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Highly conductive electrodes of graphene oxide/natural rubber latex-based electrodes by using a hyper-branched surfactant



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ABSTRACT

A custom-made surfactant called sodium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-sulfonate (TC14) was used to assist the dispersion of graphene oxide/natural rubber latex (GO/NRL) nanocomposites by the one-step method. NRL was intermixed in the electrolyte during the electrochemical exfoliation of the produced GO. The conductivity of the sample was measured by using a four-point probe measurement and was found to be 2.65×10^{-4} S cm⁻¹. The tri-chain of the hyper-branched TC14 surfactant successfully improved the dispersions and conductivity of the GO/NRL nanocomposite. Cyclic voltammetry was employed to study the supercapacitor performance of the nanocomposite. A high capacitance value of 35 F g⁻¹ was measured from the sample at a scan rate of 100 mV s⁻¹. The use of low-surface-tension triple-tail TC14 can efficiently adsorb and give triple interactions between the GO and NRL matrix. Meanwhile, a close comparison study of available commercial surfactant SDS in the fabrication of GO/NRL nanocomposites was also conducted with a similar preparation method. The conductivity obtained for SDS-GO/NRL nanocomposites was lower, which was found to be 2.59×10^{-7} S cm⁻¹. Therefore, the introduction of TC14 surfactant can uncover the possibility for the development of low cost, conductive, environmentally friendly, and flexible GO/NRL nanocomposite-based electrode for supercapacitor application.

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1. Introduction

In recent years, electrically conductive elastomeric and flexible polymer-based nanocomposites have attracted considerable interests because of their high elasticity and excellent abrasive resistance [1-4]. To obtain the benefits of the synergetic effect between nanofiller and polymer matrix, a unique graphene (GE) nanostructure was introduced into natural rubber latex (NRL). NRL is a biodegradable polymer obtained from the rubber tree (Hevea brasiliensis). It possesses excellent chemical and physical properties and environmentally friendly polymers. This elastomeric polymer is widely used in both general products (e.g. tires and gloves) and specialized fields (e.g., aerospace and biomedical) [5–9]. However, forming a conductive network within the internal rubber structure of this polymer is difficult because of the natural presence of non-rubber materials in milky colloidal NRL [10,11]. For this purpose, GE has particularly been a good candidate as nanofiller because of its extremely high electron mobility and excellent mechanical flexibility, which has generated a great deal of interests in diverse fields [12-15]. However, pristine GE cannot directly be used because of its high production cost and lack of functional groups for polymer bonding. Therefore, GE oxide (GO) has been used as an alternative raw nanofiller material because of its (i) functional groups that increase GO hydrophilicity in aqueous solutions, (ii) readily scalable materials, and (iii) versatile handling for chemical functionalization [16]. Recently, the method of GO production by chemical synthesis has been considered a favorable and convenient approach for rapidly producing GO in a massive amount compared with chemical vapor deposition method [17,18]. The GO obtained by chemical methods with the assistance of surfactant offers two advantages: the GO can be directly used in liquid form, which is highly efficient when incorporated with polymers; the GO can be dried to produce fine GO powder and then reduce GO.

Surfactants have also been recognized as the third component in the enhancement of the interfacial interaction between nanofiller and polymers [19]. Surfactants are well-known organic compounds that contain both hydrophilic (head) and hydrophobic (tails) groups. Surfactants have been categorized into four classes: anionic, cationic, non-ionic, and zwitterionic. Studies have been conducted on surfactants in GE dispersions by several researchers [20–23]. Kim et al. [20] discussed that cetyltrimethylammonium bromide (CTAB) surfactant (cationic) in multilayer GE sheets (MLGSs) increased multiple times the electrical

