



Mohamed, A., Anas, A. K., Abu Bakar, S., Ardyani, T., Zin, W. M. W., Ibrahim, S., ... Eastoe, J. (2015). Enhanced dispersion of multiwall carbon nanotubes in natural rubber latex nanocomposites by surfactants bearing phenyl groups. *Journal of Colloid and Interface Science* , 455, 179-187. DOI: 10.1016/j.jcis.2015.05.054

Peer reviewed version

Link to published version (if available):
[10.1016/j.jcis.2015.05.054](https://doi.org/10.1016/j.jcis.2015.05.054)

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Enhanced dispersion of multiwall carbon nanotubes in natural rubber latex nanocomposites through the use of benzene-containing branched hydrocarbon surfactants

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Abstract

We present here a systematic study of the dispersibility of multiwall carbon nanotubes (MWCNTs) in natural rubber latex (NR-latex) assisted by a series of single-, double-, and triple-sulphosuccinate anionic surfactants containing benzene ring moieties. Optical polarising microscopy, field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and Raman spectroscopy have been performed to obtain the dispersion-level profiles of the MWCNTs in the nanocomposites. Interestingly, a triple-chain, benzene-containing surfactant, namely sodium 1,5-dioxo-1,5-bis(3-phenylpropoxy)-3-((3-phenylpropoxy)carbonyl) pentane-2-sulphonate (TCPH), has a greater capacity the stabilisation of MWCNTs than the commercially available single-chain sodium dodecylbenzene sulphonate (SDBS) surfactant. TCPH provides significant enhancements in the electrical conductivity of nanocomposite as measured by a four-point probe instrument. These results enabled us to compile a road map for the design of surfactant architectures capable of providing the homogeneous dispersion of MWCNTs required for the next generation of polymer-carbon-nanotube materials, specifically those used in aerospace technology.

Keywords: Multiwall Carbon Nanotubes (MWCNTs), Natural Rubber Latex (NR-latex), Surfactant.

Research Highlights

- Anionic sulphosuccinate surfactants containing benzene ring moieties.
- Triple chain anionic surfactants containing benzene ring moieties.
- A highly branched, benzene-containing surfactant demonstrated the high dispersibility of MWCNTs in NR-latex.

1. Introduction

Natural rubber latex (NR-latex), a renewable polymeric material obtained from the bark of the rubber tree (*Hevea brasiliensis*), contains the milky colloidal material *cis*-1,4-polyisoprene. Additionally, NR-latex contains non-rubber materials including water, carbohydrates, protein, polypeptides, fatty acid, and phospholipids [1]. This polymer exhibits remarkable properties, such as good film-forming ability, high elasticity, and high resilience [2-4] and is therefore used in the automotive, laboratory, and medical industries [5-7]. More interestingly, it is also known to possess good biodegradability, which reduces the environmental impact of its use compared to more non-environmentally friendly polymers. Unfortunately, the implementation of this elastomeric biodegradable polymer on a large scale is not easy due to its poor electrical properties stemming from the lack of a conducting network within the internal rubber structure [8, 9]. In this respect, the employment of nanoscale filler materials (so-called nanofillers) is beneficial. Nanofiller-containing materials have been extensively studied due to their superior performance compared to that of conventional filler material [5, 10-12].

Multiwall carbon nanotubes (MWCNTs) serve as nanofillers in polymers useful in a number of fields including in hydrogen storage, electronic wires, supercapacitors, transistors, and electrochemical devices [13-16]. They are considered promising candidates for nanofiller materials for polymeric reinforcement owing to their unique structures and outstanding electrical properties [17, 18]. The use of MWCNTs as nanofillers has attracted the attention of a number of research communities, especially those interested in their ability to serve as reinforcement agents in polymers [19, 20]. However, their low dispersibility and tendency to bundle hinders their ability to disperse in polymer matrices [21]. Therefore, further experimental treatment is needed to obtain the benefits of conductive MWCNT-based nanocomposites with homogeneously dispersed nanotubes [17].

Latex technology has been widely applied in preparing electrically conductive nanocomposites [22-24]. These techniques represent new environmentally friendly, reliable, easily handled, and reproducible dispersing methods [25, 26]. This method has been applied through non-covalent functionalisation by amphiphilic molecules known as surfactants. Importantly, latex technology considered an alternative technique useful for enhancing MWCNTs/polymer interfacial interactions without disturbing the π systems inherent in the nanotube structure, as is common in their covalent functionalisation. The stabilities of colloidal nanotube systems are promoted by electrostatic (ionic surfactant) or steric (non-ionic surfactant) repulsion [27] in which their molecular chemical structures are largely responsible for their role as a third components, stabilising the colloidal system through adsorption onto the interfaces of the immiscible bulk components.

