Carbon nano-ink coated open cell polyurethane foam with multilayered skeleton for damping applications

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ABSTRACT

The improvement of the viscoelastic damping performance at small dynamic strains through interfacial slippage in polymer composites dispersed with carbon nano-fillers has been widely reported. This study utilised another mechanism to create frictional energy dissipation in high density nano-filler regions to improve damping performance of an open cell foam through nano-inks coatings. A novel carbon nano-ink coated open cell polyurethane foam with sandwich strut structure is developed by a simple two-step dipping and drying process. Nano-ink containing –COOH functionalised multi-walled carbon nanotubes were produced. The nano-inks were coated onto a pristine neat polyurethane foam structure as a sandwich core with the assistance of the silane coupling agent. Another layer of water-based polyurethane dispersion was coated on top of the nano-core as the sealing topcoat. Samples containing nanoink of 0.01, 0.05, 0.1, and 0.2wt% concentrations were fabricated and tested under both static and dynamic loading conditions for their viscoelastic damping performance. Carbon nanotube coated foams showed an overall excellent damping performance with significantly improved loss modulus and loss factor. These foams also exhibited high resiliency and energy absorption capability.

Key words: *nanocomposite, nano-ink, multilayer coating, damping*

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1. INTRODUCTION

Polymer nanocomposite foams have received much attention in recent years due to their significantly improved performance, such as superior strength [1-3], electrical conductivities [1, 4, 5], and damping [6-9] properties over the traditional foams. While their applications in various industrial sectors like flexible sensor[10] and electromagnetic shielding [1, 11] have been widely reported, very few studies focused on the damping applications for noise and vibration control. In a conventional polymer/carbon nanotube (CNT) material system with nanoparticles embedded in the polymer matrix, the three interface couplings that are considered contributing to the energy dissipations are polymer-nanotube, nanotube-nanotube interfacial sliding, and coaxial sliding of tube walls within multiwall carbon nanotube (MWNT) [12]. Polymer-nanotube sliding is determined by the CNT/polymer interfacial bonding and dispersion quality [13, 14], whereas nanotube-nanotube sliding within entangled CNTs is closely related to the filler content. The coaxial internal sliding between tube walls does not provide an appreciable increment in loss factor, however it has been shown to decrease the strain level threshold for which stick-slip dissipation occurs[15].

Foaming technique was widely reported for nanocomposites foam fabrication. Nanofillers are embedded inside the polymer skeleton, such microstructure utilise the polymer-nanotube interfacial sliding to improve damping performance. Verdejo [7] and co-workers added 0.1wt% MWNTs into flexible polyurethane (PU) foams, increased the absorption coefficient peak by 30% in the 1000-2000Hz frequency range compared with pure PU foam. With increased cell size, they attributed the increment to the polymer-nanotube 'stick-slip' mechanism solely. Bandarian [6] compared the loss factor (Tan δ) and absorption coefficient of carboxyl, hydroxyl and amide functionalised MWNTs (0.1wt%) modified open cell PU foam and also reported the foam absorption peak between 1000-2000Hz, however Bandarian concluded that the more pronounced increment in both mechanical and acoustic damping of PU/CNT-COOH and PU/CNT-OH were caused by the micro voids structure that produced by gaseous materials during reaction between functional groups on CNT surfaces and the isocyanate. The foam contains amide functionalized CNTs revealed decrement in loss factor was caused by the strong covalent bonds which inhibited the polymer-nanotube 'stick-slip' mechanism.

To realise the nanotube-nanotube interfacial sliding mechanism, a high CNT content region is required in the composite foam. Nano-ink coating process can form such microstructure for damping improvement. However, to the best of authors' knowledge, very few studies have been conducted with conductive nano-ink coating on polymer foams, they have focused mainly on pressure sensitive sensing applications with single layer ink coated on the foam skeleton [16] or infiltrated in the foam cell [17]. No report has been published regarding the damping performance utilising the nanotube-nanotube damping mechanism of the ink coating technique. In this study a novel coating method is introduced to realise the highly entangled CNT network region on the foam skeleton by a simple dip-coating process. A sandwich foam strut microstructure with MWNT as the sandwich core, and polyurethane dispersion

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(PUD) coating as sealant was fabricated. Foams containing 0.01, 0.05, 0.1, and 0.2wt% of MWNT coatings were studied regarding their coating coverage, electrical conductivity and viscoelastic damping performance.

