

2nd CIRP Conference on Composite Material Parts Manufacturing (CIRP-CCMPM 2019)

# The effect of type of mechanical processing on electrical conductivity and piezoresistive response of CNT and graphite composites

Matthew Collinson<sup>a\*</sup>, Simon Hayes<sup>b</sup>, Stefanos Petropoulos<sup>a</sup>

<sup>a</sup>Advanced Manufacturing Research Centre, Advanced Manufacturing Park, Wallis Way, Catcliffe, Rotherham, S60 5TZ

<sup>b</sup>Department of Multidisciplinary Engineering Education, The University Of Sheffield, 32 Leavygreave Road, Sheffield, S3 7RD

\* Corresponding author. Tel.: +44 (0)144-215-8032. E-mail address: [m.collinson@amrc.co.uk](mailto:m.collinson@amrc.co.uk)

## Abstract

Nanocomposite materials are attracting significant interest as matrices for conventional composite materials, where their increased electrical conductivity present the possibility of multi-functional properties, such as embedded heating and electromagnetic shielding. One problem facing the increased use of the nanocomposites is their rapid and efficient production. Three different mixing methods: 3-roll mill, shear mixing and hand mixing were tested to mix carbon nanotubes (CNTs) and graphite into epoxy resin. The electrical conductivity and piezoresistive response of the resulting nanocomposites were measured and compared to the relative rate of nanocomposite could be produced. Maximisation of the functional properties is important, but speed of throughput is also essential, thus enabling larger and production ready components to take advantage of the additional functionality. Because of health and safety concerns during material handling of nanoparticles, this study employed a premixed CNT masterbatch (Arkema) and graphite powders (Superior Graphite), as these do not require specialised health and safety equipment to process, making industrial application more viable. It was found that the 3-roll provided the largest increase in conductivity out of the three mixing methods, and hand mixing and shear mixing performed similarly. Piezoresistivity was seen in all modified samples, however gauge factors were difficult to determine due to underdeveloped sample contact and preparation methods.

© 2020 The Authors. Published by Elsevier B.V.

This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>)

Peer-review under responsibility of the scientific committee of the 2nd CIRP Conference on Composite Material Parts Manufacturing.

*Keywords:* composites; nanocomposites; CNT; carbon nanotubes; graphite; piezoresistive; conductivity; 3-roll mill; shear mixing

## 1. Introduction

Nanocomposites, the combination of a polymer matrix and a nanoscale reinforcement, have attracted significant research interest, particularly with the increased commercial availability of carbon-based nanostructures such as carbon nanotubes, graphene and graphite. Combining polymer matrices such as thermoplastics or epoxy resins, which are all electrically insulating, with these nanofillers has shown increased material properties. In particular fracture toughness and thermal conductivity, and also enhancing the material with new properties, such as conductivity and piezoresistance. The realisation of these properties allows for exciting developments in design of composite materials, in particular, multifunctional

composites. These include, but are not limited to: piezoresistive sensors, antistatic protection, localised joule effect heating and increased heat dispersion, meaning extra external devices on the part are not required.

Benefits like these are of interest to the aerospace and automotive industries, where light weighting is of significant importance due to legislation limiting emissions, which leads to reducing fuel usage, resulting in increased profitability.

Manufacturing of nanocomposites is a difficult process for most standard composite part manufacturers. Unprocessed carbon nanotubes and graphene need functionalisation, which is the enabling chemical compatibility between the filler and the matrix. This requires a strong knowledge of the nanofillers and the resin, as well as specialised chemical processes. These

nanoparticles also in their raw form require strict and costly health and safety controls, due to their comparison to asbestos and potential carcinogenic nature [1].

Once these issues are resolved, for nanocomposites to be effectively integrated into a component to enable smart functionalities, they need to be able to be processed using a medium to high throughput processes. Many previous studies have used a variety of mixing and dispersion methods, such as sonication [2], solvent evaporation [3], ball milling, dissolver disk mixing [4], shear mixing and 3-roll mill [5]. These all have varying levels of success at dispersing the nanoparticles evenly in a matrix, but have not been considered for manufacture beyond laboratory scale. Whilst it is important to obtain a high level of dispersion and therefore improvements in material properties, in this case primarily electrical conductivity, the ability to manufacture at a higher rate needs to be taken into account.

