Piezo-driven jet valve dispensing of carbon nanotube-loaded composites: optimisation and characterisation

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ABSTRACT
A new class of single walled carbon nanotubes (SWCNT)/epoxy resin ink in dimethylacetamide is successfully printed using a piezo-driven jet valve dispensing system for the fabrication of flexible nanocomposites. The optimised ink prepared by solution mixing method with a viscosity (28.54 mPa·s), surface tension (31.3 mN/m), density (0.964 g/cm³), and 0.25 wt% SWCNT is obtained through design-of-experiments. The optimisation process is carried out focusing on the ink ejectability and the electrical properties of the resulting nanocomposites. An investigation of the electrical properties of the printed structures on glass and paper substrates is performed by analysing their sheet resistances. The resulting nanocomposite exhibits sheet resistances of $15 \times 10^2$ kΩ/sq and 0.11 kΩ/sq printed on glass and paper, respectively. Finally, the interlaminar fracture properties of the nanocomposites when integrated into glass fiber reinforced polymers are investigated. The median change of the energy release ratio $G_{II_c}$ is about 3%, with almost constant standard deviation.

GRAPHICAL ABSTRACT

1. Introduction
Due to their excellent mechanical, electrical and thermal properties [1,2], carbon nanotubes (CNTs) are increasingly becoming a very important filler used to reinforce multifunctional nanocomposites [3–6]. It is proven that well-dispersed CNTs in the polymer matrix improve the fracture toughness, flexural strength, elasticity as well as the electrical and thermal conductivity of the nanocomposite [7–11]. Thus, carbon nanotube-loaded composites (CLCs) are becoming the material of choice for many current and future-oriented technical fields, especially for the aerospace, automotive, electronic devices, solar cells, wind turbine blades, etc. [12–17]. Furthermore, based on the electrical conductivity and capacitive properties of CNTs, many promising researches are being conducted to develop structural health self-monitoring systems in

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the CLCs utilising CNT fillings as sensing elements [18–23]. Also in the field of environmental remediation, CNTs based polymer membranes show a significant efficiency in water purification [24–29].

However, in contrast to the outstanding properties mentioned above, CNTs have a strong tendency to agglomerate due to their electrostatic attraction and Van der Waals forces [25,30–32]. This makes the dispersion of CNTs in the solvents or polymer matrix one of the main challenges in the fabrication process of CLCs [33–35]. The presence of such agglomerates in the matrix deteriorates the mechanical and electrical properties of the composites [36–38]. Therefore, various techniques are used to inhibit agglomeration of the CNTs and to disperse and stabilise them in their fluids and hence in the polymer matrix. These include mechanical dispersion (e.g. sonication and stirring), chemical modification of the CNT sidewalls and the addition of dispersants and stabilisers [39–42].

For the fabrication of CLCs, various methodologies have been reported, such as melt blending, resin transfer moulding, aligned CNT films, shear blending, solution mixing, etc. [25,38,43–49]. Unlike the other methods, the solution mixing process involves adding the CNTs and polymer matrix to a solvent in which the polymer matrix is dissolved. Then, the nanocomposite is formed through controlled evaporation of the solvent and a subsequent curing process [25]. An important feature of this method is that the fluid is capable of being printed with non-contact printing systems, e.g. with jet dispensers or inkjet printing technology [50]. Such printing systems offer greater flexibility and simplicity in manufacturing of the nanocomposites in a variety of patterns. In addition, they offer fast digital performance and precise ink positioning on a variety of substrates and geometries, making them an ideal choice for a wide range of applications [51–53]. Numerous printing procedures have been described in the literature for printing CNT-based fluids using various non-contact techniques, particularly inkjet printing [54–58]. Despite the many advances made, the main difficulty in printing CNT fluids, besides the agglomeration issue mentioned above, lies in the fact that the viscosity of the fluid increases significantly at higher CNT filling levels, which in most cases leads to clogging of the nozzles and thus to an interruption of the printing process [59–64].

Compared to other non-contact printing systems, piezo-driven jet valve dispensing offers a very promising potential to overcome this problem. This is due to the fact that the direct air pressure exerted on the ink, combined with the needle lift motion in the dispensing head, produces a higher jet force than by other non-contact printing systems, e.g. inkjet printing. This means that a wider range of materials with higher viscosities can be dispensed with jet valve dispensers [65,66]. Moreover, compared to aerosol jet and spray coating technologies, jet dispensers offer more flexibility in terms of controlling the ink droplet size and substrate temperature. It prints well-defined shapes and lines and does not require any complicated settings or using of special stencils. Also, with jet dispensing, the ink does not need to be atomised or exposed to carrier or sheath gases, which simplifies the process and clearly reduces the costs [52,67,68]. In addition to the dispersion techniques explained above, optimising both the physical properties of the ink and the jetting parameters of the print head is crucial for ensuring the best possible print quality. This includes, firstly, matching viscosity, surface tension and density so that the ink is dispensed consistently in well-formed drops without interruptions or formation of side droplets. Secondly, the dosing frequency, air pressure and needle lift of the jet valve must be tailored to the physical properties of the ink in order to achieve the best performance [52,66,69–71].

