EFFECT OF CNT CONCENTRATION ON MECHANICAL PROPERTIES OF COMPOSITES MANUFACTURED BY COMPRESSION RESIN TRANSFER MOLDING (CRTM)

D. Abliz[a*], G. Ziegmann[a], Y. G. Duan[b], D. C. Li[b], D. Meiners[a]

[a]*Institute of Polymer Materials and Plastics Engineering, TU Clausthal, Germany*
[b]*State Key Lab for Manufacturing Systems Engineering, Xi'an Jiaotong University, China*
**Dilmurat.abliz@tu-clausthal.de*

Keywords: CNT; polymer-matrix composites (PMCs); liquid composite molding (LCM); CRTM.

Abstract

Due to the high aspect ratio of CNT and increased viscosity of the CNT/epoxy suspension, the filtering and viscous resistance effect is a critical issue in conventional LCM processes to fabricate CNT/epoxy/fiber hybrid composites. In this paper, CNT/epoxy/fiber hybrid composites were fabricated by the CRTM process and flexural properties of the hybrid composites were tested and analyzed. The results showed that the in-plane filtering effect could be greatly improved, while the through-thickness filtering still exists as the CNT concentration exceeds a certain amount; there is an optimum concentration of the CNT to achieve the maximum mechanical properties.

1. Introduction

Carbon nanotube (CNT) is used as ideal nano-filler for polymer composite due to the following specific characteristics: firstly, CNT has outstanding mechanical, thermal and electrical properties[1, 2]; secondly, CNT has rather high aspect ratios-the diameter of CNT is normally in the nano-range but its length can be up to dozens of microns, so they can more easily form interconnected three-dimensional networks which is essential to efficiently increase the mechanical, thermal and electrical properties, with low fractions by weight or volume[3-6].

However, because of the high aspect ratio of CNT particles, one of the critical issues for the fabrication of CNT reinforced hybrid advanced polymer composites conventional LCM processes is the filtering of the CNT particles by the textiles during the impregnation, which leads to non-uniform distribution of the particles[7, 8]. During the LCM process of carbon nanoparticle filled thermosets, two main filtering mechanism, cake filtration and deep bed filtration, were identified[9, 10]. In the case of CNT/epoxy suspension injection to the textiles, cake filtration is manifested by the partly volume capture due to the larger CNT length than the intra-fiber gaps of the textiles, while deep bed filtration is characterized by the gradual capture of particles smaller than the pore channels. As long as the particles are captured by the intra-fiber gaps, the permeability of the porous medium will greatly decrease, and at the same time the viscosity of the suspension begins to rise due to the increased concentration of CNT.

In this paper, the CNT/epoxy/fiber hybrid composites were fabricated with CRTM process: during the injection process, the textiles will be under full vacuum but not be compacted, so the permeability and intra-fiber gaps of the textiles are much bigger compared to the conventional LCM processes. This would efficiently increase the impregnation speed and improve the CNT distribution in the textiles. After the injection, the textiles will be further compacted and cured with two rigid molds to improve the impregnation of the textiles and achieve the desired fiber volume fraction.

2. Experiments and Methodologies

2.1. Materials

The matrix used for the experiment is epoxy resin with corresponding hardener (RIMR 135 + RIMH 1366=10:3) from Momentive. Fiber-textile reinforcement used is biaxial non-crimp glass fiber fabric GBX450 (+45°/-45°) with an area weight of 450 g/m^2 from WELA. The CNTs used are multi-walled CNTs with (–COOH) functional groups from Nanostructured & Amorphous Materials, Inc. The outer diameter of the CNT is 10-30 nm, inner diameter is 5-10 nm and length is 10-30 μm, according to the provider.