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conductivity of MLGS/styrene butadiene rubber composites. Anionic surfactants, such as sodium dodecyl sulfate (SDS) [21], poly (sodium 4styrenesulfonate) (PSS) [22], and sodium dodecyl benzene sulfonate [23], have been demonstrated to produce defect-free GO sheets. Fernandez-Merino et al. [24] studied the role of surfactants in stabilizing reduced GO (rGO), which also affected the composite properties obtained. They found that the specific surfactants of PSS (anionic) and Tween 80 (non-ionic) influenced the capacitance of composite performance. This influence is attributed to the chemical structures of surfactants that have significant effects on rGO dispersion and composite enhancement. Guardia et al. [25] presented the ability of specific anionic surfactantstabilized GE sheets to form single and multiple layers without structural defects. Previous studies revealed that single-chained surfactants are among the most established surfactants for dispersing GO in polymer matrices [20-25]. However, in 2012, Bai et al. [26] reported the use of multiple hydrophobic tails of surfactant known as sodium bis(2-ethyhexyl) sulphosuccinate, which was successfully adsorbed onto carbon nanotube (CNT) structures and subsequently induced a temporary surface charge because of its interaction with the hydrophilic polymer. Eastoe et al. [27] successfully studied the stability enhancement of the colloidal system of water in continuous, supercritical carbon dioxide (CO₂) phase microemulsions by introducing the triple-chain surfactant known as sodium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-silphonate (TC14). They found that TC14 decreased the surface energy and packing requirements of surfactant at the CO₂-water interface, which can also control the dispersion of CNT in the polymer [26,28-33]. TC14 has been shown to enhance the electrical performance of CNT in an NRL matrix via latex technology [30]. hereafter, considering the surfactant architecture, the dispersion of CNT in NRL has been enhanced using a new different custom-made surfactants known as TCPh (sodium 1,5-dioxo-1,5-bis(3-phenylpropoxy)-3-((-phenylpropoxy)carbonyl) pentane-2sulfonate) [34]. A phenyl group located at a triple-chain surfactant has been a major reason on the improvement of the conductivities of the resulting nanocomposites. Therefore, an appropriate selection of surfactant may facilitate the formation of conductive nanocomposites between GO and NRL [35]. The careful selection and systematic study of surfactant architecture, particularly the tail group toward GO dispersion into an NRL matrix, are important.

Numerous studies have been conducted on the fabrication and characterization of GO/NRL nanocomposites and their overall performances (e.g., electrical, mechanical, and thermal properties) [36–40]. Zhan et al. [41] enhanced the electrical conductivity of GE/NRL composites produced by latex self-assembly and direct hot pressing, which is considered a new approach. Compared with twin-roll mixing, this approach has successfully formed a conductive network in GE/NRL composites. However, the use of sulfur and other additives as a cross-linking agent causes losses in the flexible properties of NRL with increasing GE concentrations, thereby limiting the use of NRL in flexible devices.

Instead of this method, our group has developed a simple and convenient approach to fabricate GO/NRL nanocomposites in an effective manner [42]. The method used is known a one-step method that can be achieved by intermixing the GO produced from the electrochemical exfoliation of graphite into NRL. The proposed method fabricates homogeneous GO/NRL nanocomposites and producing GO simultaneously. However, the surfactant used in our previous work (a single-tail SDS) has been obtained commercially; this surfactant provided insufficient interactions between GO and NRL. By contrast, triple-chain TC14 can provide a higher triple-order GO interaction to NRL molecules than single-chain SDS. To the best of our knowledge, this study is the first to report on the use of triple-chain surfactant TC14 in dispersing GO in the NRL matrix to be fabricated as an electrode material for supercapacitor applications. This attempt is believed to serve as a simple and green approach for supercapacitor electrode production with the assistance of custom-made TC14 surfactants.

This study presents novel and green hyper-branched surfactants for dispersing GO in the NRL matrix. The results showed that the

intermixed NRL in the GO production had significant improvements in electrical properties and that the TC14 surfactant formed higher GO interactions with one NRL particle in the nanocomposites. Comparison of the physical and electrical properties was conducted with SDS, and the dispersion mechanism of the GO-stabilized by TC14 and SDS were also discussed.

