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Influence of the Processing Conditions on the Morphology and the Mechanical Properties of Polyamide 6-Carbon Fibre-Carbon Nano Tube-Compounds

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Summary: Polyamide 6-compounds containing carbon nano tubes and carbon fibres are prepared by melt compounding. To investigate the influence of the processing conditions on the mechanical properties and the morphology of carbon fibre reinforced polyamide 6-nanocomposites the process parameters are varied while preparing the compounds. The processing conditions affect the mechanical properties and the morphology. The investigations reveal, that a micro-nano-compound with a PA6-matrix should be compounded at a maximum barrel temperature of 260 °C, a throughput of 15 kg/h at a screw speed of 500 min^{-1} and a screw configuration, which introduces a low amount of shear energy into the compound. These processing conditions lead to a comparatively high specific mechanical energy input of 334 Wh/kg and to the best set of mechanical properties of the investigated materials. However, the morphology of the investigated carbon fibre reinforced nanocomposites does not show significant differences and has to be further investigated.

Keywords: compounding; fillers; mechanical properties; nanocomposites; processing

Introduction

Due to an increasing demand of light weight parts with excellent mechanical properties in the automotive, the aerospace and the mechanical engineering industry, polymers with enhanced mechanical properties have a high potential to substitute metal or ceramic parts.[1–4] Commonly, polymers are filled with fillers on micrometer scale, such as glass or carbon fibers, to improve the mechanical properties compared to the neat matrix-polymer.[5]

But the filler content of glass- and carbon fiber-reinforced polymers is limited. Above filler contents of 60 wt.-% the resulting composite is not processable. Additionally, the density of the composite increases with higher filler contents, leading to an increase in weight of the part. Furthermore, high filler contents result in a more brittle part.[5,6]

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To enhance the mechanical properties of a polymer the form of the filler is of high interest. The aspect ratio of the filler specifies the ratio of the smallest to the largest dimension of the filler.[7] Other important factors are the surface chemistry and the specific surface area of the filler. A high specific surface area allows a large area for the interaction of the polymer and the filler to build physical or chemical bonds.[8,9] Table 1 summarizes particle sizes and specific surface areas of different fillers.[9]

Compared to fillers on micrometer scale the specific surface area of fillers on nanometer scale is very large. Thus, nanofillers offer a high potential alternative to microfillers in regard to the specific surface area. Since the 90's nanofillers have been investigated.[10–12]

A popular nanofiller is layered silicate. The large specific surface area and numerous

Table 1.
Specific surface areas of fillers.[9]

	Microfiller		Nanofiller
	Fibre	Talcum	Layered silicate
Particle size	20 μm	1 μm	200 nm
Specific surface area	0.2–2.0 m^2/g	1.8–6.3 m^2/g	400–800 m^2/g

compatibilizers make layered silicate a very interesting filler for polymers.[11–17] Only 5 wt.-% of layered silicate show an increase of the mechanical properties comparable to fiber reinforced parts with 20 wt.-% of glass fibers. Furthermore, only a small increase of the density and an increase of the impact strength are observed.[14,18] Besides layered silicate carbon nano tubes are very popular nanofillers. In theory carbon nano tubes feature very good mechanical, electrical and thermal properties, making carbon nano tubes a very interesting filler for polymers. Only 1 wt.-% of carbon nano tubes improves the antistatic properties and the electrical conductivity of a polymer.[7,19,20]

Even though nanofillers show good results in laboratory scale experiments, there are only few commercial applications of nanofillers. Dividing and dispersing nanofiller-agglomerates during the melt compounding process is of great importance.[21,22] During the industrial processing of composites with nanofillers, they tend to agglomerate, leading to a loss of their positive properties. Thus, only limited improvements of the mechanical properties are observed. However, discontinuous trials of Wu et. al. show, that a combination of micro- and nanofillers, possesses a high potential to improve the mechanical properties.[4] Due to synergetic effects, Akkapeddi et. al.[6] observe an improvement of the mechanical properties using a co-rotating intermeshing twin screw extruder for compounding. Other studies show similar enhanced mechanical properties for polyamide 6 and different thermosets filled with micro and nanofillers.[23–30] The most recent study of Yoo et. al.[31] reports an increase of the tensile strength and a decrease of the elongation at break for glass fibre reinforced polyamide 6-nanocomposites.

