# DEVELOPMENT OF MWCNT/CARBON FIBER REINFORCED COMPOSITE FOR AEROSPACE APPLICATIONS

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## Abstract

*In our work MWCNT/carbon fiber reinforced composites suitable for aerospace applications have been developed. During our experimental work we have focused on the development of a system being able to be easily integrated into current aerospace composite manufacturing technologies, especially for the tape-laying of prepregs. A conventional high viscosity and an extremely low viscosity epoxy prepreg resin system have been investigated. The MWCNTs have been dispersed in the reinforced matrix resin by conventional three roll milling and a novel, three step masterbatch mixing technology based on three roll milling, suitable to disperse nanoparticles in low viscosity resins. A wide range of MWCNT contents (0.1, 0.3, 0.5 and 1 mass%) has been studied to obtain the optimal composition of the hybrid composite. The viscosities and the maximal particle sizes of the prepared resins have been characterized by rheometry and fineness of grind measurements. Fiber reinforced composite samples have been prepared using the developed matrices by hand lamination assisted by vacuumbag technology. Standard tensile, three point bending, static and dynamic interlaminar shear tests have been performed on the specimens.*

## 1 Introduction

After their discovery in 1991, carbon nanotubes became one of the most intensively investigated nanosized composite reinforcing materials. They do not only provide excellent mechanical properties for the composites, but also increase their thermal and electrical conductivity significantly. Although the first assumptions and laboratory results were promising, it soon became clear that CNTs cannot replace the conventionally used carbon fibers as sole reinforcing material, but they can be used effectively as a secondary, nanosized reinforcement besides them [1]. One of the potential application areas of CNT and fiber reinforced hybrid composites is the aerospace industry. In such applications not only excellent mechanical (high static mechanical properties and fatigue resistance), but also electrical properties (electrical conductivity to some extent) are important [2]. The developed matrix resin systems also have to fulfil the requirements of the conventional aerospace prepreg production technologies [3]. Although numerous articles have been published in the field of

CNT reinforced composites and hybrid composites, only a few investigated systems would be suitable for this high performance area.

## 2 Materials and testing methods

### *2.1 Materials*

Two epoxy resin systems, both produced by IPOX Chemicals (Hungary), were selected: one for the preliminary evaluation of the production, nanotube mixing technologies, capable of room temperature curing and one group of prepreg resins for the final samples.

AH-12 aliphatic epoxy resin - T-58 amine curing agent (mixing weight ratio: 100:40) system consists of extremely low viscosity components, mainly used as thinner in higher viscosity resins, but capable of individual structural application. Capable of curing at room temperature (pot life: 120 min). Cured at 80°C for 4 hours in a Heraeus UT20 drying oven according to producer’s specifications.

AH-12 aliphatic epoxy resin with T-111 hardener (mixing weight ratio: 100:116) is a low viscosity prepreg system utilizing the extremely low viscosity epoxy resin with prepreg hardener. Capable of prepreg use, curing above 80°C. Curing has been carried out at 80°C for 8 hours in a Heraeus UT20 drying oven according to producer’s specifications and preliminary tests.

Baytubes C 150 HP (Bayer, Germany) type untreated MWCNTs and Zoltek PX35 FBUD0300 unidirectional carbon fabric was applied as reinforcement in composites.

### *2.2 Methods*

Fineness of grind tests have been performed on the prepared MWCNT filled samples using an Elcometer 2020/2 grindometer according to EN ISO 1524.

The viscosity of the resins has been tested in steady state flow rotating operation using a TA instruments RA2000 rheometer between a rotating 40 mm diameter plane disc and a controlled temperature plane sheet at 25°C.

The tensile tests have been performed according to EN ISO 527-2 on EN ISO 3167 type B specimens at 1 mm/min crosshead speed using a Zwick Z020 tensile tester. The strain has been measured by a Messphysik ME-46 Full Image Videoextensometer with a gauge length of 50 mm.

