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## Enhanced dispersion of multiwall carbon nanotubes in natural rubber latex nanocomposites by surfactants bearing phenyl groups



Azmi Mohamed <sup>a,b,\*</sup>, Argo Khoirul Anas <sup>a</sup>, Suriani Abu Bakar <sup>b,c</sup>, Tretya Ardyani <sup>a</sup>, Wan Manshol W. Zin <sup>d</sup>, Sofian Ibrahim <sup>d</sup>, Masanobu Sagisaka <sup>e</sup>, Paul Brown <sup>f</sup>, Julian Eastoe <sup>g</sup>

<sup>a</sup> Department of Chemistry, Universiti Pendidikan Sultan Idris, 35900 Tanjung Malim, Perak, Malaysia

<sup>b</sup> Nanotechnology Research Centre, Universiti Pendidikan Sultan Idris, 35900 Tanjung Malim, Perak, Malaysia

<sup>c</sup> Department of Physics, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjung Malim, Perak, Malaysia

<sup>d</sup> Malaysian Institute for Nuclear Technology Research (MINT) Bangi, 43000 Kajang, Selangor, Malaysia

e Department of Frontier Materials Chemistry, Graduate School of Science and Technology, Hirosaki University, 3 Bunkyo-cho, Hirosaki, Aomori 036-8561, Japan

<sup>f</sup> Department of Chemical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, United States

<sup>g</sup> School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, United Kingdom

## G R A P H I C A L A B S T R A C T



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#### ABSTRACT

Here is presented 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-sulfosuccinate anionic surfactants containing phenyl 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, phenyl-containing surfactant, namely sodium 1,5-dioxo-1,5-bis(3-phenylpropox y)-3-((3-phenylpropoxy)carbonyl) pentane-2-sulfonate (TCPh), has a greater capacity the stabilisation of MWCNTs than a commercially available single-chain sodium dodecylbenzenesulfonate (SDBS) surfactant. TCPh provides significant enhancements in the electrical conductivity of nanocomposites, up to  $\sim 10^{-2}$  S cm<sup>-1</sup>, as measured by a four-point probe instrument. These results have allowed compilation of a road map for the design of surfactant architectures capable of providing the homogeneous dispersion

\* Corresponding author at: Department of Chemistry, Universiti Pendidikan Sultan Idris, 35900 Tanjung Malim, Perak, Malaysia. Fax: +60 1548117296. *E-mail address:* azmi.mohamed@fsmt.upsi.edu.my (A. Mohamed). of MWCNTs required for the next generation of polymer-carbon-nanotube materials, specifically those used in aerospace technology.

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## 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 large scale implementation of this elastomeric biodegradable polymer as conductive materials 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].

#### Table 1

Surfactants used in this work.

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 is considered an alternative technique useful for enhancing MWCNTs/polymer interfacial interactions without disturbing the  $\pi$  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 dodecylsulfate (SDS) and sodium dodecylbenzenesulfonate (SDBS). Both have similar alkyl chain lengths, but differ in the inclusion of phenyl 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 surfactant structure determines its efficiency in promoting stable nanotube dispersions. It is believed that the introduction of the phenyl ring in the surfactant chains makes SDBS more effective than SDS [29]. The



existence of  $\pi$ - $\pi$  stacking is proposed as a main factor promoting the exceptional performance of SDBS in dispersing nanotubes in polymer matrices [30].

To evaluate the importance of the phenyl ring in surfactant chains, study of its role in stabilising colloidal systems of nanotubes is very important. However, to the best of our knowledge, no systematic studies on this topic exist. In previous work [31], the performance of single-, double-, and triple- chains with the aid of highly-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 highly branched methylated chains, namely sodium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-diox obutane-2-sulfonate (TC14), significantly enhanced the dispersibility of MWCNTs in the NR-latex.