In the present work, new class of single walled carbon nanotube (SWCNT)/epoxy resin inks in dimethylacetamide (DMAc) are prepared, optimised and printed using a piezo-driven jet valve dispensing system for the fabrication of flexible CNT-reinforced nanocomposites. In this regard, solution mixing method is used, whereby the SWCNTs are dispersed in the fluid by simultaneous probe ultrasonication and magnetic stirring in the presence of ethyl cellulose as a dispersant [25,72]. An optimised ink formulation is established by varying the ink component proportions using design-of-experiments and one-variable-at-a-time methods, where parameters associated with the ejectability of the ink and electrical properties of the resulting nanocomposites are considered. The finally optimised ink and the printing process are validated by printing different structures (films, conductive tracks, coils, etc.) on flexible and rigid substrates (see Figures 1 and 4). The electrical properties of the printed structures are investigated by measuring and analysing their sheet resistance. Finally, in order to demonstrate the mechanical potential of the printed CLCs when used as sensor elements, the interlaminar fracture properties are investigated when they are integrated into a glass fibre reinforced polymer (GFRP) composite. For that, ENF (End Notched Flexure) tests are performed and evaluated.

2. Materials, methods and processes

The materials used in the ink formulations as well as the optimisation strategies and finally the
dispensing procedure are explained. As for the fabrication of the CLCs, solution mixing method is used.

### 2.1. Materials

TUBALL SWCNTs with a purity of $\geq 75$ wt%, an outer diameter of $1.8 \pm 0.4 \text{nm}$ and a length of $>5 \text{nm}$ are supplied by OCSiAl. Two-component epoxy amine-based resin system, EPIKOTE resin MGS (RIMR 135) and EPIKURE curing agent MGS (RIMH 137) with a mixing ratio of 100:30 weight shares, is obtained from HEXION. ETHOCEL ethyl cellulose (EC), standard 7, is provided by DOW Chemical. N, N-dimethylacetamide with a purity of $\geq 99.8\%$ is purchased from SIGMA-ALDRICH. Fast drying conductive silver ACHESON 1415 is purchased from PLANO GmbH. Unidirectional glass fiber mats, UT-E250 and UT-E500, are supplied by GURIT.

### 2.2. Optimisation procedure

The optimisation process is carried out taking into account two features; the ejectability of the ink using a piezo-driven jet valve dispensing system and the sheet resistance of the resulting CLCs. Two optimisation strategies, design of experiments (DoE) and one-variable-at-a-time (OVAT) [73], are used to optimise SWCNT inks. To do this, DoE is applied through central composite face-centered (CCF) design. Herein, three factors, i.e. the weight fractions of SWCNT, resin, and EC, variate in two levels on the cube edges and in three levels on the axes passing through the centers of each two opposite faces (see Figure 2). In the cubical shape of CCF, different ink formulations are projected as black points. Each of them is assigned a number that refers to a single ink formulation (see Table 1). For an in-depth investigation of the direct effect of the SWCNT, an additional set of inks (the grey points on central axis) is created in accordance with OVAT design (see Figure 2), while resin and EC weight fractions are kept constant. However, the range limits for each factor are determined by several preliminary tests using trial-and-error method.

### 2.3. Ink preparation

For preparation of a 25 g of SWCNT ink, typical example, 0.577 g of the curing agent (RIMH 137) is added to 1.923 g of the epoxy resin (RIMR 135). Next, 162.5 mg of EC is added, followed by addition of 22.275 g of solvent DMAc. The resulting mixture is stirred until fully dissolved on a magnetic stirring plate at room temperature for about 1 h. Subsequently, 62.5 mg of SWCNT is added to the colorless solution and dispersed by using an ultrasonic probe (MS 73 Sonopuls HD 2070 from BANDELIN Electronics) at a power amplitude of 32% for 300 min. Simultaneously with sonication, the ink is mechanically stirred in an ice bath using a magnetic stirrer at 500 rpm. After formulation, the SWCNT ink is kept under constant stirring at 750 rpm and used within the same day.
2.4. Ink characterisation