The three point bending tests have been performed according to EN ISO 178 using a Zwick Z020 computer controlled loading frame at 2 mm/min test speed and 64 mm support span.

The notched Charpy impact tests have been performed according to EN ISO 179-2 using a Ceast Resil Impactor Junior instrumented pendulum equipped with a 2 J hammer started from 150°C (2,9 m/s impact velocity). The data has been collected using a Ceast DAS 8000 data acquisition system. The notches have been machined using a Mutronic Diadisc cutter according to the type A notch of the standard.

The dispersion achieved has been investigated by TEM using a Morgani 268D TEM. The 80 nm thick samples have been cut using a Leica Ultramicrotome EMUC6 microtome.

## 3 Results and discussion

### *3.1 Nanoparticle dispersion in epoxy resin*

To develop a competitive hybrid composite system, good nanoparticle dispersion has to be achieved. Although in the first decade after their discovery, ultrasonic stirring has been the dominant mixing method, nowadays high shear mechanical mixing technologies have taken its place because of productivity reasons. In the project we have used a previously developed three-step masterbatch technology for the dispersion of the nanotubes in the epoxy resin, and compared it to the concurrent direct mixing technology. The dispersion tests have been performed on the selected AH-12 low viscosity epoxy resin with different MWCNT contents.

The 3-step masterbatch technique (**Figure 1**) was developed to be able to utilize the mixing potential of three roll milling for low viscosity resins like the AH-12 used. In the first step an 8 weight% nanotube filled AH-12 masterbatch has been premixed for 4 hours using an IKA RW-16 overhead stirrer equipped with a Heidolph TR20 turbine type impeller. The so prepared mixture contained large, visible aggregates but its viscosity increased to the level where three roll milling became available (the neat, and loaded but no pre-dispersed resin flows down in the gap between the rolls of the three roll mill). In the second step the masterbatch has been mixed on an Enrico Molteni CIEM three roll mill, 4 pass-throughs have been carried out to reach the lowest achievable particle size. In the third step the almost solid masterbatch has been thinned with neat resin to the desired filler contents.


a) b) c) d)

**Figure 1** The steps of the masterbatch (MB) mixing technology: premixing by overhead stirrer (a), three roll milling (b), masterbatch (c), thinning under vacuum (d)

The direct mixing technique has been carried out using an IKA magic LAB® mixer with DISPAX-REACTOR® module (**Figure 2**). The machine has been set up for batch operation with constant reflux to the feed hopper. Each resin-nanotube batch has been mixed for 15 minutes at 15000 rpm. During the mixing constant stirring of the material in the hopper and cooling of the reactor has been provided.


a) b)

**Figure 2** Mixing elements of the IKA Dispax reactor (a) and mixing of the AH-12 epoxy resin in an IKA MagicLab mixer (b**)**

## *3.2 Dispersion characterization*

The direct mixing and masterbatch technologies have been compared in terms of particle size, viscosity and mechanical tests.

To compare the maximal particle size, the grinding, aggregate disintegrating effect of the two mixing technologies, fineness of grind tests have been performed on the prepared MWCNT filled samples. The fineness of grind values (the maximal particle size in microns) in case of AH-12 – T-58 system can be seen in **Figure 3**.

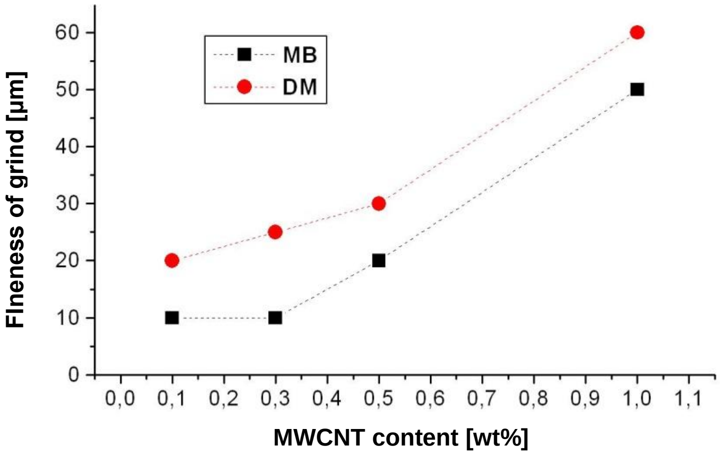

**Figure 3** Fineness of grind (maximal particle size) comparison of MWCNT filled samples prepared by masterbatch technology and direct mixing