2. EXPERIMENTAL

2.1. Nano-ink Preparation

Carboxylic functionalised MWNT with over 70% purity, average diameter of 20 nm and 10's of microns in length were supplied by Thomas Swan Ltd, UK. Transmission Electron Microscopy (TEM) images of such MWNTs are shown in Fig.1. The as-received MWNTs were dried in vacuum oven to remove moisture. Isopropanol alcohol (IPA) was used as solvent for MWNT dispersion due to its relatively low surface tension [18] at room temperature compare with deionized water [19]. IPA were added direct into dry MWNT powder, followed by ultrasonication performed with a probe sonicator for 30 min with the assistance of polyvinylpyrrolidone (PVP) as dispersant. An initial master batch of 0.2wt% solution was produced then diluted to the required wt% with additional IPA.

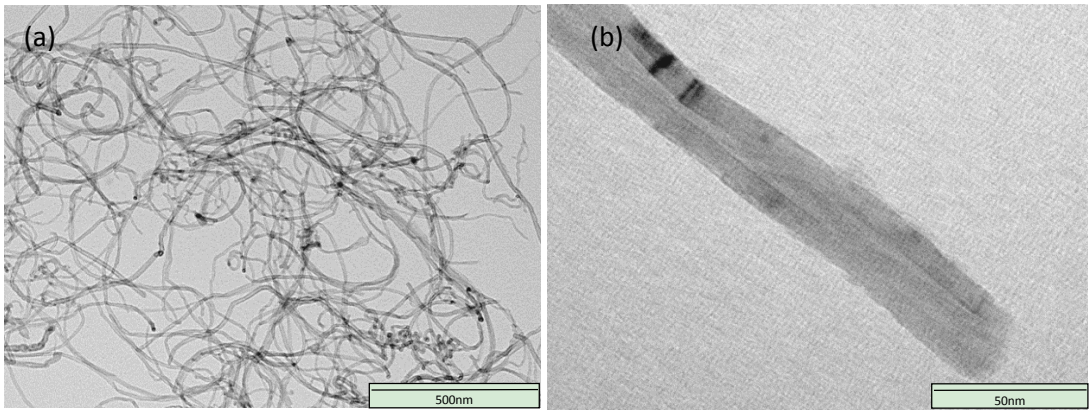

Fig. 1 TEM images of MWNT-COOH

2.2. Ink Coating Process on Open Cell Foam

The first step of coating involves a silane treatment. (3-Amin opropyl)triethoxysilane were used as coupling agent for bonding CNTs onto foam skeleton. IPA with pH value of 3.5 was used to dilute the silane concentration to 0.5wt%. Pristine PU foam (20×30×40 mm^3) obtained from SM Upholstery Ltd. (density of 27kg/m^3, with 2047-2244 pores/m) was O2 plasma treated for 1 min and then immersed and agitated in the silane solution immediately. Manual pressure helps to soak the solution faster. Before drying, the excessive solution was removed by leaving the foam on an absorbent for 30min. The silane treated foam was then dried at 80 °C for 4 hours.

In a second step the silane treated foam was immersed into MWNT ink. Agitation helped the ink infiltrate into foam cells. The foam was then removed from the ink after 20 min, placed on a 3M chemical sorbent to removed excessive material. After drying under 80 °C for 12 hours, the nanoink coated foam was removed from oven for the top coating

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Water based aliphatic polyurethane dispersion (PUD) U4101 with solids content of 39-41 and elongation at break of 1400% [20] was provided by Alberdingk Boley and used as top coating to seal the MWNT coating as a sandwich core between the base PU foam strut and PUD as illustrated in Fig. 2. The foam was then dried in the oven for 5 hours at 50 °C .

