NANO DIRECT PROCESS FOR COMPOUNDING OF NANOCOMPOSITES

Marina Matta, Coperion GmbH, Stuttgart, Germany
Paul Andersen, Coperion Corporation, Ramsey, NJ, 07446

Abstract

Numerous varieties of polymer nano-composites have been developed on the laboratory scale and characterized regarding their properties. These include, nanofiller based on exfoliated clay, nanosilver, carbon nanotubes (both single and multiple wall geometry), zinc oxide, silica, and graphene among others. Carbon nanotubes (CNT) are of particular interest as they play a special role when it comes to improving or creating electrical conductivity in a polymer matrix.

Currently most CNT based nano-composites are produced on co-rotating twin-screw compounding extruders via split feeding the polymer and the CNTs. However, processes using aqueous nano suspension are on the rise and offer new opportunities regarding technical performance, economical viability and reduction of health concerns related to the particle size of the CNTs. By using well pre-dispersed suspensions, which are already available on the market, it becomes easier to produce nanocomposites that provide the required characteristics, such as electrical conductivity. Also the usage of aqueous solutions enables dust-free handling of the carbon nanotubes.

This presentation will introduce the Nano Direct Process and show its advantages in comparison to the conventional melt-mixing process.

Introduction

Carbon nanotubes have unique properties and with their help new materials with exceptional % loading vs. performance qualities can be developed. A distinction is made between single-walled nanotubes (SWNT) and multi-walled nanotubes (MWNT), Figure 1. MWNTs consist of several rolled layers of graphene, while SWNTs consist of one tube and are more difficult and more expensive to produce. The typical diameter of the tubes is between 1 and 50 nm, whereas the length is in the micrometer range. This results in aspect ratios of up to 1:1000 [1].

Carbon nanotubes are available in the form of large aggregates, Figure 2a, that are comprised of "millions" of single CNT fibers, Figure 2b.

The properties of CNTs often exceed the characteristics of other materials. Related to their weight
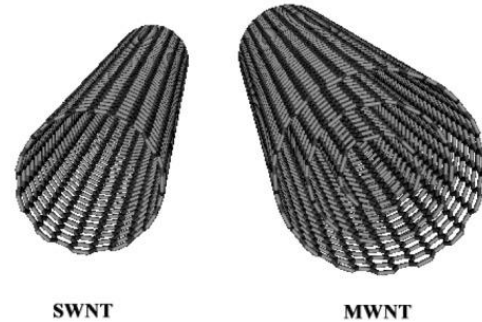

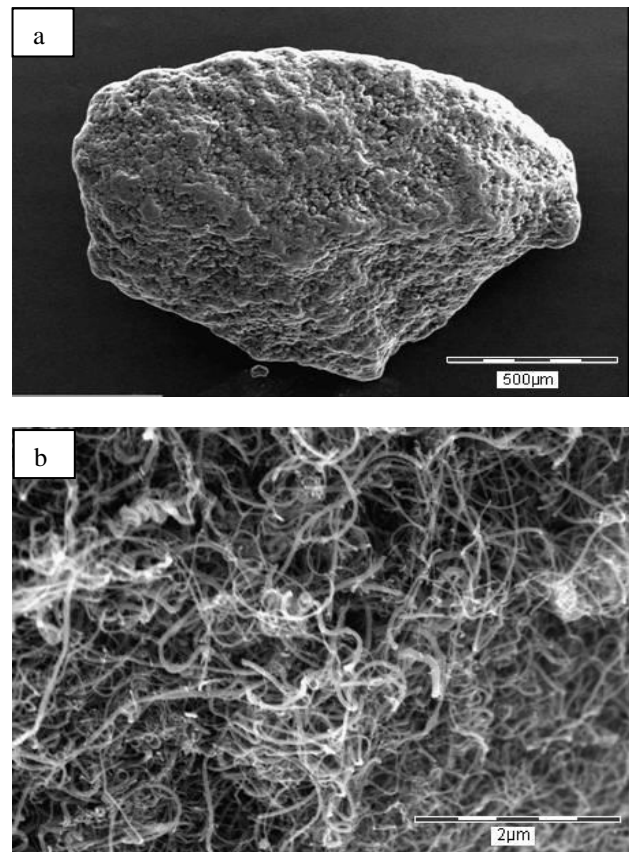Figure 1: Single-walled nanotubes (SWNT) and multi-walled nanotubes (MWNT).