To date, two commercially available ionic surfactants are frequently used to provide stable CNT-based colloidal systems. These are sodium dodecyl sulphate (SDS) and sodium dodecylbenzene sulphonate (SDBS). Both have similar alkyl chain lengths, but differ in the inclusion of benzene ring moieties in the SDBS surfactant. Bystrzejewski et al. studied the dispersibility of both SDS and SDBS in concentrations nearing the critical micelle concentration (cmc) and compared their capacity to disperse MWCNTs in aqueous media [28]. The results indicated that SDBS has better dispersing power than SDS, both below and above the cmc. This result indicates that differences in the nature of a surfactant's structure determines its efficiency in promoting the stable dispersion of nanotubes. It is believed that the introduction of the benzene ring in the surfactant chains makes SDBS more effective than SDS [29]. The existence of π - π stacking is proposed as a main factor promoting the exceptional performance of SDBS in dispersing nanotubes throughout polymer matrices [30].

To evaluate the importance of the benzene ring in surfactant chains, study of its role in stabilising colloidal systems of nanotubes is highly important. However, to the best of our

knowledge, no systematic studies on this topic exist. In our previous work [31], the performances of single-, double-, and triple- chains with the aid of hyper-methylated branched surfactants, useful for facilitating the preparation of well dispersed MWCNTs in polymer matrices, have been reported. The results showed that the introduction of a CNT-philic (a surfactant-like carbon nanotube) third chain with hyper branched methylated chains, namely sodium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-sulphonate (TC14), significantly enhanced the dispersibility of MWCNTs in the NR-latex.

In addition, to enrich the fundamental understanding of CNT-dispersing materials, we herein report a systematic study of CNT-philic surfactant architectures through the choice of a range of sulphosuccinate-type surfactants linked to benzene moieties in their alkyl chains (the chemical structure were shown in Table 1). The performance of single-, double-, and triple- chain surfactants attached to benzene moieties in the promotion of high levels of dispersion of MWCNTs in polymer matrices were investigated. These findings contribute to the molecular understanding of the phenomena and provide another option within the set of CNT-philic surfactants capable of exceptional CNTs-dispersibility. Significantly, this study suggests criteria for the molecular design of surfactants aimed at the stabilisation of nanotubes in NR-latex and gives suggestions for the development of the next generation of green, multifunctional polymer-nanotubes-based materials, such as the nanowires envisaged in aerospace applications [32, 33].

2. Materials and methods

2.1. Material

A NR-latex polymer consisting of 32.51 ± 0.08 and 33.87 ± 0.01 % dry rubber content and total solid content, respectively, was supplied from the Malaysian Institute for Nuclear

Technology Research. Details of the measurements are given elsewhere [31]. MWCNTs were self-prepared at the Universiti Sains Malaysia (USM) by a chemical vapour decomposition (CVD) technique [34] and further purified using an appropriate procedure described elsewhere [31]. The surface morphologies of the MWCNTs bundles are represented in Fig. 1, showing a diameter range from approximately 14.0 to 55.3 nm. SDS (System, 99 % purity) and SDBS (Sigma Aldrich, technical grade) were used as received. In addition, AOTPh and TCPPh were synthesised as detailed in previous reports [35-38], using 3-phenyl-1-propanol as the alcohol precursor (Acros organic). Detailed information regarding the surfactant synthesis and characterisation can be found in the supplementary material.

2.2. Preparation of nanocomposites

The general route employed for the preparation of nanocomposites is depicted in Fig. 2. The nanocomposites were prepared with the help of a latex technology method [31]. The surfactant was initially dissolved in 10 mL of deionised water, achieving concentrations between 0 and 32 mM. This surfactant solution and the MWCNTs (5 wt%) were stirred for 1 hour and sonicated (Branson 5510 sonicator, with 135 W of power and 42 KHz of an output frequency) for an additional 3 hours. The NR-latex was then added to the surfactant-nanotube colloidal mixtures, followed by additional stirring and ultrasonication. The mixture was dried in oven at 80 °C overnight before characterisation.