2.2. Manufacturing process

The manufacturing process is illustrated in the figure 1: In the first step, the fiber textiles were layed up on the lower mold. The upper mold keeps a certain gap above the textiles. So the textiles stay at the original thickness with big intra-fiber gaps without any compaction; in the second step, full vacuum was applied in the cavity and the degassed CNT/epoxy suspension was injected into the cavity, by which the suspension quickly covers the gap above the textiles; in the third step, the upper mold moved slowly until a certain distance from the lower mold to press the resin into the textiles, by which the textiles were impregnated from top to bottom direction and the desired fiber volume percentage can be achieved. After that, the mold structure was heated in an oven with 80 ℃ for 4 hours to fully cure the composites.

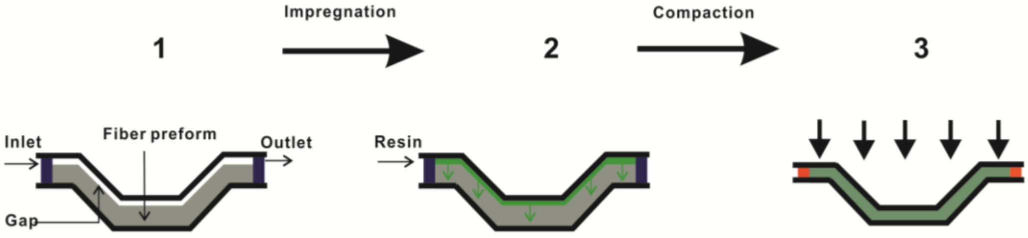

Figure 1. Illustration of the compaction resin transfer molding process.

2.3. CNT particle dispersion

The good dispersion of the CNT particles is the first critical step to take fully advantage of the nanoparticles and also to a successful injection process without filtering. A lot of different dispersion processes, including solution assisted dispersion, tip/bath sonication, three roll milling, heat stirring and etc., were investigated until now[11, 12], but the dispersion parameters differ a lot for different types of particles. In this work, three different dispersion processes were investigated and the dispersion state of the CNT particles in epoxy (0.5 wt%) were characterized.

Method 1. The CNT particles were mixed with 100 ml acetone and bath sonicated for 30 min, then the epoxy was added to the acetone and the solution was heated to 60 ℃ and magnetic stirred with a speed of 300 rpm until the acetone was fully evaporated. At the end, the solution was placed back in the bath sonicator and sonicated for another 30 min for further dispersion and cooling.

Method 2. The CNT particles were mixed directly to epoxy and the solution was bath sonicated for 30 min, after that the solution was heated to 60 ℃ and magnetic stirred with a speed of 300 rpm for 1h. At the end, the solution was placed back in the bath sonicator and sonicated for another 30 min for further dispersion and cooling.

Method 3. The CNT particles were mixed directly to epoxy and the solution was heated to 60 ℃ and stirred with a speed of 300 rpm for 15 min. After cooling down to room temperature, the solution is tip sonicated with 50% power and 0.5 circle for 5 min.

2.4. Transmission electron microscopy (TEM)

The dispersion states of the particles were characterized by transmission electron microscopy (JEM2100, JEOL).

2.5. Optical microscopy

The cross section of the samples was examined by optical digital microscope (VHX-500F, Keyence) by transmission inspection modes to investigate the microscopic morphology and inner quality. The specimens were cut, mounted and polished with an automatic polishing machine before investigation.

2.6. Flexural properties.

Flexural properties of the samples were tested by a three-point bending test with a universal material testing machine (Zwick GmbH Co. KG, Germany). The sample specifications and the testing parameters defined according to DIN EN ISO 14125 standard[13].

3. Results

3.1. CNT particle dispersion

According to the CNT dispersion state pictures below in figure 2, before dispersion the CNT particles were strongly winded to each other, as shown in figure 2(a). By the dispersion methods, the CNT particles were more homogenously dispersed in the epoxy. There were inevitably some agglomerates in all the dispersions figure 2(b-d), but in comparison, the size and quantity of the agglomerates figure 2(d) by method 3 is much smaller than the other dispersions. Moreover, the heat stirring and tip sonication that used in method 3 is the most time-saving, and the dispersion state also showed a higher fraction of single, separated CNT particles. Chandrasekaran et al.[12] also reported nearly the same interlaminar shear strength (ILSS) results for fiber composites that fabricated with 2 minutes full power tip sonicated and

20 h bath sonicated CNT/epoxy suspension. Therefore, the dispersion method 3 was chosen in this work for the particle mixing.

