

CNTs in polymer melt: The influence on dispersion by sonication

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Abstract

Nanocomposites have become more important as the implementation of nanoparticles in polymer allows additional functions in common industrial parts. Especially in the fabrication of filaments or fibres nanomodification is crucial, as only very small fillers can be added to the very fine fibres (common fibre diameter is 20 µm, fine filaments are 1 µm). [1,2]

Discharging fibres, conductive fibres and many other functional fibres raise in their importance nowadays, as the need for highly functional but flexible surfaces, such as textiles rises. Especially the dispersion quality is essential for the final enhancement of the filament properties. Homogeneously distributed particles serve function throughout the full fibre giving equal mechanical and functional properties over the length of the fibre and of the manufactured textile [3,4]. Counteracting this requirement nanoparticles tend to form agglomerates due to their high specific surface area during the manufacturing of those nanocomposites [5].

In this paper the distribution and dispersion methods are introduced. The homogenization of carbon nanoparticles in polymer melt is enhanced by a novel sonication unit of ITA and BANDELIN electronic GmbH & Co. KG. The first development steps of the semi-industrial unit fabrication as well as the first experimental results in the lab scale of the modification of the dispersion will be shown. Special focus will be laid on the sealing of the new sonication unit as well as the positioning and equipment size when being implemented in an existing melt spinning unit.

The paper will show the status of the project as well as the next steps, to show other participants the potential of the newly developed unit.

1. Introduction

Distribution (equivalent distribution over the polymer matrix) and dispersion (disaggregation of large aggregates to form single particles) of nanoparticles in a polymer matrix can be enhanced via several methods [6]:

- Melt mixing
- Solution mixing
- In-situ polymerisation
- Particle functionalization
- dispersing agent
- Ultra-sonication dispersion



Within the direct melt mixing process melt viscosity, temperature, pressure and design of twin screws are the most important process influences on the particle distribution and dispersion. Currently this is the most relevant compounding process to produce compounds efficiently. [7, 8] Though the impact of these influences depends on polymer and particle, high sheering rates and long residence times are known to counteract particle accumulation. On the contrary, both high sheer rates and long residence times can cause chain degradation of the polymers and thereby drive the decline of product quality. Additionally, besides the filler agglomerates some nanoparticles themselves, e.g. on carbon nano tubes (CNTs), tend to rupture under high shear stress. Thereby they lose their functionality. [9, 10] Finally, melt mixing cannot be applied with high sheer rated and long residence times for all mixtures.

Alternatively, solution mixing can be used, where both dissolved polymer and nanoadditives are mixed. When both mixtures have a low viscosity, high quality dispersions can be reached. Unfortunately, following the removal of the (potentially toxic) solvent, particles tend to re-agglomerate. Furthermore, the removal of the solvent can be work, and therefore cost intensive. [11, 12, 13, 14, 15]

In-situ polymerization is used for simultaneous nanocomposite production and homogenisation. For this treatment nanoparticles are added to the monomers. The monomer's viscosity is low and allows homogeneous mixtures. Unfortunately, the manufacture at industrial scale is not economical for specialized processes due to the high effort required. [16, 17]

Particle functionalization through covalent or non-covalent bonds can be achieved via linkage of atoms or molecules to reduce interactive forces between the particles. As this procedure is work intensive it is only performed in the lab scale. [18, 19, 20]

Dispersing agents are based on one of the three mechanisms as shown in **Figure 1**:

- Electrostatic (in polar fluids, acting through polar-polar repulsion)
- Steric (long-chained molecules prevent assembly)
- Electrosteric (combination of electrostatic and steric)

These dispersing agents rely on the effect that both electrostatic and steric agents enlarge the distance between the particles and thereby avoid the formation of agglomerates. The repulsion of the particles beneath each other or the use of spacers or their combination is shown respectively in **Figure 1**.