Figure 2: a) Carbon Nanotube aggregate
b) Carbon Nanotube fibers

the specific strength of the nanotubes is up to 400 times greater than the strength of steel and up to 20 times higher than that of carbon fibers [2]. Furthermore they have an extremely high electrical and thermal conductivity. Due to

the high aspect ratio it is possible to improve the electrical properties of different polymers by adding only small amounts of CNTs [3]. Specifically in the fields of electronic and electric engineering there is a high variety of applications, for example, the production of electrostatic discharge (ESD) housings to protect electrical components from overvoltage and spark discharge.

To achieve electrical conductivity the CNT aggregates first have to be de-agglomerated and the single fibers separated and distributed in the polymer matrix. Only when the CNT aggregates are broken down and dispersed well within the polymer matrix can the composite become electrically conductive.

In any system, the number of filler contact points rise with the percent filler loading. However, due to the high aspect ratio of the nanotubes there is a higher probability that they intersect and contact each other in some way as opposed to spherical particles, Figure 3. Therefore, a smaller amount of CNTs is needed to achieve electrical conductivity [4].
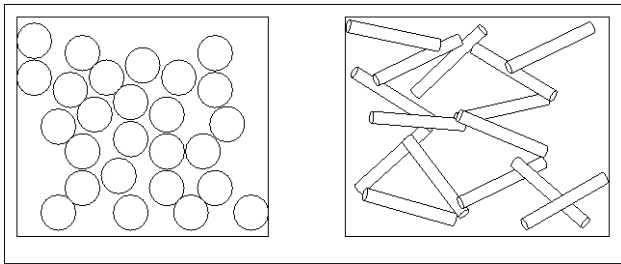

Figure 3: Comparison of the particle shape in terms of percolation.

Upon reaching certain filler concentration the percolation threshold is reached, Figure 4, and a conductive network is generated so that charge transport takes place. The aim is to achieve electrical conductivity by keeping the CNT content as low as possible
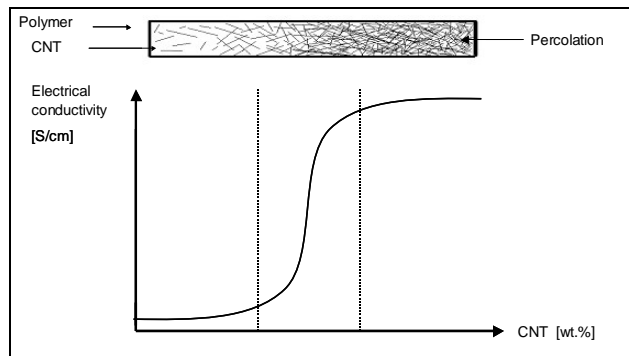

Figure 4: Electrical conductivity as function of CNT concentration.

Currently most CNT based nano-composites are produced on co-rotating twin-screw compounding extruders. The matrix polymer is fed in upstream and the CNTs introduced downstream directly into the polymer melt. However the shear energy generated by the extruder's dispersive mixing screw elements is very low compared to other possible mixing units, such as agitator bead mills [5]. For some CNTs better results might be achieved when feeding the agglomerated particles together with the polymer into the first barrel. This, however, depends on the CNT type and size of the agglomerates and it is not possible to draw any general conclusions.

Additional background information on compounding nanocomposites is available in the chapter by Andersen in the Polymer Nanocomposite Handbook [6]

Experimental

Co-rotating Twin-screw Extruder

Material transport in intermeshing, co-rotating twin-screw extruders is generally dependent on drag flow. The screws pick up the material as they rotate and where the two screws meet a complete transfer of the material from one screw to the other takes place. The tip of one screw wipes the flanks and roots of the other screw, resulting in a self-wiping action. As the material is transferred from one screw to the other, the direction of material flow is changed and new material surfaces are created with each screw revolution.

