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Smart cord-rubber composites with integrated sensing capabilities by localised carbon nanotubes using a simple swelling and infusion method

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Abstract: Smart self-sensing composites with integrated damage detection capabilities are of particular interests in various applications ranging from aerospace and automotive structural components, to wearable electronics and healthcare devices. Here, we demonstrate a feasible strategy to introduce and localise conductive nanofillers into existing elastomeric coatings of reinforcing cords for interfacial damage detection in cord-rubber composites. A simple swelling and infusion method was developed to incorporate carbon nanotubes (CNTs) into the elastomeric adhesive coating of glass cords. Conductive CNT-infused glass cords with good self-sensing functions were achieved without affecting the bonding provided by the coating with rubber matrix. The effectiveness of using these smart cords as interfacial strain and damage sensors in cord-rubber composites was demonstrated under static and cyclic loading. It showed the possibility to identify both reversible deformation and irreversible interfacial damage. The simplicity of the proposed swelling and infusion methodology provides great potential for large-scale industrial production or modification of CNT functionalised elastomeric products such as cord-rubber composites.

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1. Introduction

Since its first application in engineering composites [1], structural health monitoring (SHM) based on real-time resistivity measurements has evolved rapidly during the last few years, ranging from various conductive polymer composites (CPCs) to nano-engineered carbon or glass fibre reinforced composites [2-5]. Conductive networks based on carbon nanotubes (CNTs) or graphene have been employed to detect various failure modes particularly in electrically insulating composites. For instance, Chou *et al.* [6, 7] successfully demonstrated the possibility to identify ply delamination, transverse micro-cracking and fibre breakage in glass fibre reinforced epoxy laminates under both tensile and flexural conditions by resistivity measurements with CNTs dispersed in the epoxy matrix. By this top-down method, a resistivity change has been successfully correlated to deformation of the entire percolated CNT network throughout the bulk matrix whereas damage at the fibre-matrix interfacial region associated with stress transfer has been disregarded [8]. Moreover, nanofiller loading needs to be carefully controlled to avoid excessive resin viscosity increase and nanoparticle filtration effects during the composite manufacturing process [9].

Self-sensing smart yarns were developed as a bottom-up method to address some of the aforementioned issues by locally modifying the surface of non-conductive fibres with CNTs or graphene for interfacial strain and damage sensing [10-12]. Mäder *et al.* [8, 12] first reported an approach based on the incorporation of CNT-filled sizing on glass fibre (GF) surfaces via a solution-based process and demonstrated its potential usage as interfacial sensors upon both static and dynamic tensile loading. Bilotti *et al.* [13] fabricated a highly conductive thermoplastic polyurethane/carbon nanotube (TPU/CNT) fibre via a continuous extrusion process with good strain sensing ability. Furthermore, they demonstrated the possibility to obtain self-sensing yarns by coating a commercially available Spandex yarn with a TPU/CNT conductive polymer composite coating [10, 14]. Other techniques used to develop CNT-coated smart textile materials include electrophoretic deposition (EPD) [15, 16], chemical vapour deposition (CVD) [17, 18], electrospray [19] and spray coating [20, 21]. For instance, hierarchical CNT-GF with preferred CNT alignment was achieved by CVD and employed for *in-situ* SHM of glass fibre reinforced composites during flexural testing [11]. A novel EPD process was developed for coating CNTs onto glass fibre surfaces and these functional interphases were exploited for damage detection [15]. The effectiveness of CNT deposition onto carbon fibre prepregs by a simple spray coating technique was also reported with a good correlation between crack propagation and electrical resistivity signals during *in-situ* damage sensing tests [20].

However, most of above-mentioned research works on SHM have focused on fibre reinforced plastics (FRPs) while no study has been conducted on real-time damage detection of cord-rubber composites. One of the difficulties in developing health monitoring systems based on CNTs for cord-rubber composites is in achieving an even spatial distribution of CNTs throughout the highly viscous rubber matrix and the complexity of depositing CNTs onto the cord surface using the techniques mentioned previously. The latter is particularly complicated by the presence of an elastomeric adhesive coating on commercially available cords. Different types of cords are used in reinforced rubber products such as glass, aramid, nylon and polyester. These cords are often treated with bespoke coatings to enhance the adhesion with rubber matrix. Adhesion can be improved by varying the resorcinol formaldehyde latex (RFL) impregnation system, or by adding an external adhesive coating which is often based on chlorosulphonated polyethylene (CSM) [22-24]. The wide applications for cord-rubber composites [22, 25-27] in critical engineering such as aircraft, subsea seals, naval transportation and automotive components have resulted in an interest in developing real-time health monitoring systems during usage to maintain structural safety and avoid catastrophic failure.

Recently, Coleman *et al.* [28] pioneered an interesting novel approach to incorporate graphene into rubber bands by a simple swelling process, opening up a new route to introduce nanofillers into rubber materials without complex manufacturing procedures.

Inspired by the work of Coleman *et al.* [28-30] and taking advantage of the presence of the elastomeric coating on reinforcing cords for rubber products, in the present work, CNTs were introduced into this coating via a simple swelling and infusion method. This resulted in CNT infused glass cords with self-sensing properties that can be utilised as interfacial strain and damage sensors for cord-rubber composites. The electrical conductivity and surface morphologies of these CNT infused glass cords swollen in different CNT dispersions have been investigated. These CNT infused glass cords exhibited good strain sensing abilities and reproducibility. For the first time, *in-situ* health monitoring of cord-rubber composites has been demonstrated, unveiling insightful interfacial health conditions such as local interface failure under both static and cyclic tensile loading. Further investigations involved single cord pull-out tests while fractographic analysis revealed no detrimental effects of the presence of the CNTs on cord-rubber adhesion. The proposed methodology is an easy and efficient process to produce smart reinforcing cords with tailored sensing functionalities, which is also compatible with current cord manufacturing procedures for potential industrial scale-up. These smart cords can be used for a multitude of SHM systems of cord reinforced rubber products.

2. Experimental

2.1. Materials

The multiwall carbon nanotubes (MWCNTs) (NC7000) used in this study were supplied by Nanocyl S.A. (Belgium). The E-glass cords with an average diameter of 1.1 mm were supplied by NGF Europe Limited (UK) and used as-received. The cords had been dipped through a proprietary resorcinol formaldehyde latex (RFL) bath as the strand coating and subsequently chlorosulfonated polyethylene synthetic rubber (CSM) bath as the cord adhesive overcoat prior to reception. Both strand coating and cord coating are elastomeric coatings. The same CSM used for the preparation of the adhesive overcoat was provided in the form of dry sheets. A commercial hydrogenated acrylonitrile butadiene rubber (HNBR) compound was used as matrix for embedding the glass cord. The solvents N-methylpyrrolidone (NMP) and Dimethylformamide (DMF) were purchased from Sigma-Aldrich Company Ltd, while toluene, methanol and chloroform were purchased from VWR Chemicals. Acetone was purchased from Honeywell International Inc. Silver paint and MG Chemicals 8481 carbon conductive grease were purchased from RS Components Ltd (UK).

