

Measurement Note

NPL Report MN 10

An Introduction to the Properties of Carbon Nano-Particle Enhanced Polymers

This Measurement Note introduces and quantifies the enhancement obtained in electrical properties from nano-particle modification of polymers, for both thermosets (epoxy) and thermoplastics (polypropylene and PEEK). The nano-particles considered are nanoscale carbon-based fillers such as single walled carbon nanotubes (SWNTs), multiwalled carbon nanotubes (MWNTs) and carbon black (CB). A greater emphasis is given to MWNTs by researchers, as they are currently less costly and more easily mass produced than SWNTs. Prices in 2010 indicate that MWNT produced at industrial scale are ~£10/g compared to ~£100/g for SWNTs¹.

Data are presented for both major types of matrices showing the effect of the incorporation of carbon nano-particles. The effect of particle type, size, content loading, etc. is reviewed through published data on electrical properties. In addition to the change in electrical properties, the concurrent changes in other properties (e.g. mechanical, thermal and rheological) are documented.

It was not possible to assess the quality of the data as little evidence was given in the references cited regarding the use of standard test methods and calibrated equipment. In addition, the materials were not fully or well characterised. This lack of characterisation is partly due the absence of the accurate measurement of the degree of dispersion, which is shown to have a crucial effect on the degree of property enhancement achieved. It is particularly noted that different properties are obtained from small volumes compounded, as used in research projects, and larger amounts typical of industrial production.

The HiPerNano interest group of the Nanotechnology KTN has supported the production of this Measurement Note, which is presented in a Question and Answer format.

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June 2010

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ISSN 1754-3002

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(mechanical, thermal, rheological)

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4. SUMMARY

1. CARBON NANOPARTICLES

What are the basic electrical properties of these particles?

The following table shows a three to four orders of magnitude increase in electrical conductivity of carbon nanotubes (CNTs) as compared to a conventional filler, carbon black (CB)^{2, 3}. As CNTs are one-dimensional tubes, assuming maximum crystallinity and purity they are ballistic conductors, where electrons are not scattered and can travel at relativistic speeds for a single CNT.

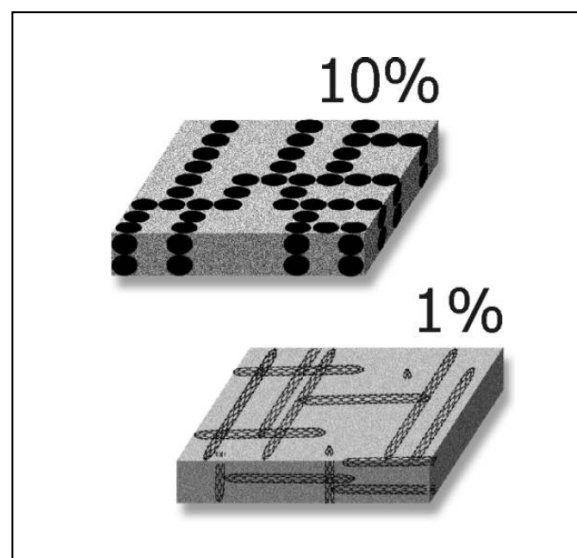
Table of properties^{4, 5, 6, 7, 8}

	Conductivity (ohm-cm)⁻¹
CNT	$2 \times 10^4 - 2 \times 10^5$
CB	$10^{-1} - 10^2$
	Thermal conductivity
CNT	3000 - 6600 W/mK
CB	4mW/mK - 1 W/mK
	Sizes
CNT	Length: 50 nm - 10 μ m Diameter: 0.3 nm - 100 nm
CB	Diameter 20 nm - 100 nm

How much carbon is needed?

The amount of carbon used depends on obtaining the extensive change in properties that occurs when percolation is achieved. That is, a network of connections is established that gives a major change in properties. Generally for both thermoplastics and thermosets, a larger amount of carbon black (CB) is required as compared to CNTs to make a fully electrical percolating path⁹. As shown in the figure below, a larger amount of circular carbon black particles are needed

compared to the carbon nanotubes in the lower schematic.



Care must be taken in whether data are quoted as a function of weight percent or volume percent. Weight is normally used in purchasing CNTs and in controlling production. Whereas, for understanding and modelling the properties the volume of CNTs incorporated is more appropriate.

As data are published against both weight and volume percent, care must be taken when reviewing and comparing published data.

Note on Annealing:

Thermal annealing may improve the conductivity of such composites by several orders of magnitude. This is due to rearrangement of the molecules into more ordered states, allowing for better charge carrier transport¹⁰.