This operation provides the mechanism of conveying, mixing and pressure build up. The mechanism is best defined through some basic geometries and these parameters, Figure 5, can be used to define all twin screw extruders.

Diameter ratio (D_o/D_i) indicates free volume of the extruder. The greater the ratio the higher the amount of material which can be transported by the screws. Also the greater the ratio the less shear on the product. However, this value cannot be increased indefinitely. Geometry constraints and mechanical properties of the screw shaft and elements limit it.
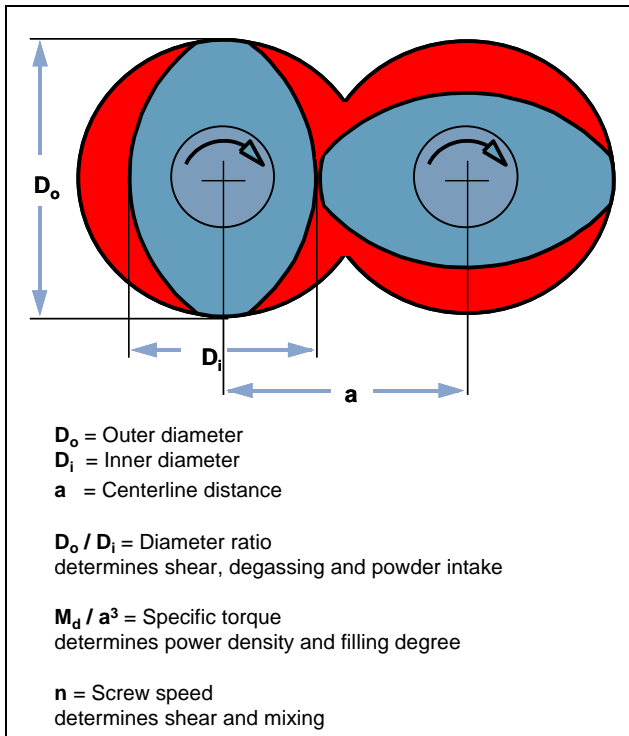
Figure 5: Geometry of twin-screw extruders.

D_o = Outer diameter
D_i = Inner diameter
a   = Centerline distance

D_o / D_i = Diameter ratio
determines shear, degassing and powder intake

M_d / a^3 = Specific torque
determines power density and filling degree

n = Screw speed
determines shear and mixing

Among conveying screw elements, co-rotating twin-screw extruders utilize staggered kneading discs to impart high shear stresses. For more gentle mixing, gear type or tooth mixing elements are employed. Like the barrels of the processing section the screw elements follow a modular design, which allows configuring specific sequencing of desired unit operations, Figure 6. For example, the polymer and fillers can be introduced at the same feed location at the beginning of the extruder, or the fillers can be metered in further downstream after the polymer has been melted.
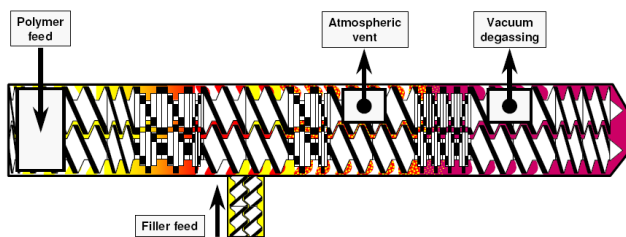

Figure 6: Co-rotating intermeshing twin-screw.

Using the conventional process for nanocomposite production the polymer is fed into the first barrel, while the CNT particles are added downstream with a side feeder directly into the melt, Figure 7. With kneading blocks the agglomerates are first dispersed and then further downstream distributed in the polymer melt. By feeding the CNTs into the polymer melt it is difficult to disperse and disentangle the agglomerates and to separate the single fibers, as high shear energy levels are needed. For some CNT types trials showed better results when feeding the agglomerated particles together with the polymer into the first barrel. This, however, depends on the CNT type and size of the agglomerates.

