Polyether Ether Ketone / Carbon Nanotube Composite Fibres – A New Material for Conductive Fiber Reinforced Plastics in Sustainable Energy Applications

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Polyether ether ketone (PEEK), a thermoplastic polymer with excellent temperature stability and mechanical properties, is modified with carbon nanotubes (CNT). Then it is processed to fibres to study the influence of CNT on the mechanical properties, the electrical conductivity and the polymer structure. Pure PEEK is compounded with CNT in different concentrations, melt spun to fibres with different winding speeds, drawn in the solid state at different temperatures and heat treated. During processing of the nano composite fibres, the mechanical properties of unmodified PEEK can be maintained while an electrical conductivity of up to 1.50 S m-1 is achieved. Furthermore, structure analysis by X-ray diffraction and differential scanning calorimetry reveals that crystallization is enhanced by CNT. The material can be processed to thermoplastic carbon fiber reinforced plastics, making it favourable for lightning protection in sustainable energy applications like wind energy plants.

1. Introduction

Commingling yarns composed of high temperature resistant polyether ether ketone (PEEK) fibres and carbon fibres (CF) offer the ability for saving complex production steps. Furthermore, by using PEEK fibres containing suitable additives, carbon nanotubes (CNT), the aimed conductivity can be achieved and the light weight potential can also be maintained. Carbon nanotubes (CNTs) are assumed to enhance physical and mechanical properties when applied in polymer nano composites. Thus, Carbon nanotubes (CNTs) have been found to increase the composite's strength and its elastic modulus according to Baughman et. al. (2007). Even at low nanotube loadings, the electrical conductivity of the polymer is elevated and the polymer structure is modified. Thereby, special consideration has to be given to a homogeneous dispersion of the CNTs in the polymer matrix (Tjong et. al., 2007). Polyether ether ketone / carbon nanotube composite fibres can be applied in various fields. Next to the aerospace technology, the chemical and automobile as well as the electrical and medical industry may profit from the fibres' strong chemical resistance, high mechanical properties under high temperature and the improved electrical conductivity (Logakis et. al., 2010).

1.1 Polyether ether ketone

The high performance polymer Polyether ether ketone (PEEK) shows a semi-crystalline structure (Kuntz, 2012). It reaches a degree of crystallinity of up to 48 %. Generally, the high performance polymer's chemical structure is based on aromatics, which are bound by either ether or ketone bridges. Depending on the ratio between ether and ketone bridges, Polyether ether ketones (PEEK) can be varied within a wide range. Therefore, the properties of the polymer are determined by the chosen ratio of ether and ketone bridges. Ether groups ensure better plasticity, higher flexibility and improve the flow behaviour in the melt due to their high molecular mobility. A higher thermal resistance is achieved through a rising number of ketone groups.

Within the range of the glass temperature at 143 °C (Allaoui et. al., 2002), Polyether ether ketone (PEEK) exhibits good mechanical properties. Thus, a high tensile and bending strength as well as advanced impact resistance and endurance strength can be registered. Regarding the characteristic temperatures of Polyether ether ketone (PEEK), a short term use temperature has been revealed close to the melting point of

approximately 300 °C. In terms of long term use, a temperature of 160 °C appears decisive (Kuntz, 2012). Next to good mechanical and thermal properties, the high performance polymer shows good chemical resistance. Additionally it is badly inflammable, self-extinguishing and demonstrates the lowest smoke gas development amongst all thermoplastics. PEEK shows low corrosiveness and toxicity as well as good electrical properties. Due to the fact, that the high performance polymer can be melt spun, PEEK may cover a broad range of applications. A disadvantage of this polymer is the comparatively high price.

1.2 PEEK nanocomposites

Generally, carbon is well known to improve a material's mechanical properties, when integrated into the polymer. Next to the possibility of mixing single (SWNT) or multi-walled (MWNT) carbon nanotubes into the material, a polymer can equally be reinforced by carbon-nanofibres. For both techniques, the key challenges remain in achieving a homogeneous dispersion, a good interfacial bonding as well as a controlled degree of alignment1. These requirements are met by using twin-screw extrusion and injection moulding.

Regarding mechanical aspects, stress-strain-tests have shown precise effects of the carbon incorporated into a polymer such as PEEK. The stress-strain-behaviour of pure PEEK almost appears to be linear. In contrast, identical stress-strain-tests of carbon nanotube / PEEK composites have turned out to be considerably nonlinear and have shown hysteresis behaviour from the extremely low strain. For integrated carbon nanofibres, the yield stress and fracture strength increase (Zheng et. al., 2004).

