OPTIMIZING THE PRODUCTION OF NANOCOMPOSITES VIA EXTRUSION TECHNIQUES USING NANOPARTICLE CONTAINING DISPERSIONS

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1 Abstract
The traditional reinforcement of thermoplastic polymers using rigid microparticles increases the stiffness but decreases the impact strength and tensile strength. Rubber particles increase the impact strength and toughness of composites, but decrease the stiffness. Nanoparticles can counteract this kind of behaviour. Via twin screw extrusion technique it is hardly possible to break up all the agglomerates by what only the incorporation of nanoparticle powders into polymer matrices does not lead automatically to an increase in toughness because of remaining agglomerates. In order to prevent those agglomerates, the incorporation of nanoparticle dispersions into polymer matrices using appropriate extrusion technology is needed.

The nanoparticle dispersions are synthesized in the dispersion agent (Bottom-up process). Thus, they are monodisperse and very well stabilized being dispersed primary particles in the dispersion agent (water).

Nanoparticle containing dispersions were incorporated in polyamide 6 (PA 6) via twin screw extrusion using a special liquid feeding system. The goal during extrusion is to Suppress re-agglomeration and a transfer of nanoparticles from the dispersing agent to the polymer matrix melt. The objective is a material with well distributed nanoparticles in a polymer matrix. The respective feeding and extrusion technology will be presented in this paper. The impact of screw configuration and extrusion parameters on the dispersion quality will be analysed and discussed, resulting in an optimized dispersion process with tailored screw design with primarily mixing elements.

A microscopical characterization of agglomerations allows the determination of a dispersion index and shows a poor nanoparticle-matrix interaction in the interphase region.

2 Introduction
Stiffness of thermoplastic polymers can be increased via reinforcement with microparticles while reducing impact and tensile strength. Nanoparticles however have the potential to increase stiffness, impact strength and tensile strength simultaneously \cite{1}. The extraordinary properties of nanocomposites depend on their huge interfacial surface area. Thus, the interface/interphase properties may become the dominant part of the macroscopic behavior of the nanoparticle-modified polymer composites. The molecular mobility of the polymer surrounding the particle is changed. Furthermore, decreasing the particle size decreases also the average interparticle distance at constant volume fraction, leading to a potential network structure based on filler-filler interactions and modified local stress distribution \cite{2}. The effect of nanoparticles on mechanical properties depends on their dimensions, size, surface area, surface chemistry and interaction as well as distribution within polymer matrix. In case of low filler-agglomerate-matrix interaction, debonding occurs, which leads to microvoids as function of agglomerate size, where stresses can be concentrated. Nanoparticles with a very good dispersion quality – down to an agglomerate
size in the nanometer range – can lead to an increase in impact strength [1]. There are two different ways to produce nanoparticle containing polymer nanocomposites: The most popular one is the deagglomeration of nanoparticle agglomerates by mechanical dispersion techniques (top-down) [3-17], the other pathway is the bottom-up technique using in situ processes to produce nanoparticles e.g. the sol-gel process [3,18]. Amongst the many different ways to produce particle-reinforced thermoplastics, the most important one is the continuous extrusion process [19]. Research has shown that shear energy input during extrusion process is not sufficient to break up all the agglomerates not even when multiple extrusion processes are applied [20,21]. Thus, the incorporation of nanoparticle containing dispersions into the extrusion process offers several advantages.

- In top-down multiple extrusion steps have to be performed. In case of bottom-up only a single extrusion step is necessary to distribute the already dispersed nanoparticles.
- Nanoparticles for itself bear a potential health risk in form of powders. The extent of the health damage risks cannot be estimated definitely, thus a contamination with nanoparticle powder should be avoided. In case of bottom-up, where nanoparticle dispersions are fed in a polymer melt in the extrusion process, the nanoparticles have to cross over from one media (dispersion) to another one (polymer melt) without being in an unbound state. Thus, the machine operators do not get in contact with unbound nanoparticles.