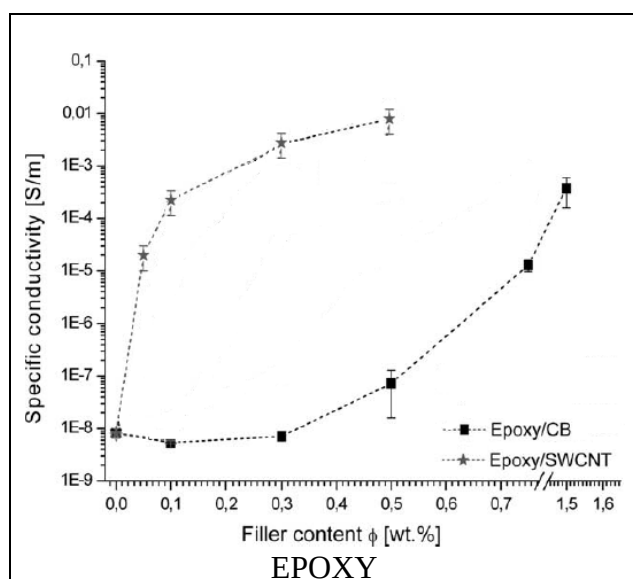
2. ELECTRICAL PROPERTIES

2.1 Thermosets – Epoxy

Do nanoparticles have a greater effect than other particles?

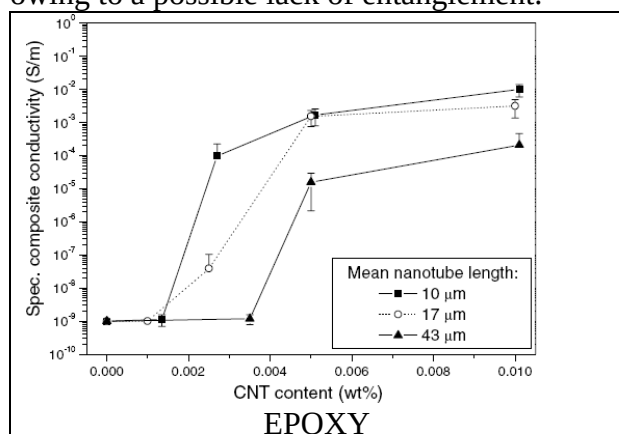
Yes. Even though the ballistic properties are lost due to integration in an amorphous to semi-crystalline polymer matrix, extensive quantum tunnelling through the high aspect ratio (100-1000 $\times$) CNT network allows for a lower percolation threshold. Conductivities

are also up to six orders of magnitude greater, as shown in the figure below ¹¹.



Does the length of carbon nanotubes have an effect?

Yes. The figure below shows that the longer the CNT length, the lower the conductivity and the higher the percolation threshold. This could be due to CNT entanglement at longer lengths ¹². It must be noted that CNT lengths can range between nanometres to millimetres, so that 10µm CNTs are already quite long. Further tests carried out with much shorter CNTs might show the opposite behaviour owing to a possible lack of entanglement.

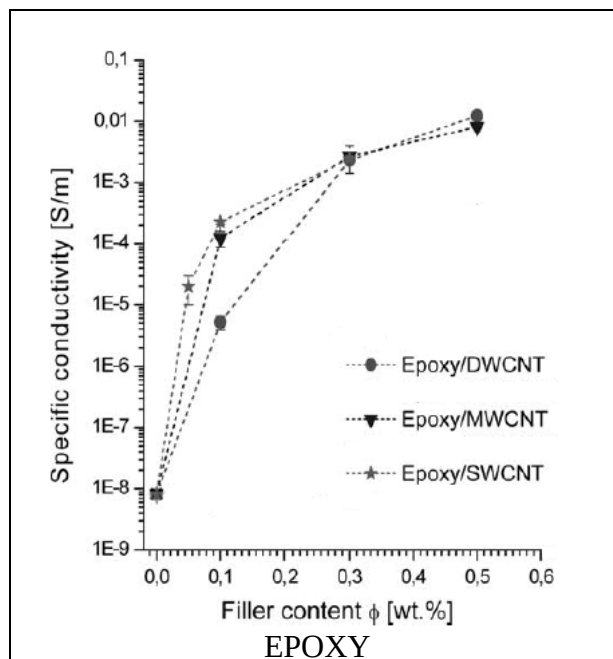


Note: Papers finding the opposite trend have been published.