The ink properties, namely viscosity ($\eta$), surface tensions ($\gamma$) and density ($\rho$), are determined as part of the process of optimising the ink’s ejectability. Thereby, viscosity of SWCNT inks is determined at a shear rate of 1000 s$^{-1}$ using a cone-plate rheometer (PHYSICA MCR 301 from ANTON PAAR). Whereas for surface tension measurements, pendant drop method and Young-Laplace fitting is employed using a drop analyzer system (DSA-100 from KRÜSS) with needle diameter 1.83 mm. A vibrating tube digital densitometer (DMA-4500 from ANTON PAAR) is used for measuring densities of the inks. All measurements are performed at 20°C and repeated 4 times so that a reliable mean value is obtained. Table 1 shows the properties of the ink formulations as well as sheet resistances of the resulting CLC films. To estimate the effect of the weight fractions on ink properties, each individual property (C), i.e. $\eta$, $\gamma$ or $\rho$, is expressed as a function of weight fraction (F), i.e. SWCNT, EC, or resin (see Figure 3). Next, the slope of each variation is calculated. Then, mean slope value (MSV) is obtained by using Eq. (1).

$$\text{MSV} = \frac{\sum_{i=1}^{N} \Delta C_i}{N}$$

$\Delta C_i$ represents the variation of a single ink property e.g. variation of viscosity $\Delta \eta$ (mPa-s). $\Delta F_i$ (wt%) represents the variation of the weight fraction of an ink component, e.g. EC. As typical example, the mean value of five slopes ($N = 5$) is calculated for the viscosity variations with changing resin weight fraction. Four of these variations occur at the cube edges and one on the central axis of the cube (see Figure 2).

2.5. Ink printing and composite specimens fabrication

SWCNT inks are printed using piezo-driven jet valve dispensing system equipped with an NJ-K-4020 piezo valve [74]. The printing head is

Table 1. Weight fractions and properties of single-walled carbon nanotube (SWCNT) inks and sheet resistances of printed carbon nanotubes-loaded composites (CLC).

| Ink No. | SWCNT | Resin$^b$ | EC$^c$ | $\rho^d$ (g/cm$^3$) | $\eta^e$ (mPa-s) | $\gamma^f$ (mN/m) | $R_s^g \times 10^2$ (k$\Omega$/sq) |
|---------|--------|-----------|--------|-------------------|-----------------|-----------------|----------------------------------|
| 1       | 0      | 10        | 0.65   | 0.9585            | 2.2             | 34.6            | –                                |
| 2       | 0.05   | 10        | 0.65   | 0.9613            | 4.0             | 34.3            | 379                              |
| 3       | 0.1    | 10        | 0.65   | 0.9633            | 4.6             | 34.1            | 408                              |
| 4       | 0.15   | 10        | 0.65   | 0.9628            | 6.5             | 34.4            | 252                              |
| 5       | 0.2    | 10        | 0.65   | 0.9631            | 13.4            | 33.7            | 89                               |
| 6       | 0.25   | 10        | 0.65   | 0.9637            | 28.5            | 31.3            | 15                               |
| 7       | 0.3    | 10        | 0.65   | 0.9643            | 49.8            | 26.1            | 3                                |
| 8       | 0.1    | 7         | 1      | 0.9593            | 8.2             | 34.3            | 416                              |
| 9       | 0.1    | 13        | 1      | 0.9678            | 9.0             | 34.1            | 388                              |
| 10      | 0.1    | 13        | 0.3    | 0.9670            | 4.3             | 34.2            | 490                              |
| 11      | 0.1    | 7         | 0.3    | 0.9576            | 4.0             | 35.0            | 151                              |
| 12      | 0.2    | 7         | 0.65   | 0.9587            | 13.5            | 33.8            | 10                               |
| 13      | 0.2    | 13        | 0.65   | 0.9683            | 11.6            | 33.7            | 210                              |
| 14      | 0.2    | 10        | 0.3    | 0.9627            | 8.1             | 34.7            | 21                               |
| 15      | 0.2    | 10        | 1      | 0.9645            | 27.8            | 33.9            | 206                              |
| 16      | 0.3    | 13        | 1      | 0.9685            | 67.5            | 28.2            | 13                               |
| 17      | 0.3    | 13        | 0.3    | 0.9676            | 60.9            | 29.2            | 5                                |
| 18      | 0.3    | 7         | 0.3    | 0.9586            | 50.2            | 31.1            | 0.4                              |
| 19      | 0.3    | 7         | 1      | 0.9603            | 62.6            | 31.2            | 3                                |

$^a$DMAc is the rest fraction up to 100 wt% in all inks.

$^b$Two-component epoxy resin system.

$^c$Ethyl cellulose.

$^d$Density.

$^e$Viscosity.

$^f$Surface tension.

$^g$Sheet resistance.
integrated to an Autodrop Compact System (purchased from MICRODROP Technologies GmbH). The nozzle used is made of carbide with an inner diameter of 300 μm. Air pressure of the printing head in range of 20–90 kPa and needle lift (70–100%) are adjusted accordingly before each printing process. All CLCs are printed with a drop spacing of 1 mm.