For this study, processability and practicality have been prioritised, from the material selection to the equipment used to manufacture the nanocomposites, in view to manufacture fibre based composites in the future. This means that conductivity vs filler content needs to be scrutinised, as manufacturing a composite with a high percentage of nanofillers is difficult due to the filtering effect when infusing. This can be alleviated with different manufacturing techniques such as pre-pregging, however are costly and prohibitive in a development environment, and also not relevant to industries such as automotive. Keeping the nanofiller weight percentage low will allow for the resin to retain its low viscosity, whilst having fewer nanoparticles to be filtered out when manufacturing along the length larger scale fibre composites.

The materials selected are either pre-functionalised in a DGEBA-CNT masterbatch (Arkema), or do not require any functionalisation, namely super expanded graphite flake (Superior Graphite) which will be mixed directly into resin. The CNTs used are Multi Walled CNTs, having 10-15 walls of 10-15nm in diameter, with an aspect ratio of 600-700. The graphite used is a super expanded graphite flake, with 90% of the particles being 17.6µm or smaller.

The mixing methods have been selected based on effectiveness, market availability, time to process and cost. The 3-roll mill was selected as it was a recommended method by the CNT masterbatch manufacturer (Arkema) as the optimal dispersion method and therefore the method has also been replicated for graphite. Another industrial method suggested by the literature and the manufacturer is a high shear mixer, which is seen more commonly in industry for efficient mixing and dispersion of solutions. The final method used in this study is hand mixing of the materials into the resin, which is used as a low effort comparative baseline, to show what conductivity can be achieved with little equipment expenditure.

CNTs were primarily investigated in this study due to their higher conductivity to weight ratio compared to graphite, and therefore more dispersions at different percentages were manufactured. Future consideration needs to be taken into account when these nanocomposites are to be used as matrices in fibre composites, where it is important that low as possible percentages of filler are used so that they can be infused and distributed between fibres evenly. When high percentages of

larger particles are used, filtration occurs between and through fibres when infusing along a fabric, and on a smaller scale, through thickness, which leads to uneven distribution, and inhomogeneous material properties [6]. Another reason to use lower percentage weight of nanoparticles is to limit the change in mechanical properties, whilst they are commonly reported as an increase, in some cases they can reduce some mechanical properties.

The piezoresistive mechanism of these nanocomposites is a complex one and not yet fully understood. It is known that there is high contact resistance between the nanoparticles in the polymer matrix, also known as the tunneling effect, of which when strained increases this contact resistance. This tunneling effect is influenced by the makeup of the internal percolation conductive network, such as weight % loading, particle conductivity, cross sectional area and particle alignment [7].

## 2. Experimental

### 2.1. Resin preparation and dispersion method

An toughened epoxy system (Gurit Prime 180 [8]) suitable for RTM and infusion was selected as the matrix for the nanocomposites, due to its low ambient viscosity and overall high processability. Two types of nanocomposites were manufactured, at different percentage loadings, to evaluate conductivity and piezoresistivity depending on the dispersion method used. The base materials for the two mixtures were MWCNTs pre-dispersed at 25% by weight in a DGEBA resin, supplied by Arkema (CS1-25), and super expanded graphite flake, supplied by Superior Graphite (FormulaBT LBG8010).

The CNT masterbatch requires mixing and coarsely dispersing into the resin, before any further mechanical mixing or processing. This was done by hand mixing the pellet style masterbatch into the resin at 80 °C, leaving overnight at temperature, then mixing by hand periodically until the pellets had visibly dispersed into the resin. CNT samples were prepared at 0.1, 0.25, 0.5, 0.75 and 1% by weight, recommended by the manufacturer and previous studies on MWCNTs [9].

The graphite nanocomposites were processed in a similar way, with the graphite being hand mixed in, then left overnight and mixed periodically until visible dispersion had been achieved. Graphite samples were prepared at 5.3% and 6.5% by weight [10].

Table 1 : Summary of materials used, processing method and weight percentages tested.

