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ORIGINAL CONTRIBUTION

Preparation of multiwall carbon nanotubes (MWCNTs) stabilised by highly branched hydrocarbon surfactants and dispersed in natural rubber latex nanocomposites

Azmi Mohamed • Argo Khoirul Anas • Suriani Abu Bakar • Azira Abd. Aziz • Masanobu Sagisaka · Paul Brown · Julian Eastoe · Azlan Kamari · Norhayati Hashim · Illyas Md Isa

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Abstract The performance of single-, double- and triple-chain anionic sulphosuccinate surfactants for dispersing multiwall carbon nanotubes (MWNCTs) in natural rubber latex (NR-latex) was studied using a range of techniques, including field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and Raman spectroscopy. The conductivities of the nanocomposites were also investigated using four-point probe measurements. Here, MWCNTs were efficiently dispersed in NR-latex with the aid of hyperbranched tri-chain sulphosuccinate anionic surfactants, specifically sodium 1,4-bis(neopentyloxy)- 3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-sulphonate (TC14). This paper highlights that TC14 performs much better than that of the commercially available surfactant sodium dodecyl sulphate (SDS), demonstrating how careful consideration of

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A. Mohamed $(\boxtimes) \cdot$ A. K. Anas \cdot A. Kamari \cdot N. Hashim \cdot I. M. Isa Department of Chemistry, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjung Malim, Perak, Malaysia

e-mail: azmi.mohamed@fsmt.upsi.edu.my

A. Mohamed : S. Abu Bakar: A. Kamari : N. Hashim : I. M. Isa Nanotechnology Research Centre, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjung Malim, Perak, Malaysia

S. Abu Bakar

Department of Physics, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjung Malim, Perak, Malaysia

A. A. Aziz

Advanced Rubber Technology Unit, Technology & Engineering Division, Malaysian Rubber Board, RRIM Research Station Sg. Buloh, Sungai Buloh 47000, Selangor, Malaysia

surfactant architecture leads to improved dispersibility of MWCNTs in NR-latex. The results should be of significant interest for improving nanowiring applications suitable for aerospace-based technology.

Keywords Multiwall carbon nanotubes (MWCNTs) . Surfactant · Natural rubber latex (NR-latex) · Nanocomposites . Sodium dodecyl sulphate (SDS)

Introduction

Multiwall carbon nanotubes (MWCNTs) exhibit numerous attractive properties that enable their use as nanofillers for

M. Sagisaka

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

P. Brown

Department of Chemical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, **USA**

J. Eastoe School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK

polymeric reinforcement [[1](#page-10-0)–[4](#page-10-0)]. They possess outstanding electrical, mechanical and thermal properties compared to conventional fillers, such as carbon black [\[5,](#page-10-0) [6](#page-10-0)], and have therefore already attracted interest in various industries for possible applications in electronics [\[7](#page-10-0)] and medicine [[8\]](#page-10-0) and as flame retardants in polyurethane and polypropylene [[9,](#page-10-0) [10\]](#page-10-0). More recently, they have also been used in aerospace-based technology [\[11](#page-10-0), [12\]](#page-10-0). Conductive materials such as copper are conventionally employed to fabricate wire components. However, they have greater mass, which is not suitable for aerospace conditions [\[12\]](#page-10-0). MWCNTs are around six times lighter than copper and are an order of magnitude more conductive. Therefore, when incorporated into polymer nanocomposites, they have the potential to replace traditional transition metal components [\[13\]](#page-10-0)

Due to the miniscule size of MWCNTs', their properties can only be exploited if they are homogenously dispersed in polymer matrices that provide good filler matrix interfacial performance. In this respect, good dispersibility of MWCNTs is still a major challenge due to strong van der Walls forces, which causes agglomeration [[14\]](#page-10-0). To overcome this hurdle, two basic methods have been developed for treating MWCNTs: (1) covalent treatments, where strong acid is used as an oxidant to functionalise MWCNTs, and (2) non-covalent treatments. In the first method, the functionalisation of the MWCNTs' surface enhances the interfacial interaction between the MWCNTs and the polymer matrix via covalent bonding. However, the electrical properties of MWCNTs have been demonstrated to be substantially affected by the disturbance of their π -electrons [\[15,](#page-10-0) [16\]](#page-10-0). In the non-covalent method, MWCNTs are incorporated into a polymer matrix with the help of a surfactant that has the ability to both assist in dispersion and modify the nanocomposite to serve various applications [[17](#page-10-0)]. The strategy of utilising a surfactant (socalled 'latex technology') results in the generation of a stable, mixed colloidal system that contains a suspension of MWCNTs in a polymer matrix. In this case, the surfactants will adsorb at the MWCNT polymer interface and reduce the interfacial tension by balancing lyophilic and lyophobic interactions. Interestingly, the unique chemical structure of the surfactants enables the formation of a stable structure via lyophilic parts (known as 'head groups') and lyophobic parts (known as 'tails'), where the tails interact with the MWCNTs.

