

Preparation of Multiwall Carbon Nanotubes/Cellulose Nanocomposites Stabilized By 1-Butyl-3-Methyl-Imidazolium (BMIM) - Surfactants

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Abstract

Multiwall carbon nanotubes (MWCNTs) ability to improve electrical, optical and mechanical properties of nanocomposites, have attracted great amount of interest for their huge potential in applying them as filler in polymer matrix. However, this application was hindered because of their low dispersion in polymer matrix and tendency to self-associate into macro-scale aggregates. Recently, diffusion of MWCNTs in cellulose polymer matrix was studied and prepared via latex technology approaches by the addition of 1-butyl-3-methyl-imidazolium (BMIM)-surfactant. The performance of BMIM-surfactants for dispersing MWCNTs in polymer was characterized using a range of techniques including field emission scanning electron microscopy (FESEM), and Thermogravimetric analysis (TGA). Meanwhile, the conductivities of the nanocomposites were also investigated using four-point probe measurements. In this study, MWCNTs were efficiently dispersed in cellulose utilizing 1-butyl-3-methyl imidazolium-dodecyl benzene sulfonate (BMIM-DBS). Interestingly, it was found that BMIM-DBS performs much better than that of the commercially available surfactant sodium dodecyl benzenesulfonate (SDBS), demonstrating the importance of the effect of surfactant counter-ion leading to improved dispersion of MWCNTs in cellulose. This finding will significantly contribute towards the improvement of properties of cellulose for nanocomposite industries.

Keywords: Multiwall carbon nanotubes (MWCNTs), surfactant, cellulose, nanocomposite

INTRODUCTION

The nanocomposites are a matrix to which nanoparticles are added to develop a specific property of materials. Nanocomposites can also be described as nanomaterials that mix one or more individual parts to produce the finest characteristics of each component. Nanocomposites maximize processing procedures for inexpensive production costs. In nanocomposite, nanoparticles (carbon nanotubes, clay and metal) act as fillers in a matrix; usually polymer matrix. Among all types of nanocomposite, the most exciting application is carbon nanotubes (CNTs)/polymer nanocomposites. The appropriate combination of high aspect ratio, very low density, small size and extreme mechanical properties make CNTs suitable and ideal candidates for reinforcing fillers of polymer materials. A huge part of the CNTs/polymer based composites exploit CNTs as conductive filler dispersed in an insulating matrix. The ranges of applications of CNTs are from electronics to aerospace sectors; for instance, electromagnetic interference (EMI), electrostatic dissipation (Hyperion Catalysis International), shielding [1] transparent conductive coatings [2] and multilayer printed circuits [3]. The key matters for generating technically motivating CNT/polymer nanocomposites are the comprehensive and proficient dispersal of separate carbon nanotubes into the polymer matrix, in addition to the force of the characteristics of the filler-matrix interface. If well dispersed, the probable filler matrix interface area

is enormous, and a suitable control of the interfacial interaction is vital for achieving optimal characteristics.

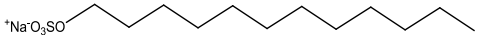
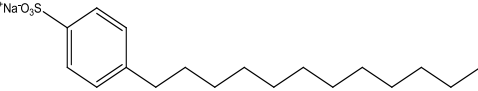
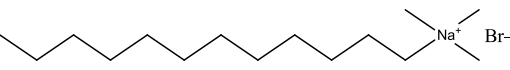
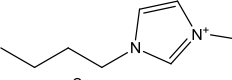
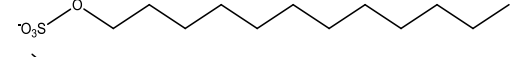
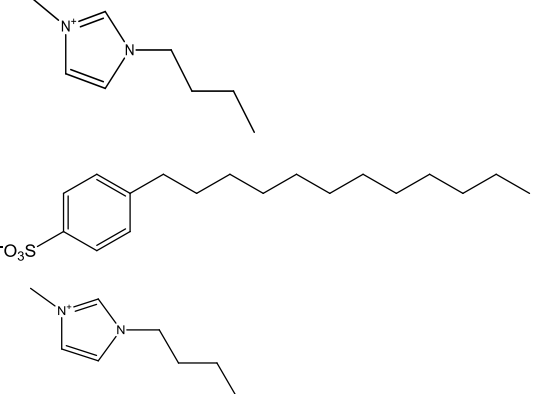
Cellulose is considered biosource, light-weight and biologically compatible [4]. The issues in improving the composites would be a dispersion of nanotubes in solvents, CNT-polymer interactions and the performance of the composite and manufacturing cost. Cellulose has attracted much consideration with expertise in diverse areas [5]. Cellulose is a renewable source-based biodegradable polymer and will be medium for presenting and transmitting information owing to its potential compatibility, mechanical stability under atmospheric conditions, and ability to absorb liquid [6]. Meanwhile, carbon nanotubes (CNTs) are referred to as one of the most versatile additives of composites because it can develop thermal, mechanical and electrical characteristics of cellulose [7]. Specifically, homogeneous distribution of CNTs in the cellulose matrix would contribute to improving its characteristics. However, the nonreactive surface and strong aggregation properties of CNTs due to van der Waals, have restricted the effectiveness of CNTs with cellulose during the time of mixing [8]. It was claimed that chemical modification of CNT, is the most successful dispersion technique. And this technique can form carboxyl functional groups on the surfaces and the ends. This carboxyl functional group binds the CNTs with cellulose very tightly. However, the chemical modification would significantly transform their desirable properties. Consequently, CNTs dispersion in solvents is a requirement to utilize the unique multifunctional properties of CNTs while preparing CNT/cellulose composites [9].