Material	Processing method	Wt. %
CNT	Shear mixed	0.1, 0.25, 0.5, 0.75 and 1%
	3-Roll milled	
	Hand mixed	
Graphite	Shear mixed	
	3-Roll milled	5.3% and 6.5%
	Hand mixed	

A batch of 500 ml resin and filler was prepared for each dispersion and mixing type, then the mixtures were dispersed further in the three different ways (Table 1). All these processes

were completed with the resin at 80 °C at the start of the mixing processes.

A 3-Roll mill (Exakt) was used to then further disperse the fillers into the resin. The resins were processed twice, from 90 microns to 30, and then from 15 to 5 microns, which was the minimum gap possible with this equipment.

Shear mixing (Greaves) was used on the pre-mixed batches at 1500 RPM for 60 minutes, using a stator mixer head.

Hand mixing was completed as per the preparation for the two mechanical dispersion methods. Heating was instead completed on a hotplate, and hand mixing was done for 30 minutes continuously, ensuring that the pellets were dispersed in the case of the CNTs

## 2.2. Sample manufacture

Once the nanocomposite blends had been prepared, hardener was added at 50% of the original resin weight used, which was mechanically mixed in with a stirrer. Immediately after stirring they were cast in dog bone style silicone moulds, at 6 casts per sample, with the sample geometry conforming to ASTM D638 [11], and placed in a curing oven at 120 °C. Particularly in the case of the CNTs, agglomeration starts immediately, which can reduce the electrical and mechanical properties of the samples. Some agglomeration is required so that a connected electrical network is made, however if allowed to develop further, the agglomerations become so large that the electrical network is lost. This is further discussed in Section 0. After curing, the meniscus of the samples was removed using a water assisted polishing wheel, which also ensured correct sample thickness was achieved.

## 2.3. Measurement of conductivity

The 4-probe resistivity method was used, which has previously been used successfully to measure conductivity of composites and nanocomposites accurately. This method can be practically applied in a composite part design situation as it doesn't require significant design changes to the composite [12].

The polishing of the samples during manufacture also provided adequate surface preparation for applying highly loaded silver epoxy adhesive (RS Components). This ensured contact resistance was minimized during conductance and piezoresistance testing. A National Instruments PXI 4080 digital multimeter was used for the 4 point conductivity measurement, which was recorded values every 100 ms during the piezoresistive testing. Resistance was automatically calculated by the National Instruments drivers, with using a current injection value depending on the resistance of the sample being tested. This allowed a large range of sample conductivities can be accounted for, whilst still providing accurate resistivity values.

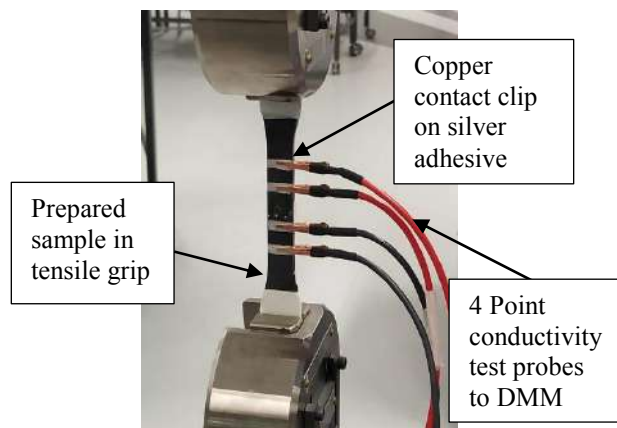


Fig. 1. Experimental setup for piezoresistive testing of dog bone samples, with the 4-point method attached to the sample whilst in the grips of the tensile testing machine.

The resistance value is then corrected for cross section of the sample, and the length between the electrodes for measuring voltage, seen in Equation 1.

$$R = \frac{V}{I} \frac{wt}{L} \Omega.cm \quad (1)$$

Where  $V$  is voltage,  $I$  is current,  $w$  &  $t$  are width and thickness of the sample, and  $L$  is the distance between the electrodes for measuring voltage.

Flat, crocodile style clips were used to clamp onto the sample, with the side not prepared with silver epoxy being insulated from the clip, of which can be seen in Fig.1. The sample was insulated from the tensile test clamp to ensure no electrical interference.