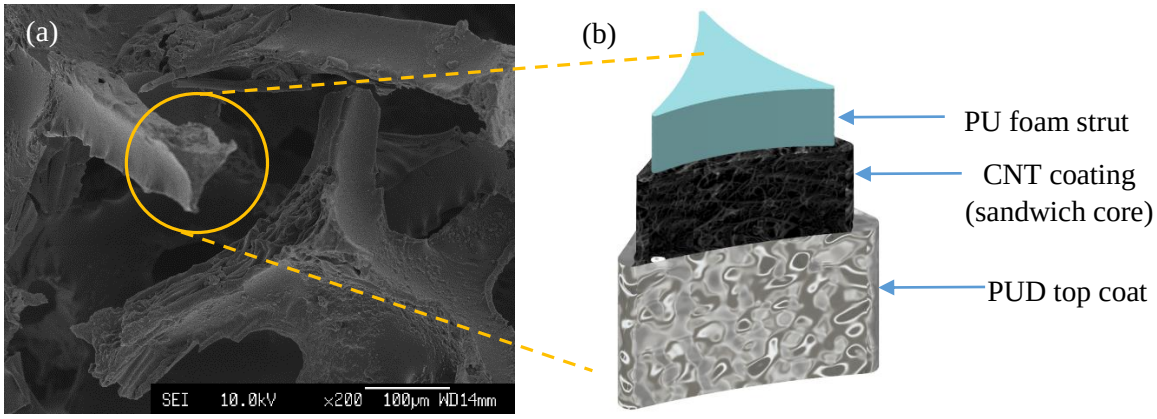

Fig. 2 SEM image of (a) pristine PU foam strut and (b) schematic illustration of the coating formed strut sandwich structure .

The surface coverage of foam struts by MWNTs is a key factor governs the damping performance. To utilise the CNT-CNT frictional slippage, the strut surface would preferably fully covered by the MWNTs ink coating. Thus one layer of MWNT ink coating with various ink concentration of 0.01wt%, 0.05wt%, 0.1wt% and 0.2wt% were produced for initial surface coverage study.

Pristine foam and PUD coated foam without MWNT ink sandwich core were also fabricated and tested for control. Fig.3 shows the as-produced foams (200×300×400 mm^3) containing ink with various concentrations.

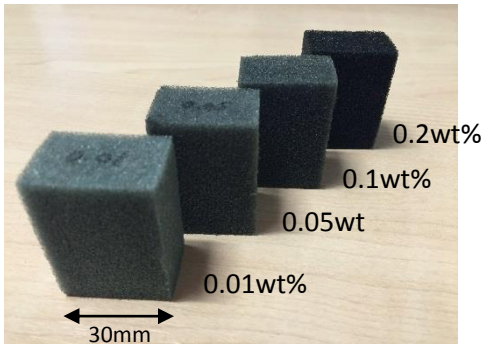

Fig. 3. As produced samples with increasing ink coating concentrations from left to right.

2.3. Properties measurements

Conductivity of foams coated with 0.01wt%~0.2wt% ink (without top coating) were measured using Keithley 2100 digital multimeter under two point measuring mode according to ASTM D4496-04, aimed to assess formation of conductive networks and therefore the coverage of ink coating on the surface.

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Quasi-static compression-compression cyclic tests were performed using Shimadzu AGS X Series universal testing machine with 1KN load cell at crosshead speed of 5mm/min under stroke control, room temperature. The aim is to obtain an overall characteristics on the static performance and provide a benchmark for the DMA data.

The amplitude, frequency and temperature dependency of the viscoelastic properties (storage modulus E', loss modulus E" and Tan δ) of multilayer coated foams were evaluated using a Dynamic Mechanical Analyser (DMA+/NUT/022/B-Metravib) under compression mode. Specimens were subjected to sinusoidal dynamic strain varying from 0.2% to 2% at a fixed frequency of 10Hz under room temperature.