It was reported that surfactant's ability to accumulate on interfaces or surfaces is extensively used to enhance steady dispersals of solids in a variety of media [10]. Those amphiphilic molecules, for example, compounds includes both nonpolar and polar categories, with the ability to adsorb without forming a homogeneous mixture when added together, for example, water and oil, water and air or solution and particles, act to decrease the surface tension.

It was also documented that surfactant possesses unique structural feature which originate from its 'duality' i.e., the tail group or the hydrophobic region that generally includes one or little hydrocarbon. Self-accumulation into supramolecular structures and adsorption at the interface are the two known significant factors, which characterize surfactants and are effectively used in dealing with constant colloidal diffusions. Surfactants adsorptions onto organic and inorganic surfaces generally rely on surfactant molecules, chemical properties of solvent and particles. The created Coulombic attractions are the driving force for the adsorption of ionic surfactants on charged surfaces; an example is the negatively charged solid surface and the surfactant's positively charged head group. The process can be explained as nonionic surfactants adsorb onto a hydrophobic surface, which depends upon the surfactant's hydrophobic tail and a strong hydrophobic attraction among the hard surfaces [11].

Challenges associated with assimilation of nano-material in particular consist of: (1) preferential alignment in melt phases and liquid; (2) uniform dispersion; and (3) mass-synthesis of material of high-purity at low prices. This paper concentrates on the second challenge that is improving homogeneous dispersions of carbon nanotubes, mainly with (surfactants) or surface active agents assistance. Diverse sources of stabilization of classical colloidal suspensions, for example, the surfactant used, adsorption mechanism and surface charge influence, will be tested to determine if they are usable to the dispersion systems of CNT [12].

Table 1 Surfactants used in this study

Surfactants name	Surfactant structure	Chemical name
SDS		sodium dodecyl sulphate
SDBS		sodium dodecylbenzenesulfonate
DTAB		dodecyl trimethyl ammonium bromide
BMIM ⁺		1-butyl-3-methyl-imidazolium ion
BMIM-DS		1-butyl-3-methyl-Imidazolium dodecyl sulphate
BMIM-DBS		1-butyl-3-methyl- imidazolium dodecyl benzene sulfonate

MATERIALS AND METHODS

Materials

Multiwall carbon nanotubes (MWCNTs) (Universiti Sains Malaysia), Cellulose (Forest Research Institute Malaysia), 1-butyl-3-methyl-imidazolium chloride (Sigma Aldrich, 89%), Ethyl acetate (System, 99.5%), Ethanol (System, 95%), Methanol (System, 99.8%), and Dichloromethane (System, 99.8%).

Preparation of 1-butyl-3-methyl-imidazolium (BMIM)-surfactant

In a 250 mL round bottom flask, 1-butyl-3-methyl-imidazolium chloride (BMIM-Cl) and surfactant were added and stirred in dichloromethane for 6 hours, resulting sodium chloride (NaCl) precipitous was later filtered off and the rotary evaporation was used to remove the solvent. The purification of crude BMIM-surfactant were done by dissolving in dry ethyl acetate and centrifuged at 6000 rpm for 20 minutes. The clean BMIM-surfactants were then dried in oven at 60°C for 24 hours. All purified BMIM-surfactants were characterized by ¹H Nuclear Magnetic Resonance Spectroscopy.

Preparation of Cellulose Nanocomposites

0.5 g of cellulose was dispersed in 10 mL deionized / distilled water and keep cooled prior using. The MWCNT/surfactant dispersion was prepared by mixing the surfactant solution and nanofiller for 1 hour, and followed by ultrasonication for 2 hours. The MWCNT/surfactant dispersion was added later to the cellulose dispersion. The mixture were stirred for 1 hour and followed by 90 minutes of ultrasonication. Lastly, MWCNT/cellulose paper was obtained after overnight drying in an oven at 60°C.

Nanocomposites characterization

Four Point Probe

The electrical conductivity of nanocomposites were measured by standard four point probe instrument model Keithley 2636A. This instrument consists of four contact leads; the current passed through two outer probe while other two inner probes were used to measure the voltage [13]. The current and voltage data was then analysed and recorded with pro-4 software, to determine sample's resistivity (ρ/ohm). The electrical conductivity ($\sigma / \text{S cm}^{-1}$) can be measured by using the following equation:

$$\sigma = \frac{1}{\rho} \quad (1)$$

In this work, the sample were cut into 1.5 cm × 1.5 cm with ~ 2 cm of thickness. All the measurements were performed in triplicate with temperature approximately 25°C. The average of three calculations was chosen as the electrical conductivity value for each sample.