Experimental Part

The experiments are conducted using a co-rotating intermeshing twin screw extruder type ZSK26Mc of Coperion GmbH, Stuttgart/Germany. The screw diameter is 26 mm. The polymer is fed into the main hopper, while the nanofillers are dosed at the 4th barrel element, whereas the microfillers are fed in the 9th barrel element. All components of the compound are dosed using appropriate gravimetric dosing systems and side feeders. The compound is degassed at the 11th barrel element, before exiting the extruder as a strand for pelletising. The complete setup is shown in Figure 1.

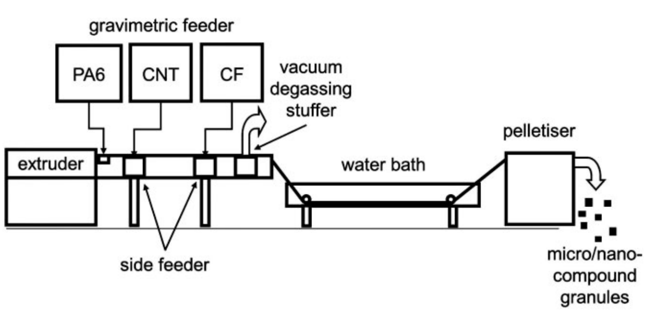

Figure 1.
Setup of the compounding process for compounding micro-nano-compounds.

Table 2.
Variation of the process parameters.

screw speed [min^{-1}]	300	400	500
throughput [kg/h]	10	15	20
max. barrel temperature [°C]	260	290	–

To investigate the influence of the process parameters on the mechanical properties and the morphology of the compound the process parameters are varied as depicted in Table 2.

Additionally, three screw configurations are investigated (Figure 2). The upper screw configuration has a high shear energy input, using four dispersive mixing sections with two kneading elements each. The third and fourth dispersive mixing section are closed with a neutral kneading element. The middle screw configuration applies a medium shear energy input having three dispersive mixing sections with two kneading elements each. The bottom screw configuration has only one dispersive mixing section with two kneading elements, introducing a low shear energy input.

The compounds are further processed to tensile and notched specimens using an injection moulding machine of Arburg GmbH & Co. KG, Loßburg/Germany, Type Allrounder 370 A 600 - 170/170. Young's modulus and the tensile strength are determined according to DIN EN ISO 527 using a tensile testing machine type Z010 of Zwick GmbH & Co. KG, Ulm/Germany. The notched impact strength is evaluated according to DIN EN ISO 179 using a pendulum of Zwick GmbH & Co. KG, Ulm/Germany. Before testing all test specimen are conditioned according to DIN EN ISO 1110 (7 days at 70 °C and 62% relative humidity) to assure uniform testing conditions. Additionally, optical microscopy is employed to visualise the carbon fibre-dispersion, while transmission electron microscopy (TEM) is applied to evaluate the dispersion of the CNT.

Materials

This paper discusses micro-nano-compounds made from the matrix polymer Polyamide 6 (PA6), the microfiller carbon fibres (CF) and the nanofiller carbon nano tubes (CNT). All compounds consist of 30 wt.-% CF and 2 wt.-% of CNT. The PA6 (BASF Ultramid B27 E01) has a relative viscosity of 2.7 and is sponsored by BASF SE, Ludwigshafen/Germany. The CF (HT C493) are prepared with a sizing suitable for PA6 and are provided by Toho Tenax Europe GmbH, Wuppertal/Germany. The CNT (NC7000) are contributed by Nanocyl S.A., Sambreville/Belgium.