2. Experimental

The methods to synthesize GO and fabricate GO/NRL nanocomposites have been described in a previous study [42,43]. The one-step method employed in the fabrication of GO/NRL nanocomposites stabilized by TC14 surfactant is summarized in Fig. 1. In this study, 0.1 M TC14 electrolyte solution was used. A static voltage of 7 V was applied to the two-graphite electrode system of the electrochemical exfoliation process. The NRL was intermixed in GO production, where the synthesis process was continued for 24 h. The dispersions obtained were then subjected to mechanical stirring at 3000 rpm and water bath sonication (500 W) for 2 h. To investigate the electrical properties and capacitance performances, the dispersions were cast-dried overnight to obtain thin films. For the electrical comparison with commercially available SDS surfactant for nanocomposites production, a 1:1 volume ratio between SDS-GO and NRL was also used. The fabrication procedures of SDS-GO/NRL nanocomposites were similar to the fabrication procedures of TC14-GO/NRL nanocomposites, wherein a 0.1 M SDS-NRL electrolyte solution was used with an applied voltage of 7 V for a 24 h synthesis process. The dispersion was then stirred (3000 rpm) and sonicated for 2 h before overnight cast-drying. A total of ~4.28 wt% of GO was consumed during the fabrication of both nanocomposites assisted by the TC14 and SDS surfactant. The nanocomposites were subjected to electrical measurement by using a Keithley 2636A instrument. Furthermore, cyclic voltammetry (C-V, Gamry Potentiostat Series-G750, USA) was performed on the assembled sample with 1 M aqueous KOH electrolytes to measure the capacitance performance of the produced nanocomposites. The capacitance value was calculated on the basis of a previous study [44]. Various techniques were used for physical characterizations, including field-emission scanning electron microscopy (FESEM, Hitachi SU8020), high-resolution transmission electron microscopy (HRTEM, JEOL JEM 2100), UV-vis absorption (Agilent 8453 Spectrophotometer), and Fourier transform infrared spectroscopy (FT-IR, Thermo scientific Nicolet 6700). The crystallinity of the GO/NRL nanocomposite samples were investigated by using micro-Raman spectroscopy (Renishaw InVia Raman Microscope) with 514 nm Ar⁺ ion laser. X-ray diffraction (XRD) patterns were collected from a PANalytical X'pert Pro monochromatized CuK α ($\lambda =$ 1.54 Å) diffractometer. Thermogravimetric analysis (TGA) was conducted by using Mettler Toledo SDTA 851 to investigate the thermal stability of the GO/NRL nanocomposite samples.

3. Results and discussion

Fig. 2(a) depicts the electrical conductivities of the TC14-GO/NRL and SDS-GO/NRL nanocomposites. The *I*—*V* curves presented in Fig. 2(a) revealed that increasing the number of single-tail SDS to triple-tail TC14 surfactant led to significant enhancement of electrical conductivity. This finding was consistent with that of Mohamed et al. [30] in dispersing CNT in the NRL matrix by the latex technology approach. The presence of TC14 surfactant resulted in the high electrical conductivity range $(2.65 \times 10^{-4} \text{ S cm}^{-1})$ compared with the single-chain SDS surfactant $(7.12 \times 10^{-7} \text{ S cm}^{-1})$. This result showed that the low surface tension of triple-chain TC14 surfactant assisted in the formation of conductive pathways between the GO and NRL matrix [45]. The conductive network was formed by allowing the hydrophobic part of the surfactant to adsorb and interact with the GO structures, thereby decreasing the surface charge of the carbon material [28,30]. Therefore, the electrical conductivity improvement of the GO/NRL



Fig. 1. Schematic of the one-step method for GO/NRL nanocomposites productions.



Fig. 2. Electrical properties and capacitance performances of the GO/NRL nanocomposites: (a) *I*–*V* curve and (b) *C*-*V* characteristic.

nanocomposites was strongly affected by the tail group of the surfactant, which was believed to improve the dispersions between GO and NRL. This finding was supported by the capacitance behavior where the TC14-GO/NRL nanocomposites samples showed high current response and large leaf shape (Fig. 2(b)). A high capacitance value of 35 F g⁻¹ was measured from the sample at a scan rate of 100 mV s⁻¹, which resulted from the good ion propagation between the electrodes and the electrolyte. These results indicated that the TC14-GO/NRL nanocomposite thin films produced have great potential to be implemented as green and low-cost supercapacitor electrodes.

