

Determination of dispersion state of Carbon Nanotubes/Epoxy suspensions prepared by different mixing techniques

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ABSTRACT

Semi-dilute carbon nanotube/epoxy suspensions are produced by dispersing CNTs in a newtonian epoxy matrix by three different mixing methods: calandring, mechanical stirring and sonication. Four different kinds of commercially available carbon nanotubes were used to investigate their dispersibility depending on the raw filler material in the same matrix.

two commercially available CNT types in high viscous polycarbonate melts. As shown by Huang et al.⁸, steady state shear flow measurements are able to directly characterize the dispersion state because the viscosity of the mixture is strictly related to the spatial and orientational distribution of the CNTs in the matrix. Bad dispersion quality, due to very low forces or insufficient mixing time, results into erratic rheological values.

INTRODUCTION

Carbon nanotubes are especially interesting as filler particles in electrically insulating polymers. By adding small amounts, the electrical conductivity of the system can be increased by a few orders of magnitude due to network formation of the fillers throughout the matrix¹⁻³. In case of carbon nanotubes (CNTs), the production technique and process parameters strongly influence the final electrical properties of CNTs based composites^{4,6}.

MATERIALS

Four different kinds of commercially available multi-wall carbon nanotubes are used: Nanocyl N7000 and N3150, Arkema C150 and Baytubes C150P. All tubes are produced by CVD process. The properties are shown in Table 1.

The key problem with the CNT based composites is the dispersability of CNTs in the matrix in order to utilize the properties of pure CNTs. The commercially available CNTs are constituted by several bundles of hundreds of carbon nanotubes that can be eventually entangled or held together by amorphous carbon. Recently, Pegel et al.⁷ showed the different dispersion behaviour of

Table 1. Properties of raw CNT material. Values marked with * refer to Ref. Rosca⁶

CNT type	Diameter (nm)	Length (µm)	Aspect ratio	Purity (%)
N7000	9.5	1.5	160	90
N3150	9.5	<1	<100	95
C150P	13	0.1-10	10-80	95
	11.6 *	~0.9 *	70 *	
C100	10-15	>1	>75	90
	12.5 *	~0.6 *	50 *	

The matrix used for the production of the suspensions are two difunctional bisphenol A/epichlorohydrin (DGEBA) based resins, EPON™ Resin 828 purchased from Hexion and LY556 from Huntsman with viscosities at room temperature of about 10-12 Pa s.

PRODUCTION

For suspension production, three most common methods were chosen, which are sonication, mechanical stirring and milling. For sonication a horn ultrasonicator (Misonix S3000) was used and milling was performed by means of a 3-roll-mill (EXAKT® 120 E). Sonication is often used to produce small batches which make it favourable for lab size application⁹⁻¹⁰. Two sonication times have been used for the suspension production (10 and 120 minutes) with an average power of 20 W.

Milling and stirring is more favourable for master batch productions and bigger amounts of material. The dispersion of the nanotubes is based on high shear. The smallest gap size used for milling was 5 µm.

Rheological measurements were carried out using a stress-controlled Ares Rheometer (Rheometric Scientific, 40 mm parallel plates) and a modified¹¹ stress-controlled rheometer (StressTech HR, Rheologica Instruments, 35 mm parallel plates). A gap size of 1 mm was chosen to

avoid constriction of shear induced agglomerates. Measurements were performed at 25°C and 60°C.

To show the quality and structure of pristine nanotubes, Scanning Electron Microscopy (SEM) was performed on the raw material. A LEO 1530 FE-SEM (Carl Zeiss GmbH, Germany) microscope was used at an acceleration voltage of 5 kV.

RESULTS AND DISCUSSION

Raw material structure

From the SEM images at two different magnifications as shown in Figure 1 one can clearly see differences in the grain size of the pristine CNTs.

Baytubes C150P shows big smooth grains with diameters up to 500 µm. The surface is quite fluffy. Arkema C100 shows small round grains with diameters around 100 µm as well as big ball-like structures up to 400-500 µm. Nanocyl 7000 shows pallet-like grains with sizes between 100-500 µm. At higher magnification a felt-like structure of small bundles becomes visible. The structure of N3150 appears to be very different, with smaller grains having maximum sizes of 100 µm and more homogeneous grain size distribution. A higher magnification image shows dreadlock-like structures.