What effect does the type of carbon nanotubes have?

Different types of CNTs can vary significantly in their electrical properties. SWNTs are generally 2/3rd semiconducting, with the remaining metallic. MWNTs are generally metallic, although conductivity may be diminished by interfering internal CNT walls

¹⁰. The figure below shows the improved effect of conductivity that SWNTs have over MWNTs and double walled nanotubes (DWNTs) ¹¹.

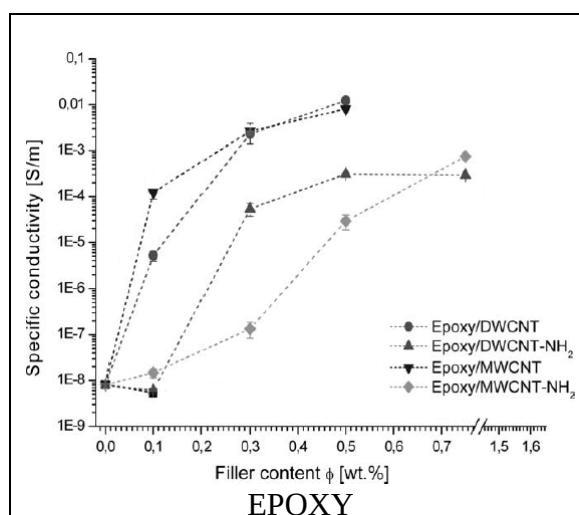


Note 1: The CNTs did not all have exactly the same length i.e. multi-walled (MWNT) 5x length of single walled (SWNT) and double (DWNT) walled.

Note 2: These percolation curves are very close to each other and change in order depending on whether one considers wt% or vol% of CNTs ¹¹.

Does the treatment (functionalisation) of the carbon nanotubes have an effect?

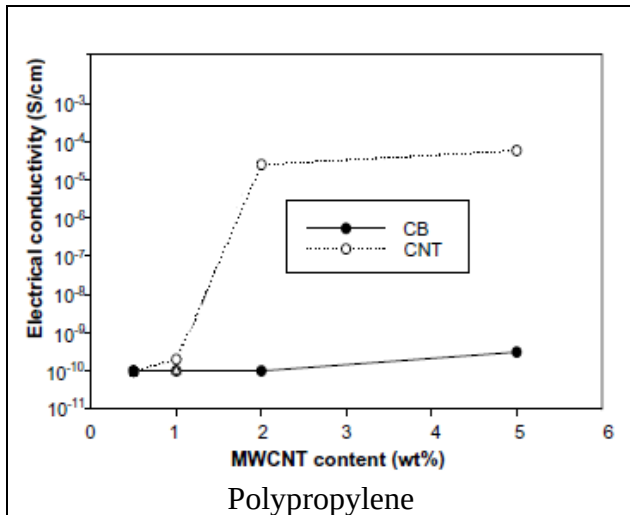
Yes. The functionalisation of CNTs has a detrimental effect as functional groups act as scattering sites for electrons. The following figure shows the decrease in conductivity and an increase in percolation threshold with the functionalisation by a typical additive, the amino group NH_2 ¹¹.



2.2 Thermoplastics – PP and PEEK

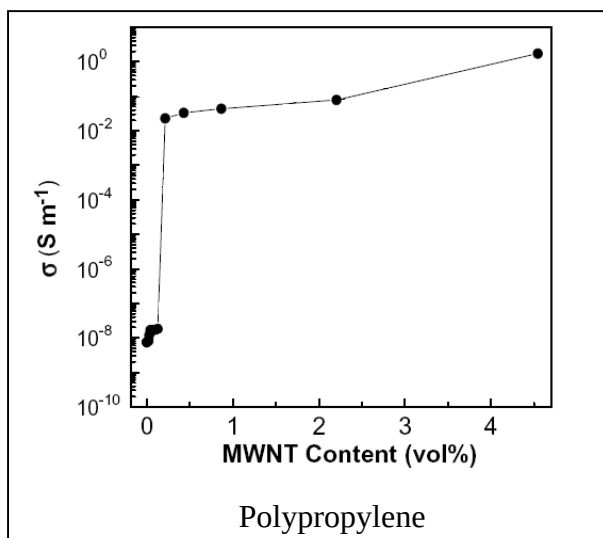
Do nanoparticles have a greater effect than other particles?

The figure below shows the percolation behaviour of MWNTs in Polypropylene (PP) as compared to CB^{10,13}.