Piezoresistance is a change in a materials resistance in response to mechanical strain. Gauge factor (GF) is a way of quantifying this response, as seen in the equation below.

$$GF = \frac{\Delta R/R_0}{\epsilon} \quad (2)$$

Where  $R$  is the resistance of the sample,  $\Delta R$  is the change in resistance and  $\epsilon$  is the strain of the sample. This allows for characterisation of the response of the material, depending on the sample tested. If a material's conductivity change can be measured in service, and the gauge factor is known, then the strain can be estimated.

## 2.4. Measurement of strain

Tensile testing was completed with a Shimadzu EZ Test machine, run at 2 mm/min as per the ASTM specification.

Machine compliance was tested using an unloaded epoxy sample with a strain gauge applied. Clip gauges were tested as a possible re-usable strain sensor, however these short circuited the resistance measurement and proved unreliable when insulated, hence the use of calibrated machine measured strain.

Strain was therefore assumed to be the change in length of the sample against the original length of the sample, as described in Equation 3 below.

$$\varepsilon = \frac{l_T - l_0}{l_0} \quad (3)$$

Where  $\varepsilon$  is strain,  $l$  is the length of the unloaded sample, and  $\delta l$  is the change in length in respect to the unloaded sample. These restrictions will mean that sample slippage in the grips will not be accounted for, which would be if a strain gauge was used for example.

### 3. Results and discussion

#### 3.1. Manufacturing observations and considerations

As seen in previous studies [13] and in practice, the manufacture of high quality dog bone samples in epoxy resin is a challenging process. Issues included manufacturing a void free sample, with defect free edges, without a meniscus, which could lead to premature sample failure. In unmodified epoxy samples, voids were visible, however in modified opaque samples, potential voids were no longer visible, particularly in highly loaded samples. For the opaque samples, manufacturing methods were improved where the voids were visible, then were eventually eliminated through improvements in procedure.

The polishing of the samples also proved to have the benefits of removing the meniscus, bringing the thickness of the samples to specification, and providing repeatable surface preparation conditions for the application of the silver epoxy adhesive.

#### 3.2. Sample conductivity

Of all the samples, the 3-roll mill proved to be a more consistent dispersion method compared to the shear mixer and the hand mixing for CNT composites, providing higher conductivities at equivalent percentage loading of fillers, summarised in Table 2 and Fig.2. Not enough data was collected to determine if this effect was experienced in the graphite mixtures, with little variance in conductivity between the manufacturing methods. Shear mixing did not provide an increase in conductivity over hand mixing in CNT samples, which would have been expected for it being a high shear process. With all mixing methods the percolation threshold was 0.25-0.5% for CNTs, with this being much closer to 0.25% for the 3-roll mill processed samples. It wasn't possible to

determine the percolation threshold for the graphite nanocomposites with the data available.

The CNT masterbatch requires high shear forces to break up the pellets and coarsely disperse into the resin, whereas it appears the graphite in powder forms require only basic mixing to disperse effectively. This is highlighted when comparing the increase in conductivity from hand mixed to the 3-roll mill for both fillers: CNTs have a large increase, whereas graphite powders do not change.

The increases between mixing methods for the CNTs may be due to the heavily loaded masterbatch requiring high shear to be broken apart properly, which the shear mixer cannot provide. Another reason, suggested by the manufacturer, is that shear mixing can on occasion damage the CNTs, breaking the walls or making them shorter. This would damage the connections within a percolation network, however there is little evidence of this in any previous studies that suggest that shear mixing doesn't have the energy density to damage CNTs [14].

Another reason for the lower conductivity of the shear mixed samples could be due to the way that the mixer head sits in a batch of epoxy-nanoparticle mixture. With this configuration, it is not always guaranteed that all the resin is processed evenly, or is passed through the mixer head an equal amount of time. Full processing of the mixture is more guaranteed with a 3-roll mill, which would be more suitable for a continuous process.