2.2. Sample preparation

Preparation of CNT infused glass cords

The various CNT dispersions were made by dispersing MWCNTs in three different solvents (NMP, DMF, acetone) at a concentration of 50 mg/100 ml using an ultrasonic processor (Sonics VCX500) for 20 min with a pulse of 2 s on and 2 s off at 25 % amplitude.

Afterwards, the as-received glass cords with lengths of ~80 mm were soaked into the various CNT dispersions using an ultrasonic bath (PS-60A, 360W) for 0.5 h, 1 h, 2 h, 3 h, 4 h, 5 h and 6 h, respectively. After this swelling and infusion step, the CNT infused glass cords were washed in ethanol without sonication for 20 s, followed by sonication in ethanol for 20 s and a final ethanol wash for 20 s to remove any CNTs that are attached loosely to the surface of the glass cords as well as residual solvent. All sonication processes were performed with ice-bath to avoid temperature build-up. The infused glass cords were then dried in an oven at 60 °C for 20 h. As-received glass cord and CNT-infused glass cord are illustrated in Figure 1 (a).

Fabrication of the glass cord-rubber pull-out sample

A specially designed mould was used for making the model composite samples (Figure 1b). Glass cords were sandwiched between two HNBR compound sheets with a 5 N preload attached to either end of the cords to ensure their straightening and then moulded using a hydraulic hot press at 180 °C for 20 min. A composite sample with a long cord extending out from either end was obtained. The middle part was then cut away using a razor blade, leaving a resulting pull-out sample with an embedded cord length of approximately 15 mm in the HNBR matrix. A cross-sectional view of the pull-out sample is shown in Figure 1 (c).

2.3. Characterisations

Electrical conductivity measurements

The various dried CNT infused glass cords were cured at 180 °C for 20 min in an oven before their conductivity was measured by a Keithley 2400 sourcemeter (Tektronix). Silver paint was applied to the circumference of the CNT infused glass cord at 20 mm intervals in order to reduce the surface contact resistance. Three measurements were taken at different positions of the treated cords.

Morphology

Scanning electron microscopy (SEM) (FEI, Inspector-F) on gold coated samples was employed to assess the CNT distribution and location from both longitudinal and cross-sectional views of the CNT infused glass cord after the curing. The fracture surfaces after pull-out tests were investigated to examine the failure mode before and after CNT infusion.

Single cord in-situ strain sensing tests

Static tensile tests of the CNT-infused cords were carried out on an Instron 5566 universal mechanical tester equipped with a 1 kN load cell at a crosshead speed of 20 mm/min coupled with simultaneous electrical measurements recorded by a 34401A multimeter (Agilent). The gauge length of the cord was 200 mm, while two electrodes were attached to the middle of the cord at distances of 100 mm with silver paint applied to the contact points.

Single cord pull-out tests

Static single cord pull-out tests were carried out on an Instron 5566 universal mechanical tester equipped with a 1 kN load cell at a crosshead speed of 20 mm/min. A minimum of three measurements for each sample were recorded. The sample was fixed in the bottom grip without compressing the lateral surfaces of the sample and the glass cord was extracted by a tensile force from the HNBR matrix. By assuming constant interfacial shear stress along the interface during the pull-out process, the interfacial shear strength (IFSS) τ was calculated from the peak pull-out force F_{max} and the cord embedded area πdl [17], given by

$$\tau = F_{max} / (\pi dl) \qquad \text{Equation 1}$$

where d is the glass cord diameter and l is the embedded length.

In-situ damage and strain sensing tests of cord-rubber composites

Both static and cyclic strain and damage sensing tests of the CNT infused cord-rubber composite pull-out samples were performed. To enable real-time electrical measurements, the entire bottom surface of the pull-out sample was coated with carbon grease, while a copper wire was attached to the sample using a high strength flexible acrylic tape as an electrode. Another electrode was directly attached to the CNT-infused glass cord at a distance of 20 mm away from the top surface of the rubber matrix using silver-paint applied to the contact points. A schematic illustration of the *in-situ* sensing test setup is shown in Figure 1 (d). Cyclic loading and unloading of the pull-out specimen was applied using different displacement levels with 1 min dwell in between each cycle at the same displacement level while the specimen was held for 5 min before being reloaded to a higher displacement level.

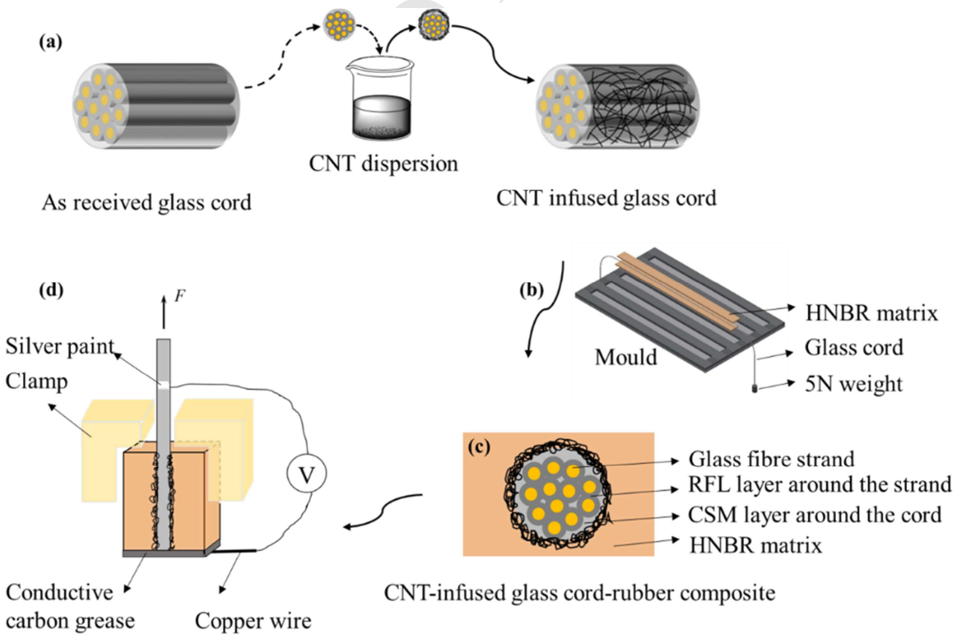

Figure 1. Schematic of (a) CNT infused glass cord preparation, (b) glass cord-HNBR pull-out specimen preparation, (c) cross-sectional view of pull-out specimen, (d) *in-situ* damage

sensing tests of pull-out of CNT infused glass cord from HNBR matrix (not drawn to scale).