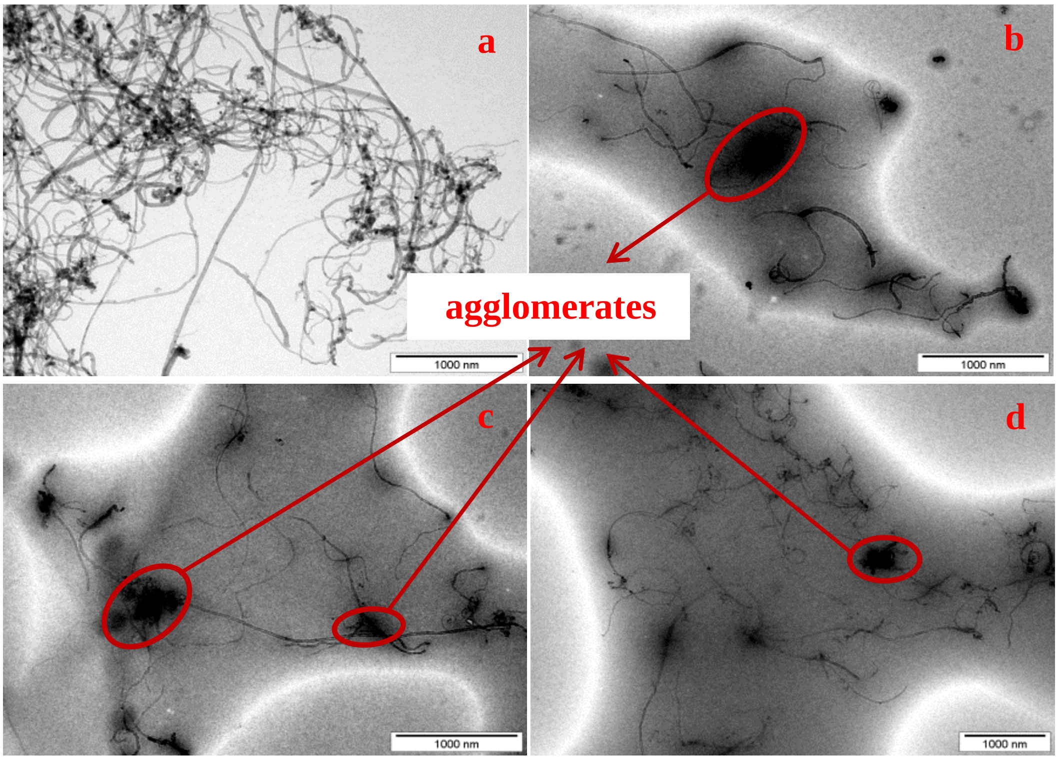

Figure 2. CNT dispersion states (TEM pictures) with different dispersion methods: a) before dispersion; b) dispersion by method 1; c) dispersion by method 2; d) dispersion by method 3.

3.2. Flexural properties

Considering the out-of-plane impregnation characteristics of the CRTM process and possible CNT filtering in the thickness direction, the flexural properties were measured from both top-bottom and bottom-top bending directions. According to the correlation of flexural properties of the multi-scale composites versus CNT concentration as shown in figure 3, both the flexural modulus and flexural strength of the hybrid composite increased sharply with the increase of the CNT concentration, until the particle concentration reached 1 wt%. At this point, the flexural modulus increased about 20 % and the flexural strength increased about 17 % compared to the baseline plate. The increase in the flexural properties is mainly due to the increase in the fiber volume fraction of the samples and the reinforcement effects of the CNT particles. However, when the CNT concentration increased above than 1 wt%, both the flexural modulus and the flexural strength began to decrease. Besides, the flexural properties from both top and bottom directions showed almost no big difference, considering the small experimental deviation.