As a result, latex technology has triggered significant efforts to uncover a molecular structure that promotes efficient stabilisation of MWCNTs in polymer matrices. Thus, the effect of several commercially available ionic surfactants, including sodium dodecyl sulphate (SDS) [[2\]](#page-10-0), sodium dodecyl benzenesulfonate (SDBS) [[17](#page-10-0)] and lithium dodecyl sulphate (LDS) [\[18\]](#page-10-0), as well as non-ionic surfactants such as Triton X-100, Tween-80, Tween-60, Tween-40 and Tween-20 [\[19\]](#page-10-0) have been investigated. The results revealed that surfactants with long, highly branched and unsaturated carbon chains are better at stabilising MWCNTs in polymer matrices.

This result is attributed to the π -electronic affinity of the surfactant toward the CNT benzene rings [\[16](#page-10-0)].

The aforementioned studies revealed the nature of the straight-chained surfactants that are most efficient at stabilising MWCNTs in polymer matrices. However, applications are limited because studies have focussed on a restricted range of commercially available surfactants and have fixated on head group selection. Thus, further systematic studies of surfactant architecture may help elucidate the general tendencies of surfactant analogues that facilitate the dispersion of MWCNTs in polymer matrices. To investigate this problem, we have chosen a range of sulphosuccinate surfactants. It is particularly 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 reported to contain multiple hydrophobic tails that adsorb onto CNTs and induce a temporary surface charge due to the interaction with the hydrophilic polymer [\[20](#page-10-0)].

Recently, a study on AOT analogue surfactants for stabilising mixed colloidal system of water in continuous, supercritical carbon dioxide $(CO₂)$ phase microemulsions (w/c) was reported by Eastoe et al. [[21](#page-10-0)]. Interestingly, this research showed that the stability of this mixed colloidal system can be dramatically enhanced via the introduction of a third, highly branched hydrocarbon and methylated chain, i.e. TC14 surfactant (sodium 1,4-bis(neopentyloxy)- 3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-sulphonate) (Table [1](#page-3-0)) [[22\]](#page-10-0). The addition of this tri-chain surfactant is generally believed to efficiently lower the surface energy and packing requirements of a surfactant at the $CO₂$ -water interface [\[22\]](#page-10-0). Interestingly, this feature precisely seemed to control MWCNT dispersibility in polymer matrix [[20](#page-10-0), [23,](#page-10-0) [24\]](#page-11-0).

To address this challenge, here, we elucidate the ability of sulphosuccinate-type surfactant analogues to disperse MWCNTs in natural rubber latex (NR-latex) and reveal their effect on the electrical properties of the resulting dispersions. Recently, De Rosa et al. [\[12\]](#page-10-0) noted the need in the aerospace industry for nanomaterials not only with superficial properties but also with high-performance components. NR-latex is one class of biosynthesised, hydrophilic polymers that exhibits numerous attractive properties, such as high resilience, good tensile strength and good tear resistance [\[23](#page-10-0)]. As a result of these outstanding features, NR-latex has been extensively used in various synthetic products, such as hoses, footwear, tires, belts, gloves, rubber-backed carpets and adhesives [\[24,](#page-11-0) [25\]](#page-11-0). Therefore, as a critical step in the development of MWCNTs imbedded in polymers for aerospace cable and wire technologies, NR-latex appears to be a promising candidate polymer.