For the Nano Direct Process the Carbon Nanotubes are pre-dispersed with a bead mill. The suspension has a CNT content of up to 10%. From visual observation, the viscosity is strongly dependent upon the CNT concentration. Therefore with higher CNT concentration the suspension becomes highly viscous and is difficult to feed. The Carbon Nanotubes are dispersed with solvents and the application of very high shear energy. Simultaneously the suspension is stabilized with additives, so that no re-agglomeration of fibers can happen in the next process steps. For more detailed description consult reference 5.

The trials were run on a ZSK18 Mega Lab twin-screw extruder with throughputs of up to 10 kg/h. The twin-screw extruder set up is ten barrels or 40/1 L/D (length/diameter). The polymer is fed into the first barrel and is melted, before the CNT suspension is injected at barrel four, directly into the melt, Figure . The highly viscous suspension is fed against the operating pressure of the extruder and is mixed into the polymer melt. After the distribution of the nano particles the carrier liquid is evaporated and the vapor is carried out via an atmospheric vent. In barrel 9, vacuum is applied to remove the remaining volatiles and the discharge takes place through a die head.

The resultant conductivity of each of the materials was measured on pressed plates with a diameter of 80 mm and a thickness of 2 mm. Therefore two stripes of conductive silver lacquer were applied on the sample with a distance of 30 mm and the surface resistivity was measured with an ohmmeter [4].
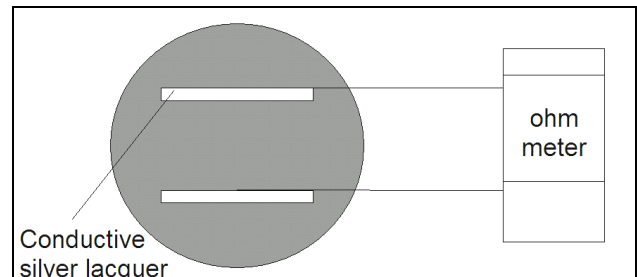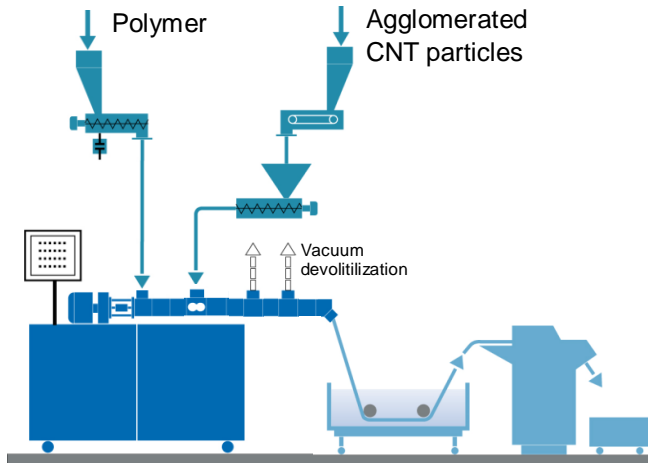

Figure 7: Measuring arrangement
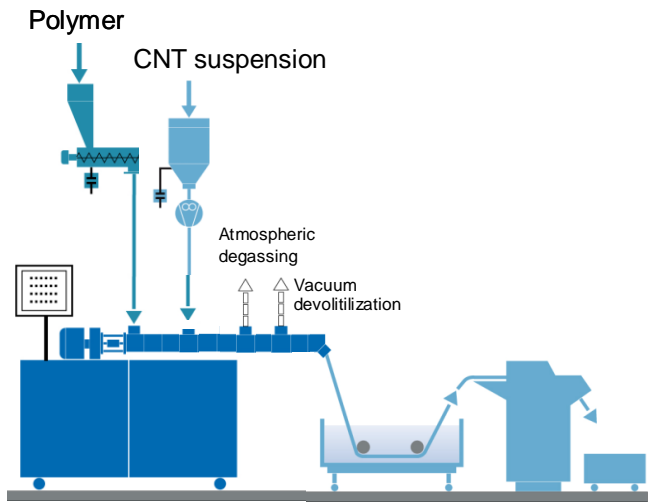
Figure 8: Conventional process.