Further characterizations of the GO produced in the NRL matrix were investigated. The FESEM images of pristine GO are shown in Fig. 3(a)-(e). The result showed that TC14-GO was successfully exfoliated into a high degree of wrinkled structures and crumpled tissue-like sheets (Fig. 3(a)). Several thick parts were observed on the TC14-GO multilayers (Fig. 3(b)) because of the intercalation of various oxygeneous groups above and below the TC14-GO structures during the oxidation process [46]. In a high magnification image, pristine GO exhibited a flake-like shape, as shown by the edge of the TC14-GO structures (Fig. 3(c)). The HRTEM image of pristine TC14-GO showed that the original graphitic-layered structure had large transparent sheets with resembled silk veil waves and folded edges (Fig. 3(d)). Similar wrinkle characteristics of GO resulting from the oxidation process can also be seen in the SDS-GO sample (Fig. 3(e)-(f)). Fig. 3(g) shows the folded GO sheets were observed, this implies that the GO has been oxidized. This result was similar to a previous study on the use of surfactant in dispersing and increasing the GE surface area [47]. Furthermore, the maximum absorbance peak from the UV-vis spectra was 226-232 nm in both GO samples (Fig. 3(h)), thus indicating the transition of $\pi - \pi^*$ bonds, disruption of aromatic GO structures, and success of the oxidation stage [48].

Fig. 4(a)–(d) show the FESEM images of the GO/NRL for both nanocomposite samples. The FESEM images showed a smooth surface with low agglomerated GO for the TC14-GO/NRL nanocomposite sample (Fig. 4(a)–(b)). This result arises from the homogeneous dispersions of the GO sheets stabilized by TC14 (shown by \rightarrow) in the NRL matrix (dark region). The high interaction between TC14-GO and NRL only resulted in small number of lumpy GO structures that were pulled out



Fig. 3. Structural properties of pristine GO (a)-(d); FESEM and HRTEM images of TC14-GO; (e)-(g) FESEM and HRTEM images of SDS-GO; and (h) UV-vis spectra.



Fig. 4. FESEM images of (a)-(b) TC14-GO/NRL nanocomposite and (c)-(d) SDS-GO/NRL nanocomposite. HRTEM images of (e) TC14-GO/NRL nanocomposites and (f) SDS-GO/NRL nanocomposites.

from the NRL matrix. By contrast, the SDS-GO/NRL nanocomposite (Fig. 4(c)–(d)) showed large agglomerated GO, as clearly shown in the high magnification image (Fig. 4(d)); this result could be attributed to the van der Waals forces and strong π – π interactions between the GO sheets [49,50]. The difference in surface morphology and homogeneity of the nanocomposites produced was presumably caused by the influence of surfactants to the composite formation during the mixing process [51].

To further investigate the GO dispersions in the nanocomposite samples, the HRTEM images of the microtomed samples are shown in Fig. 4(e)-(f). The TC14-GO dispersed as intercalated sheets in the nanocomposite, as shown by orange arrows in Fig. 4(e). This result suggested the strong interaction between GO and the NRL matrix [42,52]. By contrast, the SDS-GO/NRL nanocomposite showed the presence of highly unexfoliated sheets in the nanocomposite, as shown by the white arrows in Fig. 4(f). These results supported the ability of low surface energy of triple-tails TC14 surfactant to promote the interaction between GO and the NRL matrix [30,31,53]. This finding was verified by the homogeneous dispersions of GO in the NRL matrix.