3. Results and discussions

3.1. The distribution of CNTs on the surface of various CNT-infused cords

A good swelling capacity of the elastomeric adhesive coating material induced by the organic solvent is favourable to provide enough free volume for CNT infusion. Based on initial swelling tests of adhesive overcoat chlorosulfonated polyethylene (CSM) (see SI Fig. S1 and Table S1), NMP, DMF and acetone were chosen as potential solvents due to their good swelling capacity and compatibility with MWCNTs.

To evaluate the effectiveness of the introduction of CNTs via the swelling and infusion method, a treatment time of 1 h was used initially for the fabrication of CNT-infused glass cords. This is to limit CSM dissolution, which is of particular importance considering the very thin adhesive coating on the as-received glass cords. Figure 2 shows SEM images of the lateral surface of CNT infused glass cords and as-received glass cord prior to the swelling process. CNT networks were uniformly distributed along the entire cord surface after swelling in CNT/acetone dispersions (Figure 2a). A dense and thick CNT network was observed, indicating that a considerable amount of CNTs was attached to the cord surface. In contrast, less dense CNT networks were formed after swelling in CNT/NMP (Figure 2b) and CNT/DMF dispersions (Figure 2c) owning to the partial dissolution of CSM in the strong polar NMP and DMF solvents. Moreover, in the case of CNT/DMF dispersions, a relatively inhomogeneous CNT network was observed with the presence of some CNT agglomerates at the cord surface indicated by the arrows. The as-received glass cords (Figure 2d) exhibited a similar elastomeric surface morphology but without the presence of fibrous CNTs. As such acetone stood out as the optimum dispersion solvent in terms of CNT infusion.

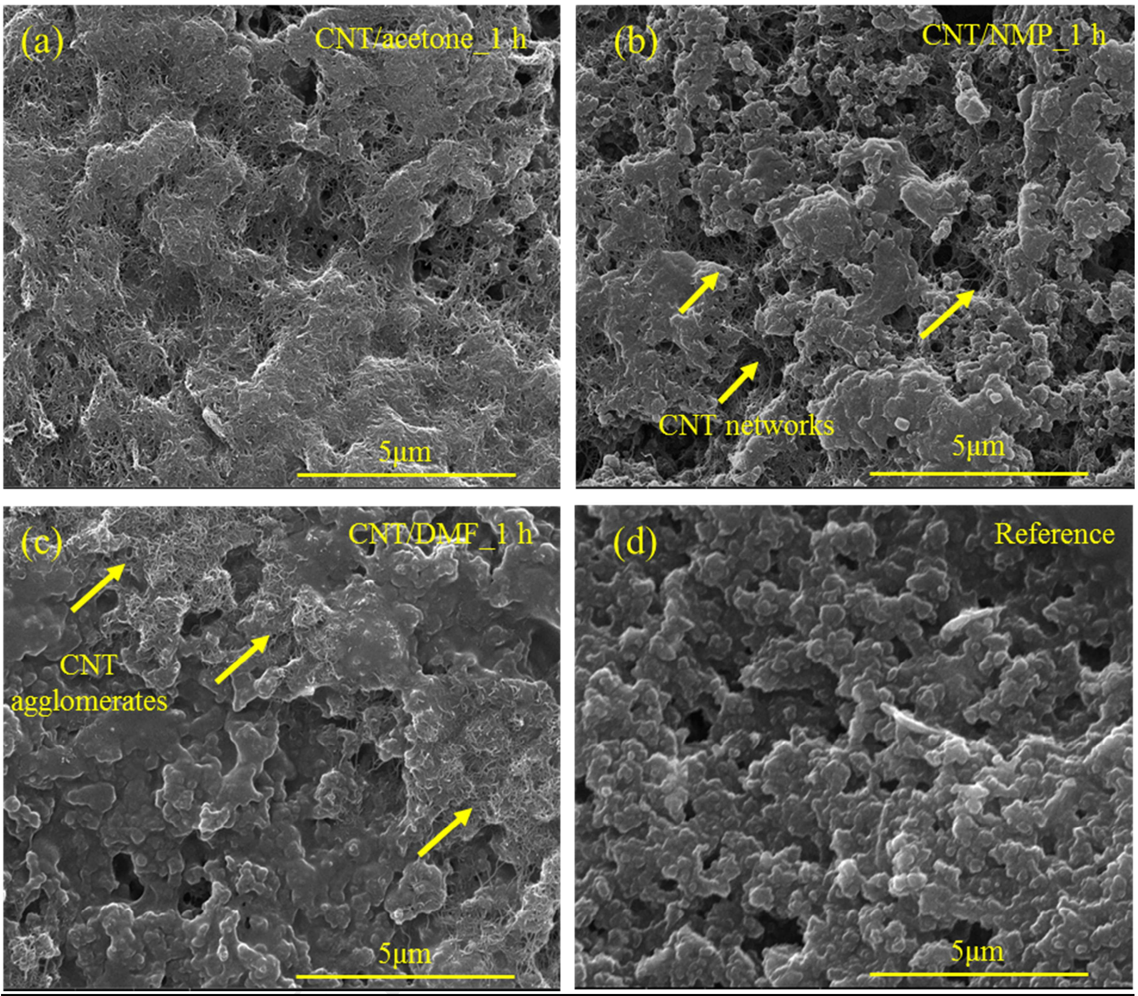

Figure 2. SEM images of the lateral surface of CNT-infused glass cords in (a) CNT/acetone, showing a uniform and dense CNT network covering the entire cord surface, (b) CNT/NMP, showing a less dense CNT network, (c) CNT/DMF, showing a relatively inhomogeneous CNT network with the presence of some CNT agglomerates indicted by the arrows for 1 h and (d) as-received glass cord prior to the swelling process without the presence of CNTs.

3.2. Morphology of CNT infused glass cords from CNT/acetone dispersions

Since acetone was selected as the most promising solvent for CNT infusion, further SEM observations of cross-sections of the cords were performed. Figure 3 shows the cross-sectional view of as-received glass cord and CNT infused glass cord from CNT/acetone dispersions for 1 h. Each glass cord has 11 strands of glass fibres (Figure 3a). A representative strand is indicated by the dashed yellow line. A two-step coating process was involved on both strands and the outer surface of the cord during manufacturing as described in experimental section, leading to two distinctive coating layers: the RFL coating on the glass fibre strand and the CSM coating on the RFL coated glass cord. The average thickness of the CSM layer around the cord is approximately 25 µm (Figure 3b) which provides improved adhesion between cord and rubber matrix. It can be seen that most of the CNTs were accumulated on the coating with an infusion depth of 2-4 µm, while very few traces of CNTs were found at a distance of 5-10 µm from the CSM layer (Figure 3d). Apparently, the current swelling and infusion process introduces CNTs preferentially into the outer CSM coating rather than in the interior of the RFL coated glass fibre strands.