The fineness of grind values clearly showed that the masterbatch technology is superior to direct mixing. During three roll milling the nearly zero gap size causes an effective grinding action besides the high shear, which can effectively grind the MWCNT aggregates. This mechanical grinding effect is not present in direct mixing, where the collision of the aggregates can be the main cause the disintegration of the aggregates. The higher particle size values at higher MWCNT loadings are probably caused by reaggregation. Reaggregation can be fully avoided, if the masterbatch is only thinned with neat resin to the desired nanotube content just before prepreg or part manufacture, because in the almost solid masterbatch the CNTs are not mobile enough to reaggregate. This has been supported by repeated measurement of freshly thinned samples, where at all applied nanotube contents maximal particle sizes below 10 microns could be measured (which is the fineness of grind of the original masterbatch before thinning).

The viscosity tests have been performed at room temperature. The results of the viscosity tests can be seen in **Figure 4**.

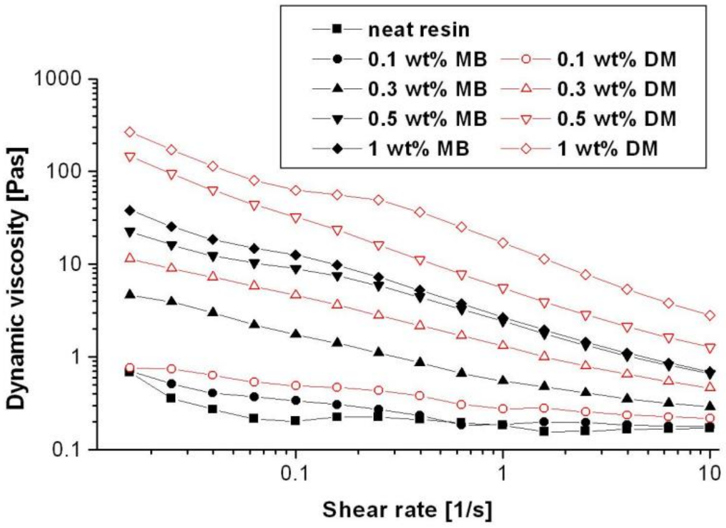

**Figure 4** Viscosity comparison of MWCNT filled epoxy resins prepared by the masterbatch technology and direct mixing

The viscosity values are in direct connection with the global dispersion state of the MWCNT reinforced system. From the results of the viscosity tests it can be clearly seen that the masterbatch technology provides not only lower maximum particle size, but also better global dispersion resulting in lower viscosity at all MWCNT contents. The more evenly dispersed, lower viscosity system is also more suitable for processing and part manufacture.

To characterize the effect of mixing method on the reinforcing potential of MWCNTs in composites mechanical tests have been carried out on cast specimens based on AH-12 – T-58 epoxy matrix loaded with MWCNTs dispersed by the two dispersion methods.