Field Emission Scanning Electron Microscopy (FESEM)

To investigate the morphologies of the sample, a field emission scanning electron microscopy was used. In principle, the specimens' surface were scanned with electron beam produced by electron gun, typically a tungsten filament [14]. This interaction produced signals containing information that was captured by a detector, processed and translated into an image which is displayed on a monitor. The FESEM investigation was performed by using FESEM Hitachi SU8020 with a voltage of 2.0 kV. Prior to the investigation, samples were coated with platinum by using Quorum Q150P S Cooled Sputter Coater to avoid poor image resolution and electrostatic charging.

Thermogravimetric analysis (TGA)

The purity of the sample was measured by thermogravimetric analysis (TGA). This measurement was reported as an effective method to evaluate the quality of MWCNTs as it is easy to handle sampling by burning at a high temperature [15]. This is applied by placing a tested material in a sample holder (commonly alumina) which is supported on analytical balance lotside of high temperature furnace. The obtained data were sent and recorded from analytical balance to produce a curve usually called as a thermogram, representing sample weight loss, measured as a function of temperature [15]. Here, thermal analysis measurements were made using TGA instrument model Perkin Elmer Pyris 1 and supported by TGA Pyris software. Thermal stability of samples were performed with nitrogen and oxygen atmosphere flow from ambient temperature to 900°C, with a constant heating rate of 40 c/min.

RESULTS AND DISCUSSION

¹H Nuclear Magnetic Resonance Spectroscopy (NMR)

Sodium dodecyl sulphate/SDS

¹HNMR (500 MHz, D₂O, TMS) (δ /ppm) 0.79-0.83 (a, m, 3H), 1.23 - 1.31 (b, m, 18H), 1.58-1.62 (c, m, 2H), 3.98-3.99 (d, m, 2H).

Sodium dodecylbenzenesulfonate/SDBS

¹HNMR (500 MHz, CDCl₃, TMS) (δ /ppm) 0.72 - 0.79 (a, m, 3H), 0.95 - 1.64 (b, m, 20H), 2.17 - 2.68 (c, s, 2H), 6.70 - 6.91 (d, s, 2H), 7.47 - 7.86 (e, s, 2H).

Dodecyl trimethyl ammonium bromide/DTAB

¹HNMR (500 MHz, CDCl₃, TMS) (δ /ppm) 0.86 - 0.89 (a, m, 3H), 1.25 - 1.37 (b, m, 18H), 1.71 - 1.77 (c, m, 2H), 3.47 - 3.59 (d, m, 4H).

1-butyl-3-methyl-Imidazolium dodecyl sulphate/BMIM-DS

¹HNMR (500 MHz, CDCl₃, TMS) (δ /ppm) 0.86 - 0.97 (a, m, 6H), 1.24 - 1.40 (b, m, 20H), 1.63 - 1.69 (c, m, 2H), 1.83 - 1.89 (d, m, 2H), 4.03 - 4.05 (e, m, 5H), 4.23 - 4.26 (f, m, 2H), 7.30 (g, m, 1H), 7.39 (h, s, 1H), 9.69 (i, s, 1H).

1-butyl-3-methyl- imidazolium dodecyl benzene sulfonate/BMIM-BDS

¹HNMR (500 MHz, CDCl₃, TMS) (δ /ppm) 0.7 - 0.91 (a, m, 6H), 0.91 - 1.36 (b, m, 20H), 1.49 - 1.58 (c, m, 2H), 1.81 - 1.85 (d, m, 2H), 2.04-2.09 (e, s, 2H), 4.05-4.09 (f, s, 2H), 4.24-4.27 (g, m, 1H), 7.06-7.20 (h, m, 2H), 7.32-7.34 (i, m, 1H), 7.70-7.86 (j, s, 2H), 10.05 (k, s, 1H).

MWCNTs/cellulose/ surfactant nanocomposites

Electrical Conductivity

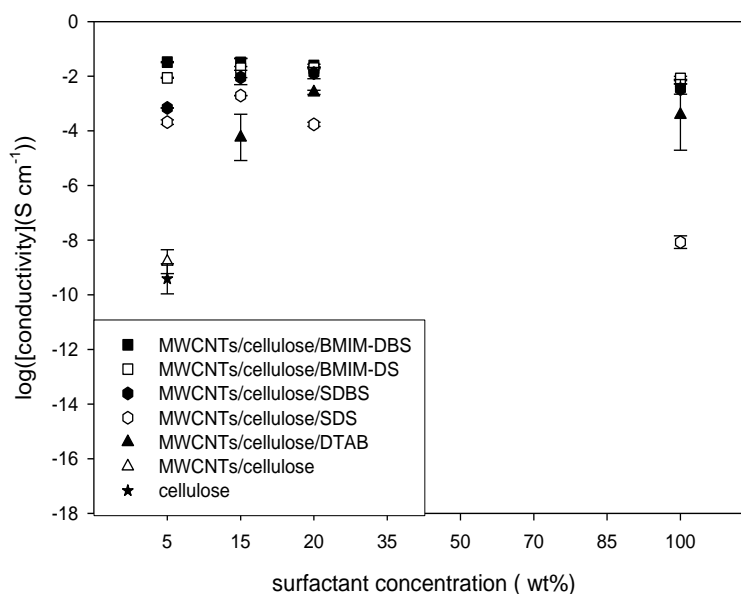


Figure 1 The electrical conductivity of MWCNTs/cellulose/surfactant nanocomposites