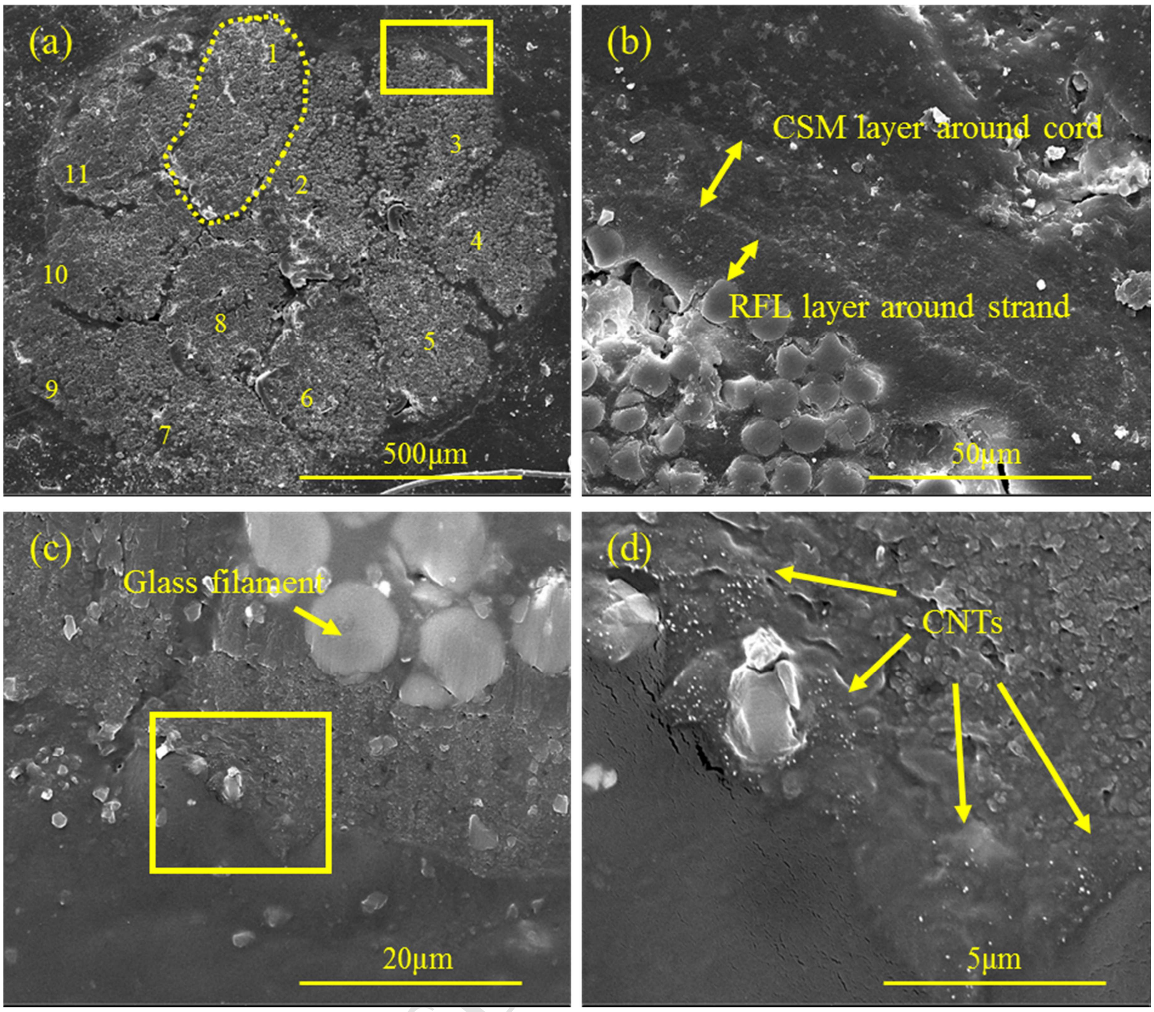

Figure 3. SEM cross-sectional views of glass cord embedded into an acrylic resin. (a) As-received glass cord consisting of 11 strands. The dashed yellow line indicates the location of a single strand in the image, (b) Higher magnification of the region as indicated by the yellow box in (a), showing RFL layer around the strand and CSM layer around the cord, (c) CNT traces in the CSM layer after swelling in CNT/acetone dispersions, (d) Higher magnification of the infused region as indicated by the yellow box in (c), showing a CNT infusion depth of 2-4 µm.

3.3. Electrical conductivity of CNT infused glass cords

Since the total amount of CNTs introduced via the simple swelling and infusion process was extremely low it was difficult to quantify the exact amount of CNT from thermogravimetric analysis (TGA) data (see SI Fig. S2). However, a good level of electrical conductivity was successfully imparted in all the intrinsically insulating glass cords. As such it demonstrates the efficiency of the proposed methodology to introduce conductive nanocarbons into glass cords with added functionalities.

Figure 4 (a) compared the electrical conductivity of CNT infused glass cords via various dispersions as a function of swelling time. Not surprisingly, glass cords swollen in CNT/acetone dispersions reached the highest electrical conductivity with levels above 10^{-2} S/m after only 30 min soaking time, implying the formation of a continuous CNT network as previously depicted in Figure 2a. No obvious change in electrical conductivity was observed with longer soaking times (> 30 min), suggesting that a saturated CNT network was formed in the swollen elastomeric coating within a relatively short period of time.

The electrical conductivity of the glass cords swollen in CNT/NMP and CNT/DMF dispersions were slightly lower compared to those swollen in CNT/acetone dispersions, in the range of 10^{-3} S/m after 30 min swelling. An increase in cord conductivity was observed for treatments with both dispersions, until a drop was seen after 3 h soaking. This decrease was attributed to a reduced amount of free volume for CNT infusion, resulting from a gradual dissolution of CSM after prolonged swelling in both dispersions. This effect was also indicated by the observed solvent colour change after swelling as-received glass cords for 1 h in acetone, DMF and NMP without CNTs under the same conditions, as shown in Figure 4 (b). Clearly, a certain amount of CSM material has been removed from the cord surface and migrated into NMP and DMF. Repeats were carried out in order to ensure batch to batch consistency on electrical performance (see SI Fig. S3). It was concluded that the obtained conductivity results of the CNT infused glass cords are highly consistent, confirming the reliability of the current method.