Also, in contrast to the increase of the storage and the tensile elastic modulus, an impact of the integrated carbon nanoparticles on the glass transition temperature T_g cannot be registered (Baughman et. al., 2007). Numerous research groups have verified a resistance against high temperatures as well as chemical and mechanical stresses (Zheng et. al., 2004; Tjong et. al., 2007).

1.3 Melt spinning of PEEK/PEEK nanocomposites

Commercially, pure Polyether ether ketone (PEEK) is distributed in several shapes and sizes (monofilaments, multifilaments, hollow fibres, staple fibers) by a number of different companies. As for PEEK nano composites, several other fabrication techniques have proven to be advantageous in terms of integrating the respective additive. Exemplary, ultra-fine filaments containing PEEK and carbon fibres of < 0.2 dtex are manufactured using a self-constructed piston-type device for low mass throughputs (Ma et. al., 2010).

Based on the current state of research, it remains challenging to set up a suitable spinning process for PEEK composites containing carbon nanotubes (Cao et. al., 2014). Due to the large influence of nanoscaled additives compounded in the polymer on the melt spinning process itself, each parameter regarding the manufacturing of fine composite fibres has to be evolved (Ahmad et. al., 2014). In preparation for the actual melt spinning, the semi-crystalline Polyether ether ketone and the carbon nanotubes are twin screw extruded. This master batch is used for the following spinning process. Thereby, the impact of the integrated carbon nanotubes on the process itself as well as the impact of the relevant melt spinning parameters on the fibre can be exposed. Meanwhile, the achievement of a homogeneous dispersion, a good interfacial bonding and a controlled degree of alignment of the CNTs remain to be the most challenging aspects (Cao et. al., 2014).

1.4 Aim of this study

The goal of this study is to manifest the possibility of spinning fibres consisting of Polyether ether ketone (PEEK) and carbon nanotubes (CNTs). There are a lot of experiments that show the possibility to produce polymer melt spun fibres with CNTs (McNally and Pötschke, 2011). In these trials more common polymers like polypropylene or polyamide are used. In this study, the results are transferred to PEEK. Within this framework, the positive impact of the carbon nanotubes (CNTs) on the mechanical and the electrical properties is scientifically verified. Regarding current research on such composite fibres, entirely new aspects are being approached. Through selective variation of the process parameters while melt spinning and a subsequent analysis, several properties of the composite fibre are outlined. The suitability of Polyether ether ketone / carbon nanotube composite fibres for the use in composites is demonstrated. Especially for the application in wind energy plants, the electrical conductivity is an important parameter to create conductive composites for lightning protection.

2. Experimental

2.1 Materials

Pure PEEK (KetaSpire KT 820 NL) from Solvay Specialty Polymers, Germany GmbH, Hannover is used as reference material. This material is blended with a PEEK master batch containing 10 weight percent multiwalled carbon nanotubes, NC7000 from Nanocyl s.a., Belgium, to vary the amount of CNTs in the

following steps: 0 %, 2 %, 4 %, 6 %, 8 % and 10 %. The CNTs have an average diameter of 9.5 nm and an average length of 1.5 µm, which results in an L/D ratio of 158.

2.2 Compounding and Melt spinning

Monofilaments with different CNT concentrations are spun with a micro extruder from DSM XPlore, Geelen, Nederland, with different die diameters (0.5 mm, 1.25 mm and 3 mm) and wind up with different winding speeds (25, 50, 100, 200 m/min). The blending of pure PEEK and PEEK with 10 % CNT takes place directly in the micro extruder. The winding speed influences the melt draw ratio (MDR). The ratio of the extrusion rate ve and the winding speed vw is a measure of the MDR. The higher winding speed the higher the melt draw ratio. With the melt draw ratio also rises the orientation of the molecules in the fibres.

2.3 Drawing and Annealing

For drawing the fibres an additional drawing unit from DSM XPlore, Geelen, Netherland, is used. Two temperatures, one near the glass transition temperature (150 °C) and one above (200 °C) are chosen. Different draw ratios (1.5; 2.2) are realized. Some of the fibres are heat treated in order to measure the difference in the structure of the fibres later. With a heating rate of 20 °C h^{-1} a temperature of 200 °C is reached and is held for two hours. After that the fibres are cooled down with 20 °C h^{-1} to room temperature.