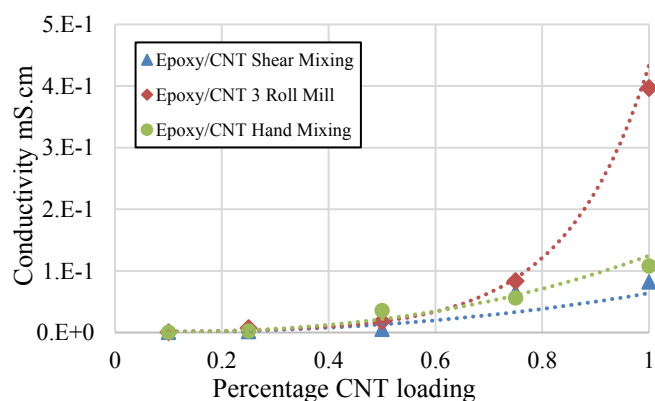


Fig. 2. Conductivity of the CNT dispersions, comparing 3-roll mill to shear mixing and hand mixing.

Table 2 : Mean conductivities for CNT and graphite, for hand mixing, shear mixing and 3-roll mill

Material & loading wt. %	Conductivity 3-roll mill mS.cm	SD	Conductivity shear mixing mS.cm	SD	Conductivity hand mixing mS.cm	SD
0.1% CNT	7.71E-04	±4.57E-04	5.85E-04	±4.00E-04	2.29E-04	±1.11E-04
0.25% CNT	7.51E-03	±1.29E-03	1.48E-03	±5.19E-04	2.66E-03	±2.52E-03
0.5% CNT	1.82E-02	±8.53E-03	5.44E-03	±3.02E-03	3.60E-02	±7.71E-03
0.75% CNT	8.35E-02	±7.11E-03	6.62E-02	±3.64E-03	5.61E-02	±1.42E-02
1% CNT	3.97E-01	±3.62E-02	8.21E-02	±8.61E-03	1.08E-01	±4.40E-02
5.3% Graphite	8.75E-04	±1.86E-05	9.19E-04	±1.36E-04	1.25E-01	±2.19E-02
7.5% Graphite	1.66E-03	±6.02E-04	2.41E-03	±1.41E-03	3.09E-01	±3.85E-03

Re-agglomeration of the nanoparticles is a crucial process that occurs enabling the conductivity of samples. A theoretically 100% distributed epoxy-particle mixture would result in no particles touching one another, which would give a homogeneous mixture, however would give the mixture electrical conductivity equivalent of the matrix, resulting in an insulator. Van der Waals forces are present between the conductive particles, leading to the particles to bunch together in groups, also known as agglomeration. The interaction of these particles leads to the conductivity of the resin increasing due to the percolation network growing, allowing more paths for the current to flow.

The agglomeration of the particles is something that continues to happen over time, leading to larger agglomerates. If left over a long period, the agglomerates continue to increase in size up to the point they become large enough so the percolation network becomes disconnected. The agglomerates no longer have links between them, therefore the conductivity is reduced, leading to a similar problem to perfectly distributed particles.

Agglomeration of CNTs in epoxy resin was investigated by Inam and Peijs [15], looking at average agglomerate size over time in epoxy resin, hardener and after mixture of the two. Agglomeration size stays low over time when mixed with just the epoxy for all variations of CNTs. Once CNTs were mixed with hardener, they agglomerated very quickly, leading to agglomerations four times larger than was observed in the epoxy after 200 minutes. This is in line with many studies that explicitly initially always mix the CNTs with the resin as opposed to the hardener component, and with what was observed by the naked eye in this study (Fig.3). CNT-Epoxy mixture was stored for days with no visual agglomerations, whereas when mixed with the hardener, agglomerations were visible if left to cure at room temperature, seen in Fig.3.

Agglomeration of the graphites were not seen visually, most likely due to the larger particle size, of which Van der Waals forces do not affect in the same way. This is also confirmed by the little difference in conductivities between mixing methods. This effect may have been further helped by the low viscosity of the resin used in this study, which would have enabled accelerated movement of particles, and therefore quicker agglomeration.



Fig. 3. Example of extreme visual CNT agglomeration in epoxy resin at 0.5% wt.

### 3.3. Sample piezoresistivity

All the epoxy samples that were modified with either CNTs or graphite showed a piezoresistive response. All graphite samples had a higher gauge factor than the CNT samples, however when corrected for their higher loading percentages, the loading efficiency was lower than the CNTs. When correcting for the wt.% loading of the filler in each sample, it appears that the lower the CNT loading, the more efficient the gauge factor response is.