3 Materials and testing methods

3.1 Materials

A commercially available polyamide 6 (Ultramid B 24 N 03 from BASF) was used. The applied nanoparticle dispersion was a commercially available SiO\textsubscript{2} containing dispersion with a mean particle size of 20 nm (Nanopol XP 20/0170 from Nanoresins GmbH) (Fig. 1). The filler content of the dispersion is 24.43 vol% (41.56 wt%). The pH-value of the dispersion is 9-10. Fig. 1 shows a very narrow particle size distribution of the applied SiO\textsubscript{2} nanoparticles. The zeta potential of the dispersion is -34.6 mV which reveals a very good stability [22].

3.2 Extrusion

Before extrusion, PA 6 was dried for 24 h at 80°C. The extrusion was performed on a co-rotating twin screw extruder from Berstorff GmbH. 6 kg/h of polymer was fed via high precision gravimetric feeder (K-tron Deutschland GmbH). The nanoparticle containing dispersion was fed into the extruder cylinder behind the melting zone via an excenter pump (type 3 RD 12-H from Viscotec GmbH, Germany). The water is first extracted atmospherically via sidefeeder followed by a vacuum pump (Fig. 2). The screw configuration was varied in the zone between nanoparticle dispersion injection and atmospheric degassing (Fig. 3).

In a first step the screw with the configuration 1 (Fig. 4) was applied to determine the extrusion processing parameters resulting in the highest dispersion index to be used for further extrusion. Therefore, nanocomposites with 2.5 vol.-\% nanoparticles were produced with different extrusion parameters. The screw rotation speed was varied (400, 200, 50 rpm) as well as the polymer throughput (3, 6, 10 kg/h) and cylinder temperature (270, 250, 225, 207 °C). The extrusion parameters resulting in the highest nanoparticle dispersion quality were found to be 250 °C cylinder temperature, 200 rpm, 6 kg/h.

In a second step, extrusion was performed with different screw designs (Fig. 4). In a third step a second granule feeding via sidefeeder was applied. The best screw design and extrusion parameters were defined by these three steps (configuration number 2, Fig. 4). With these
parameters nanocomposites with 0.4, 1.5, 1.8, 2.4, 4.7, 8.1 vol.-% SiO$_2$ were produced. Additionally, a reference of extruded PA6 with plain water injection was performed.

3.3 Charpy impact strength

Before mechanical testing the specimens were dried at 80°C for three days. The Charpy notched bar impact strength was measured according to DIN EN ISO 179 on a pendulum-type impact testing machine (CEAST GmbH). The specimens were of type 1 with a notch of type A.

3.4 Tensile Tests

Tensile tests were performed at room temperature using injection-molded specimens after drying at 80°C for three days in accordance to DIN EN ISO 527-2 standard on a universal testing machine (Zwick GmbH model 1485).

3.5 Scanning Electron Microscopy (SEM) and analysis of dispersion index

Polished surfaces were analysed using an electron microscope (Supra 40 from Zeiss and JSM 6300 from Joel) via detecting the backscattering electrons. Fracture surfaces were scanned with a secondary electron detector. All samples were coated with gold using a Sputtering Device (SCD – 050, Balzer AG). The SEM-images were analysed with an image analysis software by which the number of agglomerates of size (>$1 \mu$m) was measured. From these results the dispersion index was calculated according to equation (1) [23]:

$$ D = 1 - f \cdot \frac{A}{A_{im} \cdot \Phi_{nano}} $$

with

- $D$ $\equiv$ dispersion index
- $A$ $\equiv$ area of the agglomerates $>1 \mu$m
- $A_{im}$ $\equiv$ area of the image
- $f$ $\equiv$ shape factor
- $\Phi_{nano}$ $\equiv$ volume fraction.

A dispersion index of 1 represents a complete dispersion of the whole filler content in agglomerates $<1 \mu$m and individual nanoparticles.