2.4 Characterization

Electrical conductivity of the extruded samples and the fibres is measured with an alternating current measurement bridge LCR-819 from RS Components Ltd., Corby, Great Britain, with a measurement range up to 20 MΩ. For the measurements, frequencies of 10 Hz, 100 Hz, 1 kHz, 10 kHz and 100 kHz are chosen to detect frequency-dependent effects. Samples are clamped into the machine with three different lengths of 3 cm, 6 cm and 9 cm. With a linear regression, the resistivity per length ρ_L (in Ω m^{-1}) is determined and separated from the contact resistance R_0. Together with the cross section area A of the samples (determined by light microscopy), the specific resistivity ρ_S is calculated. The mechanical properties are analysed with a Statimat M from Textechno GmbH, Mönchengladbach, Germany. Single fibres are clamped manually into the testing machine. The measuring length is 100 mm and the testing speed is 100 mm per minute. Differential scanning calorimetry (DSC) is performed to measure the melting point, melting enthalpy (as a measure for crystallinity) and effects of the CNTs on the crystallization behaviour. Here, a DSC 1 equipped with a FRS5 sensor having 56 thermocouples from Mettler Toledo AG, Greifensee, Switzerland, is used. The different compounds are placed into crucibles with a volume of 40 µl and the samples are heated up to 450 °C, cooled down to room temperature and then heated up again. The crystallisation and orientation is analysed by wide angle x-ray diffraction (WAXD). A single-crystal image plate detection System II (STOE & Cie GmbH, Darmstadt, Germany) at the Institute of Crystallography of the RWTH Aachen is used for recording two dimensional diffraction patterns. Crystallinity is calculated from the ratio of intensity from crystalline diffraction peaks and amorphous scattering.
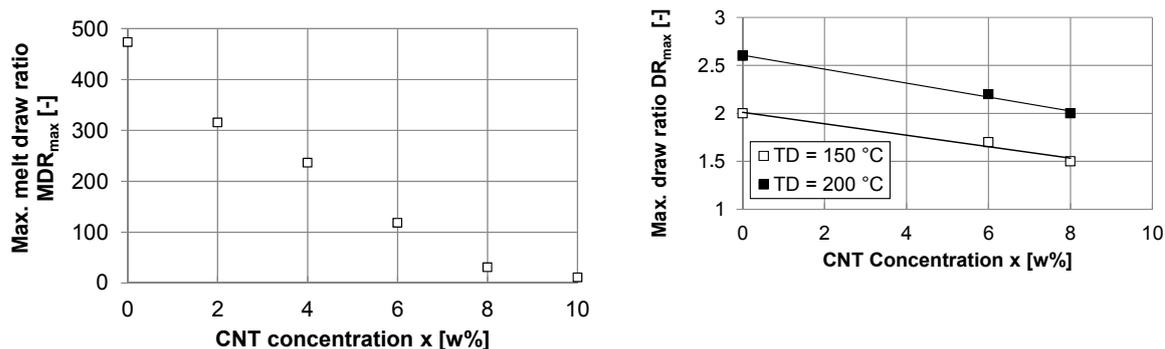
Figure 1: Results for processability to fibers as a function of CNT concentration, left: maximum melt draw ratio, right: maximum solid state draw ratio
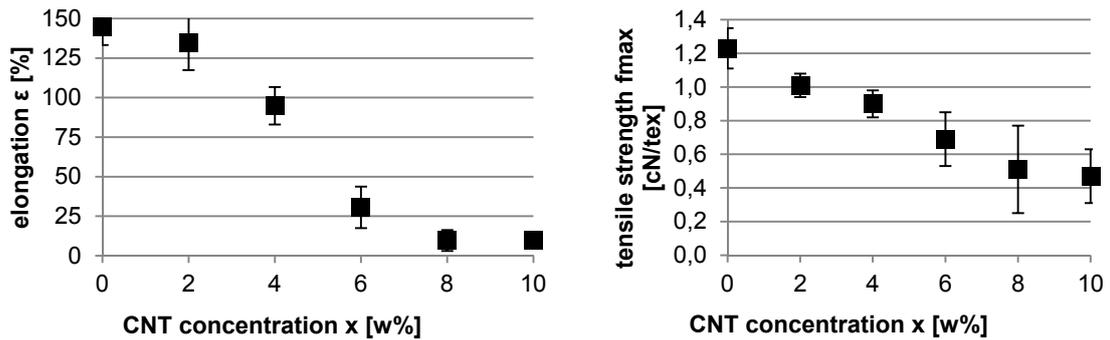
Figure 2: Mechanical properties of the nanocomposite fibers

3. Results

3.1 Processability to fibers

In order to analyse the influence of the melt draw ratio the maximum melt draw ratio is determined as a function of the CNT concentration. The result is shown in Figure 1 (left).It may be detected a linear relationship between the two variables. An influence from the melt draw ratio on the electrical conductivity cannot be established. Fibres with a melt draw ratio of 10.9 are used for the drawing experiments. The maximum draw ratio decreases with increasing CNT concentration. The result for the different fibres is shown in Figure 1 (right). The linear relationship between CNT concentration and maximum draw ratio is also valid here. In a drawing above the glass transition temperature, the maximum draw ratio is significantly higher; the decrease with increasing CNT concentration decreases like the draw ratio of the fibers drawn below glass transition temperature.