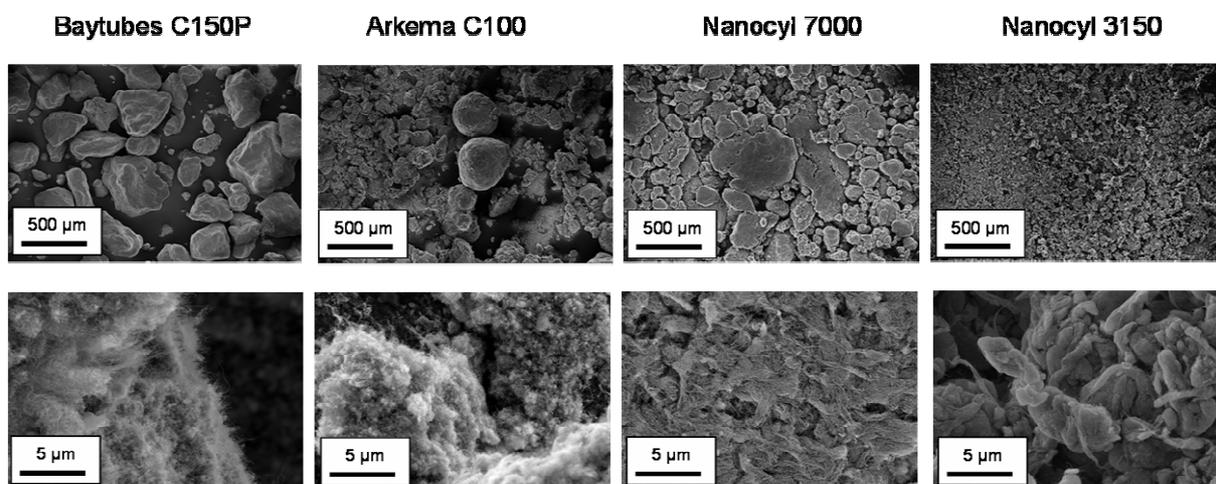


Figure 1: SEM micrographs for the as-grown CNTs. Magnification is 100x (upper row) and 10 000x (lower row).

Influence of production method

To evaluate the effect of the dispersion state on the microstructure and its electrical conductivity, shear rate sweep test with decreasing shear rates from 100 s^{-1} to 0.1 s^{-1} were performed.

In the first set of experiments, sonicated and milled samples were compared. In Figure 2, the viscosity values at a shear rate of 0.1 s^{-1} for N7000 and N3150 are compared depending on different production methods as well as storage time. For milled samples, both CNT/epoxy systems show nearly identical viscosities. Clear differences between N7000 and N3150 become obvious for short and long time sonicated suspensions. Short time sonicated N7000 suspensions show unexpected high viscosity value while the viscosity for stored N7000 samples drops nearly down to the region of the pure resin (0.25 Pa s). For N3150, values in the same region as for the unstored samples were measured.

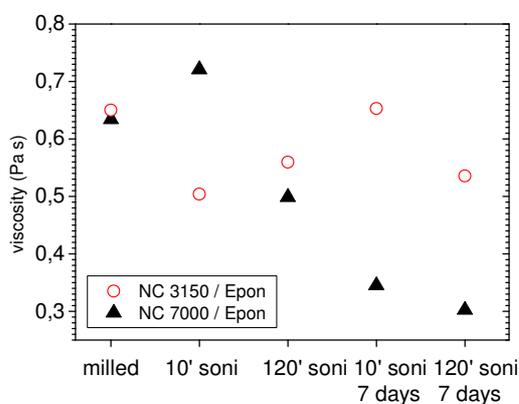


Figure 2. Steady shear viscosities at 0.1 s^{-1} for $0.05 \text{ wt}\%$ at 60°C for N7000 and N3150.

The influence on the electrical conductivity was in agreement with the viscosity measurement: for high viscous samples, high conductivity values were measured while for low viscous samples, the systems show nearly isolating behaviour. The increase in conductivity is due to shear induced network formation¹². To get further

information about the dispersion created by short sonication times, optical micrographs were taken. As one can see from Figure 2a, milling achieves a homogeneous, fine dispersion. In sonicated samples as shown in Figure 2b, big agglomerates with diameters up to $250 \mu\text{m}$ remain undispersed in the resin. We define a good dispersion if the filler particles are homogeneously distributed in the system with small variances in size. Obviously, this is not the case for short sonication times. If the suspension is bad, sedimentation or demixing effects can occur much easily during storage leading to a filler impoverished system and thus lower viscosities.

The big, undispersed agglomerates are assumed to be the main reason for the unexpected high viscosity values. As shown by Huang et al.⁸, a bad dispersion leads to erratic values in viscosity. N3150 was dispersed more effectively by sonication but even in this case, long sonication times were needed. The lower electrical conductivity values at short sonication times are understandable because the tubes sticking to the big raw material grains can not take part in the shear induced network formation. Thus the concentration of fillers taking part in the network formation process is effectively much lower.

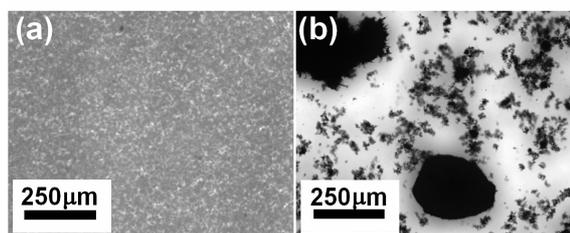


Figure 3. Light microscopy images of $0.05 \text{ wt}\%$ N7000 in Epon after shearing with 100 s^{-1} for 1 min : a) milled and b) sonicated for 10 minutes.

Because of very similar properties of the used tubes, the raw material structure seems to have the biggest influence. Based on our results, sonication seems to be applicable only for fine-grained raw material where no high forces are necessary to break up the initial structures.