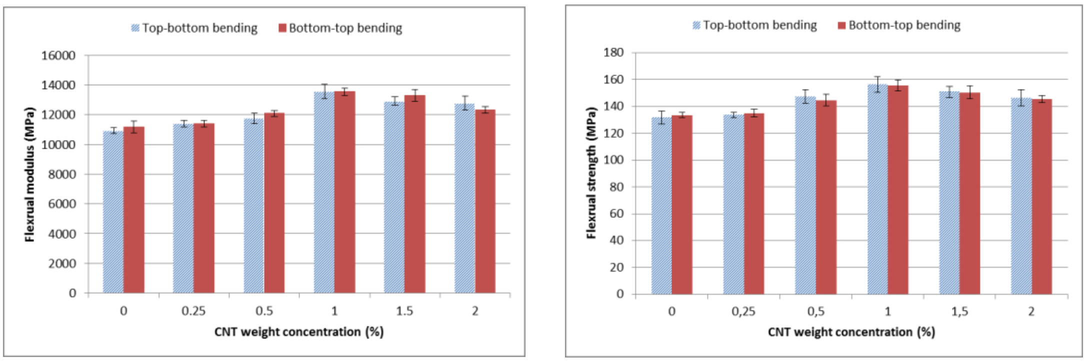

Figure 3. Change of flexural properties vs. CNT weight concentration

3.3. Morphology

The cross section side-light transmission photomicrographs of laminates with different CNT concentration are shown in figure 4. The left border of the sample that is shown in the picture is the upper surface during the impregnation, and the right border is the lower surface. It can be clearly obtained from the color distribution which shows the particle distribution that, in the samples of up to 1 wt% CNTs, the CNT/epoxy suspension fully impregnated the textiles and there was no visual filtering to be observed, as shown in figure 4(b). However, for the samples with 1.5 wt% and 2 wt%, visual transparent regions could be observed near the lower surface as shown in figure 4(c-d), which means severe filtering and not homogenous impregnation of the textiles. Besides, the baseline composite specimen without CNT particles showed almost no visible voids, as shown in figure 4(a). But as the CNT increased further to 1.5 wt% and 2 wt%, there were more and more macro voids appearing, as shown in figure 4(c-d), which is more detrimental to the flexural properties. At the same time, the size and amount of the voids increased dramatically along with the increase in CNT concentration.