Five specimens from each sample batch were tested for statistical reason.

3. RESULTS AND DISCUSSIONS

3.1 Single layer coating surface morphology and conductivity

The morphologies of the foam strut surfaces after ink coating with various MWNT concentration are depicted in SEM images in Fig. 4, the insets shows the higher magnification image. Almost no undispersed CNT bundles is observed, proves that a uniform dispersion thus uniform deposition was achieved.

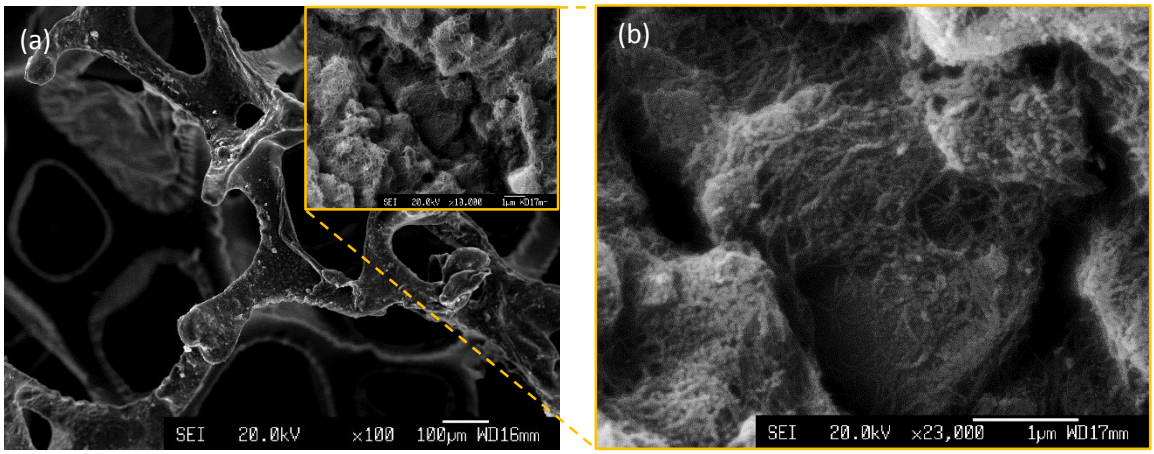

Fig. 4. SEM images of PU foam skeleton coated with 0.1wt% MWNT ink at ×100 magnification (a), and ×23000 magnification (b).

This surface morphology of MWNT coating is reflected on the foam electrical conductivity reults shown in Fig. 5, together with the actual weight percentage of MWNT coated on the foam skeleton. The percolation threshold region is between 0.05wt% and 0.1wt% ink concentration; due to the relatively high ink concentration, the 0.1wt% and 0.2wt% ink coated foam with continuous MWNT concudtive network structure revealed conductivity about 12 times higher than that of the 0.05wt% ink coated foam. Due to the saturation of surface coverage, the electrical conductivity did not reveal much

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further increment, showing only ~35% improvement with doubling the MWNT content from 0.1wt% to 0.2wt%. This surface coverage saturation is also proved by the plateau region of the 'coating weight fraction on foam' plot given in Fig. 5. Thus, the 0.1wt% MWNT ink offers the best effectiveness in foam skeleton surface coverage.