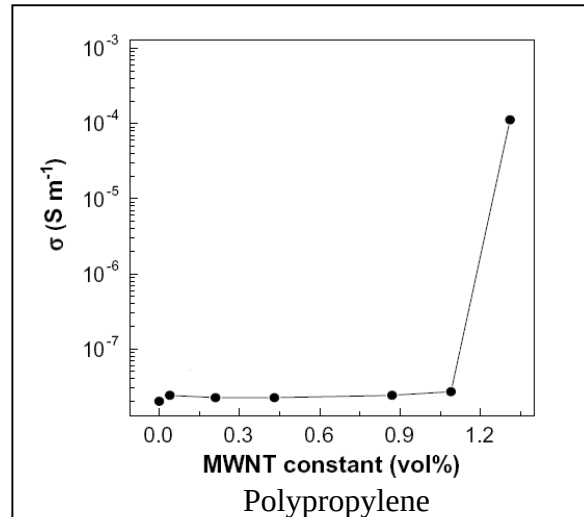
What effect does the processing method have on CNT-composites?

PP/MWNT nanocomposites prepared at high shear rates exhibit much lower percolation thresholds (indicating improved dispersion) than composites fabricated at low shear rates¹⁴. The figure below shows the variation in conductivity with MWNT content for PP/MWNT nanocomposites prepared using a high shear (Haake) mixer.



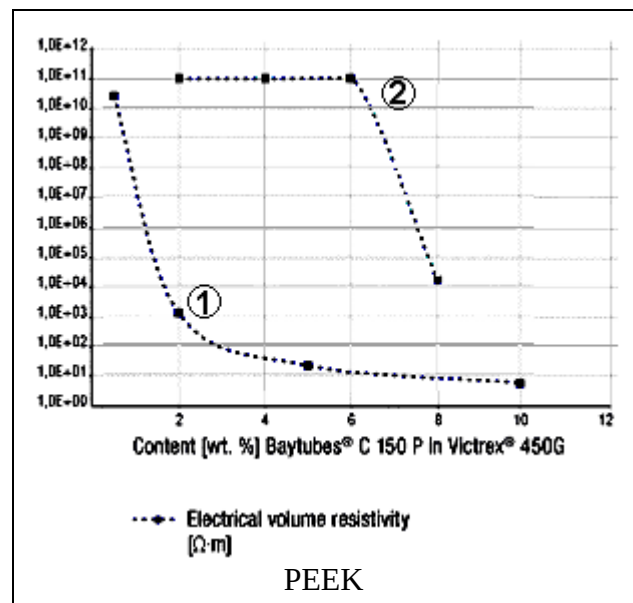
The figure below shows variations in conductivity with MWNT content for PP/MWNT nanocomposites prepared using a

low shear (Brabender) mixer. A percolation threshold of $\sim 10^{-2}$ S/m at $\sim 0.1\%$ CNT wt% content was achieved using a Haake mixer compared to a threshold of $\sim 10^{-4}$ S/m at $\sim 1\%$ CNT wt% content achieved with a Brabender mixer.



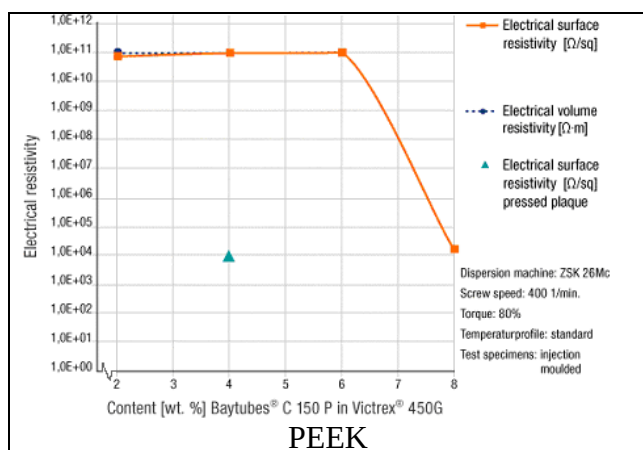
Does scaling up have an effect?

The figure below shows two curves, Number 1 represents a small “research” volume made with a DACA-Micro-Compounder (amount ~ 4 cm³ processed: Test specimens: pressed plaques). Curve Number 2 represents an industrial volume, made with a twin-screw extruder: ZSK 26Mc, amount processed: ~ 20 kg/h, test specimens: injection moulded¹⁵.