The results of the tensile tests can be seen in **Figure 5.**

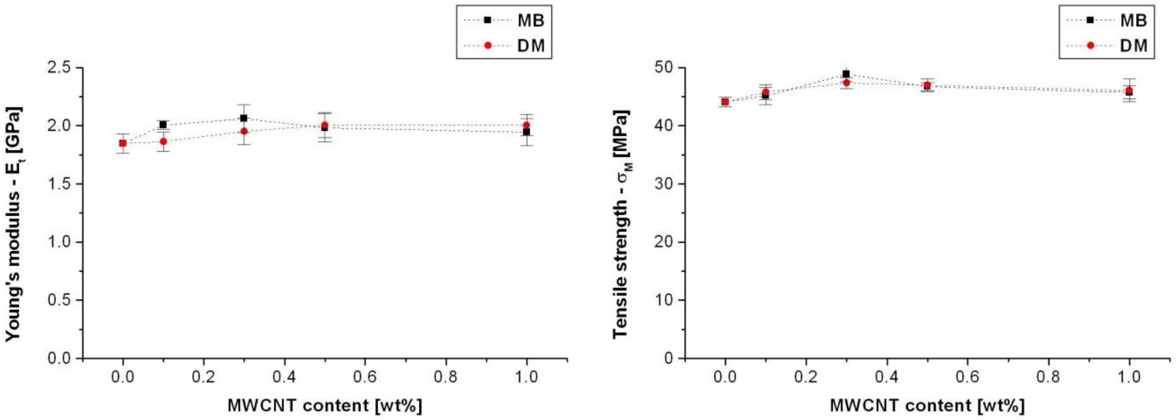

**Figure 5** Results of the tensile tests of MWCNT reinforced epoxy composites prepared by the masterbatch technology (MB) and direct mixing (DM)

The tensile test results showed no significant differences between the composites prepared by the two dispersion methods.

The results of the three point bending tests can be seen in **Figure 6**.

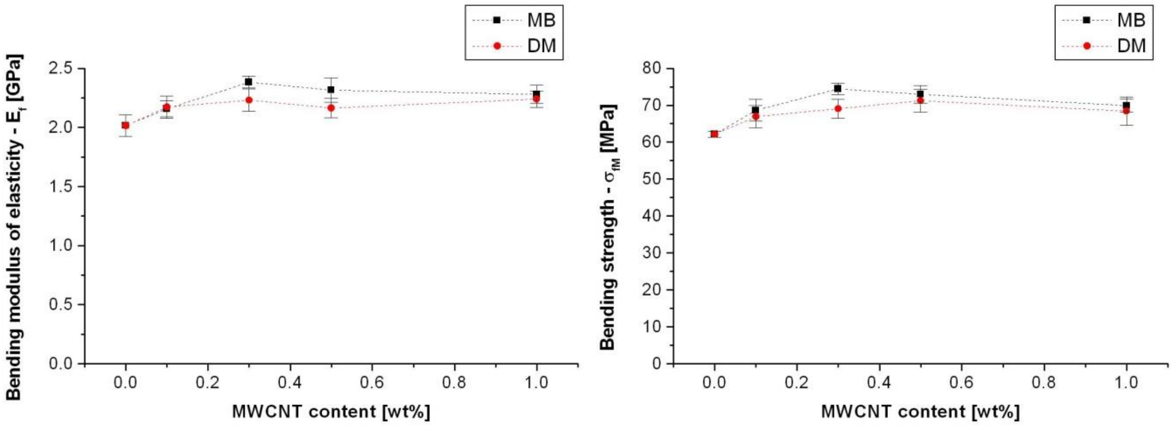

**Figure 6** Results of the three point bending tests of MWCNT reinforced epoxy composites prepared by the masterbatch technology (MB) and direct mixing (DM)

According to the three point bending test results the specimens prepared by the masterbatch technology were superior both in terms of modulus and strength to the ones prepared by direct mixing because of the better dispersion achieved.

The results of the impact tests can be seen in **Figure 7**.