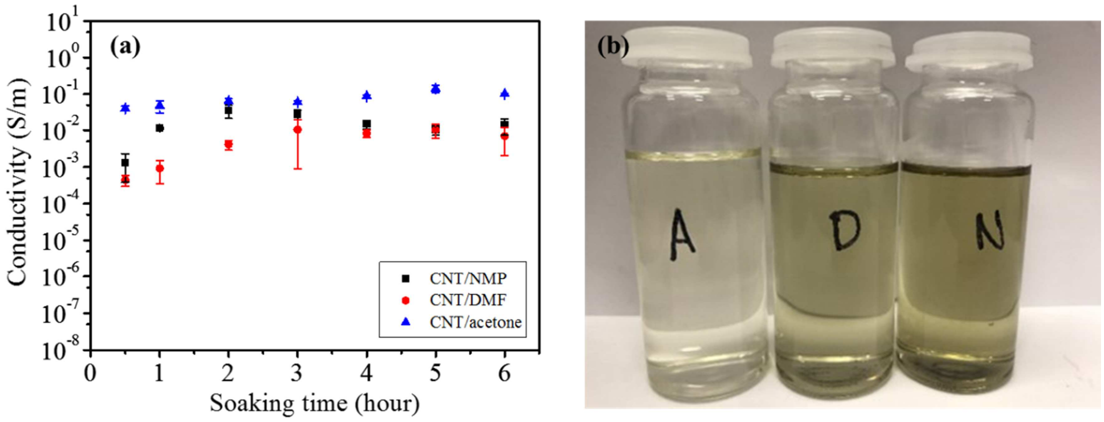

Figure 4. (a) Electrical conductivity of CNT infused glass cords via various CNT dispersions as a function of swelling time, (b) Solvent colour change after swelling of as-received glass cords in acetone, DMF and NMP for 1 h, confirming the partial removal of the CSM coating from the glass cords especially in the case of DMF and NMP.

3.4. *In-situ* strain and damage sensing during static and cyclic loading

With successful manufacturing of the conductive CNT infused glass cord, its strain sensing properties were first evaluated by recording its electrical resistance change $\Delta R / R_0$ simultaneously during static tensile loading. Subsequently these cords were embedded into a HNBR matrix. Both static and cyclic loading tests, coupled with real-time electrical measurements were performed to examine its potential as interfacial strain and damage sensors for cord-rubber composites. As CNT infused glass cords made from CNT/acetone dispersions reach the optimum conductivity after 1 h swelling and infusion, 1 h treatment time was also chosen for the other two systems for sensing investigations.

Strain sensing behaviour of CNT infused glass cord

Figure 5a shows the electrical resistance change $\Delta R / R_0$ and its relationship with load and displacement under static tensile loading of CNT infused glass cord specimens swollen in

CNT/acetone dispersions for 1 h. A small drop in the value of $\Delta R/R_0$ was initially observed due to the interlocking of glass fibre strands within the cord by straightening them along the direction of the applied force (Figure 5d), also known as setting effect [31]. This was then followed by a continuous rise in $\Delta R/R_0$ as the CNT network starts to deform with increasing applied extension until cord fracture. A nearly linear relationship between sensing signal and applied load can be seen with sensing signals ($\Delta R/R_0$) passing the zero value point, indicating a clear correlation between applied extension and sensing signal [10]. Similar findings were also observed in the other two systems (Figure 5b and 5c) with less obvious setting effects and slightly larger sensitivity owning to fewer conductive pathways arisen from a lower density of CNTs [32].

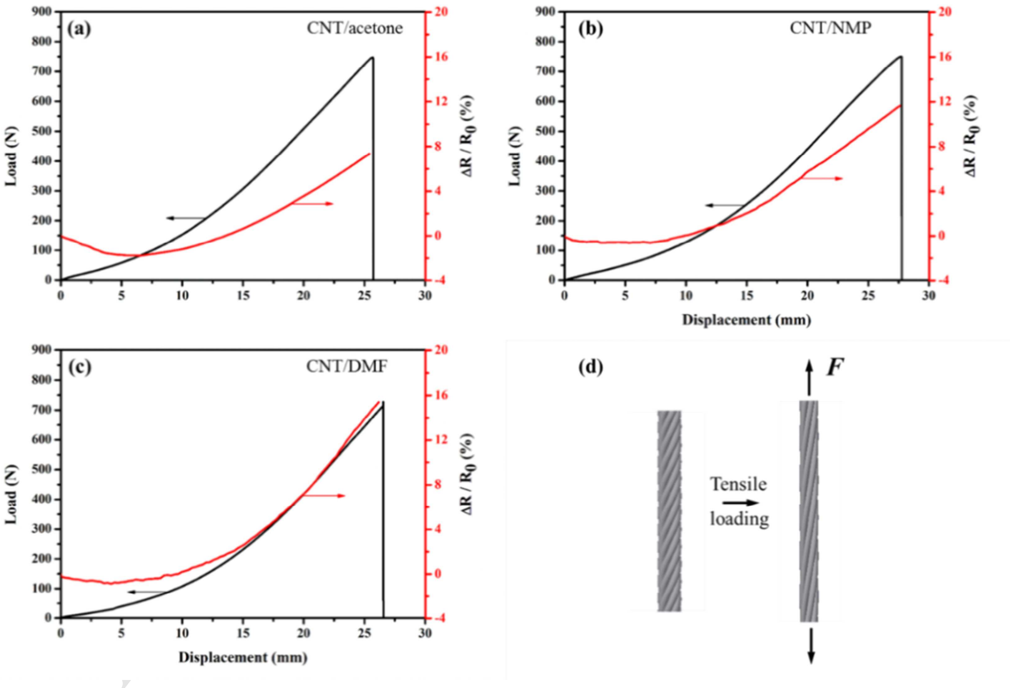

Figure 5. Static electro-mechanical response of CNT infused glass cord fabricated from (a) CNT/acetone, (b) CNT/NMP, (c) CNT/DMF, as dispersions for 1 h swelling and infusion time, (d) Straightening of twisted glass fibre strands along the direction of the applied force.

Static damage sensing of the CNT infused glass cord-rubber composites

After examining and confirming the good sensing properties of CNT infused glass cord, the sensing characterisation was applied to cord-rubber composites to demonstrate the feasibility to use these conductive cords as interfacial damage sensors.

Figure 6 shows a correlation between resistance change and applied load during pull-out tests for various CNT infused glass cord-rubber composites. Three well defined regions can be identified from the resistance change data, in agreement with findings reported by Mäder and Rausch on CNT-modified sizings on GF in PP matrix [33]. For the case of CNT/acetone dispersions, the value of $\Delta R / R_0$ increased gradually for the first 7 mm of extension. This behaviour is reversible, as confirmed later in the cyclic sensing section, and is due to the elastic deformation of the interfacial region. The first reversible region is followed by a second stage characterised by an increase in the slope of the sensing signal for the following 5 mm extension. At a critical point just before catastrophic interfacial failure, the resistance suddenly increases to beyond the multimeter limits, followed by visible macroscopic interfacial failure at the top surface of the pull-out sample as a result of shear stress concentration, propagating along the interface (see schematic (d)-②). The cord was eventually pulled out from the HNBR matrix by a frictional sliding mechanism after interface failure was complete at the end of the test (schematic (d)-③).