In addition, to enrich the fundamental understanding of CNT-dispersing materials, here is presented a systematic study of CNT-philic surfactant architectures through the choice of a range of sulfosuccinate-type surfactants linked to aromatic phenyl moieties in their alkyl chains (the chemical structure were shown in Table 1). The performance of single-, double-, and triple-chain surfactants attached to phenyl 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 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  $32.51 \pm 0.08$  and  $33.87 \pm 0.01\%$  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 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 14.0–55.3 nm. SDS (Systerm, 99% purity) and SDBS (Sigma Aldrich, technical grade) were used as received. In addition, AOTPh and TCPh 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 based 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 h and sonicated (Branson 5510 sonicator, with 135 W of power and 42 kHz of an output frequency) for an additional 3 h. 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. Characterisation

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 dimensions of  $10 \times 10$  mm and  $\sim 2$  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  $\pi$  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 aromatic surfactants, are represented in Fig. 3 and Table 2 as functions of surfactant concentration. In the absence of MWCNTs, the electrical conductivity of the pristine NR-latex was found to be approximately 10<sup>-11</sup> S cm<sup>-1</sup>. 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<sup>-1</sup>. 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  $(\sim 10^{-5} \,\mathrm{S} \,\mathrm{cm}^{-1})$  than found with the addition of SDS. As described in a previous study [40], the single-chain, phenyl-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, phenyl-functionalised AOTPh surfactant was successfully employed for the enhancement of the electrical conductivity of the nanocomposite, resulting in values







Fig. 2. The general route for nanocomposite preparation.



Fig. 3. The electrical conductivity of the NR-latex matrix and the MWCNTs/NR-latex containing phenyl-functionalised branched surfactants.

 Table 2

 Surface tension properties of the surfactants containing phenyl rings and electrical conductivities of nanocomposites.

Surfactant	cmc (mM)	$\gamma_{cmc}$ (mN m <sup>-1</sup> )	Surfactant concentration (mM)		
			16.00	24.00	32.00
			Electrical conductivity of nanocomposites (S cm <sup>-1</sup> )		
TCPh AOTPh SDBS SDS	0.5 3.6 1.5 <sup>a</sup> 8.0 <sup>b</sup>	38.9 34.9 36.5 <sup>a</sup> 34.7 <sup>b</sup>	$\begin{array}{c} 3.18\times 10^{-3} \\ 8.38\times 10^{-4} \\ 4.74\times 10^{-5} \\ 3.81\times 10^{-6} \end{array}$	$\begin{array}{c} 9.48\times 10^{-3}\\ 3.67\times 10^{-4}\\ 4.92\times 10^{-5}\\ 3.21\times 10^{-6} \end{array}$	$\begin{array}{c} 4.58\times10^{-2}\\ 4.29\times10^{-4}\\ 2.53\times10^{-4}\\ 2.94\times10^{-5} \end{array}$

<sup>a</sup> Data collected by Biswal and Paria [41].

<sup>b</sup> Data collected by Sa and Kornev [42].

up to  $\sim 10^{-4} \, \text{S cm}^{-1}$ . An outstanding improvement (up to  $\sim 10^{-2} \, \text{S cm}^{-1}$ ) was found in a MWCNTs/NR-latex nanocomposite stabilised by the triple-chain, phenyl-functionalised TCPh surfactant. A previous study [31] noted that the dispersion stability

and nanocomposite electrical conductivity are significantly affected by structural variations on the surfactant chain. Trends in electrical conductivity were found to linked closely with the surfactant limiting surface energy ( $\gamma_{cmc}$ ) achieved by the introduction of a highly methylated surfactant (TC14, electrical conductivity =  $7.96 \times 10^{-3}$  S cm<sup>-1</sup>;  $\gamma_{cmc}$  = 27.0 mN m<sup>-1</sup>). In contrast, introduction of the phenyl-functionalised surfactant resulted in a relative high  $\gamma_{\rm cmc}$  (Table 2). However, the non-aromatic surfactant di-chain analogue AOT14 (di-chain; electrical conductivity =  $7.80 \times$  $10^{-6} \,\mathrm{S} \,\mathrm{cm}^{-1}$ ) and tri-chain TC14 exhibited a lower electrical conductivity compared to the aromatic-functionalised surfactants used in this study. The phenyl-functionalised surfactant proved to be more efficient for the stabilisation of colloidal nanotube systems and thus give a pronounced nanocomposite electrical conductivity enhancement. Apparently, phenyl-functionalisation of the surfactants is a major factor to achieve favourable interactions of the surfactant chain and the MWCNTs surfaces. To further study the capacity of SDBS, AOTPh, and TCPh for stabilisation of 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 sections.