The purpose of this paper is to investigate the roles played by the chemical nature of the surfactant in the stabilisation of MWCNTs imbedded in NR-latex. The behaviour of singletail, double-tail and triple-chain sulphosuccinate analogues are compared as a function of their tail structure. These molecules

Table 1 Surfactants used in this study

Surfactant name	Surfactant structure	Chemical name	
SDS	\circ $\overline{\text{NaO}_3\text{S}}$	Sodium dodecyl sulphate	
AOT4	n O O $v_a^* \bar{o}_3 s$	Sodium bis(3,5,5-trimethyl-1- hexyl) sulphosuccinate	
AOT14	O \circ $\overline{Na} \overline{O}_3S$ ll O	Sodium bis(3,3,3-trimethyl-1- propyl) sulphosuccinate	
TC4	Ω $\stackrel{+}{\text{Na O}_3\text{S}}$ O	Sodium 1,5-dioxo-1,5- bis(3,5,5-trimethylhexyloxy)- $3-(3,5,5-$ trimethylhexyloxy)carbonyl) pentane-2-sulphonate	
TC14	C $\stackrel{+}{\text{Na O}_3\text{S}}$	Sodium 1,4- bis(neopentyloxy)-3- (neopentyloxycarbonyl)-1,4- dioxobutane-2-sulphonate	

are shown in Table 1 and consist of terminal methyl groups attached to similar hydrophilic head groups. 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 nanocomposite. The effects of the surfactant-stabilised MWCNTs/NR-latex nanocomposites on the composites' morphological and electrical properties are investigated. Significantly, this work provides additional insight into the molecular requirements of the surfactant used to incorporate MWCNTs into the NR-latex matrix and opens up the possibility for the development of frontier materials, such as advanced wiring concepts in aerospace technology [\[7](#page-10-0)].

Experimental

Materials

MWCNTs were fabricated at Universiti Sains Malaysia (USM) by a chemical vapour decomposition (CVD) method

[\[26\]](#page-11-0) and purified by refluxing in hydrochloric acid (5 M) at 100 °C for 5 h, thoroughly washed with water to pH 7 and finally dried at 90 °C overnight. The process was performed to remove impurities, including amorphous carbon and metallic catalyst [[17\]](#page-10-0). NR-latex was obtained from the Malaysian Rubber Board. The size of NR-latex particles is 10–100 nm [\[27\]](#page-11-0), with 33.86 and 32.47 % of total solid content and dry rubber content, respectively (details of the measurements are provided in the supplementary material). SDS (99 %) was purchased from Systerm and was used without purification. The AOT4, TC4 and TC14 surfactants were synthesised, characterised and purified according to the methods outlined in our previous reports [[22,](#page-10-0) [28,](#page-11-0) [29\]](#page-11-0). AOT14 was synthesised according to a method similar to that used in the preparation of AOT4 but with a modification to the alcohol precursor (Acros Organics). Further structural information is provided in the supplementary material.

Preparation of MWCNTs/NR-latex/surfactant nanocomposites

The latex technology route summarised in Fig. 1 was employed to prepare MWCNTs/NR-latex nanocomposites stabilised by a surfactant. In the first step, we prepared test dispersions (10 mL) by mixing 5 wt% MWCNTs with concentrations ranging between 0 and 32 mM; the aqueous surfactant solutions were placed in a flask. This particular concentration range was chosen as a common concentration of surfactants for latex technology [[30](#page-11-0)]. The resulting mixtures were ultrasonicated (Branson 5510 sonicator, with an output frequency of 42 KHz and power of 135 W) for 3 h at room temperature. The stable, homogenous dispersion of MWCNTs/surfactant in aqueous solution was subsequently added to the NR-latex solution. The mixture was then stirred for 1 h followed by ultrasonication for 3 h. Finally, the nanocomposite was dried overnight in an oven at 80 °C.

Characterisation of the MWCNTs/NR-latex/surfactant nanocomposites

The electrical conductivity was measured on $(10 \text{ mm} \times$ 10 mm) solid sample with ∼2 mm of thickness in triplicate using a standard four-point probe instrument (Keithley 2636A). The surface morphologies and embedded microstructure of the MWCNTs in NR-latex were confirmed using field emission scanning electron microscopy (FESEM-Hitachi SU8020) and transmission electron microscopy (TEM-JEOL 2,100F), respectively. The purity of the MWCNTs and thermal stability of the nanocomposites were investigated using thermogravimetric analysis (TGA; Perkin Elmer Pyris 1). In addition, the structural effects of the surfactants on the structure of the MWCNTs were studied using Raman spectroscopy. In this work, the measurements were performed between 100 and 4,000 cm−¹ using a Renishaw InVia Micro Raman System spectrophotometer; the spectra were collected at room temperature using an argon-ion laser (514 nm) as the light source.