3.6 Definition of the shape factor

The agglomerates (Fig. 7) do not contain 100% particles even if only particles are visible in relatively low magnifications. High resolution micrographs show a certain amount of voids inside the agglomerates, some are penetrated with polymer matrix. The resulting volumetric overestimation of the agglomerates is corrected by the shape factor $f$. It will be calculated with a control compound containing a well-defined dispersion grade of agglomerates based on a defined volume content. Therefore, we used a nano reinforced PA 6 composite with all nanoparticle existent in agglomerates $>1 \mu$m which will have a dispersion index set to zero. $f$ can be calculated by solving the equation (2).

$$ f = \left(1 - D\right) \cdot \frac{A_{im} \cdot \Phi_{nano}}{A} $$

In our case $f$ was set to 0.63.

3.7 Filler content

The total particle and agglomerate content was analysed via thermo gravimetric analysis (TGA). The material was heated with 10 K/min from 40 to 550 °C, maintaining the temperature at 550 °C for 40 min.

4 Results and Discussion

Fig. 5 gives the dispersion indices for the materials, with 2.5 vol.-% nanofiller content, produced with extrusion parameters based on experiences of previous projects. A screw speed variation, that was performed at a cylinder temperature of 250°C and a throughput-rate of 6 kg/h, resulted in the highest dispersion index at 200 rpm. The polymer and dispersion throughput was varied coming to the highest dispersion index at 6 kg/h. Changing the cylinder temperature reveals the best nanoparticle dispersion at 250 °C. The extrusion parameters chosen for the following extrusions
are 200 rpm, 250 °C and 6 kg/h (highlighted in Fig. 5).
In a second step a 2.5 vol.-% nanocomposite was produced with the above mentioned parameters and different screw designs to realize different dispersive and distributive mixing zones. A qualitative determination of the influence of the energy input by shearing and the various flow mechanisms on the transfer of the nanoparticles from the dispersion into the polymer melt and on the resulted degree of distribution is carried out. The whole screw design is presented in Fig. 3.
Details of the varied screw (between nanoparticle injection and atmospheric degassing) configurations are shown in Fig. 4. The rest of the screw design was not changed. The resulting dispersion indices for materials produced with the different screw elements are given in Fig. 6. The screw with mainly dispersive mixing elements (screw configuration 2) results in compounds with the highest dispersion quality (D = 0.7). This is due to better distribution of individual nanoparticles by mixing elements with lower tendency of agglomeration of the individual nanoparticles. Fig. 6 represents larger agglomerates in terms of a low dispersion index for screw configurations with kneading blocks in the dispersion feeding and distribution zones. A stronger melt shearing caused by kneading elements creates pronounced agglomerates and irreversible compaction takes place. Irreversible agglomerations were be found in the highly pressurized zones in the extruder [24, 25]. And pigment powders were compacted to agglomerates on the blades of a high speed mixer [26]. Thus the agglomerates found in this project are formed during extrusion processing. The configuration no. 6 was taken to apply a second polymer feeding via a downstream sidefeeder (Fig. 3) to modify the viscosity and therefore the melt shearing conditions in the following processing zone. The resulting dispersion index was 0.53. The screw configurations 6 and 2 contain identical mixing elements and lead to the best distribution index. The observed reduced dispersion index caused by addition of polymer granulates, which 1) reduce the local melt temperature, 2) increase the melt shearing and 3) increase energy input is in agreement with the reduction of the dispersion index by screw designs with more pronounced melt shearing and energy input by kneading elements.
The optimized parameters (200 rpm, 250 °C and 6 kg/h) and the screw no. 2 were taken in order to perform materials with different nanoparticle contents in a second production cycle. The dispersion quality (Fig. 8) shows less dependency from the particle content. There appears a slight maximum of the dispersion index at 1.8 vol.-% (Fig. 7) and then it converges to a value around 0.4 for higher concentrations.
The exhausted water from the atmospheric degassing was condensed, collected and analysed via TGA (Fig. 9). The ash content of the condensate was close to zero (0.00-0.15 wt.-%). Thus, the nanoparticles transfer completely from the dispersion agent (water) into the polymer melt.
The notched Charpy impact energy shows a decreasing tendency with higher volume concentrations (Fig. 10). According to Lazzeri et al. smaller particles have detrimental effect on toughness due to the presence of large individual particles and agglomerates, which act as stress-concentrating defects that trigger brittle fracture [27]. The Young’s modulus (2820 MPa) of the unfilled polyamide is significantly increased (approx. 10%) with only 0.5 vol.-% nanoparticles. A further increase of the nanoparticle concentration (Fig. 11) represents a linear increase to 3740 MPa with 8 vol.-%. The tensile strength shown in Fig. 12 shows a clear reduction by small amounts of nanoparticles. The tensile strength increases with higher filler amounts to a maximum at 2.4 vol.-% where the strength is on the same level as the references.
As the mechanical behavior is determined by the particle-matrix interaction leading to a change in polymer flexibility in the particle-matrix interphase [28], the particle-matrix interaction was analyzed via SEM. Fig. 7 shows weak nanoparticle agglomerate-matrix interaction. There is a gap between agglomerate and matrix. This lack of adhesion in the interface region can also be seen in Figure 13. The single nanoparticles inside the agglomerate can be clearly seen in this micrograph.