## 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 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, optical polarising microscopy was employed to observe the micro-scale dispersion of MWCNTs, and surface morphologies were observed by FESEM.

Figs. 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.



Fig. 4. Optical polarising microscope images of MWCNTs/NR-latex: at the absence of surfactant (a); with SDBS (b); with AOTPh (c); with TCPh (d). — and  $\rightarrow$  represent the MWCNTs agglomerated and dispersed in NR-latex, respectively.

The presence of surfactant was crucial for stabilising the nanotubes in the latexes. 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/—) and very few individual nanotubes (signed by stealth arrow/ $\rightarrow$ ) on the surfaces of nanocomposites (Fig. 5a and a'). The images show that the MWCNTs are represented by the bright bars and spots against the dark polymer matrix. This contrast stems from the different charge transport capabilities of the conductive nanotubes and the insulating polymer matrix [23,30]. Interestingly, the introduction of the commercially available SDBS decreased the number of nanotube bundles and slightly increased the number of individual nanotubes observed (Figs. 4b; 5b 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 (Figs. 4c; 5c and c'), indicating that the twice-phenyl-functionalised surfactant provides more effective dispersion of MWCNTs than SDBS surfactant chains bearing only one phenyl moiety. Remarkably, the addition of the tri-chain phenyl-functionalised surfactant (TCPh) exhibited the most notable improvement in the level of dispersion of MWCNTs in the NR-latex matrix (Figs. 4d; 5d and d'). FESEM images showed smooth surface morphologies with homogeneously dispersed MWCNTs. These results convincingly suggest that increasing the number of aromatic rings per surfactant molecule from one to three 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 as 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 treated with incorporated 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 in mind, a possible mechanism of surfactant-induced MWCNT stabilisation was proposed, described in the following section.

#### 3.4. Raman spectroscopy measurements

As discussed above, surfactant chains bearing phenyl rings have a significant influence on maximising 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  $\pi$  systems of the nanotube structures [44].

There are two characteristic Raman bands appearing at  $\sim$ 1340 cm<sup>-1</sup> and  $\sim$ 1580 cm<sup>-1</sup> 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. 5. FESEM images of MWCNTs/NR-latex: in the absence of surfactant (a and a'); with SDBS (b and b'); with AOTPh (c and c'); with TCPh (d and d').

Fig. 7, there are only very slight increases or decreases in the comparative  $I_D/I_G$  values, verifying that, in general, the sp<sup>2</sup> hybridised carbon atoms in the graphitic structure of MWCNTs have been not converted to sp<sup>3</sup> hybridised atoms. This result also confirms that the non-covalent functionalisation by the surfactants employed in this work did not disrupt the  $\pi$  systems comprising the nanotube structure. The small changes in the  $I_D/I_G$  values were caused by nanotube-surfactant interactions, which tend to induce physical strain and field disturbance in the graphite sheets [46]. Based on this study, it is now possible to schematically illustrate the  $\pi$ - $\pi$  interactions between the phenyl rings in the surfactant chains and the nanotubes, covered in the following sections.