Results and discussion

Electrical conductivity measurements

The electrical conductivities of the MWCNTs/NR-latex stabilised using different ionic surfactant are depicted in Fig. 2 and Table [2](#page-6-0) as functions of the surfactant concentrations. The measurements were conducted at similar surfactant concentrations to enable close comparison of the electrical conductivities of the nanocomposites. As discussed in the literature, NR-latex is a fluid containing *cis*-1,4-polyisoprene polymer as its main component. The lower range of electrical conductivity of the NR-latex measured in this study was $\sim 10^{-10}$ S cm⁻¹, which generally reflects elastomer behaviour with insulating material properties [[33](#page-11-0)]. The addition of 5 wt% of MWCNTs to NR-latex results in an increase in the electrical conductivity of three orders of magnitude to $\sim 10^{-7}$ S cm⁻¹. This increase in electrical conductivity suggests the formation of a network of percolated MWCNTs in the polymer matrix that exceeds the percolation threshold [[6](#page-10-0), [15](#page-10-0)].

Interestingly, the addition of commercially available SDS to MWCNTs/NR-latex nanocomposites resulted in an increase in conductivity of almost an order of magnitude to the $\sim 10^{-6}$ S cm⁻¹ range. Single-chain SDS has previously been reported to function as a good stabiliser for MWCNTs in polymer matrices by allowing the hydrophobic part of the surfactant to adsorb onto the MWCNTs' surface, which induces a temporary surface charge [[34](#page-11-0)]. Double-chain surfactants with terminal methyl groups, i.e. AOT4 and AOT14, substantially affected the conductivity of the composite, improving it to 10^{-5} S cm⁻¹. Remarkably, the addition of a triplechain surfactant with a terminal methyl group, i.e. TC14, led to an enhancement of conductivity to 10^{-3} S cm⁻¹ under these experimental conditions.

Fig. 2 The electrical conductivity of the NR-latex matrix and the MWCNTs/NR-latex containing surfactant

As evident in Fig. 2, the MWCNTs/NR-latex containing 24.00 mM TC14 exhibited the highest electrical conductivity. A comparison of the conductivity results for the series of SDS (mono-chain), AOT14 (di-chain) and TC14 (tri-chain) revealed a clear trend of increasing electrical conductivity with increasing number of tails, as reported previously [\[22](#page-10-0), [35](#page-11-0), [36\]](#page-11-0). However, a discrepancy in conductivity can be seen for TC14 systems with below cmc (21.63 mM) due to dynamic equilibrium behaviour of surfactant at MWCNT interface. The results suggest that the conductivity of composite is subject to surfactant concentration [\[32](#page-11-0), [36\]](#page-11-0). The addition of a third chain to the surfactant structure is believed to be important for decreasing the surface energy (as found in $\gamma_{\rm cm}$ in Table [2\)](#page-6-0) and then strongly interacting with the MWCNTs. FESEM was used to confirm the ability of TC14 to disperse and stabilise MWCNTs in NR-latex; the results are discussed in the following section.