Figure 9: Nano Direct Process.

Results

Trials based on the traditional melting / mixing process have shown that the achievable electrical conductivity of the composites is dependent upon the viscosity of the polymer, Figures 10, 11. The higher the viscosity of the polymer (within a shear rate of 100-1000 s^{-1}), the higher the shear stress and therefore the better the dispersion of the CNT agglomerates.

The trials have shown that the higher viscosity of the mLLDPE results in the low surface resistance of the composite at reduced CNT concentrations. With LDPE and HDPE, which have a lower viscosity, much higher CNT concentrations of 7-8 wt% are needed to reach the percolation threshold.

Using the Nano Direct Process, the conductivity, Figure 12, seems not to be dependant on the polymer type and its properties. In many respects this is not surprising

since the CNTs have been pre-dispersed in what could be considered a suspension masterbatch. Also from additional data to be included during the ANTEC presentation, conventional processing based on a pre-dispersed CNT masterbatch improved the percolation results, but nowhere near the level of the Nano Direct process. As a consequence of this improved dispersion within the polymer matrix, percolation is reached at much lower CNT concentrations of about 1.5 to 2 wt.-%.
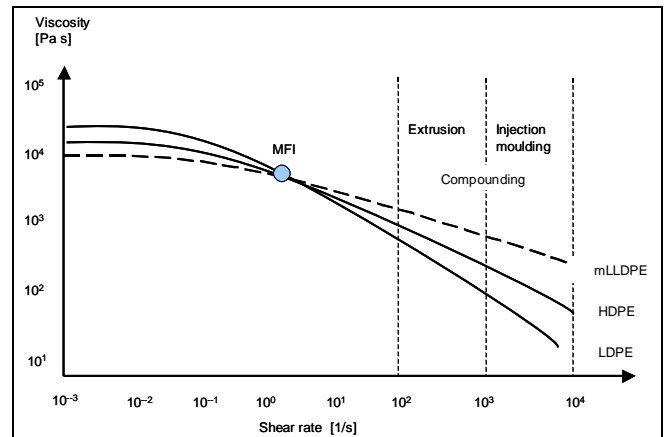

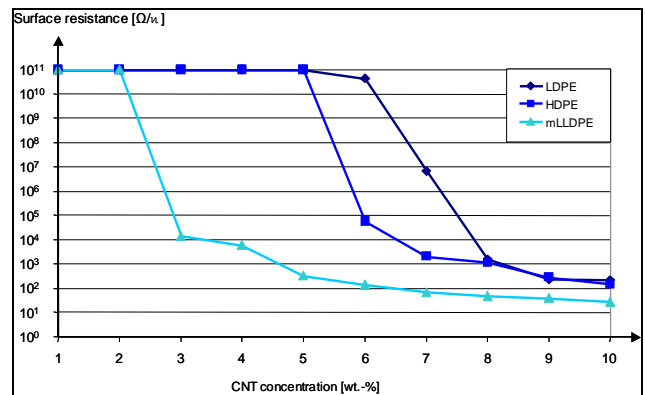Figure 10: Viscosity as function of shear rate.

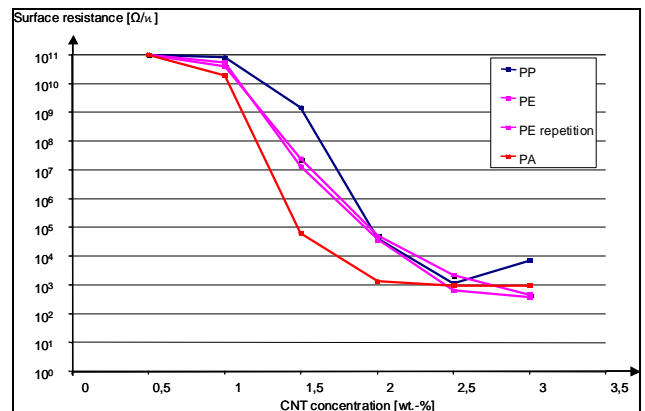Figure 11: Percolation curves, conventional process.

