STUDY OF CARBON NANOTUBE FILLER DISPERSION IN POLYMER COMPOSITES BY VARIOUS MICROSCOPIC METHODS

PhD thesis booklet

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1. Introduction and literature survey

In the past two decades, remarkable interest was given to the outstanding properties of carbon nanotubes (CNT) due to their unique electronic structure. This interest manifested in extensive research on carbon nanotube synthesis, characterization, and development of their application. The exploitation of such properties could mean their application as fillers for polymer composites by means of mechanical or electrical properties improvement. The mechanical reinforcement or the appearance for electrical conductivity in CNT filled polymer composites and its measure is a function of the CNT dispersion and distribution.

Concerning industrial applications, a product could hit the market if a price barrier is achieved by a synergy between the filler’s price and the improvements of the composite’ properties. Practically, the Van der Waals interactions between nanotubes induce the formation of compact nanotube agglomerates. The shear forces during composite processing needs to be larger than the agglomerate strength, for loosening and distributing the tubes properly in the composite.

However the nanotubes align due to too high shear forces in the polymer matrix, the decrease in tube-tube contacts significantly decrease or cause the disappearance of

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conductivity. Practically the interconnected loose clusters formation means the optimal case. By now an established theory had been formed for the effect of process parameters on the nanotube clusters formation, but the experimental investigation of CNT morphology has an outstanding importance as well.

The most common investigation method mainly in the industrial research and development is the transmission optical microscopy, which is very effective in the $10^{-3}$-$10^{-6}$ m range. When the investigated sample’s morphology does not change at this dimension scale and other unanswered question are still present the application of a better resolution microscope is advantageous. Scanning electron microscopy (SEM, $10^{-3}$-$10^{-9}$ m) besides transmission electron microscopy (TEM $10^{-5}$-$10^{-10}$ m) and conductive tip atomic force microscopy (C-AFM $10^{-5}$-$10^{-9}$ m) could be counted as further possibilities.

The aim of my work was to effectively characterize the microstructure of nanotube filled polymer composites by microscopic methods, and interpret the effect of process parameters on the properties of such composites of different material groups. The first researched topic was the three roll milled epoxy suspension loaded with 0.01 and 0.1 wt. % multiwall carbon nanotubes (MWCNTs), and I have investigated the dispersion of nanotubes in the suspension. As the second topic, I studied different extruded MWCNT loaded polystyrene composites and the effect of process parameters on the properties of composites. The third topic was the investigation of 3 wt. % MWCNT loaded, injection moulded polycarbonate composites with different process parameters and I have studied the effect of injection moulded parameters on the properties of parts.

2. Microscopic sample preparation and analysis

I have prepared the MWCNT/epoxy suspensions for TOM study by placing a drop of suspension between two glass plates and then I have investigated the morphology of the suspension.

The MWCNT filled polystyrene composite extruded strands were prepared for TOM analysis similarly to the injection moulded composite plate visualized on Figure 1.

A bar was cut from the middle of the injection moulded parts (Figure 1), from which a 5 µm thick slice was cut by a Leica Ultracut UCT microtome, then 70-100 nm thick slices were removed for transmission electron microscopy (TEM) analysis.

The optical microscopy images were performed by an Olympus BH2 microscope equipped with a Leica DFC 280 digital camera. The microscopy images were converted
in black and white bitmaps by Gimp 2.5 software, and the numerical values were obtained using another free software ImageJ developed in Fraunhofer ICT. Thus I have calculated the area occupied by black dots relative to the total area, named area fraction ($A_f$). The number of agglomerates was also calculated.

TEM investigation was carried out on a Philips CM20 transmission electron microscope operated at 200 kV using a LaB$_6$ cathode.

Scanning electron microscopy (SEM) and conductive tip atomic force microscopy (C-AFM) analysis was performed on flat surfaces of the samples previously cut by microtome, the back side of these pieces were fixed on metallic sample holder by conductive carbon paste.

SEM analysis was done using a LEO 1540Xb field emission scanning electron microscope (FASEM) operating a 5 kV and equipped with an Everhart-Thornley seconder electron detector.