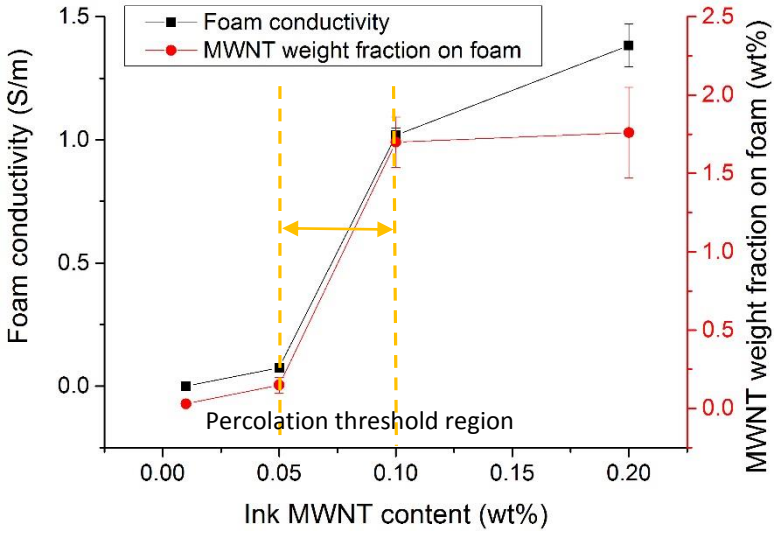

Fig. 5. Eectrical conductivity and CNT weight fraction of ink coated foams versus ink concentration.

3.2 Compression tests.

Uniaxial compression test results are shown in Fig.6. Both MWNT ink layer and PUD layer contributed to the variation in mechanical performance of foams. As shown in Fig. 6, pristine PU foam revealed the smallest elastic modulus (E) and stress at 10% strain ($\sigma_{0.1}$) of 8.5kPa among the tested foams, whereas the '0.01wt%', '0.05wt%', and '0.1wt%' samples with increasing ink MWNT concentration revealed very similar E and $\sigma_{0.1}$. Foam coated with 0.2wt% MWNT ink exhibits ~94% and ~97% increment in E and $\sigma_{0.1}$, respectively, comparing with the pristine foam. Such significant improvement in mechanical performance can be attributed to two reasons, namely, the strengthening effect of PUD layer and that of the MWNT core layer. By comparing the mechanical properties of 'pristine', '0.1wt%' and '0.2wt%' foams shown in Fig. 6a and b, one can conclude that the PUD layer can only improve the mechanical performance to a certain level, the further improvement from '0.1wt%' to '0.2wt%' was solely caused by the strengthening effect of MWNT core layer. The amino group on the silane coated foam reacted with the carboxyl group on WMNT surface to form a strong chemical bonding (\/\$H^+H_3^-$OOC), together with the entangled MWNTs network structure shown in Fig. 4 formed a rigid sheath around the flexible PU foam skeleton, and improved its mechanical performance thusly.

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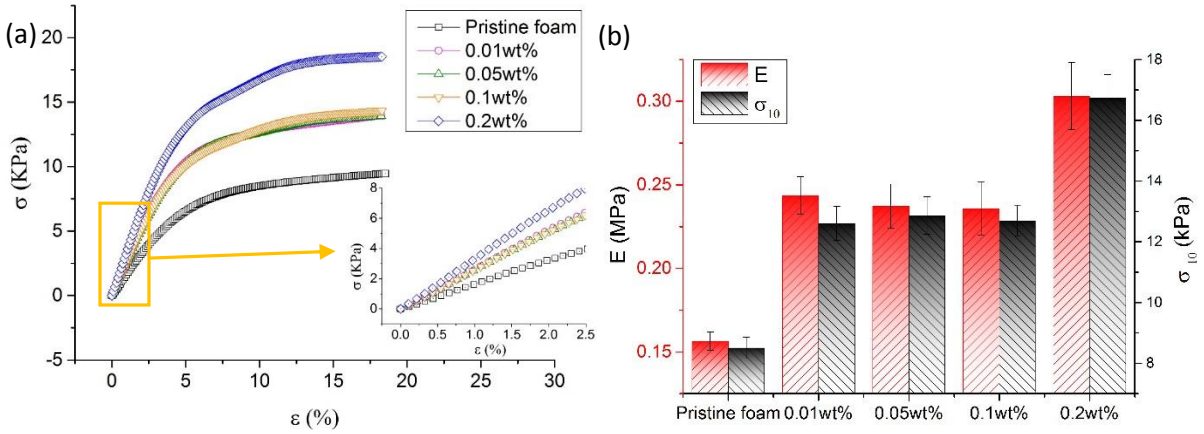

Fig. 6. Plot of compression stress-strain curve (a), and elastic modulus and stress at 10% strain (b) of foams coated with various concentrated MWNT ink.