Similar trends of the electro-mechanical response were observed in cord-rubber composite specimens with conductive glass cords made from CNT/NMP and CNT/DMF dispersions respectively (Figure 6b and 6c). However, unlike the CNT/acetone specimen, the other conductive glass cords were only able to detect damage that occurred at the early stages of the test, which was then followed by a sharp increase in electrical resistance beyond the measurable range much earlier before catastrophic interface failure. This early signal loss was attributed to the relatively high initial resistance compared to that of the glass cord infused in a CNT/acetone dispersion. It is worthy to point out that the sensing properties of these cords made from CNT/NMP and CNT/DMF dispersions could be tuned and improved by adjusting the period of swelling and infusion treatment time.

In addition, the observed $\Delta R / R_0$ change for the CNT/acetone specimen was also much higher (up to 850 %) than that of other composite pull-out specimens, demonstrating a strongly enhanced interface damage monitoring capability. The sensing properties of different systems including displacement values corresponding to the last measurable electrical signal point ΔD_1 and maximum pull-out force ΔD_2 are summarized (see SI Table S2).

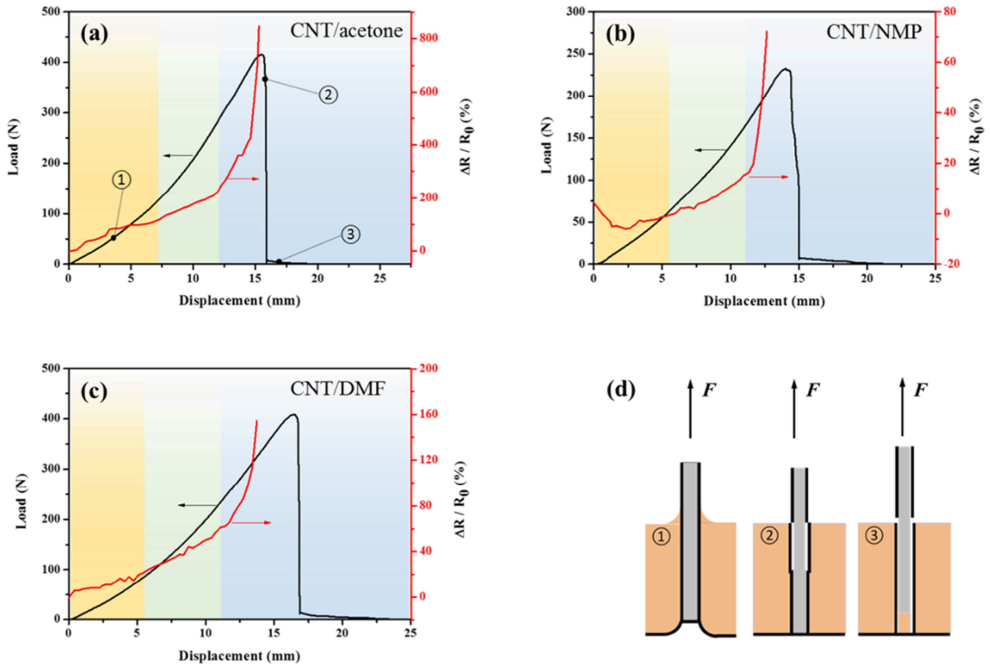

Figure 6. Static electro-mechanical response of the pull-out of a CNT infused glass cord from a HNBR matrix using (a) CNT/acetone, (b) CNT/NMP, (c) CNT/DMF, as dispersions for a swelling and infusion time of 1 h, (d) Illustration showing the interfacial failure

process during single cord pull-out: ① perfectly bonded to matrix, ② crack initiation at the top surface, ③ completely debonded interface with the cord pulled out by frictional sliding.

Cyclic strain and damage sensing of CNT infused glass cord-rubber composites

As the glass cord swollen in CNT/acetone dispersions had a more continuous and sensitive sensing signal among all other composite samples when applied as interfacial damage sensor under static loading, it was selected for further evaluation in cyclic *in-situ* damage sensing.

Figure 7 shows the cyclic electro-mechanical behaviour of the same composite pull-out specimen subjected to a series of cyclic loading conditions before the application of a static tensile load to ultimate interfacial failure. At low displacement levels (Figure 7a) with an applied cyclic extension from 3.5 mm to 7 mm, the sensing signals increased up to 80 % with applied load while recovered to initial levels upon unloading, indicating good reversibility at given extension levels. This was attributed to the reversible deformation of the elastomeric interphase without the permanent break-down of the CNT network. This is consistent with previous static sensing results of glass cord-rubber composite pull-out specimens (see Figure 6a) where the resistance change was roughly the same value when displaced to 7 mm.

When the applied strain increased from an extension level of 3.5 mm to 10.5 mm (Figure 7b), a clear change in $\Delta R / R_0$ values (about 50~80 % increment) was observed after the first loading cycle. Instead of returning to initial levels, the following sensing signals went up gradually upon unloading, which can be explained by a partial interruption of conductive paths as a result of some degree of permanent interfacial damage. Upon further static tensile loading (Figure 7c), the sensing signals increased continuously with a sharp and clear jump until catastrophic interface failure was achieved.

The potential of conductive glass cords made using the proposed infusion method for structural integrity monitoring of interfacial damage in cord-rubber composites has, therefore, been demonstrated. Glass cords made by swelling in CNT/acetone dispersions offered the most sensitive and continuous sensing signals just before catastrophic interfacial failure.

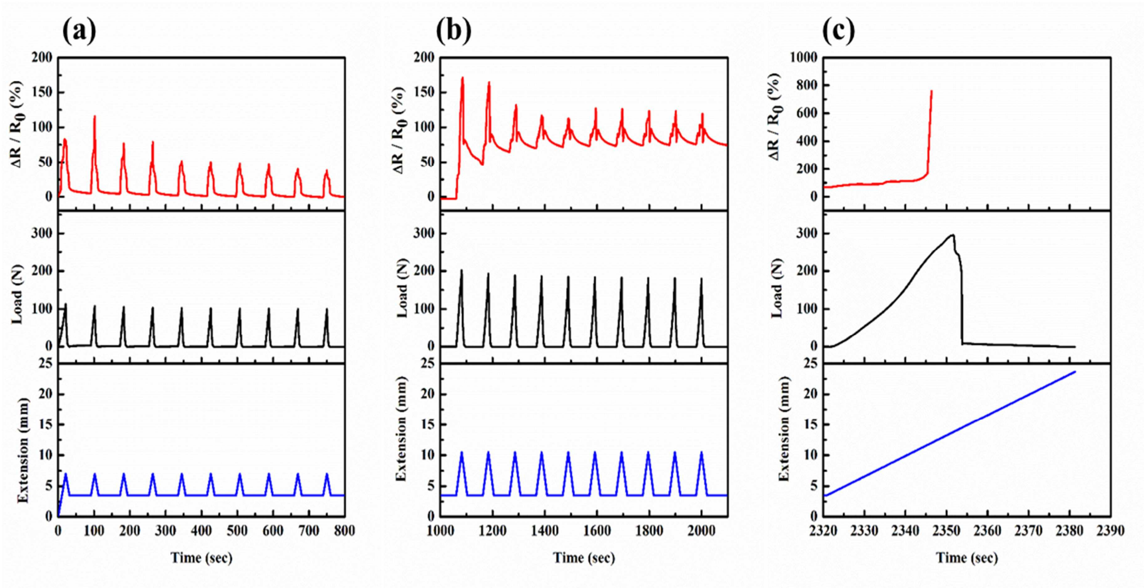

Figure 7. Cyclic electro-mechanical characterisation of the CNT infused glass cord-rubber composite pull-out specimen using CNT/acetone dispersions subjected to cyclic extension from (a) 3.5 mm to 7.0 mm with 1 min relaxation time between each cycle, showing reversible interfacial deformation, (b) 3.5 mm to 10.5 mm extension with 1 min relaxation time, showing some degree of permanent interfacial damage, (c) continuous increased extension until complete pull-out, with a clear sharp increment in sensing signals. Note: The specimen was held for 5 min before reloaded to a higher displacement level.