2.3. Characterisations

Measurements of the electrical conductivities of the nanocomposites were performed with a four-point probe instrument (Keithley 2636A). This measurement was repeated three times, on samples with the dimensions of 10 x 10 mm and ~2 mm thickness. Images of nanotube micro-dispersions were captured using an optical polarising microscope (Nikon, Eclipse 501).

A field emission electron microscope (FESEM-Hitachi SU8020) was used to observe the surface morphologies of the nanocomposites. In addition, the embedded microstructures of the nanocomposites were confirmed by transmission electron microscopy (TEM-JEOL 2100F). A Renishaw InVia micro Raman system spectrophotometer with a 514 nm argon-ion laser source was used to evaluate the disruption of the π systems in the nanotubes structure.

3. Results and Discussion

3.1. Electrical conductivity measurements

The experimentally determined electrical conductivities of the MWCNTs/NR-latex nanocomposites, stabilised by ionic surfactants bearing benzene rings, are represented in Fig. 3 and Table 2 as functions of the surfactant concentrations. In the absence of MWCNTs, the electrical conductivity of the pristine NR-latex was found to be approximately 10^{-11} S cm⁻¹. However, the addition of MWCNTs served to construct a conductive network within the structure of the nanocomposites [25, 39], and gave improvement in conductivity up to 10^{-7} S cm⁻¹. The use of SDS as a dispersing agent for the MWCNTs in NR-latex was beneficial, enhancing the electrical conductivity of nanocomposite by an order of magnitude. The introduction of commercially available SDBS to the MWCNTs/NR-latex nanocomposites resulted in a higher electrical conductivity ($\sim 10^{-5}$ S cm⁻¹) than found with the addition of SDS. As described in a previous study [40], the single-chain, benzene-functionalised SDBS surfactant is thought to be a good stabiliser for MWCNTs in polymer matrices due to its ability to increase the interfacial interactions between the MWCNTs and the polymer via $\pi - \pi$ interactions [29].

Interestingly, a double-chain, benzene-functionalised AOTPh surfactant was successfully employed for the enhancement of the electrical conductivity of the nanocomposite, resulting in values up to $\sim 10^{-4}$ S cm⁻¹. An outstanding improvement (up to $\sim 10^{-2}$ S cm⁻¹) was found in a

MWCNTs/NR-latex nanocomposite stabilised by the triple-chain, benzene-functionalised TCPH surfactant. Our previous study [31] noted that the low surface energy (γ_{cmc}) achieved by the introduction of a hyper methylated surfactant (TC14, $\gamma_{\text{cmc}} = 27.0 \text{ mN m}^{-1}$) was a major factor in stabilising the nanotube-colloidal system. In contrast, introduction of the benzene-functionalised surfactant resulted in a relative high γ_{cmc} (Table 2). Thus, in case of surfactants bearing benzene functionalities, $\pi - \pi$ interactions between the surfactant chain and the MWCNT surfaces are favourable and represent the major factor in the stabilisation of colloidal nanotube systems. To further study the capacity of SDBS, AOTPh, and TCPH to stabilise MWCNTs/NR-latex nanocomposites, the dispersion levels of the nanotubes were observed by optical polarising microscopy, FESEM, and TEM. The results are discussed in the following section.

3.2. Observations of MWCNTs dispersion in NR-latex

As previously discussed, the introduction of the SDBS, AOTPh, and TCPH surfactants generated an obvious increase in the electrical conductivity of the MWCNTs/NR-latex nanocomposites. It is believed that the different levels of MWCNT dispersion provided by each surfactant are responsible for the nanocomposite's electrical conductivity. To investigate the importance of the MWCNT dispersion level in the optimisation of the conducting network within the internal structure of nanocomposites, the micro-scale structures and surface morphologies of the material require investigation [30]. To these ends, an optical polarising microscope was employed to observe the micro-scale dispersion of MWCNTs, while their surface morphologies were observed by FESEM.