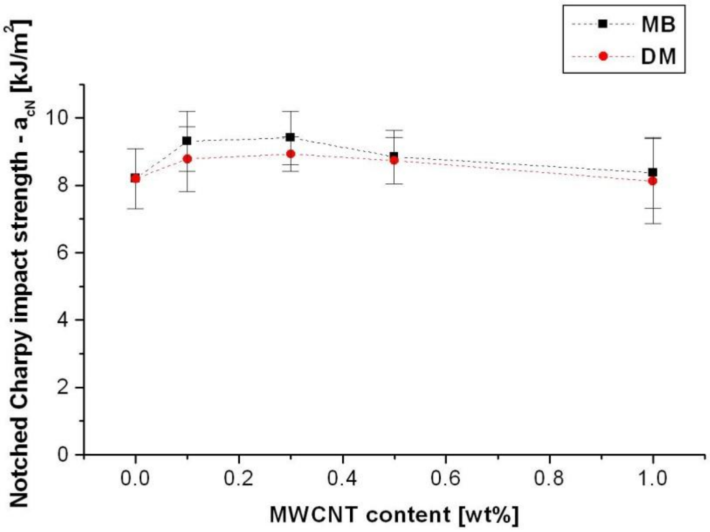

**Figure 7** Result of the notched Charpy impact tests of MWCNT reinforced epoxy composites prepared by the masterbatch technology (MB) and direct mixing (DM)

In the results of the notched Charpy impact tests also the better performance of the masterbatch technology prepared specimens can be observed, especially around the optimal MWCNT content of 0.3 wt%.

The results of the mechanical tests showed that the masterbatch technology is capable of the production of high performance nanocomposites, and that it provides higher mechanical properties than the competitor direct mixing technology, therefore the use of the masterbatch technology is preferable.

The dispersion achieved by the masterbatch technology has been investigated by TEM on AH-12 – T-111 matrix 0.3 wt% MWCNT reinforced cast specimens. Two typical TEM micrographs of the samples can be seen in **Figure 8**.

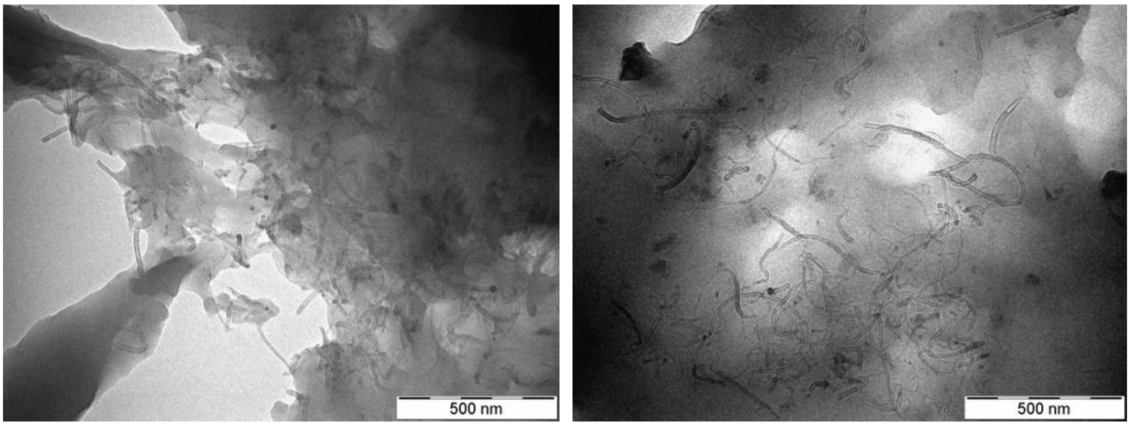

**Figure 8 TEM micrograhps of the 0.3 wt% MWCNT reinforced AH-12 – T-111 epoxy matrix specimens**

In the TEM micrographs well distributed individual MWCNTs can be observed. This further supports that the masterbatch technology has been successful in the dispersion of the MWCNTs in the epoxy resin.

## Conclusions

The masterbatch dispersion method, developed for use with low viscosity resins has been characterized by rheological, particle size measurements and has been compared to a competitor direct mixing technology. The dispersion achieved by the used masterbatch technology has been characterized by TEM. According to the tests the masterbatch mixing technology provides good nanoparticle dispersion, without the risk of MWCNT reaggregation.

According to the results of the mechanical tests performed on MWCNT/CF reinforced hybrid composites prepared by vacuumbag technology (tensile, three point bending, interlaminar shear, DMA) 0.3 wt% MWCNT provided the best results.

## Acknowledgement

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