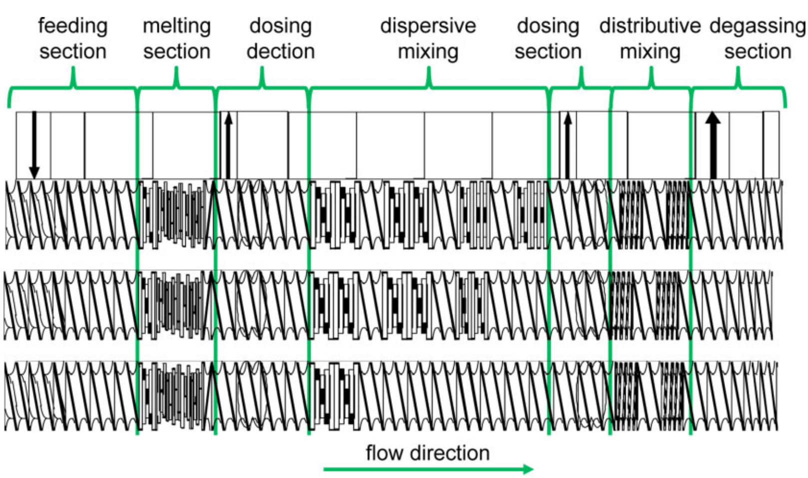

Figure 2.
Screw configurations used in the experimental setup.

Results and Discussion

For analysing the influence of the processing conditions on the mechanical properties and the morphology of the micro-nano-compounds, the influence of the process parameters on the mechanical properties are discussed first, followed by a brief comparison of the morphology of two different compounds.

In Figure 3 Young's modulus and the tensile strength are depicted for different process parameters in dependency of the maximum barrel temperature. Figure 4 displays the notched impact strength. The results are shown for the screw configuration, which introduces a low level of shear energy into the compound.

Young's modulus, the tensile strength and the notched impact strength show the tendency to be slightly higher for a comparable set of process parameters, when the compound is processed with a temperature profile resulting in a maximum barrel temperature of 290 °C. The higher barrel temperatures lead to a decrease in melt viscosity. Thus, coating the fillers with polymer is easier. Comparable results are

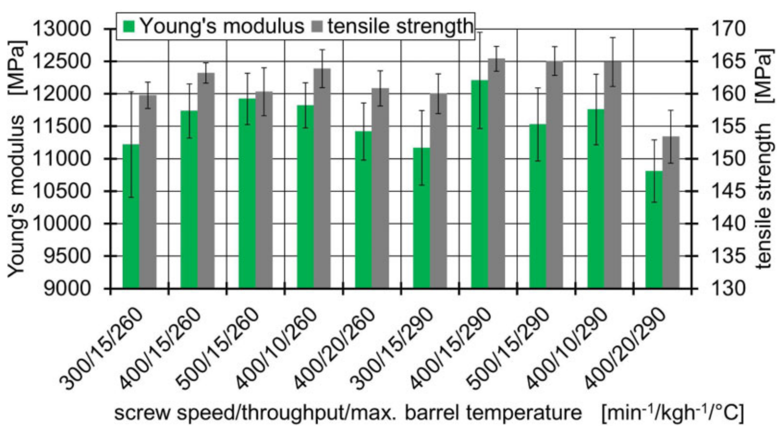

Figure 3.
Young's modulus and tensile strength for different process parameters at a maximum barrel temperatures of 260 and 290 °C.

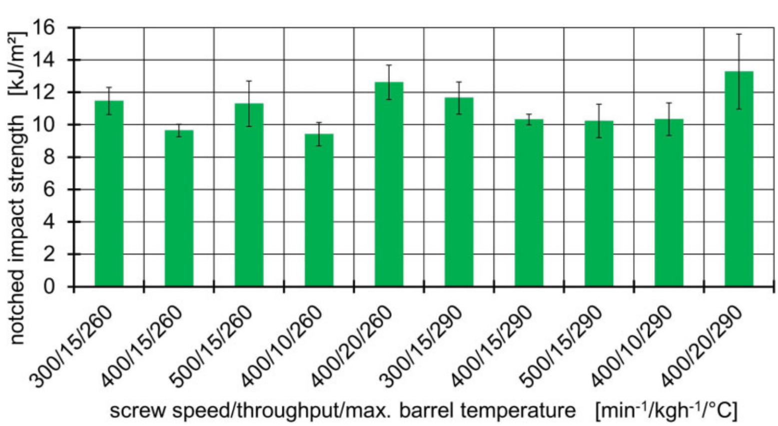

Figure 4.
Notched impact strength for different process parameters at a maximum barrel temperatures of 260 and 290 °C.

observed for the other screw configurations. However, the increased melt temperature may lead to a degradation of the carbon fiber sizing and a loss in the molecular weight of the PA6.