FESEM observations

As described in the previous section, the presence of TC14, which has a third chain with a terminal methyl group, induces a significant improvement in the electrical conductivity of the MWCNTs/NR-latex nanocomposite. Further investigation of the dispersion of MWCNTs in NR-latex matrices, which plays an important role in improving the electrical and thermal properties of the nanocomposites, is therefore important [\[15](#page-10-0)]. Consequently, we characterised the dispersion of the MWCNTs in the NR-latex matrix using FESEM to help identify the internal structure of the conductive MWCNT networks with NR-latex assisted by the surfactants [\[37](#page-11-0)]. FESEM images of MWCNTs can only be seen in Fig. [3\(a,](#page-7-0) [a](#page-7-0)'). In Fig. [3\(b](#page-7-0)–d), the stealth arrows (\rightarrow) and diamond arrows (\rightarrow) represent individual and bundled MWCNTs, respectively. In the absence of surfactant [Fig. [3\(b, b](#page-7-0)′)], the MWCNTs exhibited diameters of ∼260 nm; the MWCNTs were entangled and poorly dispersed in the NR-latex matrix. The poor distribution was determined from the large bundles of MWCNTs that appeared at high magnification. However, after the introduction of SDS [Fig. [3\(c, c](#page-7-0)′)], the morphology of the nanocomposite differed substantially from that of the surfactant-free system. The number of agglomerated nanotubes decreased slightly in agreement with the results of a previous study [\[38\]](#page-11-0). An alternative approach to enhance the dispersion of MWCNTs in a polymer matrix is the addition of a tri-chain surfactant. Interestingly, prior to the addition of the TC14 surfactant, the morphology of the nanocomposite was remarkably well dispersed with no agglomeration, and the diameters of the individual MWCNTs were approximately 15–60 nm; the TC14 was thus demonstrated to be a promising surfactants for latex technology. These results strongly suggest that the introduction of a surfactant with a third chain

Surfactant	cm (mM)	γ_{cmc} (mN m ⁻¹)	Surfactant concentration (mM)		
			16.00	24.00 Electrical conductivity of nanocomposites $(S \text{ cm}^{-1})$	32.00
TC14	$21.63^{\rm a}$	$27.0^{\rm a}$	3.09×10^{-4}	7.96×10^{-3}	1.52×10^{-3}
TC ₄	$0.0125^{\rm a}$	$29.7^{\rm a}$	3.43×10^{-5}	2.69×10^{-4}	5.17×10^{-4}
AOT ₄	1.10^{b}	28.0 ^b	7.45×10^{-5}	1.18×10^{-4}	1.84×10^{-4}
AOT ₁₄	2.40	28.6	2.18×10^{-5}	7.80×10^{-6}	1.55×10^{-6}
SDS	8.00 ^c	34.7°	3.81×10^{-6}	3.21×10^{-6}	2.94×10^{-5}

Table 2 Surface tension properties of surfactants and electrical conductivities of nanocomposites

^a Data collected by Mohamed et al. [[22\]](#page-10-0)

 b Data collected by Nave et al. [[31](#page-11-0)]</sup>

c Data collected by Sa and Kornev [\[32](#page-11-0)]

containing a terminal methyl group can efficiently debundle MWCNTs in NR-latex matrices.

TEM observations

In the preceding section, FESEM images highlighted the different morphologies for dispersed MWCNTs in NRlatex before and after treatment with the surfactant. In order to support these observations, TEM studies were conducted to understand the embedded microstructure of MWCNTs/NR-latex nanocomposite (see Fig. [4\)](#page-8-0). It is clear that the introduction of TC14 surfactant efficiently loosens the MWCNT bundles. This result indicates that TC14 surfactant was successful in generating homogeneous dispersions of MWCNTs in NR-latex and strongly supporting the proposed mechanism of MWCNT stabilisation that can be found in the next section.

Thermal stability measurements

The thermal stability of the various nanocomposites was measured using thermogravimetric analysis (TGA). Figure [5](#page-8-0) shows the weight loss percentage as a function of the temperature for NR-latex, MWCNTs/NR-latex, MWCNTs/NR-latex/SDS and MWCNTs/NR-latex/TC14. The TGA of NR-latex matrix [Fig. [5\(a\)](#page-8-0)] shows a weight loss of approximately 4 % between room temperature and 200 °C, which corresponds to decomposition of water and ammonia residue [[39](#page-11-0)]. However, upon introduction of a surfactant, the curves for the nanocomposite [Fig. [5\(c, d\)\]](#page-8-0) differed slightly from that of NR-latex, with a weight loss of ∼5 % in the temperature range 200– 300 °C, consistent with the weight loss of the free surfactant that remained in the polymer matrix and low boiling point constituents [[40,](#page-11-0) [41\]](#page-11-0). The weight loss of the NR-latex occurred in the temperature range of 300– 440 °C (88 %) and at temperatures greater than 440 °C

(8 %), corresponding to a degradation of the non-volatile residues [[42\]](#page-11-0).