C-AFM investigation was carried out using a Multimode 8 AFM (Bruker) with 20 nm Pt-Ir coated tips. The following parameters were used under normal conditions: 100 pA sensitivity and 100 mV DC bias, 10 μm scanning window, and 512x512 pixel resolution. The principle of C-AFM measurement is that a 20 nm diameter tip scans a flat surface. During the scans the surface topography is mapped, and the electrical conductance of the surface is measured point-by-point. The C-AFM images could be handled as bitmaps, and the area occupied by conductive spots could be calculated, and correlated to the total investigated area. Ten images were averaged for each sample.

![Figure 1. Sample preparation for microscopy analysis of injection moulded composites.](image)
3. Results

3.1. Three-roll milled MWCNT/epoxy suspensions

The aim of the analysis was the observation what improvement could be obtained in nanotube dispersion by increasing the roll speed of the three roll mill and by increasing the number of passes in case of 0.01 and 0.1 wt. % loadings. The samples were prepared by two roll speeds (180 and 270 rpm) and with one and five passes. I have investigated the suspension by transmission optical microscopy, and then I have converted the optical micrographs in bitmaps (some examples are displayed on Figure 2) and I have evaluated them statistically (which results are displayed on Figure 3). Comparing the bitmaps it is notable that in case of the studied parameters the increase in number of passes decreased more significantly the MWCNT quantity in agglomerate state than the increase in roll speed.

Figure 2. Bitmaps of transmission optical microscopy images of three-roll milled MWCNT/epoxy suspensions for 180 and 270 rpm screw speed, and 0.01, 0.1 wt. % MCNT loadings.
The effect of the process parameters on the nanotube agglomerates dispersion could be noted on Figure 3. Figure 3 „B” displays the significant decrease in the agglomerate area fraction by the increase in the number of passes for both compositions and roll speeds while the decrease of agglomerate counts (Figure 3 „A”) seems to be smaller. Furthermore, this agglomerate count decrease is more significant in case of higher rather than lower roll speed samples of both compositions.

I have interpreted the above observations based on the different characteristics of the two possible dispersion mechanisms of MWCNT agglomerates. One of them, the exfoliation akin to dissolution: mobile polymer chains in the liquid intrude between the MWCNTs, wet them, and gradually peel them off the agglomerate. The other mechanism, rupture is a faster process, if the shear forces are high enough, the agglomerate breaks into smaller pieces on its weakest sites.

Considering that the agglomerate strength is reversely proportional to its surface area, obviously the larger agglomerates break into smaller pieces relatively fast. The surface area of individual agglomerates becomes smaller, therefore their strength increases and their further rupture is less and less probable. They achieve such a size, where at a given shear their rupture is not but only their exfoliation is possible, which is however a slower process. Therefore it is expected that the ratio of the smaller agglomerates will increase during processing.

At higher shear forces, accordingly at higher roll speed the characteristic size (below which no further rupture of agglomerates takes place) will be smaller, so their size decreases faster below the optical diffraction limit.

Figure 3. Summary of statistical evaluation of the TOM images of suspensions containing 0.01, 0.1 wt. % MWCNT and processed by 180 and 270 rpm roll speeds, by 1 and 5 passes each. (A): number of agglomerates; (B): agglomerate area factions.
3.2. Extruded MWCNT/polystyrene composites

The motivation of this analysis was to compare the effects of the screw speed and throughput used in a twin screw extruder on the dispersion of nanotubes in different MWCNT loading MWCNT/polystyrene composites. Figure 4 displays the TOM bitmaps obtained from 3-, and 5 wt. % MWCNT loaded extruded polystyrene composites, where the black objects correspond to the nanotube agglomerates while the background is associated to the polymer matrix. It is clearly visible that there are much less agglomerates remained in cases of 1100 rpm than 500 rpm screw speed for both 3 and 5 wt. % MWCNT concentrations.