#### 3.5. Stabilisation of MWCNTs by aromatic surfactants

The presence of phenyl moieties in the surfactant chains exerts a notable stabilising effect on MWCNTs in NR-latex matrices. The homogenous dispersion of MWCNTs in NR-latex stabilised by phenyl-bearing surfactants is strongly believed to be due to the attractive interaction of the conjugated-systems of the MWCNTs and the aromatic moieties in the surfactant tails [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 separate phenyl units



Fig. 6. TEM image of MWCNTs/NR-latex with the TCPh surfactant.

contained in the tail groups [49]. Due to the inclusion of three phenyl 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 aromatic moieties, the proposed mechanism for the dispersal of MWCNTs in NR-latex is given in Fig. 8. When single-chain SDBS was associated with the MWCNT surfaces, the sulfonate head groups of the surfactant are exposed to latex particles, while their phenyl-containing tails groups are positioned close to the MWCNT surfaces via physical adsorption. According to work by Matarredona et al. [50] the final arrangement of SDBS adsorption on nanotube surfaces tend to



Fig. 7. Raman spectra of (a) NR-latex matrix, (b) MWCNTs, (c) MWCNTs/NR-latex, (d) MWCNTs/NR-latex/SDS, (e) MWCNTs/NR-latex/SDBS, (f) MWCNTs/NR-latex/AOTPh, and (g) MWCNTs/NR-latex/TCPh.



Fig. 8. Mechanism of MWCNTs/NR-latex nanocomposite stabilisation by phenylfunctionalised branched surfactants.

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 aqueous phase for dissolution. Hence, self-assembly structure of the adsorbed surfactants on the nanotube surfaces can modify the aggregation tendency of nanotubes thereby preventing re-aggregation of the individualised CNTs.

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 < nitroaromatics. The adsorption of aromatic compounds onto MWCNTs was found to be stronger than found for aliphatic compounds, indicating that  $\pi$ - $\pi$  interactions are important in the adsorption of organic compounds onto MWCNTs. Interestingly, an increased number of phenyl rings in the molecule further enhances the favourable  $\pi$ - $\pi$  interactions between the dispersants and the MWCNT surfaces.

In the present study, the use of a double aromatic chain surfactant (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 aromatic chain surfactant (TCPh) significantly enhances the stability of the colloidal system and led to the highest level of MWCNT dispersion. Increasing numbers of phenyl rings are expected to alter the overall extent of  $\pi$ - $\pi$  interactions between the surfactant tails and MWCNT surfaces by giving rise to stronger interactions involving  $\pi$ -orbitals of the respective materials. The new results presented here for the series of SDBS (monochain), AOTPh (di-chain), and TCPh (tri-chain) indicate a clear trend of increasing the stabilities of nanotube-colloidal systems with surfactant aromatic chain structure, leading to significant improvements of the nanocomposite electrical properties.

## 4. Conclusions

To more fully develop multifunctional nanocomposites applied in aerospace technology, intensive research into methods for optimising 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 extent of aromaticity with single-, double-, and triple-sulfosuccinate type surfactants. The results showed that the use of a triple-chain surfactant functionalised with three phenyl 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 bearing only one phenyl group. In addition, increasing numbers of phenyl rings included in the surfactant tails (from one to three) can offer favourable  $\pi$ - $\pi$  interactions between surfactant tails and MWCNT surfaces.

Taking all the results together, the phenyl rings functionalization here is consistent with past works that suggested aromatic moieties on the surfactant molecular structure is of primary importance to conferring high dispersion stability [47,50]. Similar electrical properties enhancement were presented but for Gemini with two phenyl rings and nonionic Triton-X100 surfactants in nanocomposites of MWCNTs/polystyrene and MWCNTs/epoxy, respectively [30,45]. Hence, the findings here appear quite general, strengthening frequent claims that aromatic bearing surfactants offer CNT-compatibility improvement over and above of that of the single, di- and tri-chain non-aromatic rings analogues [31]. This is considered to be one of the distinguishing features explaining why surfactants containing aromatic rings are preferable for applications in carbon nanomaterial. These results indicate the importance of including phenyl rings in surfactant chains designed to enhance the dispersibility of MWNCTs in polymer matrices.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcis.2015.05.054.

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