This result was reinforced by the FT-IR analysis results as shown in Fig. 5. The typical FT-IR spectrum for GO which is in good agreement with the previously reported data [42]. Several peaks detected were located at 3336-3347, 1655-1675, 873-878, 1045-1060, and 1310–1380 cm^{-1} , which indicated the O—H (water molecules), CC (carboxylic acid), CO (carbonyl groups), C-O (epoxy groups), and O—H (hydroxyl groups), respectively [54–56]. The presence of various oxygen functional groups in the sample creates a strong hydrophilicity of GO, which facilitates it to be water-soluble in a water-based polymer. Upon introduction of GO in the NRL matrix, the FT-IR spectra (Fig. 5(a)) showed the existence of several functional groups in both nanocomposites. The FT-IR analyses in Fig. 5(a) shows a weak and small absorption peak at 1384 cm⁻¹, which is attributed to the CO—H group. Furthermore, the peaks around 1436–1448 and 833–843 cm⁻¹ were attributed to the intercalated surfactant TC14 and SDS within the GO layers, respectively [24]. This result revealed that both GO/NRL nanocomposite samples consist of conductive network that was strongly built from the GO dispersions. The introduction of GO shifted the peak around \sim 3300 cm⁻¹ to a higher wavelength around \sim 3500 cm⁻¹ in both nanocomposites. The red-shift may be due to the newly formed hydrogen bonds between NRL and oxidized GO sheets [25]. Furthermore, the observed CC skeletal vibration peak [57] shifted from 1655 to 1639 cm^{-1} in the TC14-GO/NRL nanocomposite, thus indicating that a high interaction occurred between both GO and the NRL matrix compared with the SDS-GO/NRL nanocomposite, which only showed a small shifted peak of approximately 12 cm^{-1} . These results strongly suggested that the introduction of triple-tail TC14 surfactant could efficiently facilitate the dispersion of exfoliated GO in the NRL matrix.

As shown in the TC14-GO/NRL nanocomposite micro-Raman spectrum (Fig. 5(b)), the I_D/I_G ratio obtained after the introduction of the NRL intermix in the TC14-GO dispersions was 0.95, which was relatively higher than that of the pristine TC14-GO ($I_D/I_G = 0.82$), SDS-GO $(I_D/I_G = 0.89)$ and the SDS-GO/NRL nanocomposite $(I_D/I_G = 0.93)$. The increase in the ratio of D to G intensity is attributed to the high interaction from the triple-tail TC14 surfactant wrapping process and the additional impurities obtained from the intermixed NRL matrix [58-59]. Furthermore, the lattice disorder was suggested because of the atomic reactions of the newly formed bond between TC14-GO and the NRL matrix. The additional band (G + band) around 1620–1622 cm⁻¹ was observed in the nanocomposite samples, thus indicating that the edges of TC14-GO and SDS-GO sheets intercalated between the NRL matrices [58]. Therefore, the triple-chain surfactant TC14 used in this study did not show any additional "disturbance" behavior to the π -systems of the GO structures but efficiently stabilized GO in the NRL matrix.

The homogeneous dispersions of the TC14-GO/NRL nanocomposite were also verified by the XRD analysis as shown in Fig. 5(c). An intense peak was observed around ~ 10.9° - 11.7° for the pristine TC14-GO and



Fig. 5. Interfacial interaction analyses of TC14-GO/NRL and SDS-GO/NRL nanocomposites (a) FT-IR spectra, (b) micro-Raman spectra and (c) XRD analyses.

SDS-GO spectra, respectively [59–60]. This finding confirmed the existence of various oxygeneous groups in the GO structures after the oxidation process. The absence of graphite or oxidized graphite peak (26°) in the XRD spectrum indicated that both TC14 and SDS were anchored along the GO sheets, which led to homogeneous dispersion in nanocomposite. However, the existence of a clearer graphitization peak at ~17.6° than SDS-GO/NRL nanocomposite, which only showed a weak diffraction peak at around 18.4°, could be attributed to the better spontaneous interaction between TC14-GO and NRL matrix than the GO-stabilized by SDS [42,61].