The electrical conductivity of nanocomposites are stabilized by various types of surfactant as shown in (Figure 1). The conductivity was observed at low value of $1 \times 10^{-10} \text{ S cm}^{-1}$ for the pure cellulose due to highly insulation material [13]. However, the MWCNTs filled cellulose with the absence of surfactant showed conductivity enhancement to be about $1 \times 10^{-9} \text{ S cm}^{-1}$. Yet, the electrical conductivity was significantly increased by the addition of five different surfactant into the MWCNTs/cellulose nanocomposites, namely; SDS, BMIM-DS, SDBS, BMIM-DBS, and DTAB. The addition of linear single chain DTAB shows a slight increase in electrical conductivity which is $4 \times 10^{-4} \text{ S cm}^{-1}$, also SDS shows a slight increase in electrical conductivity which stands at $7.86 \times 10^{-5} \text{ S cm}^{-1}$. But, the surfactants' modified-tail structure by the addition of SDBS benzene ring, shows a significant increase in electrical conductivity which stands at $2.48 \times 10^{-4} \text{ S cm}^{-1}$. The result has proved that the benzene ring factor contributes a significant effect in electrical properties of nanocomposites. In order to enhance the dispersion quality of MWCNTs/cellulose nanocomposites, imidazolium counter ion system known as BMIM-surfactant of SDS and SDBS was introduced. The result showed the electrical conductivity improved significantly which stood at $1.1 \times 10^{-2} \text{ S cm}^{-1}$ and $1.1 \times 10^{-2} \text{ S cm}^{-1}$ respectively.

Based on the above result, the electrical conductivity shows a relationship with the dispersion properties of surfactant. From the analysis result, BMIM-DBS shows the better dispersion on MWCNTs cellulose nanocomposites followed by BMIM-DS, SDBS, SDS and DTAB. The result indicates that the introduction of imidazolium counter ion gives higher impact on the electrical conductivity compared to the single surfactant system. The result is in agreement with earlier finding by Mohamed [13]. The presence of benzene rings moieties in the chain of sulphosuccinate surfactants exhibits notable effect in stabilizing MWCNTs in polymer matrix. The formation of well dispersed MWCNTs in cellulose, stabilized by surfactant attached benzene ring, is strongly believed to be caused by the interaction between π -system of the MWCNTs and the π -system of conjugated benzene ring moieties introduced in surfactant tails and usually called π - π staking.

Table 2 Electrical conductivities of nanocomposites

Surfactant	Surfactant concentration (wt %)			
	5%	15%	20%	100%
Electrical conductivity of nanocomposites (mS cm^{-1})				
BMIM-DBS	0.0328 ± 0.0015	0.0334 ± 0.0103	0.0246 ± 0.0027	0.0064 ± 0.0011
BMIM-DS	0.0087 ± 0.004	0.0236 ± 0.0146	0.0198 ± 0.0011	0.0837 ± 0.0015
SDBS	0.0006 ± 8.9427	0.010 ± 0.0056	0.0141 ± 0.0067	0.0035 ± 0.0012
SDS	0.0002 ± 3.8584	0.0019 ± 2.33546	0.0001 ± 3.1928	$9.2259 \times 10^{-9} \pm 4.0355$
DTAB	—	0.0001 ± 0.0001	0.0025 ± 0.0004	0.0014 ± 0.0012

Field Emission Scanning Electron Microscopy (FESEM)

As discussed earlier, the addition of BMIM-surfactant has an imidazolium counter ion which induces a notable enhancement in MWCNTs/cellulose nanocomposites electrical conductivity. Additional investigation of MWCNTs dispersion in cellulose matrixes that takes a significant role in enhancing the electrical conductivity of the nanocomposites, is therefore important [16]. Consequently, we characterized the dispersion of the MWCNTs in the cellulose matrix using FESEM to help characterize

the surface morphological structure of the electrical conductive MWCNTs networks with cellulose assisted by surfactants.

The length of the nanotubes are difficult to determine definitely because of entangle arrangement and the order of microns. It can be seen that the surface morphology of cellulose appeared to be smooth with relatively dark area. Moreover, as a result of their high conductivity, the bright regions in the images were attributed to the MWCNTs, and the MWCNTs were disturbed evenly in the cellulose pellicle irrespective of aggregation [17]. The original MWCNTs tends to form largely in bundles due to Van der Waals interactions. Nanotubes diameters ranges approximately from 17 to 38 nm. These characteristic are helpful to observe the dispersion state of MWCNTs in cellulose matrix, discussed in the following paragraph.

FESEM images of Figure 2 (a-a~) show the agglomerates of MWCNTs when dispersed in cellulose. The bright phase represents the cellulose matrix while the dark phase corresponds to the nanotubes. The bright phase are strongly entrenched to the cellulose matrix. The bigger diameters shown suggest that the MWCNTs were folded in a cellulose layer. This shows good adhesion between the cellulose and MWCNTs with an outer diameter of 21.9 -210 nm [18]. Comparing FESEM images of (Figure 2 a-a~) with other five figures, all surface area and size agglomeration are changed. The different result was observed before adding imidazolium counter ion, SDBS (Figure 2 b-b~), SDS (Figure 2 c-c~), and DTAB (Figure 2 d-d~).