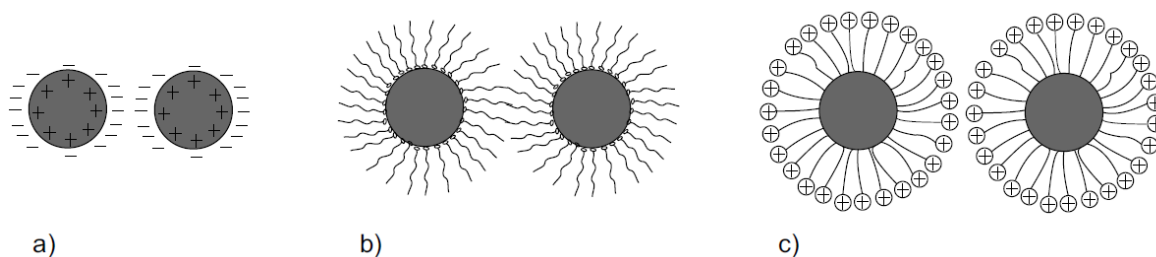


Figure 1. Mechanisms of dispersing agents for nanoparticles; a) electrostatic, b) steric, c) electrosteric [21]

In ultra-sonication dispersion cavitation effects, based on the implosion of cavitation bubbles forming micro-currents (jets) at high sonication intensities, are used. While this method is common for the rupture of 3D networks of vulcanised rubber [22, 23], the dispersion of nanoparticles in polymer melt has only been used at the lab scale [20, 24, 25, 26]. Here the method was successful at destroying agglomerates and achieving homogeneous particle distributions. The implementation of this method in a semi-industrial spinning line is covered in the following. The potential use of dispersing agents in such a system is so far not covered, to avoid interactions.

2. Theoretical unit design

A common melt spinning process consists of an extrusion unit, a spinning unit and a take-up unit. For the implementation of a sonication unit in such a process, only the extrusion unit has to be modified, as this is the part, where the polymer is available as liquid melt. The implementation of the sonication unit is achievable at several positions. As the particles tend to re-agglomerate, though they were primarily homogeneously dispersed in the extruder, the implementation of the sonication unit at the latest point possible is recommended. Therefore the unit is implemented right before the spin pack. The spin pack consists of several filtration units (filter meshes and filter sands) and therefore requires a melt without agglomerates. The set-up is shown in *Figure 2*.