The weight loss between 390 and 440 °C (see the inset in Fig. [5\)](#page-8-0) gives a clearer picture of the effect of the surfactant on the thermal stability of the nanocomposites. The inset clearly shows a steeper gradient for the MWCNTs/NR-latex nanocomposite than for the NR-latex-only sample. These results were attributed to an enhancement of the thermal stability of NR-latex as consequence of the barrier effect in MWCNTs [\[10](#page-10-0)]. Interestingly, TC14 has been demonstrated to provide a notable performance improvement over commercially available SDS by dispersing MWCNTs with greater thermal stability. This thermal stability is related to the homogeneous dispersion of the nanocomposite by TC14, as discussed in the '[FESEM observations](#page-5-0)' and 'TEM observations'. Therefore, the homogeneous dispersion of MWCNTs in the polymer matrix by the tri-chain surfactant with terminal methyl groups produced a higher density of filler-matrix interactions in the nanocomposite [[43](#page-11-0)].

Raman spectroscopy measurements

Raman spectroscopy measurements are helpful for studying the characteristics of MWCNTs subjected to a non-covalent treatment and provide useful information about the role of the surfactant as the dispersing agent. Figure [6](#page-8-0) shows Raman spectra of MWCNTs in NR-latex with TC14 and SDS surfactants. The results depicted in Fig. [6\(b\)](#page-8-0) agree well with the literature with respect to the two characteristic peaks of MWCNTs at approximately 1,340 and 1,580 cm⁻¹; these peaks correspond to the disorder band (D-band) and graphite band (G-band), respectively [\[44](#page-11-0)].

The intensity ratio of the D- and G-bands (I_D/I_G) is commonly used to describe the disruption of the π -system in graphite sheets [\[6\]](#page-10-0). As evident in Fig. [6,](#page-8-0) after the addition of the surfactant, the I_D/I_G ratio slightly increased generally because of surfactant wrapping and the $sp²$ hybridisation of

Fig. 3 FESEM images of MWCNTs only $(a \text{ and } a')$ and MWCNTs/NR-latex: in the absence of surfactant $(b \text{ and } b')$, with SDS (c and c') or with TC14 $(d \text{ and } d')$

the graphite sheet was not altered to $sp³$ hybridisation. Furthermore, an increase in the I_D/I_G ratio for MWCNTs/ NR-latex was also observed as a consequence of the wrapping process by isoprene monomers in the NRlatex [[45](#page-11-0)]. We confirmed that the surfactant treatments

used in this study did not disturb the π -systems of the MWCNTs in the nanocomposites. On the basis of this study, the possible mechanism by which the TC14 surfactant effectively disperses MWCNTs in NR-latex can be investigated.

Proposed mechanism of MWCNT stabilisation

As discussed in the previous section, the tri-chain surfactant TC14 exhibits a much greater ability for stabilising MWCNTs in NR-latex than the single-chain SDS surfactant. The formation of homogeneously dispersed MWCNTs in NR-latex is believed to be due to hydrophilic/hydrophobic interactions [\[46\]](#page-11-0). The surface of NR-latex particles are covered by both positive charges of protein molecules and negative charges of phospholipid molecules [\[47,](#page-11-0) [48\]](#page-11-0); therefore, the hydrophilic heads are forced to interact with the NR-latex and the hydrophobic tails of the surfactants adsorb onto the MWCNTs' surface. In this case, ultrasonication provides a high local shear force that opens spaces on the ends of the carbon nanotube bundles [[16\]](#page-10-0) (see Fig. [7](#page-9-0)). Surfactants, which easily adsorb onto the carbon nanotube surface, subsequently diffuse into these spaces [[49](#page-11-0)]. In previous reports, the effectiveness of a surfactant as a dispersing agent was demonstrated to be

governed by the low surface energy of the tail group [\[22,](#page-10-0) [29,](#page-11-0) [50](#page-11-0)]. With respect to low surface energy, TC14 effectively diffuses into the open spaces in MWCNTs and easily adsorbs onto the surface, as expected given TC14's bulky surfactant tail that results from the introduction of a third chain with a terminal methyl group.