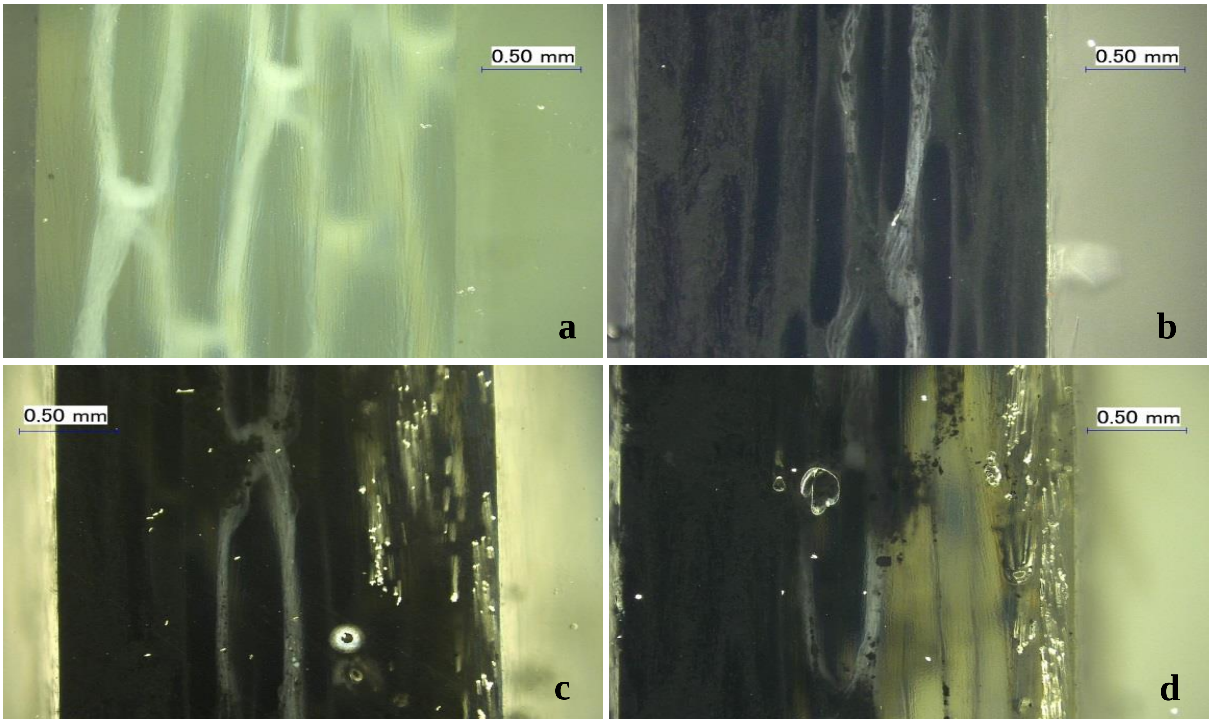

Figure 4. Change Cross section side-light transmission photomicrographs of laminates with different CNT concentration: (a) Reference (0 wt%); (b) 1 wt%; (c) 1.5 wt%; (d) 2 wt%.

4. Discussion

As the concentration of the particles increased, the flexural properties of the composites increased until CNT percolation threshold concentration of 1 wt% (already tested in other experiments). However, after the critical concentration point, the flexural properties of the composite began to decrease. The decrease in the flexural properties could be well explained combining the cross section side-light transmission and surface photomicrographs of the samples as shown in figure 4: the samples with CNT concentration of higher than 1 wt% showed more particle filtering and critical inner defects. Especially, when the CNT concentration is above 1 wt%, the macro voids also increased exponentially with the increase of the CNT concentration, which is detrimental to the flexural properties of the composites. The CNTs increase the mechanical properties, but the inner defects caused by the unavoidable adverse effect of the CNT concentration on the process parameters would decrease the electrical and mechanical properties. There would be a balance between the two effects. At CNT concentration of lower than 1 wt%, the increasing effect by the CNT was larger than that of the adverse effect, so the mechanical properties increased with increase in CNT concentration; However, at CNT concentration of higher than 1 wt%, the rapid increase of the inner defects would compromise or even surpass the enhancement effect of the CNT, so both the mechanical properties began to decrease. This is the main reason why the flexural properties of the samples began to decrease at higher CNT concentration.

The results showed that there is an optimum CNT concentration for manufacturing of multi-scale composites by the proposed process, considering the adverse effects of the CNT to the process parameters, i.e. the particle re-agglomeration and increase in suspension viscosity. The increase in the filtering effect and the amount of the inner defects, i.e. macro and micro voids, that lead to the decrease in the mechanical properties when the CNT concentration is too high are expectable. But in most cases, as long as the CNTs concentration is above the percolation threshold, there is also no need to inject extra amount of the CNT to the composites. But the percolation thresholds and the influence of the CNTs to the suspension viscosity are different considering the different length, dispersibility and polymer matrix. In this work, the optimal CNT concentration for the maximum improvement in the flexural properties is proved to be 1 wt%.