3.3 Viscoelastic damping performance

The amplitude dependency of the viscoelastic properties (storage modulus E', loss modulus E") of samples were evaluated using Dynamic Mechanical Analyser. Fig.7. (a), (b) and (c) show the storage modulus, loss modulus and loss factor of the tested specimens. The storage modulus E' (Fig.7 (a)) which is an indication of foam stiffness did not show a significant increment with increasing ink concentration until 0.2wt%, abotu78% increment in E' was achieved with 0.2wt% ink coated foam compared with the pristine foam. Such result agreed with the trend obtained from static compression test (Fig. 6 (b)) indicating that the MWNT core layers revealed strengthening effect on the foam at 0.2wt% ink concentration. However, the magnitude of the elastic modulus is higher than that of the storage modulus obtained from DMA test. One possible reason is that the elastic modulus was calculated with strain up to 3% whereas the DMA only presented the dynamic strain up to 2%. Together with the differences in testing frequency and the input signal (sinusoidal for DMA, triangular for quasi-static test) which led to different level of energy input per cycle, it is difficult to find a corresponding relationship between the results obtained from these two tests.

The loss modulus (Fig.7 (b)), which is an indication of energy dissipation capability, revealed the same trend with that of the storage modulus; the 0.01, 0.05, and 0.1wt% ink coated foams exhibited similar E" cross the tested strain range. With ink concentration increased further to 0.2wt%, the peak loss modulus improved a further 68% compare with that of the 0.1wt%. A total 144% increment in loss modulus of '0.2wt%' was achieved at 1.08% strain comparing with the baseline pristine foam. As discussed previously, such significant increment attributed to both the viscoelasticity of PUD layers and the frictional sliding of MWNT core, additionally, two possible damping mechanism within the MWNT core layers could be further accounted for as following.

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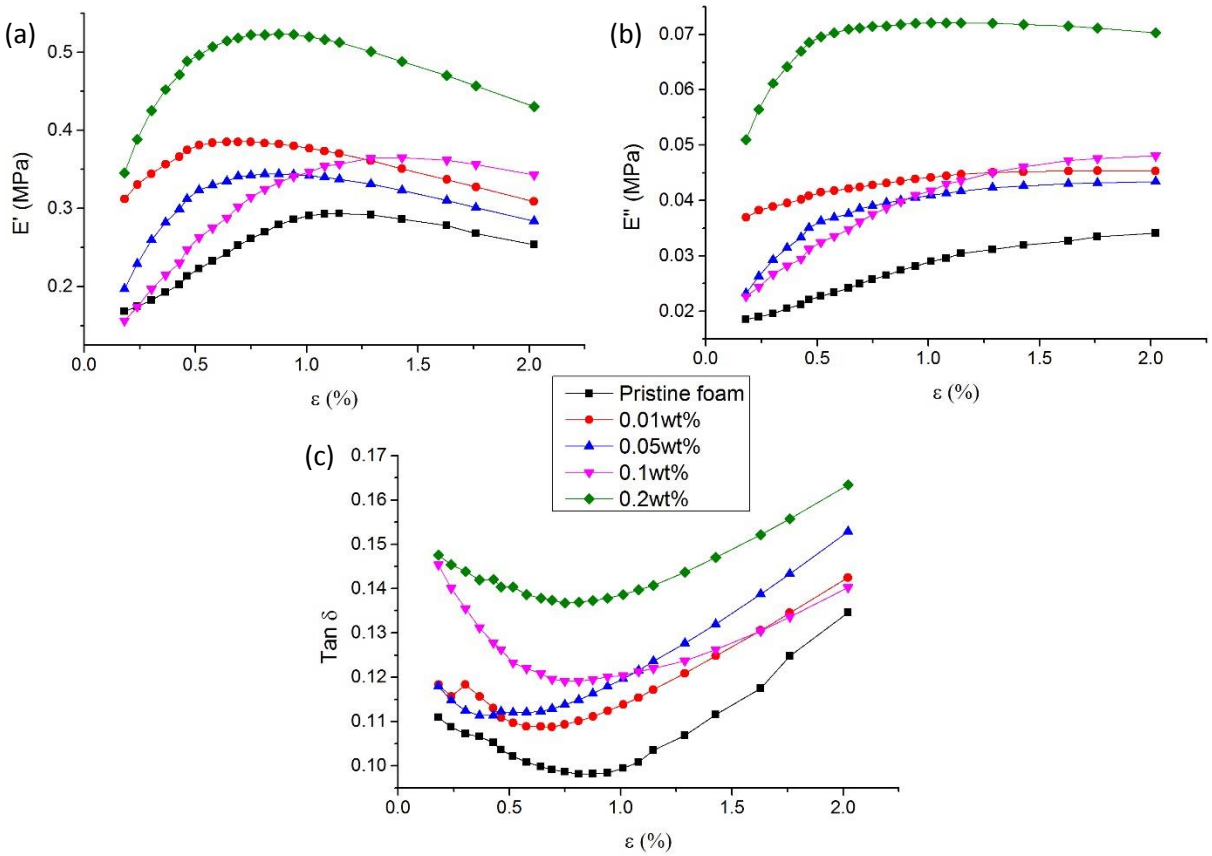