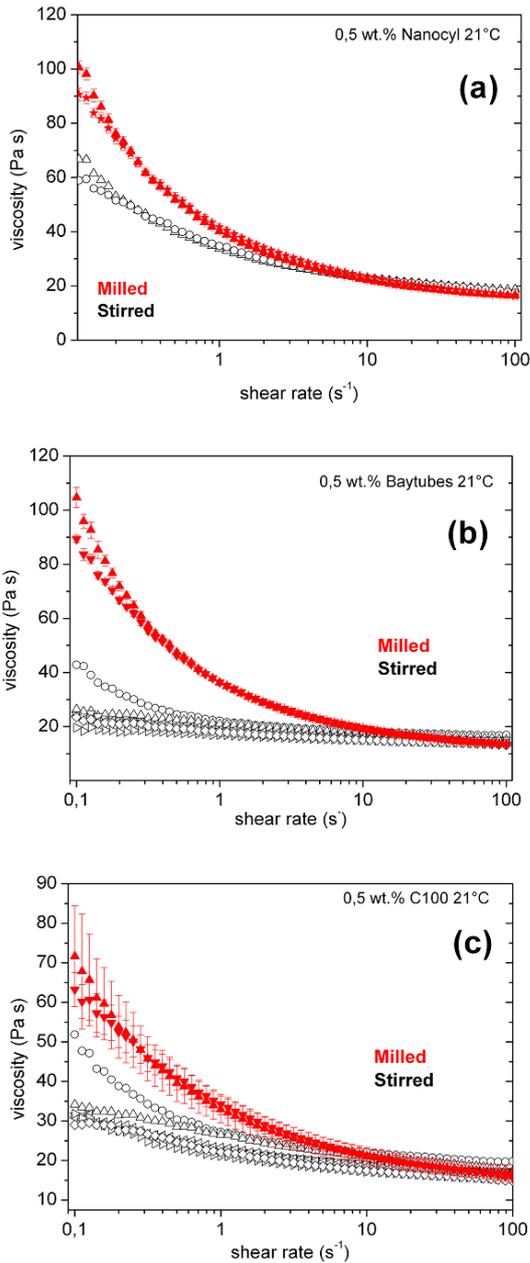


Figure 4. Shear rate sweep test of different CNT/epoxy systems at 21°C prepared by milling (closed, red symbols) or stirring (open, black symbols).

Mechanical stirring induces higher shear forces in bigger amounts of material compared to sonication. As sonication was not able to disperse N7000 efficiently, milling and stirring was performed for N7000, C150P and C100 to check if these methods are able to disperse raw material with initial big agglomerates/grains.

Shear rate sweep tests were performed on milled and stirred material with shear rates from 100-0.1 s⁻¹ at 21°C. The results are shown in Figure 4. Milling induces higher shear forces compared to stirring thus, leading to a finer dispersion. The dispersion quality is directly reflected by the viscosity, higher resistance against flow is measured for small and homogeneous dispersed particles. For N7000/epoxy, reproducible viscosity values can be obtained by both production methods with slightly higher viscosities at low shear rates for milled suspensions (comp. Fig. 4a).

CNTs with lower aspect ratio and coarse-grained raw material as C150P and C100 also show reproducible rheological behaviour with higher viscosities at low shear rates for milled systems due to agglomeration and network formation. For stirred samples, higher viscosities were measured in the first shear rate sweep starting at 100s⁻¹, when decreasing the applied shear rate. This is by analogy with the milled systems. However thereafter, deviant behaviour was observed. It was not possible to reproduce the viscosity values of the first sweep by further measurements. The viscosity values even at low shear rates decreases strongly by more than 50 % showing almost linear viscosities over the applied shear rate regime. This behaviour is more pronounced for C150P (Figure 4b) than for C100. We assume that stirring is not able to totally disperse the raw material of C100 and C150P. Big grains of initial material, comparable to those optically observed for short sonicated samples, may remain in the resin. The lower viscosities indicate a worse dispersion compared to

milled samples. Additionally, the flattening of the viscosity curve may be explained by migration of the big particles into the centre of the plates. Due to the plate-plate setup, a shear force gradient is present with highest shear rates at the edges and zero shear in the middle of the plate. Big agglomerates may drift towards the middle where they do not have to resist against the shear flow and thus do not affect the viscosity. Thus, a system with effectively lower CNT concentration is measured. This is just an assumption and is not yet further proved but it explains the linear viscosity behaviour usually occurring for concentration much lower than the used 0.5 wt%.

As a result we can conclude that high forces are necessary to break up dense raw material structures. Other filler properties such as length, aspect ratio or purity do not seem to play a crucial role while the raw material structure influences the dispersibility mostly.

CONCLUSION

It was found that despite using CNTs with similar properties, the dispersability of the raw material and the time stability of the suspensions are quite different. Independent of the used CNT raw material, milling showed to be the only mixing technique in achieving a homogeneous dispersion without remaining raw material agglomerates. Raw material with initially small particles seems to be easier dispersible. Big particles need quite high forces to break up and can thus not be sufficiently dispersed by low power methods.

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