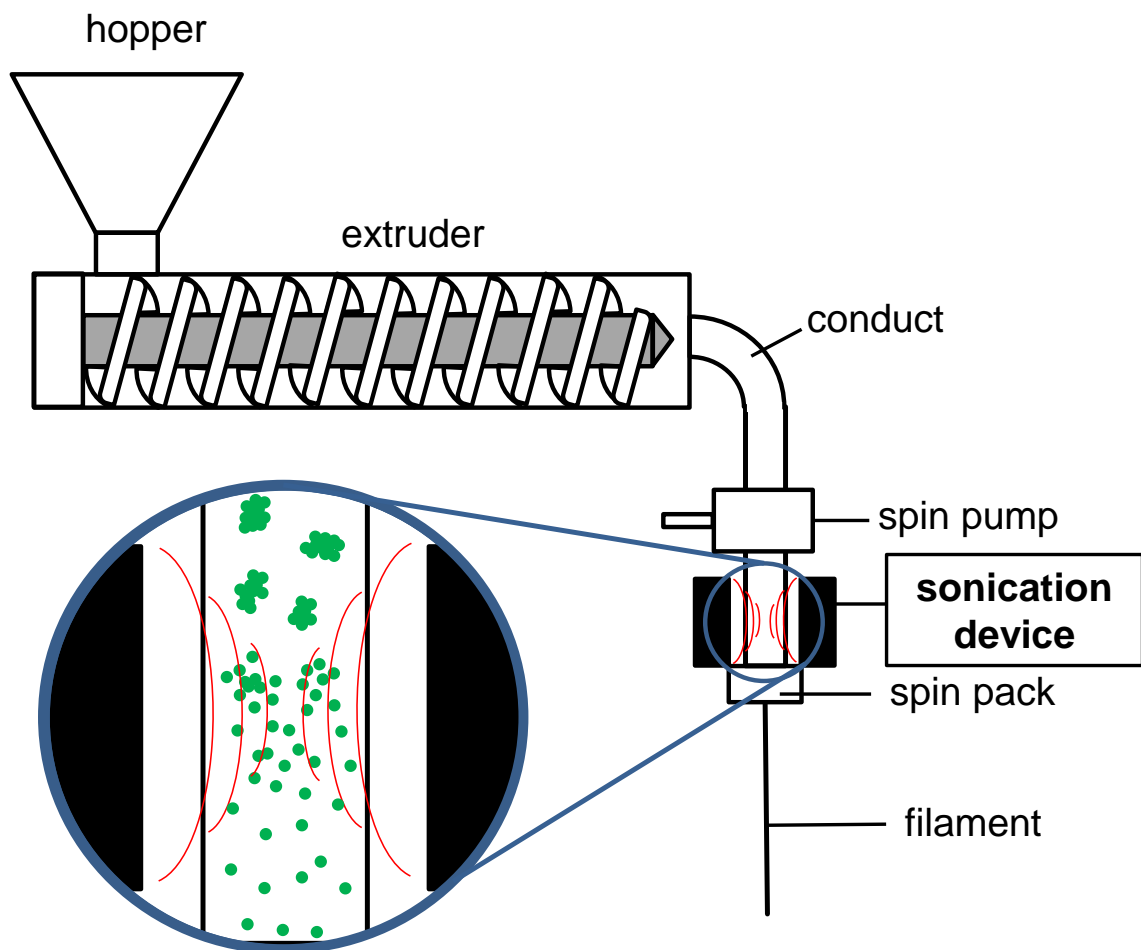


Figure 2. Position of the implementation of a sonication unit in a spinning line at the latest possible step of the extrusion unit

The ultra-sound can be applied via several set-ups. Number of sonication units, direction of implementation and strength of implementation of the ultra-sound are considered in this set-up. So far the units are going to be implemented individually. This allows to determine the effect of dispersion of one sonication device, but could also give information on multiple sonication units, when the material is re-entering the extruder after the first trial. For this study the implementation direction design involves both radial insertion from all sides through four units as well as a linear exposure through a rod sonotrode, that is implemented to the melt path from one side only. The aim is to achieve a maximum intensity of 400 W with a single sonotrode, while the radial unit can add up to 1.000 W. As

the implementation of both units does not allow to visually investigate the dispersion quality in the melt duct right after sonication application separate tests were conducted on the lab scale.

3. Test design

Lab scale sonication tests are conducted as the direct sonication impact cannot be visualized directly in the melt spinning process, as the system is enclosed. Sonication influences can only be measured by investigation of final particle dispersion in the melt/filament and/or by examination of the remains, e.g. particle lumps and their position, in the filters. Here agglomerates and inhomogeneous distributions can be detected visually via microscopy. Nevertheless it is important to understand further influences, as melt behaviour, jet formation and temperature variation in the sonication area as well, which cannot be detected afterwards. Therefore a sonication test is designed.

For simple set up a rod sonotrode is used. Radial sonication is preliminarily excluded, as the system is then already enclosed from four sides and does not allow as much insight as the rod system. For the experimental design a standard ultrasonic transducer type UW 200 equipped with a sonotrode type TS 410 and a sonopuls ultrasonic homogenizer HD 4100 by BANDELIN electronic GmbH & Co. KG, Berlin, Germany is used. In an oven by Fourné, Maschinenbau GmbH, Alfter, Germany, roughly 20 g of polycaprolactone (PCL) Capa 6506 supplied by Perstorp Specialty Chemicals AB, Perstorp, Schweden, is melted at 200 °C in a 100 ml glass beaker for 240 min. The beaker is then transferred a heating plate, positioned underneath the sonication device to retain the temperature. Multiwall carbon nanotubes (MWCNTs) type NC7000, produced as a powder via vapor deposition, supplied by Nanocyl NA, Sambreville, Belgium are added on the melt via a spatula. Through lowering the sonotrode into the powder, it is pushed into the melt. No further stirring is applied. The sonotrode is inserted into the melt by about 1 cm and sonication is applied at an amplitude of 100 % without pulsation for 90 seconds to include an energy of 19.413kJ. The set-up is shown in **Figure 3**.