2.5.1. Specimen fabrication for electrical test
For the electrical test (see Secs. 2.6 and 3.2), samples of CLC are prepared on both glass and paper substrates. On glass slides, SWCNT inks are printed in a rectangular geometry of 10 x 40 mm in 4 layers (see Figure 4b). After that, the specimens are transferred to an oven (M 53 from BINDER GmbH) for curing. The curing cycles are carried out at 23°C for 24 h and for 15 h at 80°C. Next, the CLC films are sanded gently with fine 220 grit sandpaper in order to remove the insulating resin layer formed on the outer surface of the composites during fabrication [75–77]. Then, two 10 x 10 mm contacting square-shaped electrodes are deposited on each of the opposite edges of the rectangle using a quick-drying silver conductive paste. In the next step, the silver electrodes are wired using a single core wire with a diameter of 0.23 mm (see Figure 4c). To investigate the effect of layer number variation and sheet resistance of SWCNT independent of the ink insulating components, a conductive path in shape of a meander coil with a width of 1.6 mm and a length of 1050 mm is printed on paper (see Figure 5). The curing procedure for the CLCs specimens printed on paper is similar to the one described above.

2.5.2. Specimen fabrication for mechanical test
For the mechanical test (see Sec. 2.7), square-shaped CLC films (110 x 110 mm) are printed on PTFE foils with a thickness of 0.025 mm (obtained from GOODFELLOW GmbH). After printing, the films are left at room temperature for 120 h to ensure complete solvent evaporation. In the next step, the CLC films are peeled off the PTFE foils and integrated in the symmetry plane of 6 layers of unidirectional glass fiber mats from GURIT (1 layer of UT-E250 on top and bottom of the CLC film plus 2 additional layers UT-E500 on both sides). An artificial precrack is applied by positioning a 30 mm wide PTFE strip flush to the CLC films perpendicular to the fiber direction of the mats. The laminate is impregnated with the same epoxy resin described in Sec. 2.1 in a vacuum-assisted resin transfer molding process. It is first cured at 50°C for 16 h and finally post-cured for 16 h at 80°C. After that, the plates are cut into rectangular geometry (125 x 15 mm) with the fiber-direction equal to the specimen longitudinal direction using a circular saw with a diamond blade.

Figure 3. Exemplary illustration for the relationship between a single ink property (C) and the weight fraction of a single ink component (F).

Figure 4. Rectangular thin film of carbon nanotube-loaded composite (CLC) for electrical investigation. (a) Schematic configuration of coplanar silver paste (Ag) electrodes deposited on a CLC film, printed on glass substrate for resistance (R) measurement; (b) CLC film after curing; (c) Wired coplanar Ag electrodes of a CLC film.

Figure 5. Conductive path with a width of 1.6 mm in a meander coil shape of carbon nanotubes-loaded composite (CLC) printed on paper substrate for electrical investigation.
2.6. Electrical test

The resistances of the CLC films printed on glass are measured using a multimeter/data acquisition system (Model 2700 from KEITHLEY). Since both contacting electrodes are laid on the same plane (see Figure 4a), coplanar method is applied for the measurements [78–80].

Direct current resistance \( R \) indicated by the multimeter is used to calculate the sheet resistances \( R_s \) (see Eq. (2)), taking into account the distance between the electrodes \( S \) and the width \( B \) of the rectangular geometry.

\[
R_s = \frac{R \cdot B}{S} \quad (2)
\]

For measurement of the resistance \( R \) of the conductive path printed on paper (grammage of 80 g/m\(^2\)) (see Figure 5), a digital multimeter (TRUE RMS 177 from FLUKE) is used. The meander coil is first numbered at specific intervals. One of the multimeter probes is fixed on point \( t_1 \) and the other probe is varied on all the remaining points along the coil path, from \( t_2 \) to the opposite edge at point \( t_{33} \). At each variation of the distance \( S \), the resistance value \( R \) is measured. Since the width \( B \) of the path is known (1.6 mm), the sheet resistance \( R_s \) is calculated according to Eq. (2). For both CLCs, printed on glass and paper, the measurement is repeated at least four times on different substrates so that a reliable mean value is obtained.

2.7. Mechanical test

ENF tests are performed on CLC thin films integrated in GFRP and, for comparative evaluation, on neat GFRP specimens with the same configuration. The ENF test is carried out on a Tira Test 2810 testing machine in three-point bending configuration (see Figure 6). A mandrel and supports with 5 mm radius according to ASTM D 7905 [81] are used. The support span \( 2L \) is set to a value of 50 mm. First, the crack tip position and the adjacent support position are marked on the specimen. Their distance defines the precrack length \( a_0 \). The nominal value is 8 mm, deviations are recorded and taken into account later in the evaluation. Additionally, the specimen width \( w \) and the total thickness \( 2h \) are measured four times to obtain a final mean value. After the specimen is properly set on the test fixture, the test is performed in a displacement-controlled manner. The mandrel has a constant velocity of 1 mm/min. The applied force increases continuously until a critical value \( P_c \) is reached at a critical displacement \( \Delta_c \) (see Figure 7). The force suddenly drops as the crack abruptly propagates. The experiment is then stopped manually. Experimental information about \( P \) and \( \Delta \) are logged in increments of 0.02 s.