5 Summary
The reduction of the environmental pollution with nanoparticles during the processing of powders can be eliminated by incorporation of water dispersed nanoparticles. The processing via twin screw extrusion requires adapted screw configurations and optimized processing parameters. Several process optimization steps of a polyamide-6 filled with SiO$_2$-nanoparticles from a dispersion show significantly improved dispersion qualities.

- Contrary to mixing mechanisms of powderous nanoparticles where higher melt shearing and energy input improves the dispersion quality a sufficient distribution of dispersion based nanoparticles requires lower melt shearing to avoid the creation and compaction of agglomerates.
- Typical improvements of the modulus by rigid particles were observed in combination of slightly reduced charpy impact toughness and minor influenced tensile strength.
- A correlation of the quantitative dispersion quality characterizing dispersion index with mechanical parameters (modulus, impact toughness or strength) is not possible.
- A microscopical characterization of agglomerations shows a poor nanoparticle-matrix interaction in the interphase region.
- The poor stress transfer between matrix and nanoparticles could be a reason for the toughness and strength reduction and impossible correlations to the dispersion index.

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References


Figure 1. Particle size distribution of applied nanoparticles (Nanopol XP 20/0170) showing a monodispers nanoparticle dispersion.
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Figure 2. Scheme of the build-up of the liquid feeding system and the extrusion technology.

Figure 3. Screw design for adding nanoparticle dispersions within extrusion process.

Screw configuration 1: Conveying elements

Screw configuration 2: Mixing elements

Screw configuration 3: Kneading elements

Screw configuration 4: Mixing and kneading elements

Screw configuration 5: Kneading elements at dispersion input

Screw configuration 6: Blister filling elements

Figure 4. Scheme of the screw design in the varied part of the screw.

Figure 5. Dispersion index of compounds with 2.5 vol.-% nanoparticles resulting from extrusion with different extrusion parameters. The varied parameter is framed.

Figure 6. Dispersion index resulting from extrusion of different mainly used screw configurations.
Figure 7. SEM image of polyamide 6 with 1.78 vol% SiO₂ nanoparticle content from incorporation of nanoparticle dispersion.

Figure 8. Dispersion index of PA6 nanocomposites with different SiO₂ nanoparticle concentration (Nanopol XP 20/0170).

Figure 9. Condensate from the atmospheric degassing.

Figure 10. Charpy notch impact energy for nanoparticle reinforced PA6 versus nanoparticle concentration. The references are neat PA6, once extruded PA6, and once extruded PA6 including water.

Figure 11. Young’s modulus for SiO₂ reinforced nanocomposites versus particle concentration. The references are neat PA6, once extruded PA6, and once extruded PA6 including water.

Figure 12. Tensile strength for SiO₂ reinforced nanocomposites versus particle concentration. The references are neat PA6, once extruded PA6 and once extruded PA6 including water.
Figure 13. SiO₂-nanoparticle agglomerate in a PA 6 matrix. There gap between agglomerate and matrix showing a lack of adhesion is encircled.