One of the largest factors in obtaining a good quality piezoresistive signal was the quality of the connection between the DMM and the sample, with clip connectors seen in Fig.1. Poor connections and electrical interference from the conducting grips on the tensile testing machine led to noisy results, which were inconclusive. Tighter grips and insulating the part from the grips led to more consistent results, of which an example can be seen in Fig.4. These responses were consistently in line with the axial strain when normalised. The change in resistance and the axial stress were normalised in respect to axial strain, of which the response of the resistance change is directly related to the stress. Whilst there were only a few of these samples that showed this positive response, showing good replication of the samples, the overall method had poor repeatability.

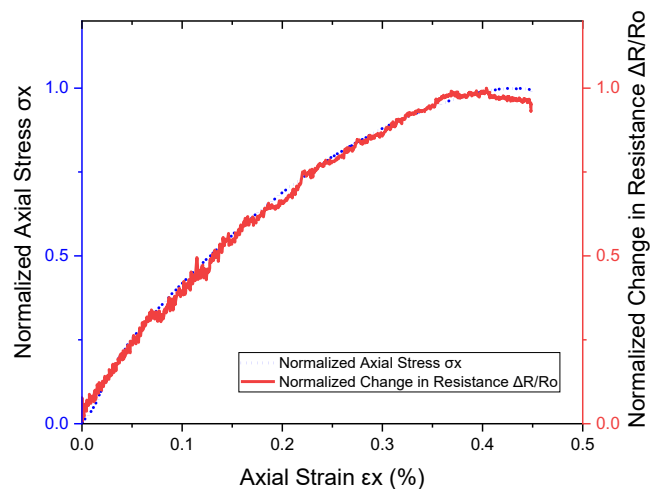


Fig. 4. Example of a piezoresistive response from a 0.25% by wt. CNT epoxy sample processed in the 3-roll mill.

Gauge factor was determined for each concentration and manufacturing method, which ranged from 0.5 to 3.1 for CNT composites, and from 7.8 to 33.4 for graphite composites, as summarised in Table 3.

Even though there were 6 samples manufactured per method and concentration, there were only one or two good results per set. This led to large variability and inconsistency in the results, which have been presented in Table 3. Where results aren't presented, it wasn't possible to get a piezoresistive response.

Table 3 : Mean gauge factors for all samples tested.

Material & loading	Gauge factor 3-roll mill	Gauge factor shear mixing	Gauge factor hand mixing
0.1% CNT	0.49	N/A	N/A
0.25% CNT	2.85	1.37	1.10
0.5% CNT	3.09	0.72	2.10
0.75% CNT	2.39	2.62	1.88
1% CNT	0.89	2.94	1.87
5.3% Graphite	7.84	8.81	13.6
7.5% Graphite	27.75	33.39	7.40

For the graphite samples, an increase in gauge factor was seen in the mechanically mixed samples when loading was increased, however this same pattern did not occur for the hand mixed samples. It seems that when using high shear mixing methods on the graphite samples, the gauge factors are similar, however see a large change, for better or worse when hand mixing is used. This may be due to lack of consistency of the hand mixing method, of which is significantly less controlled than the mechanical mixing methods.

The noise issues and variances in gauge factor may have also been affected by the resistivity and therefore gauge factor of the connection method, which could have dominated the response. Whilst attempts to reduce contact resistance were taken, it is possible that the negative gauge factors of the contacts were interfering with the results. This is more frequently seen in the measurement of CFRP piezoresistive samples [16], but still could be possible in the testing completed here.

It would be recommended to directly bond on the wires to the samples with conductive adhesive, rather than using clips, to ensure that the connection is more repeatable and consistent. On in service parts, the connectors are likely to be integrated into the part during manufacture and therefore be more durable, however there is limited research in this area and therefore wasn't pursued during this study.

The responses and gauge factors seen in the samples allows for potential composite smart functionalities, if these resins were to be integrated into or applied to the surface of composites. The gauge factors seen in this study would allow for smart sensors, replacing strain gauges at low cost, where typically a gauge factor of a Constantan or nickel-chromium strain gauge is around 2 [17]. The quality of the response, when a good connection was available was high, giving a very consistent and high quality response, comparable to a strain gauge. This case, and other investigations on nanocomposites consistently get within this gauge factor range [18]. This could allow lower cost and less sensitive equipment to detect strain, and eventually damage in composites, without having to apply a strain gauge to the structure, which is a time consuming and expensive operation.