The mode II interlaminar energy release ratio (ERR) \( G_{II,c} \) as given by

\[
G_{II,c} = \frac{9(a_0 + 0.42y/h)^2 \cdot P_c \cdot \Delta_c}{2L^3 + 3(a_0 + 0.42y/h)^3 \cdot 2w} \quad (3)
\]

defines the energy required to propagate a crack of width \( w \) over length \( da \) under in-plane shear load [81]. It is calculated from experimentally obtained data \( P_c \) and \( \Delta_c \), specimen dimensions \( w \) and \( h \), and test configuration \( L \) and \( a_0 \). A shear correction \( 0.42y/h \) [82,83] extends the basic approach as presented e.g. by Mi et al. [84]. The factor \( \chi = 0.663 \) is calculated in accordance with Harper et al. [83] and Reeder et al. [82] considering a Poisson’s ratio of 0.3. The test is performed 12 times for neat GFRP specimens and 17 times for the configuration with integrated CLC film. Each test gives a single \( G_{II,c} \) value. All specimens, i.e. neat GFRP and with integrated CLC film, are manufactured from the same GFRP batch to increase the comparability between both configurations.

2.8. Microscopic investigation

In order to evaluate the distribution as well as the agglomeration behaviour of SWCNTs in the CLC matrix after curing, microscopic investigation is carried out. For that, a single layer of CLC film printed on glass substrate is illuminated from below while being examined from above with a digital microscope (VHX-5000 from KEYENCE) at a magnification of 20 times.
3. Results and discussion

The results for the electrical and mechanical properties of CLCs as well as for the optimisation of the ink are discussed in detail.

3.1. Ink optimisation

As shown in Sec. 2.4, CCF combined with OVAT designs are used to investigate the effect of each ink component weight fraction on viscosity, surface tension, and density.

3.1.1. Effects on the viscosity

It is found that all ink weight fractions have a certain effect on viscosity, but in different proportions. Ink 11 (0.1 wt% SWCNT, 7 wt% resin and 0.3 wt% EC) with a viscosity value of 4.0 mPa.s is taken as a typical example (see Table 1). With a shift on the axis of SWCNT from ink 11 to 18 (0.3 wt% SWCNT) keeping the EC and resin fractions constant (see Figure 2), the viscosity increases dramatically to 50.2 mPa.s (i.e. 13 times greater than the value at ink 11). Similarly, when shifting on the EC axis from ink 11 to 8 (1 wt% EC), the viscosity increases to 8.2 mPa.s, which is 2 times greater than the value at ink 11. Whereas, when shifting on the resin axis from ink 11 to ink 10 (13 wt% resin), a very small increase in viscosity occurs (~0.3 mPa.s). For a closer understanding of the viscosity behaviour, the MSV of the viscosity changes with varying ink compositions is calculated according to Eq. (1). It shows that SWCNT has the most significant effect on the viscosity with an MSV of 258.03 mPa.s/[wt%], which confirms the same trend shown by ink 11. This is, according to Zare et al. [76], due to the large aspect ratio (length per diameter) of carbon nanotubes which produces a huge interfacial area between polymer matrix and nanoparticles enhancing the viscosity. In addition, as the amount of CNT increases, a network of entangled CNTs is formed, leading to a very strong increase in viscosity [63, 85].

As a secondary effect comes the influence of EC with an MSV of 12.79 mPa.s/[wt%]. Whereas the resin fraction with an MSV of 0.4 mPa.s/[wt%] exhibits the least influence on viscosity, which is attributable to its low viscosity as provided from the manufacturer. Figure 9(a) shows the variation curve of viscosity when SWCNT content changes while EC and resin content are kept constant. At low SWCNT contents (0–0.15 wt%), a slight increase in viscosity is observed, while at high SWCNT contents (0.2–0.3 wt%), the viscosity increases dramatically, in a nonlinear manner up to values around 50 mPa.s, e.g. ink 5 (0.3 wt% SWCNT).