The nanotubes clusters begin aggregation for the nanocomposite in some areas. The surface morphology agglomerates seem not as loose as that MWCNTs/cellulose/ BMIM-DBS and MWCNTs/cellulose/ BMIM-DS (Figure 3), (e-e~), (f-f~), (g-g~), and (h-h~) Somehow, the typical agglomerates size of MWCNTs by using BMIM-DBS and BMIM-DS (Figure 4), (i-i~), (j-j~), (k-k~), and (l-l~) are rather smoother and regular in which the size diameter of 21.7-45.5 nm compared to SDBS size aggregates of (21.9 - 36.5 nm) and SDS (24.2 - 46.8 nm).

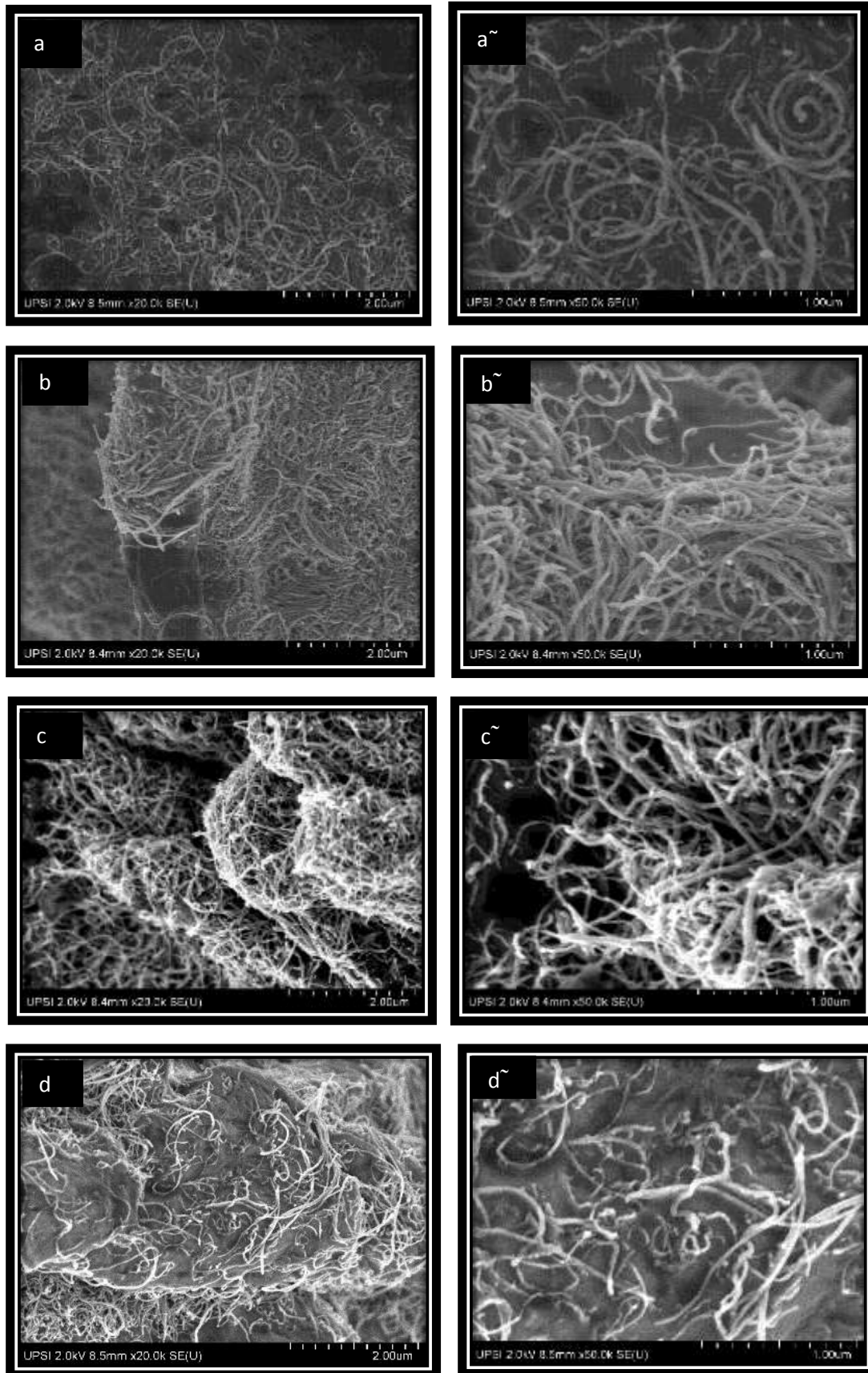


Figure 2 FESEM images of MWCNTs/Cellulose: in the absence of surfactant (a and a[~]); with SDBS (b and b[~]); with SDS (c and c[~]); with DTAB (d and d[~])