Fig. 4 and 5 (a – d) show micrographs and FESEM images of the MWCNTs dispersed in NR-latex. These figures compare the micro-dispersion and surface morphologies of the MWCNTs at a given dispersion level with and without surfactant treatment. The presence of

surfactant was crucial for stabilising the nanotubes. Fig. 4a indicates that the absence of surfactant caused low level dispersion of MWCNTs, which was evident in the FESEM images through the observation of bundles (signed by diamond arrow / \blacklozenge) and very few individual nanotubes (signed by stealth arrow / \rightarrow) on the surfaces of nanocomposites (Fig. 5, a and a'). Interestingly, the introduction of the commercially available SDBS surfactant decreased the number of nanotubes bundles and slightly increased the number of individual nanotubes observed (Fig. 4b; Fig. 5, b and b'). This result is in agreement with previous studies [43] wherein treatment with SDBS surfactants did not obviously shorten the MWCNT structures, indicating that $\pi - \pi$ interactions between the tails of the SDBS surfactant and the MWCNT surfaces did not modify the physical characteristics of the nanotubes, especially their electrical properties.

The introduction of AOTPh resulted in a more effective dispersion of MWCNTs in the NR-latex (Fig. 4c; Fig. 5, c and c'), indicating that the twice-benzene-functionalised system provided more effective dispersibility of MWCNTs than surfactant chains with only one benzene moiety. Remarkably, the addition of a tri-chain, benzene-functionalised surfactant (TCPh) exhibited the most notable improvement in the level of dispersion of MWCNTs in the NR-latex matrix (Fig. 4d; Fig. 5, d and d'). FESEM images showed smooth surface morphologies with homogeneously dispersed MWCNTs. These results convincingly suggest that increasing the number of benzene rings from one to three in the surfactants chains leads to more effective dispersal of MWCNTs in NR-latex matrices. To further investigate the dispersion level of MWCNTs in NR-latex assisted by the TCPh surfactant, TEM observations were employed and are discussed in the following section.

3.3. TEM observations

In the study of nanocomposite systems, TEM is a powerful technique by which the state of nanofiller dispersion can be assessed [25]. The use of TEM on extremely thin microtomed sections of the nanocomposites allowed the direct imaging the carbon nanotube dispersion inside the NR matrices. This process helps provide insight into the mechanisms behind the observed improvements in electrical conductivity. Fig. 6 depicts the dispersibility of MWCNTs in NR-latex non-covalently treated with TCPH. The TEM image indicates that TCPH surfactant efficiently aided in disentangling the MWCNT bundles, giving a homogeneous dispersion in the NR-latex. With this information in mind, we set out to construct a possible mechanism of surfactant-induced MWCNT stabilisation. This mechanism is described in the following section.

3.4. Raman spectroscopy measurements

As discussed above, surfactant chains bearing benzene rings have a significant influence on maximising the surfactant-nanotube interactions. This effect is indicated in the MWCNT dispersion profiles for materials treated with the individual surfactants used in this study. The surfactant tails were physically adsorbed onto the MWCNT surfaces via $\pi - \pi$ interactions. As such, it is important to identify the effects of these non-covalent interactions on the graphitic structural characteristics of the nanotubes. Raman spectroscopy is a technique capable of verifying the structural characteristics of the MWCNTs, providing important information on the disruption of the π systems of the nanotube structures [44].

There are two characteristic Raman bands appearing at $\sim 1340\text{ cm}^{-1}$ and $\sim 1580\text{ cm}^{-1}$ known as the graphite (G-band) and defect (D-band), respectively. The intensity ratio of D- and G- band (I_D/I_G) indicates the degree of disordering of the nanotubes caused by non-covalent functionalisation [45]. As depicted in Fig. 7, there are only very slight increases or

decreases in the comparative I_D/I_G values, verifying that, in general, the sp^2 hybridised carbon atoms in the graphitic structure of MWCNTs have been not converted to sp^3 hybridised atoms. This result also confirms that the non-covalent functionalisation by the surfactants employed in this work did not disrupt the π systems comprising the nanotube structure. The small changes in the I_D/I_G values were caused by nanotubes-surfactant interactions, which tend to induce physical strain and field disturbance in the graphite sheet [46]. Based on this study, it is now possible to schematically illustrate the $\pi - \pi$ interactions between the benzene ring in the surfactant chain and the nanotubes. This description can be found in the following sections.

3.5. Stabilisation of MWCNTs by surfactant attached benzene ring

The presence of benzene moieties in the surfactant chain exerts a notable stabilising effect on MWCNTs in NR-latex matrices. The homogenous dispersion of MWCNTs in NR-latex stabilised by benzene-bearing surfactant is strongly believed to be due to the interaction of the π -systems of the MWCNTs and the aromatic moieties in the surfactant tails. This phenomenon is commonly known as $\pi - \pi$ stacking [47]. With regard to the un-zipping mechanism of nanotube stabilisation [31, 48], as the surfactant diffuses into the spaces between the bundles of MWCNTs, the effectiveness of surfactant as a dispersant has been demonstrated to be governed by number of benzene units contained in the tail groups [49]. Due to the inclusion of three benzene moieties in TcPh, this surfactant most effectively diffused into the open spaces between the MWCNTs bundles and easily adsorbed onto the nanotube surfaces.