3.1.2. Effects on the surface tension

In a similar way, the effect of the individual ink fractions on the surface tension is evaluated. It is found that the surface tension exhibits relatively stable values against variations in EC and resin content, with MSV not exceeding –0.7 [mN/m]/[wt%]. However, the most remarkable effect on surface tension is observed by changing the SWCNT content. As the SWCNT content increases, the surface tension decreases with an MSV of –25.93 [mN/m]/[wt%]. Figure 9(b) shows a constant plateau of the surface tension curve around 34.4 mN/m at low SWCNT contents. When the SWCNT fractions reach values ≥0.2 wt%, the surface tension starts to decrease in a nonlinear behaviour. This is attributed to the increase in ink viscosity at values ≥0.2 wt% of SWCNT (see Figure 9a). However, this behaviour is described by Pelofsky [86], who proposed an empirical equation for the relationship between surface tension γ and the viscosity η as given by

$$\ln \gamma = \ln A + \frac{B}{\eta}$$

where A and B are substance-dependent constants.

3.1.3. Effects on the density

Finally, investigation of ink density behaviour with variation of the component fractions shows that the density increases only very slightly with increasing ink component fractions, where the MSV lies in the vicinity of 26 × 10^{-4} [mN/m]/[wt%] by all fraction changes. Figure 9(c) shows the density development curve with increasing SWCNT content. It indicates that the change in density over the entire variation range of SWCNT content from 0.05–0.3 wt% does not exceed 3 × 10^{-3} g/cm^3.

3.1.4. Selection of the optimised ink

To conclude, as experimentally demonstrated, the density of the formulated inks shows relatively stable values against ink fraction variations. While surface tension decreases only at high loading levels of SWCNT. Furthermore, the measured values of density and surface tension listed in Table 1 show no negative effects on the ejectability. The viscosity of the SWCNT ink is the only ink property that is significantly affected by the variation of SWCNT and, to a lesser extent, EC content. The variation of the resin content shows very little effect on the viscosity of the ink. Indeed, inks 7, 16, 17, 18 and 19 with 0.3 wt% SWCNTs have higher viscosity values than other ink formulations (see Table 1). At this SWCNT weight fraction, viscosity values remain consistently high (at ≥49.8 mPa.s), regardless of EC and resin contents. Moreover, as Esmaeili and Ferreira reported [34, 35], increasing carbon nanotube content leads to greater agglomeration in both
ink and resulting composite. Microscopic examination of CLC films printed with 0.3 wt% SWCNT inks confirms the presence of agglomerates with diameters of 500–1000 µm (see Figure 8c). As well, it shows gaps with diameters of 100–300 µm distributed in the CLC films, most likely, formed by non-removable air bubbles in the high viscous ink during the homogenisation process.

Consequently, both together, agglomeration combined with high viscosity reduce ink ejectability and lead to frequent clogging in the printhead nozzle. Moreover, an increase in the needle lift up to 100%
or air pressure of the printhead up to 90 kPa does not improve the situation. Thus, inks with 0.3 wt% SWCNT are excluded from selection process of the optimised ink.

Since EC plays an important role as a dispersant and stabilizer in the ink [41,87–92], low EC contents, i.e. 0.3 wt%, lead also to frequent printing interruptions due to the agglomeration. Thus, inks 11 and 14 containing low EC contents are discarded too.

Regarding resin content, ink 12 with low resin level (7 wt%) is excluded. This is because, according to Yang et al. [93], low resin content can lead to a reduction in the mechanical properties of CLC.

Conversely, since both EC and resin components are non-conductive materials, increasing their weight fractions to 1% and 13%, respectively, leads to a remarkable increase in sheet resistance of the CLC films (see Table 1). For this reason, inks 8, 9, 10, 13 and 15 having high levels of EC and/or resin are excluded. The remaining two inks, 3 and 5, differ from each other in SWCNT content (0.1 wt% at 3 and 0.2 wt% at 5), whereas both have the same EC (0.65 wt%) and resin (10 wt%) contents. The sheet resistance measurements of CLC films printed with ink 5 exhibit, due to the higher SWCNT filling level, a lower sheet resistance value ($89 \times 10^2 \text{ k}\Omega/\text{sq}$) than the films printed with ink 3 ($408 \times 10^2 \text{ k}\Omega/\text{sq}$).

Therefore, ink 5 is given priority in the selection process. In this ink, the weight fractions of EC (0.65 wt%) and resin (1 wt%) are fully optimised with respect to ejectability and electrical testing.

In terms of SWCNT content, microscopic examination of the cured CLC films of ink 5 shows a poor and inhomogeneous distribution of SWCNTs with agglomerates in the range of 100–400 μm (see Figure 8a). Therefore, the SWCNT content is increased to 0.25 wt% in another ink formulation (i.e. ink 6) located on the central axis of the DoE cube. At this SWCNT fraction (0.25 wt%), high agglomeration rate seen by inks with 0.3% SWCNT is avoided. In addition, the higher amount of SWCNT (0.25 wt%) in ink 6 lead to a clear improvement in the electrical properties in CLC films (see Sec. 3.2.1).