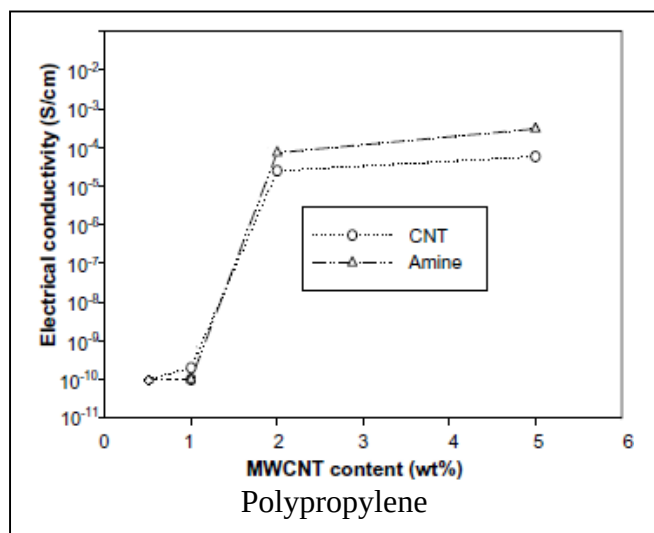
Does the format of the material make a difference?

Yes. The figure below shows the percolation behaviour of small diameter nanotubes from Bayer (Baytubes) in polyetheretherketone (PEEK) as compared to a pressed plaque¹⁵. The conductivity of a pressed plaque at 4 wt% CNTs is 7 orders of magnitude greater than that of an injection moulded material, using the same compounded material.



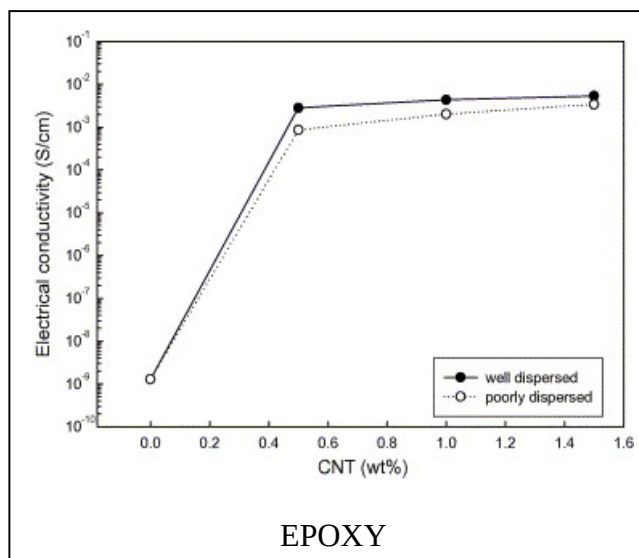
Does the treatment (functionalisation) of the carbon nanotube have an effect?

Although most publications show a decrease in the conductivity of the composite due to CNT functionalisation, some papers contradict and show slight improvements in electrical conductivity. An example of this is shown below¹⁰.



What effect does the degree of dispersion of CNTs have?

The better the dispersion, the lower will be the percolation threshold. The figure below shows the electrical conductivity of differing amounts of MWNT weight percentages in epoxy for well-dispersed and badly dispersed carbon nanotubes¹⁶.