![Figure 4. Bitmaps obtained from transmission optical microscopy images of 3- and 5 wt. % MWCNT loaded polystyrene composites.](image)

The statistical analysis summary of the TOM images of 2-, 3- and 5 wt.% nanotube containing polystyrene composites extruded with 500 and 1100 rpm with 7.5 and 10 Kg/h throughput at extruder temperatures followed a special profile (P) and of uniform 210 °C is presented on Figure 5. Part „A” of figure displays the area fractions of the agglomerates as well as the so-called special mechanical energy (SME - mechanical energy conveyed from the extruder to the extrudate in a certain process) values. Figure 5 part “B” shows the number of agglomerates per mm². It is visible that the area fraction depends strongly on nanotube loading, besides it decreases significantly with the growth of screw speed. An approximate reverse proportionality between SME values and area fractions can be observed.
It is visible that in the case of lower, 500 rpm screw speed the rise of MWCNT filler content involved not only the increase of the agglomerates area fraction, but their number has increased as well. This increase in agglomerate number is about proportional with the variation of nanotube loading. In case of the higher, 1100 rpm screw speed samples this tendency is not present, at higher loadings the number of agglomerates in most cases decreased more than expected. I have explained this phenomenon by the smaller shear in case of lower screw speed or lower loading samples. It makes larger the critical size below which rupture of agglomerates does not take place, but only the slower exfoliation mechanism can decrease their size. Consequently the proportion of smaller size agglomerates increases. In contrast with this, higher viscosity in case of the higher loading samples and higher screw speed makes shear high enough to decrease the critical size significantly. Therefore rupture of smaller agglomerates is possible, so their proportion is smaller in these samples.

3.3. Injection moulded 3 wt. % MWCNT/polycarbonate composites

Diluting by a twin screw extruder the masterbatch resulted in 3 wt. % MWCNT containing polycarbonate raw material used for injection moulding. This was processed using different settings. Among the injection moulding parameters the melt temperature (280, 300, 320 °C) and the injection velocity (6, 18, 30, 30 mm/s) were varied.

I have measured the electrical resistivity of the resulted parts and I have observed magnitude differences between the resistivity values. Therefore I carried out transmission optical microscopy analysis in order to understand what caused such differences. On the optical scale there was no significant difference between the samples,
so I have investigated them by scanning- and transmission electron microscopy.

SEM results revealed that in case of some parameters the polymer chains were wetted in different grade.

TEM investigation showed some differences in the morphology of formed nanotube networks, but these results did not explain the reason of such difference in electrical resistivity.

![Figure 6. Conductive tip AFM images of the used raw material (Rm) and the injection moulded 3 wt. % MWCNT/PC composites.](image)

Therefore I have used C-AFM to analyse the raw material used for injection moulding and the results of injection moulding. Figure 6 displays clearly the difference between the various injection moulding settings, and their effect on the morphology of conductive network.

The conductive images can also be used as bitmaps and the area occupied by conductive spots can be calculated. I have demonstrated that this reflects well the differences in the morphology of conductive networks in the samples supposedly produced by the different injection moulding parameters, moreover they are in correlation with the bulk volume resistivity results. Thus, by increasing the shear during injection moulding decrease in the conductive spot’s size and area fraction were found, due to the increase of nanotube separation. I have observed a contrasting effect at the highest melt temperature: the formation of larger conductive sports could be explained by the reagglomeration of the tubes due to the lower shear forces and the higher mobility of the polymer chains.

4. Theses

1. a. I have investigated the dispersion of carbon nanotubes in bisphenol-A-digycidyl-ether epoxy resin processed through three-roll mill by transmission optical microscopy. I have determined that in the investigated parameter range the number of agglomerates
observable by optical microscopy can be more effectively decreased in three roll milling by repeated processing than through higher roll speeds [6.1.1./2, 3, 4].

1. b. I have observed, that in case of lower roll speed the multiple milling decreases more significantly the size of agglomerates, while their number decreases only moderately. Using higher roll speed, multiple milling decreases significantly not only the number of agglomerates, but their sizes as well. I have explained the difference by the change in the ratio of dispersion mechanisms which happens at different agglomerate sizes, due to different shear [6.1.1./2, 3, 4].