Figure 5 shows Young's modulus and the tensile strength against the screw speed, whereas Figure 6 shows the notched impact strength. The results are shown for the three different screw configurations. The results are shown for compounds produced with a throughput of 15 kg/h and a maximum barrel temperature of 260 °C.

Using a screw, which introduces a low amount of shear energy into the compound, the maximum of Young's modulus is achieved at a screw speed of 500 min^{-1}, whereas the application of screws, which introduce higher amounts of shear energy, leads to a maximum of Young's modulus at a screw speed of 400 min^{-1}. For all compounds a maximum of the tensile strength is observed at 400 min^{-1}. A possible explanation for the decrease of the tensile strength at 500 min^{-1}, could be a deterioration of the CF. The notched impact strength shows a minimum at a screw speed of 400 min^{-1} for the screw with a low shear energy input, whereas at the same screw speed a maximum of the

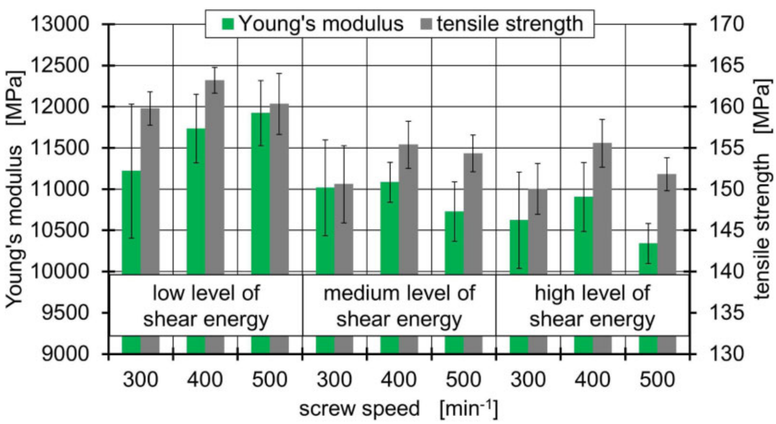

Figure 5.
Young's modulus and tensile strength for different screw configurations at 300, 400 and 500 min^{-1}.

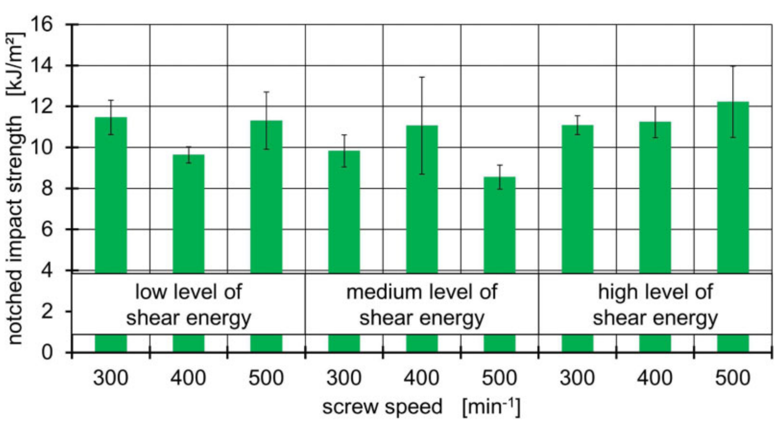

Figure 6.
Notched impact strength for different screw configurations at 300, 400 and 500 min^{-1}.

notched impact strength is achieved when using a screw configuration, which introduces a medium level of shear energy. For the screw configuration with a high shear energy input the notched impact strength increases with increasing screw speed. Since the higher screw speed decreases the viscosity of the PA6, the wetting of the fillers in the polymer may be easier, leading to the same effect, which can be observed, when the barrel temperature is increased.