To describe the thermal stability of the GO, NRL, and GO/NRL nano-composites, TGA was conducted at a heating rate of 10 $^\circ$ C/min. As



Fig. 6. TGA analyses of GO, NRL, TC14-GO/NRL and SDS-GO/NRL nanocomposites.

shown in Fig. 6, the initial weight loss of approximately 4% between room temperature and 200 °C in both nanocomposite samples stabilized by TC14 and SDS was ascribed to the evaporation of the adsorbed water in the GO/NRL nanocomposites followed by the main mass loss corresponding to polymer degradation. The nanocomposite samples showed degradation behavior at 300–500 °C because of the degradation of the polymer backbone, which was mainly attributed to the thermooxidative degradation of the polymer chain and the non-volatile residues [62-63]. The TC14-GO/NRL nanocomposite sample was completely burned above 450 °C, whereas the pristine TC14-GO and SDS-GO decomposed slowly up to 800 °C. In comparison, the nanocomposite sample stabilized by SDS showed an early decomposition stage at 300 °C. The SDS-GO/NRL nanocomposites had low thermal degradation temperature because the SDS surfactant displayed dopant anion role in the polymer chain, and SDS itself exhibited a low decomposition temperature [63]. Furthermore, the significant changes in thermal stability were related to the strong interfacial bonding effect of GO, which involved covalent bonding and a high cross-linking system [64]. Therefore, the thermal stability obtained was closely related to the homogeneous dispersions facilitated by the triple-tail surfactant, TC14, compared with single-tail SDS. Hence, the TGA analysis showed that GO was stabilized across NRL polymer by custom-made hyperbranched surfactant and that TC14 had better thermal stability than commercially available SDS surfactant.

The GO/NRL nanocomposite dispersion mechanism of the GOstabilized TC14 and SDS suspensions is illustrated in Fig. 7. The mechanism for the fabrication of GO/NRL nanocomposite by one-step synthesis method was thoroughly discussed in our previous study [42]. However, in the present study, a custom-made triple-chain hyperbranched TC14 surfactant was used as an electrolyte instead of the single-chain SDS. The oxidative cleavage reaction through the electrochemical exfoliation method was assisted by an external voltage of 7 V to open the graphite layers, which subsequently interacted with the existing NRL molecules pre-coated with the hydrophilic head group of TC14. The surfactant tails were then intercalated into the graphite layers to self-arrange along the GO surface because of the low surface tension of the tail group of TC14 ($\gamma_{cmc}=27.0~mN~m^{-1})$ and the behavior of the surfactant itself [28,30-34]. Compared with the SDS surfactant, the interactions of GO to the NRL molecules using TC14 were three orders higher than those of the single-chain of SDS (schematic comparison is shown in Fig. 5(b)-(c)). Hence, the formation of conductive nanocomposite may be attributed to the high GO interactions assisted by the triple-tail surfactant TC14. Furthermore, the TC14 concentration was prepared above the critical micelle concentration level to assist the optimum exfoliation process of the precipitated GO sheets and enhance the homogeneity and electrical conductivity of the TC14-GO/NRL nanocomposite [15,21].

4. Conclusions

Well dispersed, uniform, and conductive nanocomposite electrodes were successfully prepared by using TC14 surfactant as a stabilizing agent by a one-step method. The high conductivity of the TC14-GO/NRL nanocomposites $(2.65 \times 10^{-4} \text{ S cm}^{-1})$ and the capacitance value



Fig. 7. Proposed mechanism of TC14-GO/NRL nanocomposites production through one-step method. (a) The NRL-coated TC14 formed a micelle, and the tail group of TC14 interacted with the exfoliated GO layers. (b) High GO interactions to one NRL particle. (c) Comparison of the growth mechanism for the SDS-GO/NRL nanocomposites.

of 35 F g⁻¹ were also measured. The high interaction of the noncovalent TC14 surfactant to the GO sheets is the key to excellent electrical conductivities. Thus, the conductive TC14-GO/NRL nanocomposites produced are useful as new flexible electrode materials. The green and low-cost fabrication process proposed in this work can be used in supercapacitor applications.

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