Interestingly, the MWCNTs/cellulose dispersed by BMIM-DBS and BMIM-DS surfactant Figure 3 and 4 shown the good dispersion when almost all nanotubes particles are homogeneously distributed throughout cellulose matrix. The aggregation sizes of 21.1 - 45.3 nm determined is increased compared to using other surfactants as dispersing agent. Since there was no physical damages or shortening of MWCNTs were remarkable and observed in all samples, this shows treatment using surfactants is mild and physical surface changes that are saved in the morphological structure of the nanotubes that are folded up and agglomerations of tubes could be clearly observed. The debundling of the nanotubes was thought to be caused by modification of these surfactants [19]. Yet, the morphological examinations revealed few surfactants could play the same role during MWCNTs diffusion in the surfactant solution. It was observed that the degree of nanotube debundling depends upon surfactant. The surface surfactants for surface changing has different similarity to the MWCNTs surfaces. This caused the different degree of effectiveness in the reduction of MWCNTs agglomeration. There exist a common agreement that it is very difficult to totally open up and debundle all nanotubes into individual tubes. Yet, to a very minimum extent, it was observed in particular that the BMIM-DBS diffused MWCNTs emerges to be less bundled, which suggest that the most promising surfactant to debundle the MWCNTs is BMIM-DBS [19]. Besides, there is no clear separation of phases observed, suggesting the good miscibility between cellulose and MWCNTs.

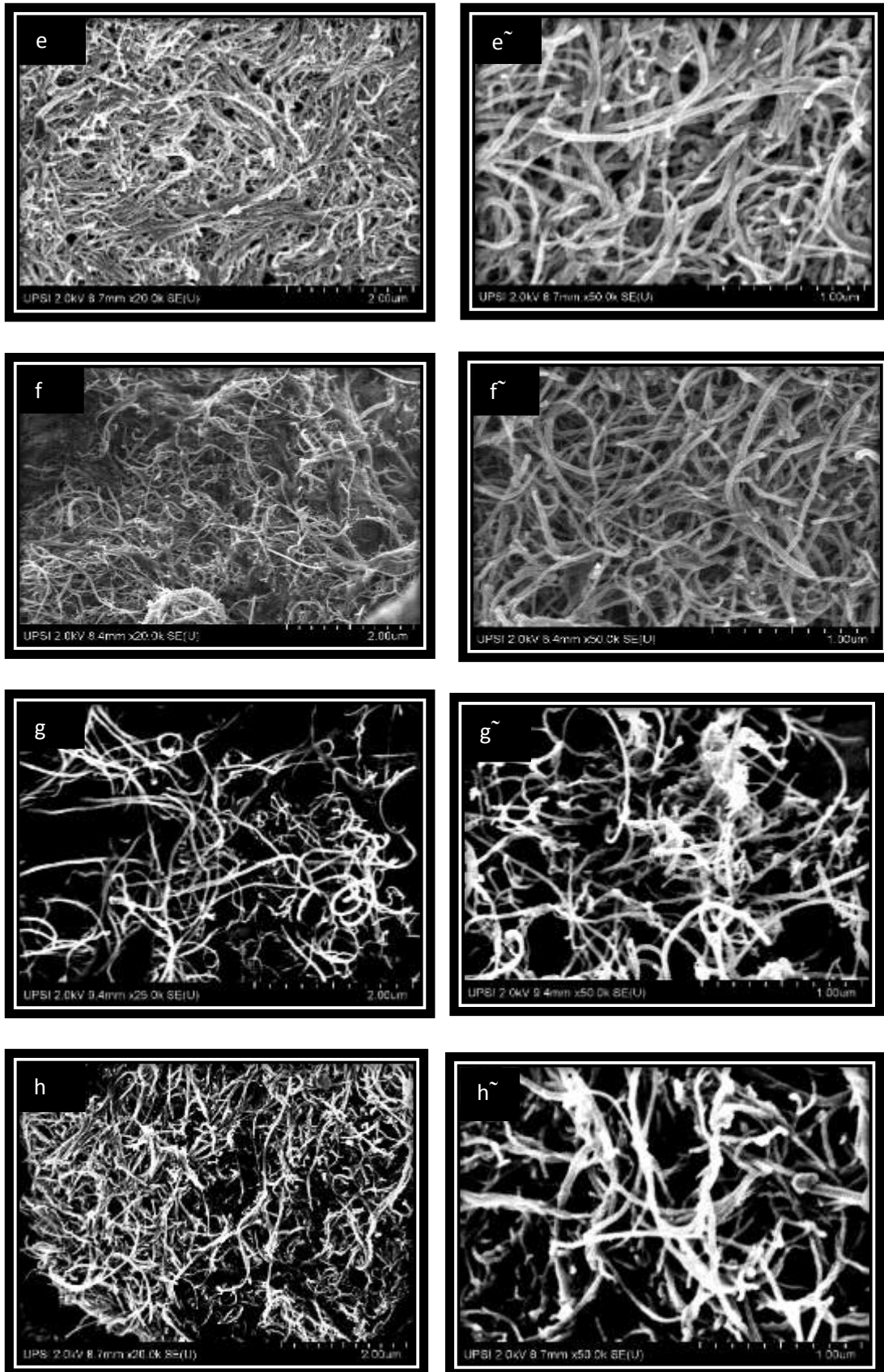


Figure 3 FESEM images of MWCNTs/Cellulose using different concentration of BMIM-DS; (e-e~) 5%, (f-f~) 15%, (g-g~) 20%, and (h-h~) 100%.