Consistency of the measuring of composite samples is still an issue, of which a standard test method needs to be developed and agreed upon. Even when taking in to account recommendations from previous studies, it is still a challenge

to get consistent contact resistance when applying electrodes to a sample.

### 3.4. Manufacturing rate

3-Roll mill, high shear mixing and hand mixing were selected as mixing methods as they vary largely in initial cost, ease of use and processing time. 3-roll mill and shear mixing are commonly used techniques for particle dispersion in mixtures, with hand mixing used as example of minimum effort and cost of what can be achieved.

To compare the methods, literature was examined to ensure the highest level of dispersion was achieved using each method, taking into account the low viscosity resin being used, as described in section 2.1.

The 3-roll mill was the most time consuming and hands on method for dispersion, as the resin mixture has to be fed through slowly, and requires careful cleanup after use. To feed through 500 ml of resin containing fillers takes around 20 minutes, which increases in duration as the gap between the rollers is reduced. This process has to be repeated more than once and requires user supervision throughout. The pouring of the resin from old containers to new, to not contaminate samples, leads to resin waste, as does resin that is stuck on rollers and not processed. This process could be adapted to be run continuously, which would not require cleaning as often, and would reduce wastage.

High shear mixing is easier to run when working with batches, as the mixture can be left to run without supervision. The samples for this study were mixed for 60 minutes, but were left unsupervised during this time, making it more suitable as an industrial process. Mixers of this type are also available that convert the method from a batch process to a continuous one.

Hand mixing was the most simple, however most labour intensive, and operator dependent on the final dispersion. In small batches this method is a useful comparison, but unlike the other methods, it isn't suitable for scaling up to large manufacturing rates.

In the case of the CNTs, the high shear methods were the only ones that provided the higher conductivities and therefore more even distribution. This is partly due to the highly loaded masterbatch format they are provided in, requiring force and heat to break them apart.

Graphite mixtures did not benefit from the mechanical dispersion methods as shown by the conductivities seen in Table 2.

### 3.5. Future use cases

With all the research activity around nanocomposites, particularly around their benefits to increasing material properties, it is important to know how to process and test the resulting nanocomposites to ensure that they are being manufactured optimally and obtaining the expected final properties. This study was completed to understand these dispersion methods and the factors that affect the final

conductivities of the samples, particularly the interface method between the sensing equipment and the nanocomposites.

Being able to measure the conductivity and piezoresistivity of a composite, or nanocomposite accurately opens up opportunities for multifunctional composites, beyond a structural material. The primary additional function would be integrated structural health monitoring (SHM) systems, being able measure strain in a structure, as well as impact damages. Other uses for conductive composites could be for other electrical interfaces, such as effective static dissipation and joule heating applications such as direct electric cure.

#### 4. Conclusion

The processing and mixing methods of fillers in epoxies are critical to getting the required performance, in this case electrical conductivity, and subsequently piezoresistivity. CNT-epoxy composites had higher conductivities compared to graphite-epoxy composites for a much higher loading content. Significantly higher conductivities were found when mixing in CNT masterbatch when using the 3-roll mill, compared to the shear mixer and hand mixing, which performed similarly.

Piezoresistivity was found in all composite samples, with there being no significant change in gauge factor between manufacturing methods and loading percentage.

Measuring conductivity whilst loading the sample proved difficult, with signals dropping out, and giving consistently different gauge factors within the same set of samples, even when conductive paint and copper clips were used to achieve a high conductivity connection. More research is required to enable consistent piezoresistive testing, so that studies can be compared more easily, and results within studies are more consistent.

This study has shown that it is possible to manufacture and process nanoparticle modified resins with high conductivities, without requiring high expenditure equipment or health and safety controls or processes, enabling more accessible research and product development into multifunctional materials.

#### 5. Acknowledgements

This work was funded by the European Union's Horizon 2020 research programme under grant agreement No 760940, under the project titled MASTRO.