Fig. 7. Storage modulus (a), loss modulus (b), and loss factor (c) as a function of the dynamic strain obtained from DMA analysis.

In a similar way to any conventional CNTs embedded in polymer matrix nanocomposites two main damping mechanism exist in the MWNT core: the energy dissipation caused by (a) CNT-polymer interfacial sliding and (b)energy dissipation caused by the CNT-CNT sliding [12]. Unlike conventional polymer based nanocomposites that are mainly characterised by the stick-slip mechanism at the CNT-polymer interface, the MWNT core contains more entangled CNTs that provide more tube-tube contact point, and therefore would dissipate energy mainly through the CNT-CNT interfacial sliding. When considering the chemical bond formed by the –COOH functional group between the MWNTs and the PUDs, the CNT-polymer interface retain a much stronger bonding and therefore required higher critical shear strain (stress) to activate the CNT-polymer interfacial sliding mechanism compared to the case of the interfacial sliding between CNTs[12]. Hence, as indicated in Fig. 7 (b), the sharp increment in loss modulus of '0.2wt%' at lower dynamic strain is caused primarily by the CNT-CNT interfacial sliding mechanism. With the increase of the dynamic strain the other CNT-polymer damping mechanism started to contribute to the overall damping performance, reaching a peak of storage and loss modulus at a specific strain with the two damping mechanism been fully activated.

Finally, the loss factor (Tan δ) is plotted in Fig.7 (c). Although sample '0.1wt%' revealed similar loss modulus compare with '0.01wt%' and '0.05wt%', due to their low storage modulus at lower strain

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region their loss factor below 0.1% strain is higher than that of the other two samples. Foam coated with 0.2wt% MWNT revealed the highest loss factor of ~0.163 at 2% strain, increased by ~30% compare with the baseline PU foam.

4. CONCLUSIONS

A simple and scalable method for fabricating CNT ink coated PU foam was reported. Such simple dip-coating technique formed a sandwich skeleton structure treating the highly entangled MWNTs as the sandwich core, and water based PUD as the topcoat, exploited the nanotube-nanotube interfacial sliding damping mechanism within the core layer and realised a pronounced increment in foam damping performance. The electrical conductivity of the ink layer was also measured to assess the surface coating coverage, and with 0.1wt% MWNT ink concentration full coverage was achieved with foam electrical conductivity increased dramatically to ~1 S/m. The micro-architectured foam nanocomposites show significant increments in terms of both the elastic modulus and the loss modulus, with an optimal performance achieved with 0.2wt% ink concentration.

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