2. a. I was first to prove by transmission optical microscopy analysis that a reverse correlation exists between the so-called specific mechanical energy transmitted to mass unit of material and the total size of undispersed agglomerates in extruded MWCNT/polystyrene composites of different compositions produced by various combinations of process parameters [6.1.1./2, 4, 5].

2. b. I have observed that in all the cases at lower screw speed both the total size and number of agglomerates increases with increased MWCNT loadings while for higher screw speed the increase of the agglomerate size is not followed by the increase of number of agglomerates. I have explained the phenomenon as the dispersion of smallest visible agglomerates happens not only through exfoliation, dominating at lower shear, but due to higher sheer caused by higher screw speed, where the rupture mechanism is significant [6.1.1./2, 4, 5].

3. I was first to apply conductive tip atomic force microscopy for characterization of local conductive properties of injection moulded MWCNT polycarbonate composites prepared with different injection speeds and melt temperatures. I have observed that in correlation with bulk conductivity, the average distance of conductive spots increases and their total area decreases with the growth of injection velocity in the samples produced at the same melt temperature. I have explained the phenomenon in correlation with TEM results that the higher shear caused by the injection velocity increase separates nanotubes from each other, reducing the density of the conductive network. At the highest melt temperature I have observed the increase of the conductive spot sizes. I have interpreted this as the reagglomeration of nanotubes due to the higher mobility of the polymer chains [6.1.1./1, 2, 4].
5. Application possibilities

The determined correspondence between the process parameters and the material’s properties as well as the new knowledge concerning the materials microstructure can directly be exploited in the industrial materials design for all the three investigated systems.

The conductive tip atomic force microscopy investigation methodology can be applied for the study of local electrical conductivity in high resolution, therefore it can contribute to the understanding of the conductive network formation, and to the selection of correct process parameters in the development of various conductive composites.

6. Dissemination

6.1. Scientific papers

6.1.1. Scientific papers related to the thesis points

1. Visualization of the conductive paths in injection moulded MWCNT/polycarbonate nanocomposites by conductive AFM; Bernadeth Kiss-Pataki, Jyri Tiusanen, Gergely Dobrik, Zofia Vértesy, Zsolt Endre Horváth; Composite Science and Technology, 90, 2014, 102-109. IF: 3.328


3. Influence of process parameters on the morphology, rheological and dielectric properties of three-roll-milled multiwalled carbon nanotube/epoxy suspensions; Ganiu Olowojoba, Shyam Sathyanarayana, Burak Caglar, Bernadeth Kiss-Pataki, Irma Mikonsaari, Christof Hübner, Peter Elsner; Polymer, 54, 2013, 188-198. IF: 3.379


6.1.2. Scientific publications not related to the thesis points


6.2. Presentations

6.2.1. Presentations related to the research topic


Vuorinen, (EN, poster).


6.2.2. Presentations not related to the thesis points


6. XVII Internal Symposium of Analytical and Environmental Problems, Szeged, Hungary, 2011. 17th of September: Multi-element characterization of archaeological ceramic shards from the Tasnad-Sere site, Tasnad, Romania, Bernadeth Pataki, Marta Ballók, Andras Bartha, Zofia Vértesy, Laszlo Kékedy-Nagy, Ioan Bratu, Emil Indrea,
Erzsebet Veress, (EN Poster).


14. Colloquium Spectroscopicum Internationale XXXVI, Budapest, Hungary, 2009, 30th August – 3rd September, FT-IR spectroscopic and XRD study of ceramic artifacts from Satu Mare county archaeological sites, Romania, Bernadeth Pataki, Ioan Bratu, Emil Indrea, Liviu Dărăban, Corina Ionescu, Róbert Gindele, Erzsébet Veress, (EN,


17. VII. Magyar Tudomány Napja Erdélyben Nemzetközi Konferencia, Cluj Napoca, Romania, 2008. 21-22nd of November, Provenance study by XRF analysis of ceramic artifacts found on Satu Mare county archaeological sites, Romania. Bernadeth Pataki, Róbert Gindele, Liviu Dărăban, Erzsébet Veress, (HU, poster).