3.5. Interfacial shear strength

After demonstrating the potential of the developed CNT infused glass cord as smart reinforcements for rubber products, with added interfacial damage and strain sensing capabilities, efforts were made to evaluate the effect of CNT infusion on adhesion between cord and rubber.

Several micromechanical characterisations can be used to quantitatively evaluate the interfacial shear strength (IFSS) between a reinforcing fibre and its surrounding matrix, including single fibre pull-out and fibre fragmentation tests [34]. Figure 8a presents the single cord pull-out test results of various CNT infused glass cord-rubber and as-received glass cord-rubber composites swollen in various solvents without the presence of CNTs (acetone, NMP, and DMF, respectively) for 1 h under the same conditions before embedded into the HNBR matrix. It can be seen that no significant change in IFSS values was observed, within typical experimental error [16, 19, 35]. Fractographic analysis (Figure 8b and 8c) of fracture surfaces after pull-out indicated a change from failure mode of the elastomeric coating/HNBR interface failure to failure at the elastomeric coating/glass fibre interface, indicating a toughening of the elastomeric coating/HNBR interphase due to the presence of CNTs.

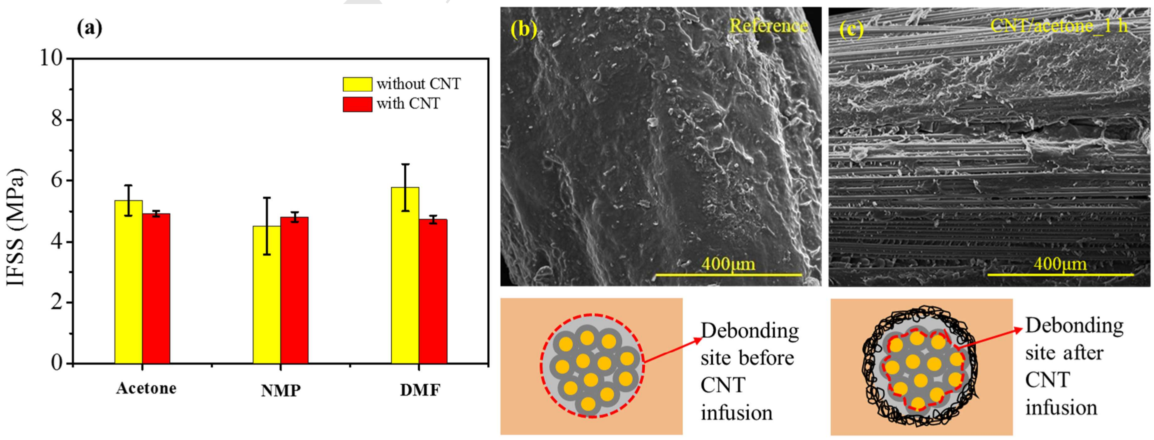

Figure 8. (a) Single cord pull-out test results of glass cord-rubber composites with and without CNT treatment. (b) Fracture surface of reference cord specimens after pull-out

testing, showing failure at the elastomeric coating/HNBR interface with most of the elastomeric coating remaining present on the cord surface, (c) Fracture surface of cord specimens swelled in CNT/acetone dispersions showing failure at the elastomeric coating/glass fibre interface with glass fibres exposed at the fracture surface.

4. Conclusions

A simple and efficient method was developed for the fabrication of self-sensing CNT infused glass cords based on a swelling and infusion process. The percolated CNT network has been successfully localised into the existing elastomeric coating present on the reinforcing cords, acting as an integrated interfacial strain and damage sensors for cord-rubber composites. The effect of various solvents on CNT infusion has been investigated. Good electrical conductivity (10^{-2} S/m) was achieved with extremely low amounts of CNTs after only 30 min of swelling, with no detrimental effects on original mechanical performance of the composites.

For the first time, the internal health status of cord-rubber composites has been *in-situ* monitored based on fabricated smart sensing cords. Stable and repeatable sensing signals were obtained under both static and cyclic loading conditions, providing insightful information of the interfacial structural integrity of the system. With such smart hierarchical cord-rubber composites, early detection of interfacial damage before catastrophic failure becomes viable.

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References

[1] K. Schulte, C. Baron, Load and failure analyses of CFRP laminates by means of electrical resistivity measurements, Composites science and technology 36(1) (1989) 63-76.