The microscopic examination of the cured CLC film printed with ink 6 shows better homogeneous and intense SWCNT distribution in the composite matrix compared to 5 (0.2 wt% SWCNT) and 7 (0.3 wt% SWCNT) (see Figure 8a–c). Furthermore, the physical properties of ink 6, namely viscosity (28.54 mPa·s), surface tension (31.3 mN/m) and density (0.964 g/cm³), meet the requirements of the ink ejection at the jet valve dispensing system with minimum interruption rate. Therefore, ink 6 (0.25 wt% SWCNT, 0.65 wt% EC and 10 wt% resin) is selected as final and all-optimised ink.
3.2. Electrical properties

The electrical properties of the CLCs are evaluated by measuring the sheet resistance of films printed on glass substrates, while the number of printed layers and the SWCNT filling level effects are evaluated by measuring the sheet resistance of CLCs printed on paper substrates.

3.2.1. Sheet resistance of CLC films

Table 1 shows the results of the measured sheet resistance values in cured composites prepared according to Sec. 2.6. Due to the fact that SWCNTs are the only conductive component among the others of the inks, increasing the content of SWCNT leads to a clear decrease in the sheet resistance of the composites. As example, composites printed with ink formulation series 7, 16, 17, 18, and 19, which contain high levels of SWCNTs at 0.3 wt%, have lower values for sheet resistance than others printed with inks containing less than 0.3 wt% SWCNTs. In this series, the lowest value of sheet resistance is observed in the CLC films printed with ink 18, which is 0.4 × 10^2 kΩ/sq. In this ink, compared to others, non-conductive EC and resin contents are at lowest levels with 0.3 wt% and 7 wt%, respectively. As the content of EC and resin increases in the ink, the sheet resistance value increases accordingly in the cured composites and reaches the highest value of 13 × 10^2 kΩ/sq at CLC films printed with ink 16 when EC and resin are at 1 wt% and 13 wt%, respectively. Following this principle, all sheet resistance values of the composites behave accordingly the same. Figure 9(d) shows the sheet resistance values of the composites printed with inks ranging from 0 wt% to 0.3 wt% SWCNT content in steps of 0.05 wt%, with EC and resin fixed at 0.65 wt% and 10 wt%, respectively. Although, the composites printed with inks containing 0.3 wt% SWCNT have the lowest sheet resistance values, none of these composites are considered as optimal for the reasons described in Sec. 3.1. Instead, the CLC printed with ink 6 shows a sheet resistance of 15 × 10^2 kΩ/sq is selected as an optimal composite and used for the mechanical test (see Sec. 3.3).

3.2.2. Effect of number of printing layers and SWCNT filling

In the literature, the interfacial adhesion between carbon nanotube filler and polymeric matrices in nanocomposites is already reported. It is found that a strong bond can be established between them and, in some cases, the entire surface of the carbon nanotubes is covered with a polymer layer [75–77]. Therefore, when measuring the sheet resistance of the cured composite films, gentle abrading is required to remove the insulating layer of the epoxy resin covering the SWCNT (see Sec. 2.5.1). Consequently, part of the total SWCNT amount in the film can be discarded. Therefore, to investigate the influence of variation in number of printed layers, SWCNT inks are printed on paper substrates (see Figure 5). This is because the paper readily absorbs the solvent (i.e. DMAc as well as the EC and resin dissolved in DMAc) and strongly bonds with the CNTs, thus, a major part of the insulating additives dissolved in the solvent are removed [94]. In Figure 10(a), the sheet resistance of CLC paths printed on paper with inks 4, 5, and 6 and having different SWCNT weight fractions, 0.15 wt%, 0.20 wt%, and 0.25 wt%, respectively, is correlated to the corresponding distances along the conductive path (see Figure 5). This means, the resistances along the conductive path are measured at different distances S starting at point t2 and ending at t33 (see Figure 5). Then, the corresponding sheet resistances are then calculated according to Eq. (2). It is seen in Figure 10(a) that the sheet resistances of CLCs on paper are dramatically lower than those printed on glass substrate. For example, the sheet resistance for CLCs printed with ink 6 is 14.9 × 10^2 kΩ/sq on glass, whereas it is 0.11 kΩ/sq on paper. This is due to the fact, that the insulating components of the ink remain in the CLC films printed on glass substrates. Moreover, the decrement of sheet resistances of the CLCs printed with inks 4, 5 and 6 with increasing SWCNT content shows a nonlinear behaviour. This is possibly due to that the intensity of the interconnections between the carbon nanotubes increases in an exponential-like way at higher SWCNT content which, in its turn, decreases the sheet resistance in the same way.