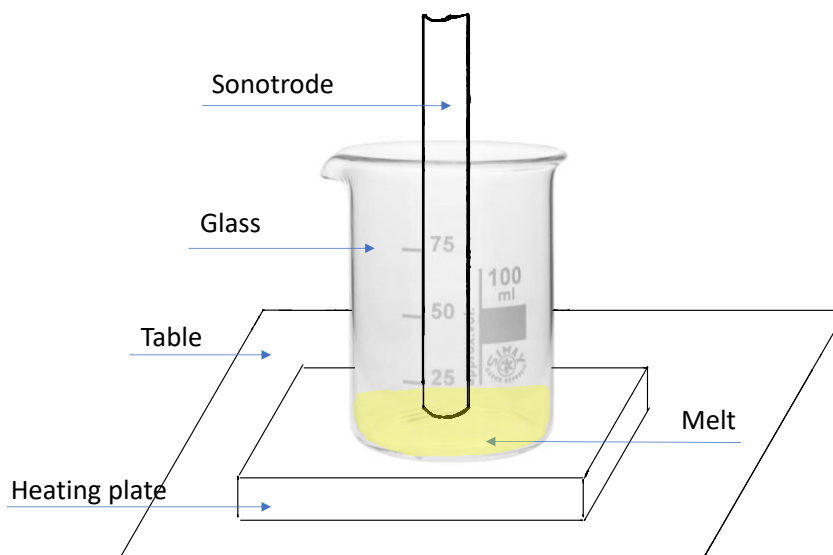


Figure 3. Schematic set-up of the sonication device and beaker

Throughout the experiment melt temperature measurements are conducted on a thermal camera type Flir SC 640 by Flir Systems, Wilsonville, USA.

After sonication the final mixture is poured out to form a thick film. This film break in sharp edges and these breaking edges are investigated in microscopy to investigate the particle distribution.

4. Results and discussion

When exposing a polymer melt and added CNTs to ultrasound, a mixture was successfully prepared. Prove of principal was therefore successful. The used sonotrode is able to initiate ultrasonic energy into the polymer melt. The results of the thermal camera measurements are shown in **Figure 4**. Here it can be seen, that the preheated melt quickly loses its temperature when positioned outside of the oven. On the other hand the sonication implied heating starts to heat the system after 45 s as the dissipating energy is smaller, that the sonication energy applied. This combination of applied energy to form heat in the system, resulting in lower melt viscosity, and start of a mixing process enables high quality mixing of polymer melt and CNTs via ultrasonic dispersion. By microscopy it was able to show that agglomerates can be destroyed.

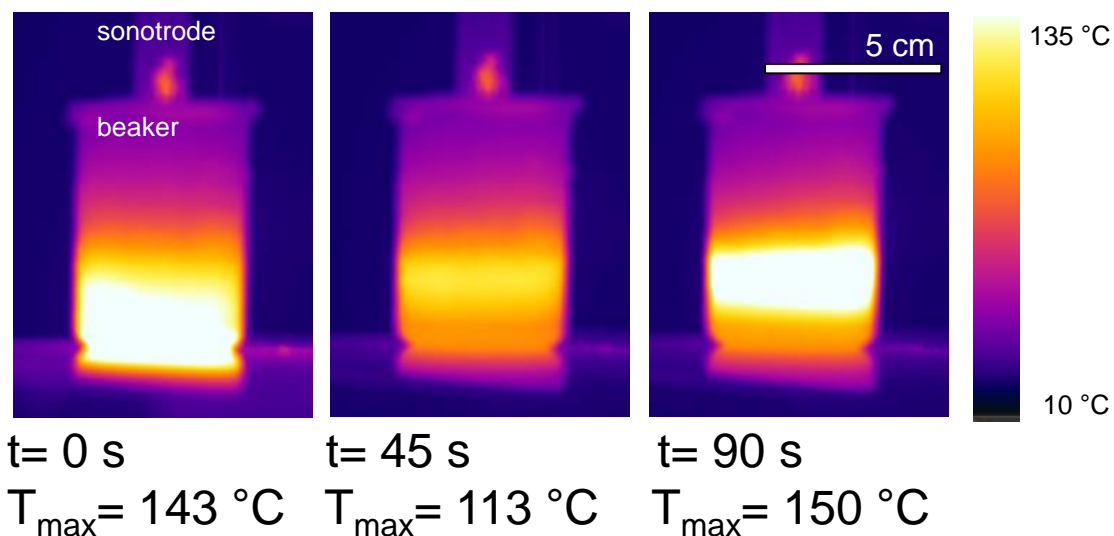


Figure 4. Thermal pictures of the beaker with melt at time $t = 0\text{ s}$, 45 s and 90 s with the according maximum melt temperature.

5. Outlook

After giving first proof of principal for the used sonotrode the finalization of sonication device design has to be done. Here especially the sealing of parts against melt flow is important to consider and investigate. When the concept is finalized, the ultrasound device is manufactured and implemented in the melt spinning line. From a CNT polymer compound fibres will be produced, which will then be analysis via conductivity tests, to ensure homogeneous antistatic properties, and additionally, microscopy is used to check for homogeneous distribution of CNTs in the fibre and to measure the particle size of remaining particles/agglomerates to ensure great distribution.

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