#### References

- [1] C.A. Poland, et al., Carbon nanotubes introduced into the abdominal cavity of mice show asbestos-like pathogenicity in a pilot study, *Nat. Nanotechnol.* 3 (2008) 423–428. doi:10.1038/nnano.2008.111.
- [2] P.C. Ma, et al., Dispersion, interfacial interaction and re-agglomeration of functionalized carbon nanotubes in epoxy composites, *Carbon N. Y.* 48 (2010) 1824–1834. doi:10.1016/j.carbon.2010.01.028.
- [3] S. Kim, et al., Assessment of carbon nanotube dispersion and mechanical property of epoxy nanocomposites by curing reaction heat measurement, *J. Reinf. Plast. Compos.* 35 (2016) 71–80. doi:10.1177/0731684415613704.
- [4] J.K.W. Sandler, et al., Ultra-low electrical percolation threshold in carbon-nanotube-epoxy composites, *Polymer (Guildf).* 44 (2003) 5893–5899. doi:10.1016/S0032-3861(03)00539-1.
- [5] I.D. Rosca, S. V. Hoa, Highly conductive multiwall carbon nanotube and epoxy composites produced by three-roll milling, *Carbon N. Y.* 47 (2009) 1958–1968. doi:10.1016/j.carbon.2009.03.039.
- [6] S.G. Miller, et al., Mionitoring nanoparticle filtration in a RTM processed epoxy/carbon fiber composite, 2011. <https://ntrs.nasa.gov/search.jsp?R=20110014529> (accessed June 27, 2019).
- [7] Alamus, et al., Piezoresistive strain sensors made from carbon nanotubes based polymer nanocomposites, *Sensors.* 11 (2011) 10691–10723. doi:10.3390/s111110691.
- [8] G.H. AG, Prime™ 180, (n.d.) 1–4. [http://www.gurit.com/-/media/Gurit/Datasheets/PRIME\\_180.pdf](http://www.gurit.com/-/media/Gurit/Datasheets/PRIME_180.pdf).
- [9] R. Khare, S. Bose, Carbon nanotube-based composites - A Review, *J. Miner. Mater. Charact. Eng.* 4 (2005) 31–46. doi:10.1016/B978-0-12-803581-8.10313-3.
- [10] S. Gantayat, et al., Expanded graphite as a filler for epoxy matrix composites to improve their thermal, mechanical and electrical properties, *New Carbon Mater.* 30 (2015) 432–437. doi:10.1016/S1872-5805(15)60200-1.
- [11] ASTM D638, Standard test method for tensile properties of plastics, *ASTM Int.* 08 (2015) 46–58. doi:10.1520/D0638-14.1.
- [12] K.T. Ilkardaslar, F. Delale, Self-sensing damage in CNT infused epoxy panels with and without glass-fibre reinforcement, *Strain.* 54 (2018). doi:10.1111/str.12268.
- [13] T.T. Chiao, et al., Fabrication and testing of epoxide resin tensile specimens, *Composites.* 3 (1972) 10–15. doi:10.1016/0010-4361(72)90465-X.
- [14] Y.Y. Huang, et al., Dispersion of Carbon Nanotubes: Mixing, Sonication, Stabilization, and Composite Properties, *Polymers (Basel).* 4 (2012) 275–295. doi:10.3390/polym4010275.
- [15] F. Inam, T. Peijs, Re-agglomeration of Carbon nanotubes in two-part epoxy system ; Influence of the concentration, 2007. [http://nrl.northumbria.ac.uk/12712/1/IBCAST\\_Proc.\\_May\\_2007.pdf](http://nrl.northumbria.ac.uk/12712/1/IBCAST_Proc._May_2007.pdf) (accessed August 14, 2018).
- [16] G. Georgousis, et al., Piezoresistivity of conductive polymer nanocomposites: Experiment and modeling, *J. Reinf. Plast. Compos.* 37 (2018) 1085–1098. doi:10.1177/0731684418783051.
- [17] A. Technologies, Practical Strain Gage Measurements, 1999. [https://www.omega.co.uk/techref/pdf/StrainGage\\_Measurement.pdf](https://www.omega.co.uk/techref/pdf/StrainGage_Measurement.pdf) (accessed June 11, 2019).
- [18] A. Sanli, et al., Piezoresistive performance characterization of strain sensitive multi-walled carbon nanotube-epoxy nanocomposites, *Sensors Actuators A Phys.* 254 (2017) 61–68. doi:10.1016/j.sna.2016.12.011.