[2] N. Alexopoulos, C. Bartholome, P. Poulin, Z. Marioli-Riga, Structural health monitoring of glass fiber reinforced composites using embedded carbon nanotube (CNT) fibers, Composites Science and Technology 70(2) (2010) 260-271.
[3] J.-M. Park, P.-G. Kim, J.-H. Jang, Z. Wang, J.-W. Kim, W.-I. Lee, J.-G. Park, K.L. DeVries, Self-sensing and dispersive evaluation of single carbon fiber/carbon nanotube (CNT)-epoxy composites using electro-micromechanical technique and nondestructive acoustic emission, Composites Part B: Engineering 39(7) (2008) 1170-1182.
[4] L. Böger, M.H. Wichmann, L.O. Meyer, K. Schulte, Load and health monitoring in glass fibre reinforced composites with an electrically conductive nanocomposite epoxy matrix, Composites Science and Technology 68(7) (2008) 1886-1894.
[5] H. Zhang, E. Bilotti, T. Peijs, The use of carbon nanotubes for damage sensing and structural health monitoring in laminated composites: a review, Nanocomposites 1(4) (2015) 167-184.
[6] L. Gao, E.T. Thostenson, Z. Zhang, T.W. Chou, Sensing of damage mechanisms in fiber-reinforced composites under cyclic loading using carbon nanotubes, Advanced Functional Materials 19(1) (2009) 123-130.
[7] E.T. Thostenson, T.W. Chou, Carbon nanotube networks: sensing of distributed strain and damage for life prediction and self healing, Advanced Materials 18(21) (2006) 2837-2841.
[8] J. Rausch, E. Mäder, Health monitoring in continuous glass fibre reinforced thermoplastics: Manufacturing and application of interphase sensors based on carbon nanotubes, Composites Science and Technology 70(11) (2010) 1589-1596.
[9] H. Zhang, Y. Liu, S. Huo, J. Briscoe, W. Tu, O.T. Picot, A. Rezai, E. Bilotti, T. Peijs, Filtration effects of graphene nanoplatelets in resin infusion processes: Problems and possible solutions, Composites Science and Technology 139 (2017) 138-145.
[10] R. Zhang, H. Deng, R. Valenca, J. Jin, Q. Fu, E. Bilotti, T. Peijs, Carbon nanotube polymer coatings for textile yarns with good strain sensing capability, Sensors and Actuators A: Physical 179 (2012) 83-91.
[11] D.L. He, B.H. Fan, H. Zhao, X.X. Lu, M.H. Yang, Y. Liu, J.B. Bai, Design of electrically conductive structural composites by modulating aligned CVD-Grown carbon nanotube length on Glass Fibers, ACS Applied Materials & Interfaces 9(3) (2017) 2948-2958.
[12] S.L. Gao, R.C. Zhuang, J. Zhang, J.W. Liu, E. Mader, Glass fibers with carbon nanotube networks as multifunctional sensors, Advanced Functional Materials 20(12) (2010) 1885-1893.
[13] E. Bilotti, R. Zhang, H. Deng, M. Baxendale, T. Peijs, Fabrication and property prediction of conductive and strain sensing TPU/CNT nanocomposite fibres, Journal of Materials Chemistry, 20(42) (2010) 9449-9455.
[14] R. Zhang, H. Deng, R. Valenca, J. Jin, Q. Fu, E. Bilotti, T. Peijs, Strain sensing behaviour of elastomeric composite films containing carbon nanotubes under cyclic loading, Composites Science and Technology 74 (2013) 1-5.
[15] J. Zhang, R. Zhuang, J. Liu, E. Mäder, G. Heinrich, S. Gao, Functional interphases with multi-walled carbon nanotubes in glass fibre/epoxy composites, Carbon 48(8) (2010) 2273-2281.
[16] S. Tamrakar, Q. An, E.T. Thostenson, A.N. Rider, B.Z. Haque, J.W. Gillespie, Tailoring interfacial properties by controlling carbon nanotube coating thickness on glass fibers using electrophoretic deposition, ACS Applied Materials & Interfaces 8(2) (2016) 1501-1510.
[17] H. Qian, A. Bismarck, E.S. Greenhalgh, G. Kalinka, M.S. Shaffer, Hierarchical composites reinforced with carbon nanotube grafted fibers: the potential assessed at the single fiber level, Chemistry of Materials 20(5) (2008) 1862-1869.
[18] J. Sebastian, N. Schehl, M. Bouchard, M. Boehle, L. Li, A. Lagounov, K. Lafdi, Health monitoring of structural composites with embedded carbon nanotube coated glass fiber sensors, Carbon 66 (2014) 191-200.
[19] Q.X. Li, J.S. Church, M. Naebe, B.L. Fox, Interfacial characterization and reinforcing mechanism of novel carbon nanotube - Carbon fibre hybrid composites, Carbon 109 (2016) 74-86.

[20] H. Zhang, Y. Liu, M. Kuwata, E. Bilotti, T. Peijs, Improved fracture toughness and integrated damage sensing capability by spray coated CNTs on carbon fibre prepreg, Composites Part A: Applied Science and Manufacturing 70 (2015) 102-110.
[21] H. Zhang, M. Kuwata, E. Bilotti, T. Peijs, Integrated damage sensing in fibre-reinforced composites with extremely low carbon nanotube loadings, Journal of Nanomaterials (2015) 16(1):243.
[22] C. Valantin, F. Lacroix, M.P. Deffarges, J. Morcel, N. Aït Hocine, Interfacial damage on fatigue-loaded textile–rubber composites, Journal of Applied Polymer Science 132(4) (2015).
[23] W.B. Wennekes, J.W.M. Noordermeer, R.N. Datta, Mechanistic Investigations into the Adhesion between RFL-Treated Cords and Rubber. Part I: The Influence of Rubber Curatives, Rubber Chemistry and Technology 80(4) (2007) 545-564.
[24] R.B. Durairaj, Resorcinol formaldehyde latex (RFL) adhesives and applications, Resorcinol: Chemistry, Technology and Applications (2005) 263-339.
[25] B. Lee, D. Liu, M. Chawla, P. Ulrich, Fatigue of cord-rubber composites, Rubber Chemistry and Technology 67(5) (1994) 761-774.
[26] H. Iizuka, K. Watanabe, S. Mashimo, Observations of fatigue failure in synchronous belts, Fatigue & Fracture of Engineering Materials & Structures 17(7) (1994) 783-790.
[27] H. Yang, X.F. Yao, H. Yan, Y.N. Yuan, Y.F. Dong, Y.H. Liu, Anisotropic hyper-viscoelastic behaviors of fabric reinforced rubber composites, Composite Structures 187 (2018) 116-121.
[28] C.S. Boland, U. Khan, C. Backes, A. O'Neill, J. McCauley, S. Duane, R. Shanker, Y. Liu, I. Jurewicz, A.B. Dalton, J.N. Coleman, Sensitive, High-strain, High-rate bodily motion sensors based on graphene-rubber composites, ACS Nano 8(9) (2014) 8819-8830.
[29] I. O'Connor, S. De, J.N. Coleman, Y.K. Gun'ko, Development of transparent, conducting composites by surface infiltration of nanotubes into commercial polymer films, Carbon 47(8) (2009) 1983-1988.
[30] I. O'Connor, H. Hayden, J.N. Coleman, Y.K. Gun'ko, High-strength, high-toughness composite fibers by swelling Kevlar in nanotube suspensions, Small 5(4) (2009) 466-469.
[31] J.W.S. Hearle, L.W.C. Miles, The setting of fibres and fabrics, Merrow Publishing Company Limited, 1971.
[32] J. Lee, M. Lim, J. Yoon, M.S. Kim, B. Choi, D.M. Kim, D.H. Kim, I. Park, S.-J. Choi, Transparent, flexible strain sensor based on a solution-processed carbon nanotube network, ACS Applied Materials & Interfaces 9(31) (2017) 26279-26285.
[33] J. Rausch, E. Mäder, Health monitoring in continuous glass fibre reinforced thermoplastics: Tailored sensitivity and cyclic loading of CNT-based interphase sensors, Composites Science and Technology 70(13) (2010) 2023-2030.
[34] D. Hull, T. Clyne, An introduction to composite materials, Cambridge University Press, 1996.
[35] S. Aziz, S.A. Rashid, S. Rahmanian, M.A. Salleh, Experimental evaluation of the interfacial properties of carbon nanotube coated carbon fiber reinforced hybrid composites, Polymer Composites 36(10) (2015) 1941-1950.