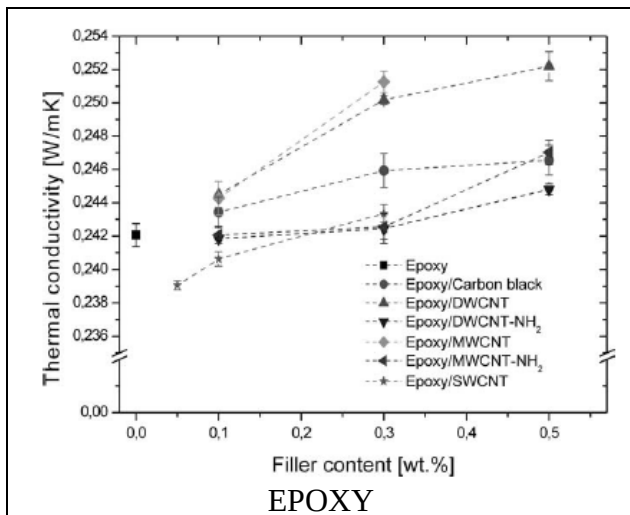


3. OTHER PROPERTIES

3.1 Thermosets

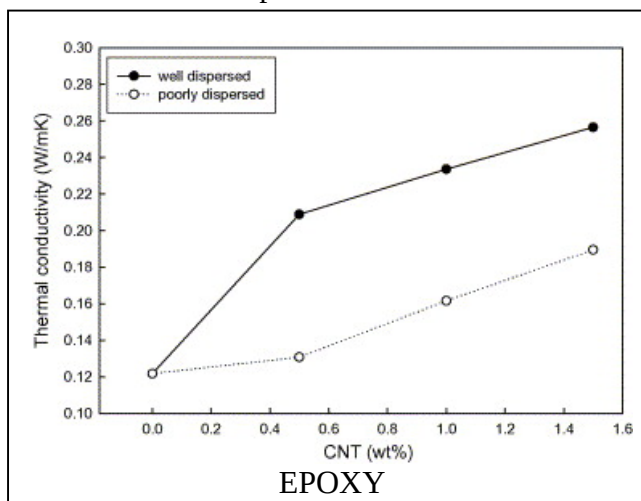
How do the thermal properties vary at the same time?

As can be seen below, CNTs improve the thermal conductivity of epoxy. The greatest thermal conductivity values are obtained when non-functionalised CNTs are used, as this minimises phonon scattering at defects (functional groups)¹¹. Thermal conductivity enhancement is not as great as electrical conductivity enhancement, as it occurs via a different type of propagation: electrons can tunnel between polymer chains, phonons (that give rise to thermal conduction) cannot¹⁷.



What effect does the degree of CNT dispersion have on the thermal conductivity?

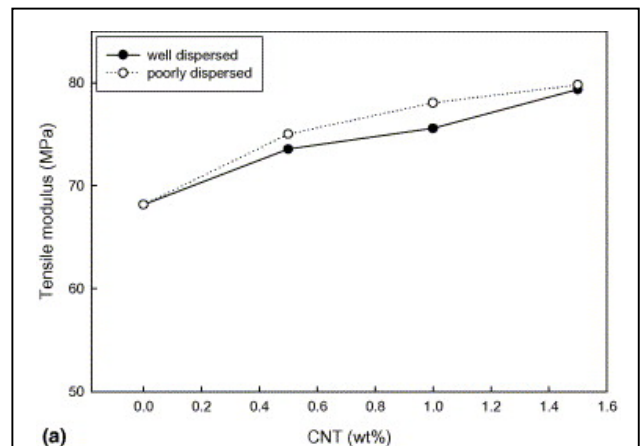
The figure below shows the thermal conductivity of the nanocomposites with respect to carbon loading with well and poorly dispersed MWNT. “Well dispersed” CNTs show two-fold improvements.



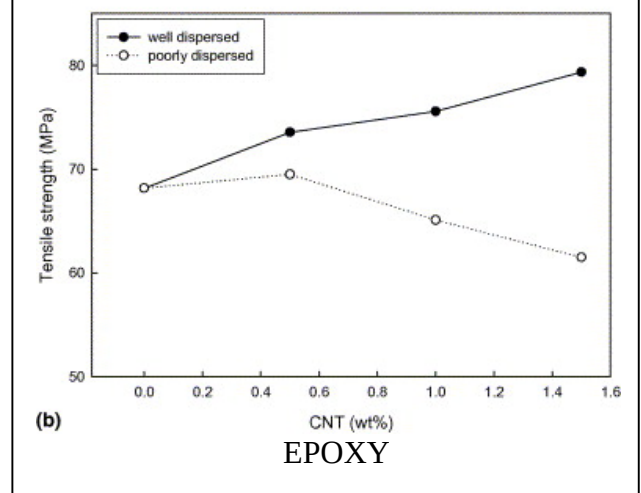
How do the mechanical properties vary at the same time?

The curves below show the mechanical properties of MWNT/epoxy composites: (a) tensile modulus, (b) tensile strength of MWNTs/epoxy composites and (c) elongation at break with respect to CNT loading, for *well* and *poorly* dispersed MWNTs¹⁶. The strength and elongation at break were significantly higher at high CNT concentrations for well dispersed compared to poorly dispersed CNTs, the tensile modulus showed the opposite trend. This could be due to bundled CNTs in poor dispersions where the weak Van der Waals forces between the graphitic planes