To further demonstrate the importance of the benzene moieties, the proposed mechanism for the dispersal of MWCNTs in NR-latex is given in Fig. 8. When single-chain SDBS was layered on the MWCNT surfaces, the sulphonate head groups of the surfactant are exposed to

latex particles, while their benzene-containing tails groups are positioned close to the MWCNT surfaces via physical adsorption. These SDBS/nanotube aggregates are tend to appear as cylindrical micelles surrounding an inner nanotube [50]. In this model, the monolayers are formed by adsorbed surfactant in a vertical orientation with the negatively charged head groups directed towards the colloidal system. Hence, the nanotubes are contained within the interior of a cylindrical micelle within colloidal systems that rely on the surfactants for stability.

A study by Kragulj et al. [51] demonstrated that $\pi - \pi$ interactions between aromatic organic compounds increased with increasing number of aromatic rings. As part of this study, the adsorption ability of aliphatic and aromatic organic compounds onto MWCNT surfaces is also investigated. In their experimental study, the adsorption abilities of organic compounds were ranked as follows: non-polar aliphatics < monoaromatics < polycyclic aromatic hydrocarbons < nitriaromatics. The adsorption of aromatic compound onto MWCNTs was found to be stronger than found for aliphatic compounds, indicating that $\pi - \pi$ interaction are important in the adsorption of organic compounds onto MWCNTs. Interestingly, an increased number of benzene rings in the molecule further enhances the $\pi - \pi$ interactions between aromatic compounds and MWCNT surfaces.

In the present study, the use double chains surfactants, with each chain containing a benzene ring (AOTPh), affected the dispersibility of MWCNTs in NR-latex. This effect was reflected by the decreasing number of MWCNT bundles after the introduction AOTPh, as previously discussed. The introduction of triple chains surfactant (TCPh), again with each chain containing a benzene group, significantly enhances the stability of the colloidal system and led to the highest level of MWCNT dispersion. Evidently, increasing numbers of benzene rings tend to increase the hydrophobicity of the surfactant tails, which significantly increases the π - π interactions between the surfactants tails and MWCNT surfaces. In this respect, the

results for the series of SDBS (monochain), AOTPh (di-chain), and TCPH (tri-chain) indicates a clear trend of increasing hydrophobicity with increasing numbers of benzene rings, leading to significant improvements in the stabilities of nanotube-colloidal systems.

4. Conclusions

To more fully develop the green multifunctional nanocomposites applied in aerospace technology, intensive research into methods for optimal dispersion of individual MWCNTs is crucial [8, 21, 32, 33]. In this work, homogeneously dispersed MWCNTs in NR-latex have been successfully prepared via non-covalent treatment with surfactants. This study was conducted with a goal of systematically studying the importance of the inclusion of benzene rings in single-, double-, and triple-sulphosuccinate type surfactants. The results showed that the use of a triple-chain surfactant functionalised with three benzene groups provided remarkable stabilisation of a colloidal mixture of MWCNTs dispersed in an NR-latex matrix compared to that of a commercially available SDBS surfactant. In addition, the hydrophobicity of surfactant evidently increased with increasing numbers of benzene rings included in the surfactant tails (from single to triple), further strengthening the importance of π - π interactions between surfactants tails and MWCNT surfaces. These results indicate the importance of including benzene rings in surfactant chains designed to enhance the dispersibility of MWNCTs in polymer matrices.

Acknowledgements

The authors would like to acknowledge University Research Grant (GPU-UPSI; Grant code: 2012-0113-102-01), the Research Acculturation Grant Scheme (RAGS; Grant code: 2013-0001-101-72), the Malaysia Toray Science Foundation (MTSF; Grant code: 2012-0138-102-11), JEOL Ltd. and the Universiti Pendidikan Sultan Idris for financial and facilities support.

MS thanks JSPS and Leading Research Organisations under the G8 Research Councils Initiative for Multilateral Research Funding –G8-2012.

Supplementary material

Additional details on surfactant synthesis and characterisation.

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