The dependency of Young's modulus and the tensile strength on the throughput is depicted in Figure 7. The notched impact strength is displayed in Figure 8.

If the screw configuration with a low shear energy input is applied, increasing the throughput leads to a decrease in Young's modulus and the tensile strength, whereas for the other screw configurations the opposite effect is observed. A possible explanation for the different results may be, that for the screw with a low shear energy input a decreasing throughput and the resulting increase in residence time leads to a better dispersion of the fillers. In contrast, the increasing residence time leads to a deterioration of the fillers, when the screw configurations are used, which introduce a medium and a high amount of

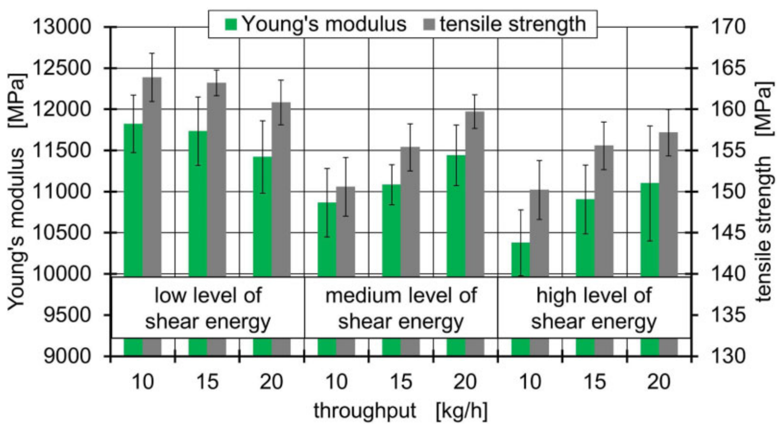

Figure 7.
Young's modulus and tensile strength for different screw configurations at 10, 15 and 20 kg/h.

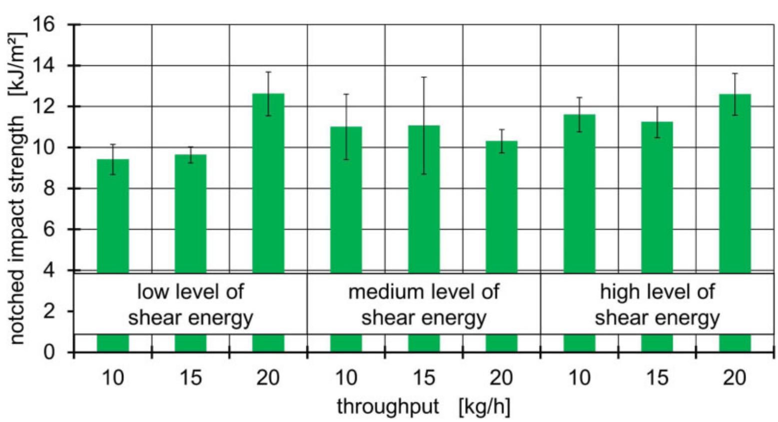

Figure 8.
Notched impact strength for different screw configurations at 10, 15 and 20 kg/h.

shear energy, respectively. The maximum of the tensile strength is achieved at 20 kg/h for the screw configurations with a low and a high shear energy input, while the tensile strength of the compounds, which are processed with the screw configuration, which introduces medium shear energy input remains nearly constant. Concerning the notched impact strength of the compounds processed using the screw configurations with a low and a high shear energy input, a low throughput and the resulting high residence time might lead to a reagglomeration of the CNT. Hence, a short residence time may lead to favourable results of the impact strength. Comparing the process parameter variations, apparently the opposite effect of Young's modulus and the tensile strength on one hand and the notched impact strength on the other hand can be observed.