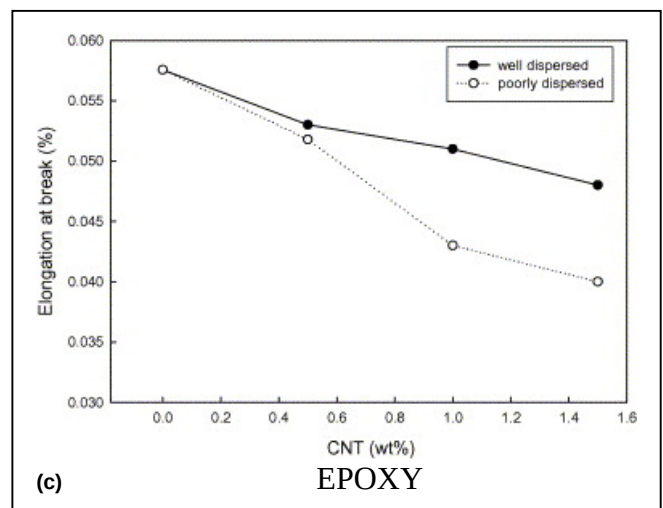
cause CNTs to slip past each other thus decreasing the elongation at break¹⁶.



(a)



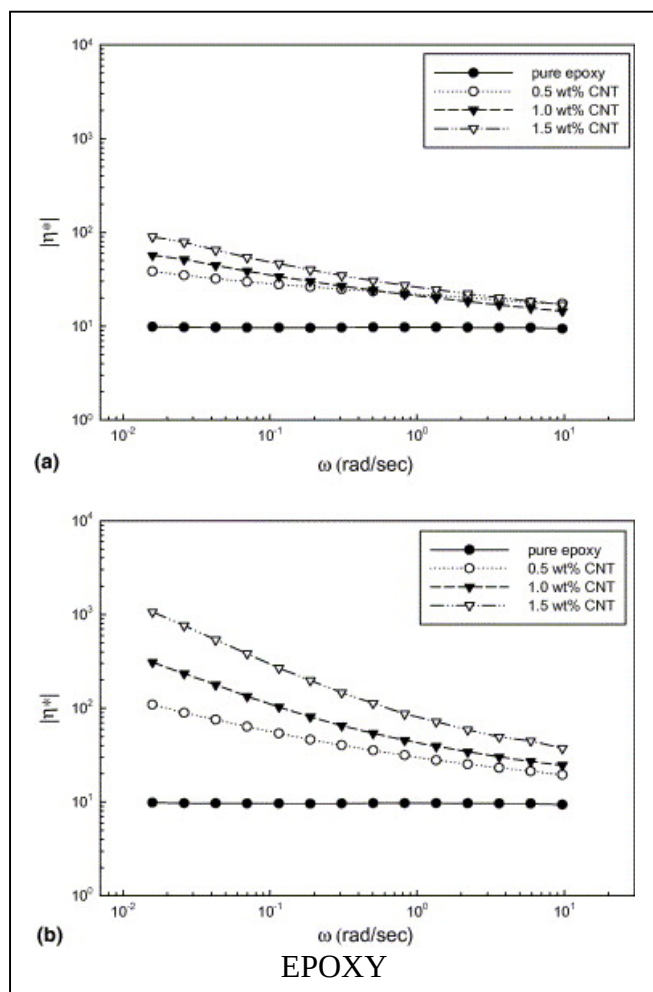
(b)



(c)

How does the rheology vary with CNT additions?

The figure below shows complex viscosities of epoxy nanocomposites filled with (a) well dispersed and (b) poorly dispersed CNTs. The viscosity is greater when CNTs are poorly dispersed. It was suggested that the agglomerates in the poorly dispersed CNT nanocomposites act as large particles as if higher filler loading were present at specific points. The agglomerates are thought to trap some of the polymer resin in the voids between CNTs, resulting in the nanocomposite behaving as if it had a lower volume fraction of polymer matrix¹⁶.