Figure 12: Percolation curves, Nano Direct Process.

Figure 13 shows the light optical microscope photos of the HDPE composites produced with 2 wt.-% of CNTs. Sample A was produced with the conventional melting /mixing process and shows poorer dispersion with a significant number of large agglomerates. Sample B was produced with the Nano Direct Process and shows a much better dispersion, with only a few small agglomerates.
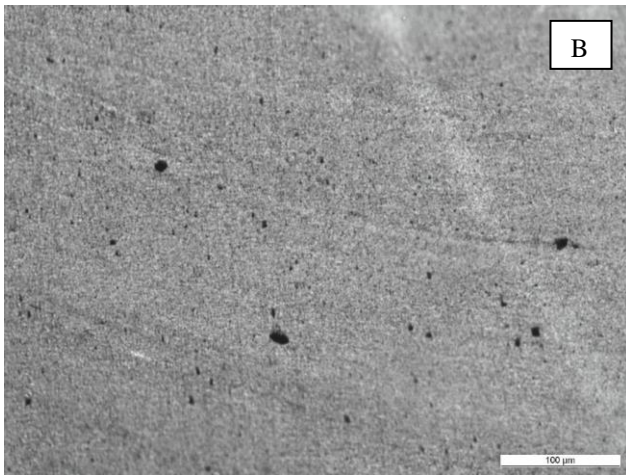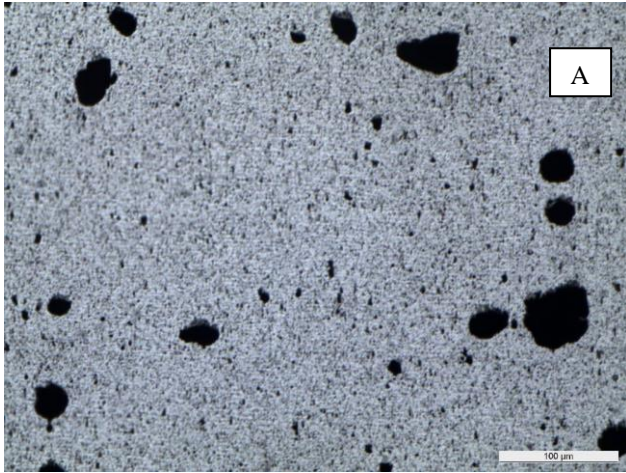
Figure 13: Dispersion of 2% CNTs in HDPE
        A) Conventional process
        B) Nano Direct Process

The main process task of the Nano Direct Process is to devolitalize the water out of the system and to keep the temperature high in the injection zone. As the water takes the evaporation enthalpy from the polymer melt, the melt has to be prevented from freezing. Kneading elements bring the necessary energy, in form of shear energy. As the CNTs are already well dispersed, the percolation can be reached at much lower CNT concentrations.

A potential limitation of the Nano Direct Process is the amount of water or solvent that can be removed reliably. In the course of the trials it was possible to devolitalize 30 wt.-% of water in relation to the compound produced.

Summary

Comparing both processes the results of the Nano Direct Process are better, as the carbon nanotubes are already well dispersed in the suspension and do not have to be de-agglomerated in the twin-screw extruder. The well-dispersed material is fed into the extruder and is distributed within the melt, so there is no need to disperse the agglomerates in the extruder and percolation can be achieved with lower CNT concentrations.

Using the Nano Direct Process the dispersion is independent of the polymer type and it's viscosity, to the greatest possible extent.

The Nano Direct process was successfully tested for other polymers and nano particles, such as polyamide with nano clays.

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