3.2 Mechanical properties

With the addition of CNT to PEEK the mechanical properties of the fibres decrease. Both, the elongation at break ε and the tensile strength, decrease with increased CNT concentration, Figure 2.

The elongation at break decreases from 144.8 % ± 11.6 % (0 % CNT) to 9.7 % ± 2.2 % (10 % CNT) for fibres spun at a winding speed of 50 m min^{-1}. The maximum tenacity force, thus the tensile strength, decreases for these fibres from 1.23 ± 0.12 cN/tex to 0.47 ± 0.16 cN/tex. Visible CNT agglomerates are vulnerabilities in the fibres making them break faster. The lower elongation at break relates to the increased crystallinity of the samples with higher CNT contents. With less amorphous regions, many polymer molecules in the fibre cannot align under tensile loading, since they are already oriented within the crystalline regions, and there prevail stronger attractive forces between them.

3.3 Electrical properties

The percolation threshold is found at 2,6 vol.- % CNT. As expected, the electrical conductivity increases with CNT concentration (Figure 3). For modelling the percolation behaviour, Equation 1 is applied:

$$\sigma(p) = \sigma_{max} \cdot \left(\frac{p - p_c}{p_{max} - p_c}\right)^{\beta}$$

(1)
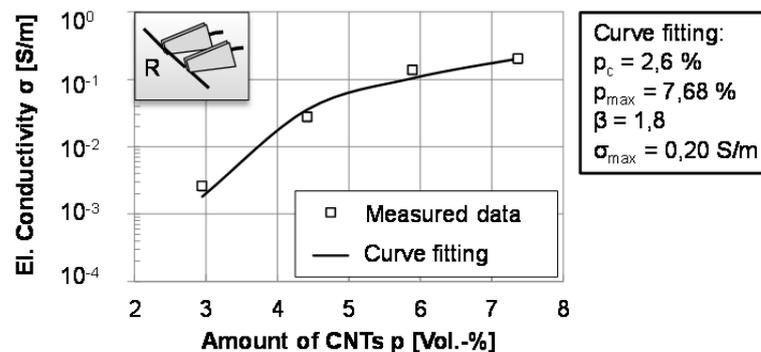
Figure 3: Electrical conductivity of the nanocomposite fibers as a function of CNT concentration
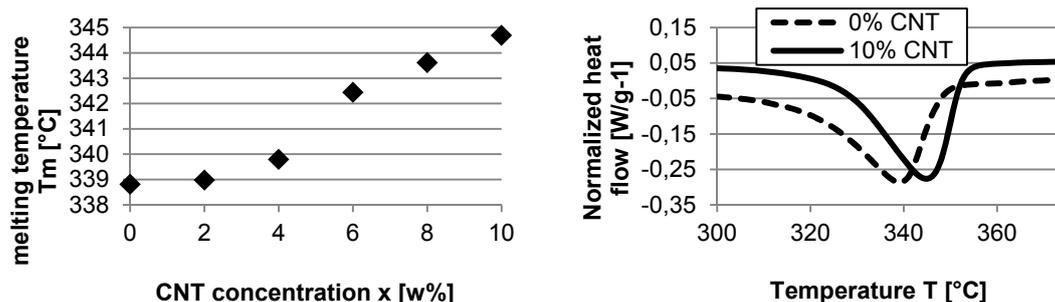
Figure 4: Melting temperature as a function of CNT concentration (left), DSC thermograms (right)

The parameters from curve fitting can be found in Figure 3. The maximum electrical conductivity is achieved with 7.86 vol.- % CNTs having a value of 0.2 S/m^{-1}. The electrical conductivity increases with higher winding speed. This is verified, since the electrical conductivity for the fibre with 6 % CNT, a die diameter of 0.5 mm and winding speed of 25 m/min^{-1} is 1.22 S/m^{-1}. Compared to a fibre spun under same condition except a winding speed of 100 m/min^{-1} shows a higher electrical conductivity of 1.50 S/m^{-1}. This effect can be seen at every CNT-concentration. The electrical conductivity decreases in the fibres stretched below the glass transition temperature. The fibres drawn at higher temperature have a higher or lower electrical conductivity depending on the CNT concentration. During the drawing process, CNT are aligned in fibre direction, which leads to a lower amount of conductive paths in the fibres and therefore to a lower conductivity. By the heat treatment, the electrical conductivity of the fibres increases. So, the electrical conductivity raises from 0.31 S/m^{-1} to 0.91 S/m^{-1} (150 °C) and up to 1.10 S/m^{-1} for 200 °C treatment temperature due to a relaxation of the polymer chains leading to a lower CNT orientation and more conductive paths in the fibres.