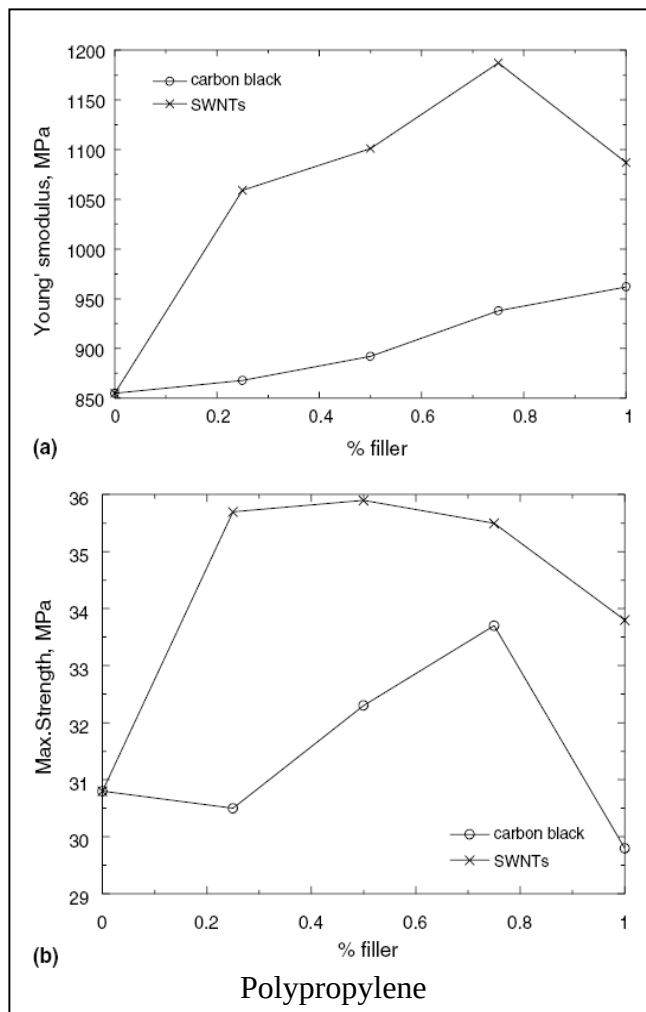


3.2 Thermoplastics

How do the mechanical properties vary at the same time?

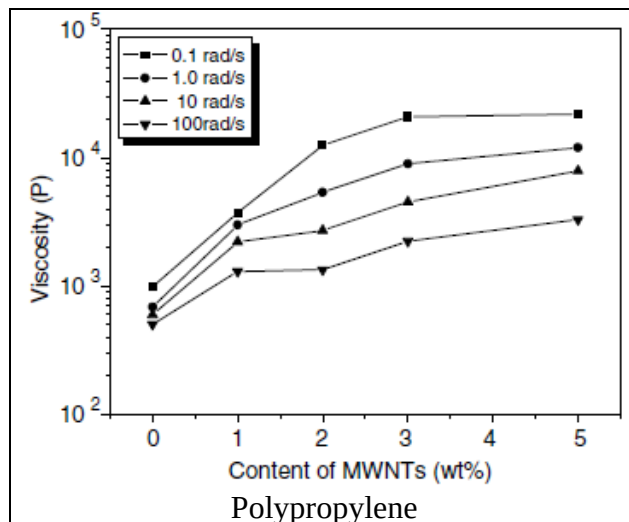
It's often observed that both the Young's modulus and the tensile strength increase more significantly with increasing CNT weight percentage as compared to the more steady increase with the CB fillers¹⁸. This is

associated with the CNTs' high aspect. Such properties, may easily be lost due to bundling of the CNTs, allowing slippage and decreasing the effective aspect ratio of the CNTs¹⁸.



How does the rheology vary with CNT additions?

Viscosity of MWNT/PP composites measured at 170 °C for different nanotubes content¹⁹.



4. Conclusion

It is clear that the properties obtained in nano-particle modified systems depend on many aspects. In particular, the properties are dependent on the degree of dispersion, which is currently difficult to measure.

The incorporation of CNT causes much larger changes in the electrical properties than the mechanical properties. Hence, electrical application of these modified materials is particularly favoured.

As measurements of electrical conductivity versus CNT amounts are expressed in units of mass or volume, one of these measurements should be standardised, keeping in mind that mass percentage is useful for production and volume percentage is useful for modelling.

Electrical, optical, thermal and mechanical tests often do not report CNT dispersion data or they are qualitative (e.g. well or poorly dispersed from subjective TEM studies). These should be reported in conjunction with other data (wherever possible). This highlights a need for dispersion measurements.

There is little confidence in published data due to significantly different results on performance dependence on CNT types and differing experimental set-ups, equipment, parameters used and so on. It could be possible to obtain standard electrical, optical, thermal and mechanical tests on well-characterised reference materials (thermosets and thermoplastics).

There is no standard measurement technique for the dispersion of CNTs. This should encourage international development of new measurement methods.

In future, participants measuring material properties should be encouraged to use:

- calibrated equipment,
- standard test methods, and
- well-characterised material.

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Acknowledgments

The authors are grateful to colleagues at NPL, Dr Bill Broughton, Dr Alexandre Cuenat and Laurie Winkless for consultations during this work. The authors acknowledge the input and financial support of Dr Martin Kemp on behalf of the HiPerNano interest group of the Nanotechnology KTN.