Another consideration that affects the electrical conductivity of MWCNTs in polymer matrices essentially arises from the surfactant concentration and generally requires concentrations greater than the critical micelle concentration (cmc) [[51\]](#page-11-0). Thus, the cmc values, which are given in Table [2](#page-6-0), are used to compare the electrical conductivities of the nanocomposites prepared with different surfactants. As observed in Fig. [1](#page-4-0), the effect of TC14 on the electrical conductivity of nanocomposites is greatest when the concentration of surfactant exceeds its cmc (24.00 and 32.00 mM). Interestingly, TC14 induces a higher electrical conductivity than the other surfactants when

Fig. 5 TGA curves for the (a) NR-latex matrix, (b) MWCNTs/NR-latex, (c) MWCNTs/NR-latex/SDS and (d) MWCNTs/NR-latex/TC14

Fig. 6 Raman spectra of (a) NR-latex matrix, (b) MWCNTs, (c) MWCNTs/NR-latex, (d) MWCNTs/NR-latex/SDS and (e) MWCNTs/ NR-latex/TC14

Fig. 7 Stabilisation of individual MWCNTs by a surfactant: a MWCNTs bundles, b high local shear is formed, c the surfactant begins to adsorb onto the MWCNT surface and d the individual MWCNTs stabilised by surfactant are separated from the bundles

present at concentrations less than the cmc, which is clear from the electrical conductivity data for all of the samples with surfactants (shown in Fig. [1](#page-4-0)), and is consistent with the cmc values mentioned in a previous study [\[38\]](#page-11-0).

To understand why the TC14 surfactant concentration is so influential, we illustrate the proposed mechanism of MWCNT dispersion in an NR-latex matrix [[17](#page-10-0), [52\]](#page-11-0) (see Fig. 8). When the TC14 surfactant is present at a concentration less than the cmc, its adsorption onto the MWCNTs' interface is in dynamic equilibrium, with molecules adsorbing and desorbing at an equal rate [[53](#page-11-0)]. During this stage, the range of surfactant concentration is of no importance for nanocomposite system since only minimum MWCNTs are covered with surfactant [\[32](#page-11-0), [38](#page-11-0)]. However, when the maximum coverage at the interface is nearly achieved (i.e. at the cmc), the rate that surfactant molecules adsorb onto the MWCNTs drastically increases and the surfactant molecules form multilayers on the nanotube surfaces to minimise the system-free energy. In this case, the effectiveness of the surfactant at reducing interfacial tension at the cmc is reflected in the surface tension ($\gamma_{\rm cmc}$). Compared to SDS (Table [2\)](#page-6-0), TC14 resulted in a decrease in γ_{cmc} (27 mN m⁻¹). This low value of $\gamma_{\rm cmc}$ is attributed to the increase in hydrophobicity due to the incorporation of the low surface energies of the terminal methyl groups [[35,](#page-11-0) [36](#page-11-0), [50](#page-11-0)], which is considered to be one of the underlying factors responsible for maximising the interactions between the surfactant tails and the nanotubes and, consequently, for improving the dispersion of the MWCNTs [[22\]](#page-10-0). In addition, when the surfactants are present in concentrations greater than the cmc, the system is in equilibrium, with no clear difference observed in the morphologies of the different surfactants. At this stage, homogeneous dispersion of the MWCNTs occurred, and the electrical conductivities of the nanocomposites were significantly enhanced.

Fig. 8 Mechanism of surfactant micelle formation in the MWCNTs dispersion

Conclusions

Attempts to improve the outstanding electrical, thermal and mechanical properties of MWCNTs by improving their dispersion in NR-latex are important in the development of better components for use in nanowires in aerospace applications [11, 12]. In this study, a stable, colloidal mixture of MWCNTs in a polymer matrix was obtained through latex technology via surfactant utilisation [15]. Here, systematic studies of MWCNTs dispersed in NR-latex using single-, double- and triple-chain sulphosuccinate-type surfactants were performed. The results revealed that the introduction of the third chain with terminal methyl groups on the surfactant chains profoundly influence the homogenisation of MWCNTs in NRlatex matrices. Interestingly, the results are consistent with the results of surface tension studies [22], where the introduction of a third chain with a highly methylated group lowers the surface energy, resulting in efficient partitioning at the MWCNTs/NR-latex interface. Therefore, the TC14 surfactant provides a better option compared to the single-chain SDS surfactant. These results will aid in expanding our understanding of the dispersion behaviour of MWCNTs in the presence of surfactants and will advance the theory of surfactant design for MWCNTs.

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