Girifalco, Hodak, & Lee, 2000). Various methods have been used to obtain good dispersion of carbon nanotubes in the polymer matrix. Heinrich et al.,(2009) reported the use of ionic liquid, ethanol and carboxylated hydrogenated butadiene rubber as very effective dispersing agents for CNTs in rubber matrix (Le, et,. al, 2013). Non-covalent methods are preferred over the covalent methods since the π system in graphene sheets remains undisturbed and inherent properties of the nanotubes are preserved. Surfactants have been reported for obtaining stable aqueous dispersions of carbon nanotubes (Tkalya, Ghislandi, & Koning, 2012; Ponnamma, et, al, 2014). Addition of surfactants to the aqueous suspensions of CNTs followed by sonication can very effectively debundle the CNT aggregates resulting in a homogeneous dispersion. But the sonication energy and CNT to surfactant ratio needs to be optimised to prevent any detrimental effect on the inherent properties of the nanotubes (Vichchulada et,. al, 2010).

It has been reported that the surfactant's ability to accumulate on interfaces or surfaces is extensively used to enhance steady dispersals of solids in a variety of media (Seelenmeyer, & Ballauff, 2000; Singh, Menchavez, Takai, Fuji & Takahashi, 2005). Those amphiphilic molecules (Figure 1.1), for example, compounds includes both nonpolar and polar categories, with the ability to adsorb without forming a homogeneous mixture when added together, for example, water and oil, water and air or solution and particles, act to decrease the surface tension.

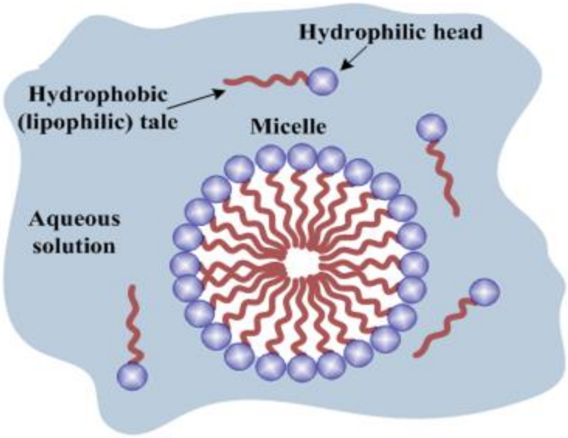

Figure 1.1. Amphiphilic structure of surfactant molecules

It has been stated that the surfactants possess a unique structural feature and it originates from its ‘duality’: the tail group or the hydrophobic region that generally includes one or little hydrocarbon. There are four categories of surfactants which are; nonionic or zwitterionic, anionic, cationic and amphoteric surfactants. Two significant factors, which characterize surfactants, namely self-accumulation into supramolecular structures and adsorption at the interface, are effectively used in dealing with constant colloidal diffusions. Surfactants adsorptions onto organic and inorganic surfaces generally rely on surfactant molecules, chemical properties of solvent and particles. The created Coulombic attractions are the driving force for the adsorption of ionic surfactants on charged surfaces. For instance, among the negatively charged solid surface and the surfactant's positively charged head group.

The process can be explained as nonionic surfactants adsorb onto a hydrophobic surface, is depended on the surfactant's hydrophobic tail and a strong hydrophobic attraction among the hard surfaces (Assouline, et al., 2003; Haggenmueller, Gommans, Rinzler, Fischer, & Winey, 2000; Wang, & Hobbie, 2003).

Challenges associated with assimilation of nano-material in particular consist of (1) preferential alignment in melt phases and liquid; (2) uniform dispersion; and (3) mass-synthesis of material of high-purity at low prices. This research concentrates on the second challenge that is improving homogeneous dispersions of carbon nanotubes, mainly with (surfactants) or surface active agents assistance. Diverse sources of stabilization of classical colloidal suspensions, for example, the surfactant used, adsorption mechanism and surface charge influence, will be tested to determine if they are usable to dispersion systems of CNT (Vaisman, Wachtel, Wagner, & Marom, 2007).

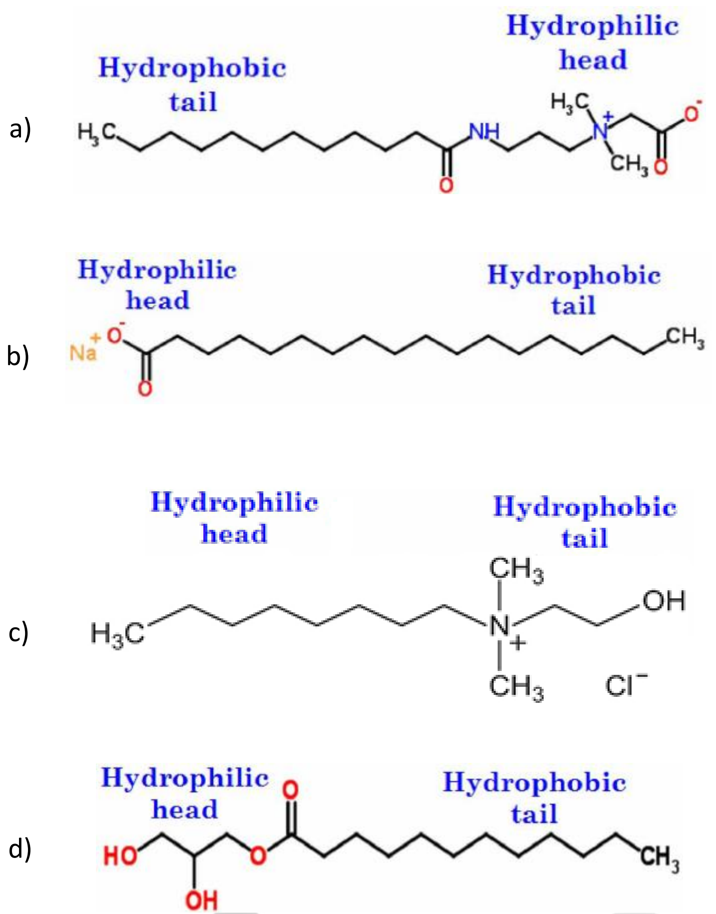

Figure 1.2. (a) Chemical structure of an amphoteric surfactant; (b) Chemical structure of an anionic surfactant; (c) Chemical structure of a cationic surfactant; (d) Chemical structure of a nonionic or zwitterionic surfactant.

1.2 Research Objectives

The following are the objectives this research aims to achieve:

1. To synthesize and characterize 1-butyl-3-methyl-imidazolium (BMIM)-surfactants.
2. To study morphology and electrical properties of MWNTs/cellulose/1-butyl-3-methyl imidazolium (BMIM) surfactant nanocomposites.