For studying the effect of printing layer number, CLC films are printed on paper substrate with the same ink 5, however, in 2 and 4 layers. In the ones with 2 layers, the sheet resistance shows value of 0.21 kΩ/sq, while in 4 layers it decreases to be 0.059 kΩ/sq. It is obvious that doubling the SWCNT content in the ink does not reduce the sheet resistance to half its value in a linear way, but rather reduces it by a factor of 0.72, which confirms the exponential-like decrease in sheet resistance as described above.

3.3. Mechanical properties

The results of the ENF tests are shown as boxplots in Figure 11. The box contains values between the 25th and the 75th percentile. The middle horizontal line indicates the median value and the vertical lines (whiskers) show the range from lowest to the highest value. Values more than 1.5 times the
interquartile outside the box are defined as outliers. The data for the neat unidirectional GFRP specimens are shown in white, while the boxplot related to the specimens with integrated CLC film is shaded in grey. Two main effects are visible: (I) The median value slightly increases when the CLC film is integrated interlaminar to the GFRP and (II) the standard deviation, without considering outliers, is not affected.

With respect to (I), the median value of the neat GFRP specimens is 2174 N/m. The corresponding value for the case with integrated CLC film is 2238 N/m, which is 3% higher and thus almost unchanged. A key factor for high ERR is the quality of the cohesive bond between adjacent GFRP layers. In the reference configuration, the load-bearing glass fibres in the fracture zone can be optimally wetted by the infused matrix resin to achieve good cohesion properties. Experimental data for the configuration with CLC film prove that its integration does not have a strong effect on these bonding properties. The load transfer between the top and bottom of the specimens is thus not deteriorated by the film which locally separates adjacent glass fibres at the interface. This indicates sufficient adhesion between the integrated film and the GFRP.

Regarding effect (II), standard deviations of 181 N/m for the neat GFRP specimens and 178 N/m for specimens with CLC films are similar. The coefficient of variation (CoV), the ratio between the standard deviation and the mean value, is 0.08 for both configurations. Three outliers are identified for the specimens with CLC film. One of them ($G_{II,c} = 3350$ N/m) clearly overestimates the obtained median value of the configuration. As ENF specimens are sensitive to the precrack geometry, flush alignment of the PTFE strip to the CLC film is required during manufacturing. Any spacing allows the infusion resin to penetrate the precrack and thus change its effective length. This may cause larger ERR than in neat GFRP specimens. Two other data points ($G_{II,c} = 1413$ N/m and $G_{II,c} = 1684$ N/m) are defined as outliers since they deviate to much from the rest of the data set. Potential reasons for these weak values can be manufacturing issues such as non-uniform distribution of the CLC film components, irregular printing quality and incorrect handling of the uncured material. However, only two $G_{II,c}$ values are lower than the minimum reference value from the GFRP specimens.

Two major conclusions can be drawn from the mechanical results. First, integration of CLC films does not decrease the median energy release ratio under mode II load. Considering that smaller electrodes shall be applied in practice that will not fully cover the substrate (see Figure 1), no notable effects on the ERR are expected. Secondly, assuring high process capability of the CLC film printing is a key factor to obtain similar variations in the mechanical results as in the reference configuration. A standard deviation comparable to the data set with neat GFRP specimens must be aspired.

4. Summary and conclusion

Flexible CLCs were successfully fabricated by printing SWCNT/resin inks using a piezo-driven jet valve dispenser. First, the ink was prepared by solution mixing method in DMAc, where SWCNTs were dispersed in the ink medium by simultaneous probe sonication and magnetic stirring, with presence of EC as a dispersant. The optimisation of the ink involved the ejectability from the piezo-driven jet valve dispenser as well as the electrical properties of the resulting CLCs. Based on these two boundaries, an optimised ink has been selected using CCF and OVAT strategies. Thus, the component fractions of the ink were varied, while the viscosity, surface tension, density of the ink and sheet resistance of the resulting CLCs were evaluated. As a potential application, the CLCs are integrated interlaminar into...
unidirectional GFRP laminates. It is found that the CLC films integrated into the GFRPs does not lower the median values of the mechanical fracture properties under mode II load compared to the neat GFRPs tested. Further, the experimental variation was found to be comparable to the reference set. Despite the mechanical fracture behaviour was not an optimisation parameter, acceptable properties were achieved.

Piezo-driven nozzle valve dispensers allow printing of inks with higher viscosity values, which could open the possibility of printing inks with higher carbon nanotube loading. Future work will focus on the preparation of inks with higher SWCNT levels as well as replacing the insulating additives, e.g. EC, in the ink with other removable additives, e.g. ethylene glycol, to improve the electrical properties of the resulting CLCs. Also, an investigation is intended to develop a concept for structural health monitoring of GFRP laminates based on the obtained electrical and mechanical properties of the resulting nanocomposite.

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