5. Conclusion and outlook

Liquid composite molding (LCM) processes are widely used for manufacturing of the advanced polymer composites. However, the conventional LCM processes face critical issues when it comes to injection of CNT or similar particle mixed thermoset suspensions. This paper used CRTM process for manufacturing of the CNT/epoxy/fiber hybrid composites, by which the through-thickness impregnation of the fiber textiles before compaction could be achieved. The main findings in this work can be summarized as follows:

- The process was proven to be effective for efficiently injecting CNT loaded suspensions with high viscosity, which greatly decreases the fabrication cycle time.
- For the experimental materials that are used, the optimum CNT concentration to achieve the maximum flexural properties of the samples is proved to be 1 wt%. The CNTs with 1 wt% increased the flexural modulus by 20 % and the flexural strength by 17 % compared to the baseline plate.
- According to the optical observation, the filtering of the CNTs in the through-thickness direction still exists at higher loads, which is considered due to the re-agglomeration in CNT and the dramatic viscosity increase of the suspension.

Considering the re-agglomeration of CNTs and the increase of the suspension viscosity, injection process modification with regard to the better dispersing and stabilizing the CNTs at higher loads, optimized injection temperature, pressure and etc. might be the critical steps for further researches.

References

[1] Thostenson ET, Ren ZF, Chou TW. Advances in the science and technology of carbon nanotubes and their composites: a review. *Compos Sci Technol*. 2001;61(13):1899-912.

[2] Lau KT, Hui D. The revolutionary creation of new advanced materials - carbon nanotube composites. *Compos Part B-eng*. 2002;33(4):263-77.

[3] Zhu Y, Bakis CE, Adair JH. Effects of carbon nanofiller functionalization and distribution on interlaminar fracture toughness of multi-scale reinforced polymer composites. *Carbon*. 2012;50(3):1316-31.

[4] Wang Q, Dai J, Li W, Wei Z, Jiang J. The effects of CNT alignment on electrical conductivity and mechanical properties of SWNT/epoxy nanocomposites. *Compos Sci Technol*. 2008;68(7-8):1644-8.

[5] Lonjon A, Demont P, Dantras E, Lacabanne C. Electrical conductivity improvement of aeronautical carbon fiber reinforced polyepoxy composites by insertion of carbon nanotubes. *J Non-cryst Solids*. 2012;358(15):1859-62.

[6] Han Z, Fina A. Thermal conductivity of carbon nanotubes and their polymer nanocomposites: A review. *Prog Polym Sci*. 2011;36(7):914-44.

[7] Qiu J, Zhang C, Wang B, Liang R. Carbon nanotube integrated multifunctional multiscale composites. *Nanot*. 2007;18(27).

[8] da Costa EFR, Skordos AA, Partridge IK, Rezai A. RTM processing and electrical performance of carbon nanotube modified epoxy/fibre composites. *Compos Part A-appl S*. 2012;43(4):593-602.

[9] Lefevre D, Comas-Cardona S, Binetruy C, Krawczak P. Coupling filtration and flow during liquid composite molding: Experimental investigation and simulation. *Compos Sci Technol*. 2009;69(13):2127-34.

[10] da Costa EFR, Skordos AA. Modelling flow and filtration in liquid composite moulding of nanoparticle loaded thermosets. *Compos Sci Technol*. 2012;72(7):799-805.

[11] Tomas Roll Frømyr FKH, and Torbjørn Olsen. The Optimum Dispersion of Carbon Nanotubes for Epoxy Nanocomposites: Evolution of the Particle Size Distribution by Ultrasonic Treatment. *Journal of Nanotechnology*. 2012;2:14.

[12] Chandrasekaran VCS, Advani SG, Santare MH. Role of processing on interlaminar shear strength enhancement of epoxy/glass fiber/multi-walled carbon nanotube hybrid composites. *Carbon*. 2010;48(13):3692-9.

[13] DIN EN ISO 14125: Fiber reinforced plastic composites - Determination of flexural properties.