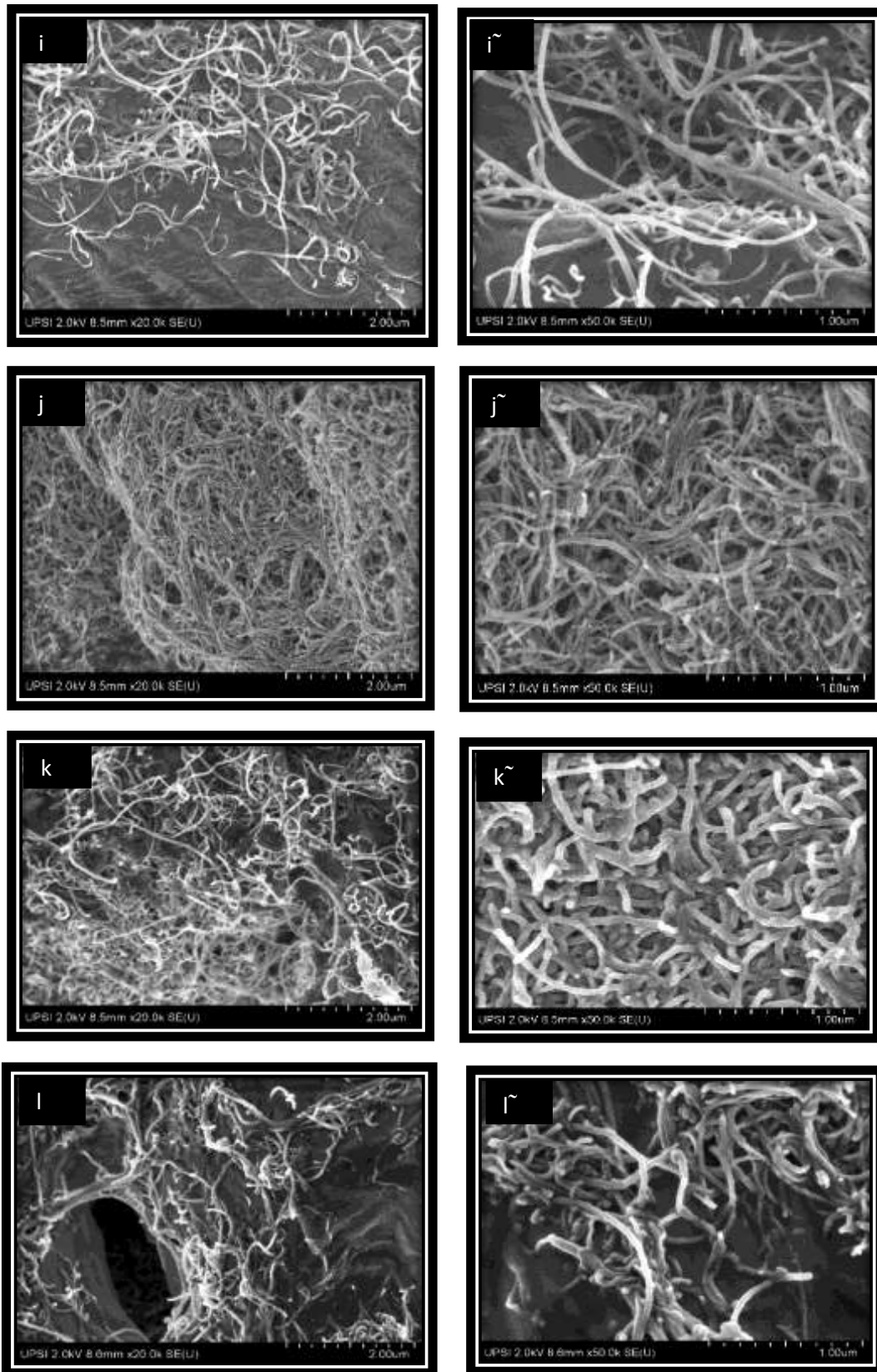


Figure 4 FESEM images of MWCNTs/Cellulose using different concentration of BMIM-DBS; (i-i[~]) 5%, (j-j[~]) 15%, (k-k[~]) 20%, and (l-l[~]) 100%

Thermogravimetric analysis (TGA)