3.4 Thermal properties

The melting temperature increases with increasing CNT concentration (see Figure 4 left). CNT molecules in the polymer matrix have an inhibiting effect during the melting process. Figure 4 (right) shows the DSC curves of PEEK fibres with 0 % and 10 % CNT, the shift in the melting temperature is visible. With variation of the cooling rate a shift of the crystallization temperature appears, it decreases with growing cooling rate for PEEK and PEEK with CNTs. Due to the rapid cooling, undercooling of the melt occurs, and the crystallization takes place at lower temperatures. In general, the crystallization temperatures of polymer with carbon nanotubes are higher than that for pure PEEK, because the CNTs are used as nuclei for the heterogeneous nucleation. With a further increase of the CNT concentration, it is possible that the CNT molecules limit the polymer chains in their mobility, thus hindering the formation of crystals, as Díez-Pascual et. al. (2012) have observed.

3.5 Structural properties

The orientation factor of the fibres depends firstly on the CNT concentration and secondly on the winding speed. Without CNTs in the fibres the orientation factor is higher, because the orientation of the molecular chains in the fibre direction is hindered by CNT molecules. In addition, the orientation of molecular chains increases with the winding speed and hence melt draw ratio. Also, the crystallinity of the fibres is determined with WAXD. By the addition of CNTs, the crystallinity of the material increased, Figure 5, since the CNT molecules serve as nuclei for the heterogeneous nucleation (Jin et. al., 2012).
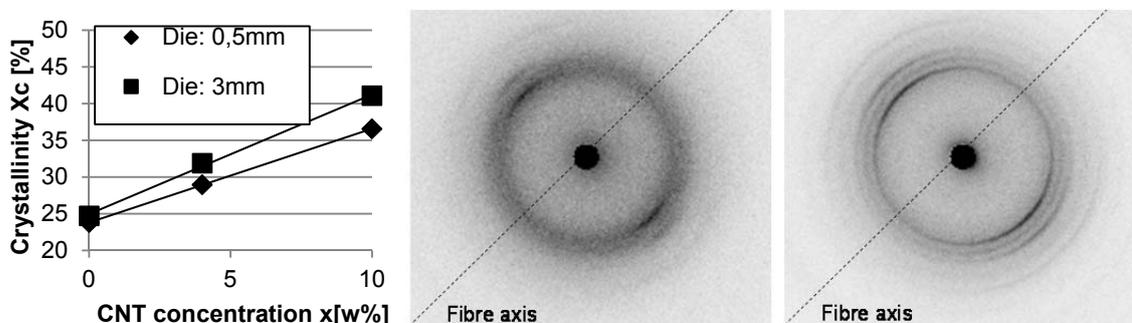
Figure 5: Crystallinity as a function of CNT concentration (left) and diffraction patterns of fibers with 0 w% (middle) and 10 w % CNT (right)

4. Conclusion

Not all spinning parameters can be realized at high CNT concentrations because the maximum melt draw ratio decreases. A maximum electrical conductivity of 1.22 S m^{-1} is achieved in the fiber. The determination of polymer structure shows an increasing crystallinity with increasing CNT content while the orientation factor decreased. It can be increased by increasing the winding speed, whereby it does not reach the orientation factor of pure PEEK. Beside aggregates in the CNT-modified fibers, the decrease of crystallinity is another reason for the decrease of the tensile strength of the fibers. The influence of all material and process parameters is summarized in Table 1.

Table 1: Summary of the influences of different parameters on the nanocomposite fiber properties

	CNT con-centration x	Melt draw ratio MDR	Solid state draw ratio DR	Temp. of heat treatment T
Electrical conductivity σ	↗	↗	→	↗
Maximum melt draw ratio MDR$_{max}$	↘	-	-	-
Maximum draw ratio DR$_{max}$	↘	↘	-	↗
Tensile strength F$_{max}$	↘	→	↘	↗
Maximum elongation ε$_{max}$	↘	↘	↘	↗
Melting temperature T$_m$	↗	→	→	→
Crystallinity X$_c$	↗	↘	↗	↘
Orientation factor f	↗	↗	↗	→

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