In Figure 9 the dispersion of the CF is compared for two different compounds prepared with a low and a high specific mechanical energy input. The specific mechanical energy input (SME) can be calculated from the process parameters according to Equation 1.[32]

$$SME = \frac{\frac{n}{n_{\max}} \cdot \frac{U}{100} - \frac{n}{n_{\max}} \cdot \frac{U_{\min}}{100}}{\dot{m}} \cdot P_{\max} \qquad (1)$$

In Equation 1 n is the actual screw speed in $\min^{-1}$ and n_{max} the maximum screw speed of the twin screw extruder. The efficiency of the twin screw extruder is denoted U in %, while the minimum efficiency of the twin screw extruder is U_{min}. The throughput is represented by $\dot{m}$ in kg/h and the maximum output power of the twin screw extruder is P_{max} in W. The maximum screw speed of the twin screw extruder is 1 200 $\min^{-1}$ and the maximum output power is 28 000 W, while the minimal efficiency of the machine measures 5%. The compound on the left is prepared with a SME of 154 Wh/kg, while the material on the right is compounded with a SME of 334 Wh/kg. The compounds are prepared at a throughput of 20 kg/h and 15 kg/h respectively, using a screw configuration, which introduces a low level of shear energy into the material.

The optical microscopy pictures show, that employing a higher SME while preparing the compound does not necessarily lead to better dispersion of the CF. However, the optical microscopy pictures at this magnification do not reveal agglomerates of the CNT.

Figure 10 compares the same two compounds shown in Figure 9, using TEM to evaluate the dispersion of the CNT.

In both pictures CNT-agglomerates are visible. The size of the agglomerates is approximately the same for both SME. No significant differences can be observed.

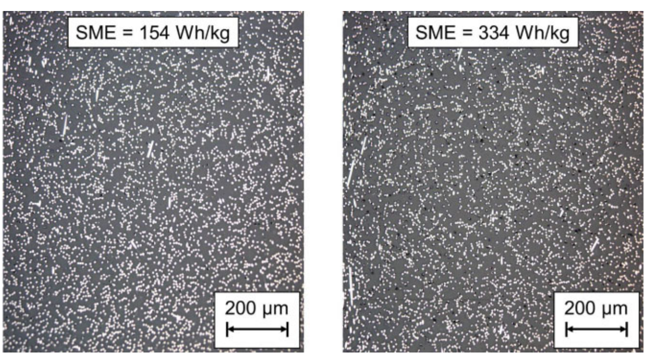

Figure 9.
Dispersion of CF for two compounds made with different SME using optical microscopy.

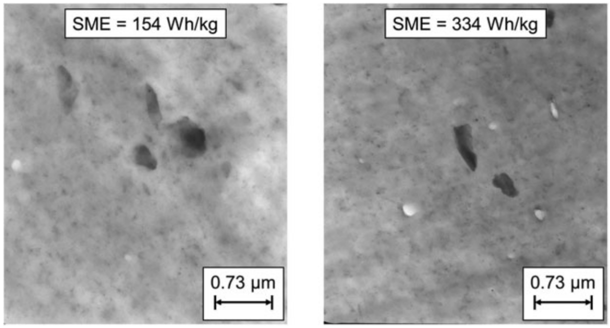

Figure 10.
Dispersion of CNT for two compounds made with different SME using TEM.

Conclusion

This paper shows that processing of compounds containing micro- and nano-filler is possible. The variation of process parameters demonstrates that the processing conditions affect the mechanical properties of the micro-nano-compounds. However, the process parameters have an opposite influence on Young's modulus and the tensile strength on one hand and the notched impact strength on the other hand. Thus, the design of a compounding process for micro-nano-compounds is challenging. To further investigate carbon fibre reinforced nanocomposites a maximum barrel temperature of 260 °C, a throughput of 15 kg/h at a screw speed of 500 min^{-1} and the screw configuration, which introduces a low amount of shear energy into the compound, should be applied. These processing conditions lead to a comparatively high specific mechanical energy input of 334 Wh/kg and to the best set of mechanical properties.

However, the morphology of the investigated micro-nano-compounds does not show significant differences and has to be further investigated. Additionally, carbon fibre reinforced nanocomposites containing different amounts of micro- and nanofillers have to be tested to benefit from the combination of fillers on micro- and nanometer scale and to achieve the best mechanical properties possible.

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