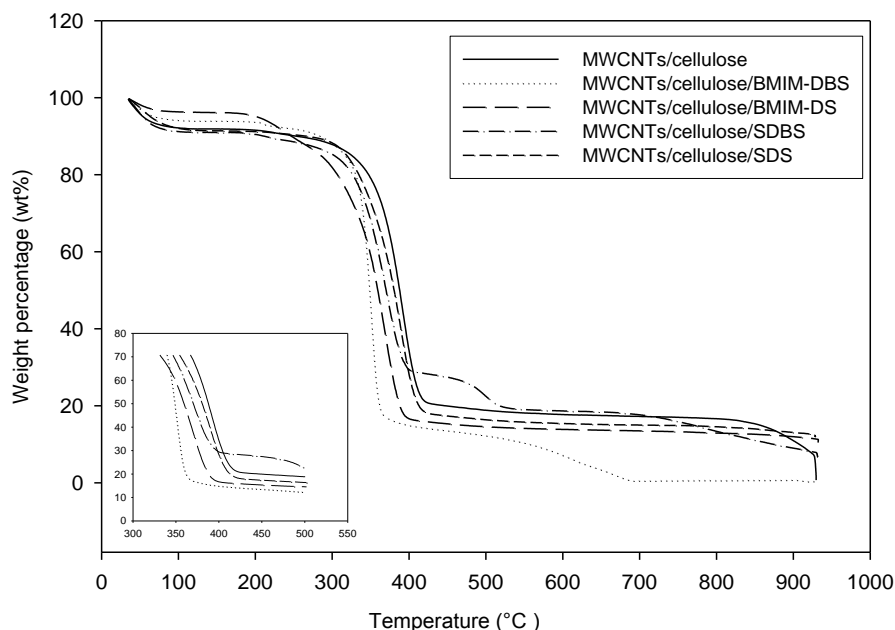


Figure 5 TGA curves for the MWCNTs/Cellulose matrix, MWCNTs/Cellulose/SDS, MWCNTs/Cellulose/SDBS, MWCNTs/Cellulose/BMIM-DS, MWCNTs/Cellulose/ BMIM-DBS

Thermal-degradation of the MWCNTs/cellulose matrix in a nitrogen and ammonia atmosphere was calculated and plotted in Figure 5. The figure shows the percentage of weight loss as a function of cellulose temperature, MWCNTs/cellulose, MWCNTs/cellulose/SDS, MWCNTs/cellulose/SDBS, MWCNTs/cellulose/BMIM-DS and MWCNTs/cellulose/BMIM-DBS. For MWCNTs/cellulose composite, weight loss curve, was at the temperature from the range of 300 to 430°C and has occurred as a result of evaporation of physically immersed water molecules and disintegration of cellulose respectively [20]. The weight loss range between 270 and 410°C (in Figure 5) provides a clearer elaboration of the impact of the surfactant on nanocomposites thermal stability. The result shows MWCNTs/Cellulose/BMIM-DBS has a steeper gradient than for the MWCNTs/cellulose without surfactant. Interestingly, BMIM-DBS and BMIM-BDS were shown to provide a remarkable performance enhancement than commercially available SDS, and SDBS, by spreading MWCNTs with good amount of thermal stability.

Hence, the consistent diffusion of MWCNTs in the polymer matrix through the introduction of imidazolium counter ion gives impact on the thermal stability compared to the single surfactant system. Terminal methyl groups of surfactant produce higher concentration of filler matrix interactions in the nanocomposite. This stability of thermal is found to relate to the consistent dispersal of nanocomposite by BMIM-DBS and BMIM-DS, as discussed in the FESEM observations.

CONCLUSION

To conclude, novel properties and/or improved performance are required in materials of new technologies compared to the conventionally processed components. In this perspective, to meet the emerging demands arising from scientific and technological advances, nanocomposites are the most appropriate materials. The central challenge in preparing electrical conductive nanocomposites is how

to fully disperse individual MWCNTs in polymer matrix. With regard to this study, a stable colloidal system consisting MWCNTs in a polymer matrix was prepared using cellulose and assisted by surfactant. The utilization of surfactants is very important due to their abilities to stabilise MWCNTs through hydrophobic/hydrophilic interfacial interaction. Furthermore, unlike acidic treatment called covalent functionalization, the use of surfactant does not disturb the π system of nanotube. Here, dispersion and orientation of MWCNTs in cellulose simultaneously created a better electrical conductivity material. The results shows that the introduction of imidazolium counter ion gives higher impact on the electrical conductivity compared to the single surfactant system which tremendously influences the high level of dispersion of MWCNTs in cellulose matrixes.

Meanwhile, the attachment of benzene ring moieties in the BMIM-DBS-type surfactants also exhibited remarkable performance for stabilising MWCNTs. The dispersion quality and electrical conductivity have increased as a function of using a different concentration of BMIM - surfactant from 5% to 100%. The 4-point probe result conclude that the addition of BMIM-surfactant system provide the maximum and minimum conductivity value of $8.87 \times 10^{-2} \text{Scm}^{-1}$ and $1.81 \times 10^{-10} \text{Scm}^{-1}$ respectively. FESEM result seems to show agreement with conductivity behaviour since BMIM-DBS and BMIM-DS has high tendency to well-stabilize the MWCNTs/ cellulose compared to another surfactant. Meanwhile, the TGA analysis also proved that the addition of surfactant brings weight loss insignificant chemical effect to the MWCNTs system. The results of this study will contribute in exploring the understanding of the dispersal characteristics of MWCNTs in the presence of surfactant and will enhance the theory of surfactant design and development of MWCNTs. It is also really important to provide additional insight into molecular requirement for MWCNT-BMIM- surfactant architecture which can be used in cellulose approach.

ACKNOWLEDGEMENT

The work funded under grants from kurita water and Environment Foundation (Grant Code: 16P003), and the Fundamental Research Grant Scheme (FRGS; Grant code: 2015-0155-101-020

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