NANO REINFORCED INTERFACES FOR ADVANCED GLASS FIBRE/EPOXY COMPOSITES

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1 Introduction

In recent years, the incorporation of nanoparticles into polymers has been attracting great interest. Numerous studies deal with the effect of nanoparticles on the mechanical properties of composite materials. Besides the modification of the whole matrix volume, certain studies report on more localized approaches dealing with nanoparticle reinforced interphases [1-3]. In this context, it was reported that nanoparticle reinforced interphases can be obtained by applying sizing systems containing predispersed nanoparticles. An advantage of this approach is the possibility to apply the nanoparticles together with the sizing during the fibre spinning, i.e. without additional processing steps. Moreover, the fibres are not subjected to elevated temperatures as it is commonly necessary for growing CNTs directly on the fibre surface. Therefore, the sizing properties are preserved and consequently the chemical interaction between fibre and matrix is not adversely affected.

In this study, we report on the effect of nanoparticle modified sizings on the mechanical properties of glass fibre (GF)/epoxy (EP) composites. Namely CNTs and titanium dioxide (TiO_2) particles were used in the sizing formulations in order to serve as local reinforcements of the composites interphase.

2 Experimental

2.1 Materials

E-glass fibres having an average diameter of 17 μm were spun at the Leibniz Institute of Polymer Research Dresden and sized with an epoxy compatible sizing containing different quantities of predispersed CNTs (Aquacyl IPFDD, Nanocyl S.A., Belgium) and TiO_2 (Hombitec RM400 WP, Sachtleben Chemie GmbH, Germany), respectively. In detail, the film former content was varied from 3 to 15 wt% within the sizing system while the nanoparticle concentration was gradually increased up to 20 wt% relative to the solid content of the film former. Filament winding and vacuum assisted resin infusion was used to manufacture unidirectional GF/EP composites containing 58±2 vol% GF. The matrix system was based on an epoxy resin and hardener (Epikote RIMR135 and Epikure RIMH137, weight ratio 100:30, both Momentive) and was cured at 80°C for 6h. After the curing, specimens for mechanical testing were cut out of the unidirectional plates using a rotating diamond saw.

2.2 Characterization

Micro- and macromechanical test methods were applied in order to evaluate the effect of the nanoparticles on the fibre/matrix bonding. This involved single fibre pull-out (SFPO) tests (see [4] for details) as well as transverse tensile and Charpy impact tests according to ISO 527-5 and ISO 179-1, respectively. In addition, the compression shear test (CST) was used to evaluate the compression shear strength.

Micrographs of the fibre surfaces were obtained using a scanning electron microscope (SEM, Ultra 35 Carl Zeiss SMT AG, Germany).

3 Results and Discussion

Nanoparticles as CNTs and TiO_2 are known to affect the mechanical properties when being incorporated into polymeric matrices [5,6]. This involves different mechanisms e.g. increase of Young's modulus, crack deflection, CNT-crack bridging, and CNT pull-out. As the interphase is known to be a failure prone region in composite materials, it is of special interest to investigate how and to what extend the presence of nanoparticles affects the failure mechanisms.

3.1 SEM Surface Analysis of As-Spun GF

Figure 1 shows SEM micrographs of GF surfaces. In detail, as-spun fibre surfaces containing CNTs and TiO_2 particles are shown in figure 1a and 1b, respectively. It can be seen that the application of modified sizing formulations during GF spinning results in a thin nanoparticle-rich coating on the fibre surface. The nanoparticles are embedded into the sizing, acting as highly localized reinforcement in this region. However, the predispersed nanoparticles need to be compatible to the aqueous sizing system in order to prevent precipitation and agglomeration on the GF surface.

3.2 Microcomecanical Characterization – Single Fibre Pull Out Test

In order to investigate whether the CNTs or TiO_2 on the GF surface actively participate with the crack propagation in the interface, single fibre model composites (GF/Epoxy) were prepared and characterized.

At a first stage, the fractured surfaces of GF without nanofillers in the interface were investigated as reference materials. Figure 2 shows their surfaces after single fibre pull-out test. It can be seen, that the GF surface after pull-out is relatively smooth apart from some regions where matrix resin is attached to the fibre. This kind of failure pattern indicates a predominantly adhesive failure. On the contrary, in figure 1c and 1d fractured surfaces of CNT and TiO_2-sized GF after pull-out are shown for direct comparison with figure 2. The fracture patterns have noticeably changed, which becomes evident from the comparably rough GF surface. Small regions with adhering matrix resin are distributed all over the fractured surface, indicating that the fracture mechanism has changed to a rather cohesive failure. As can be inferred from figure 1c and 1d, the higher magnifications of the small regions with epoxy on the fractured surfaces are either filled with CNTs or TiO_2.

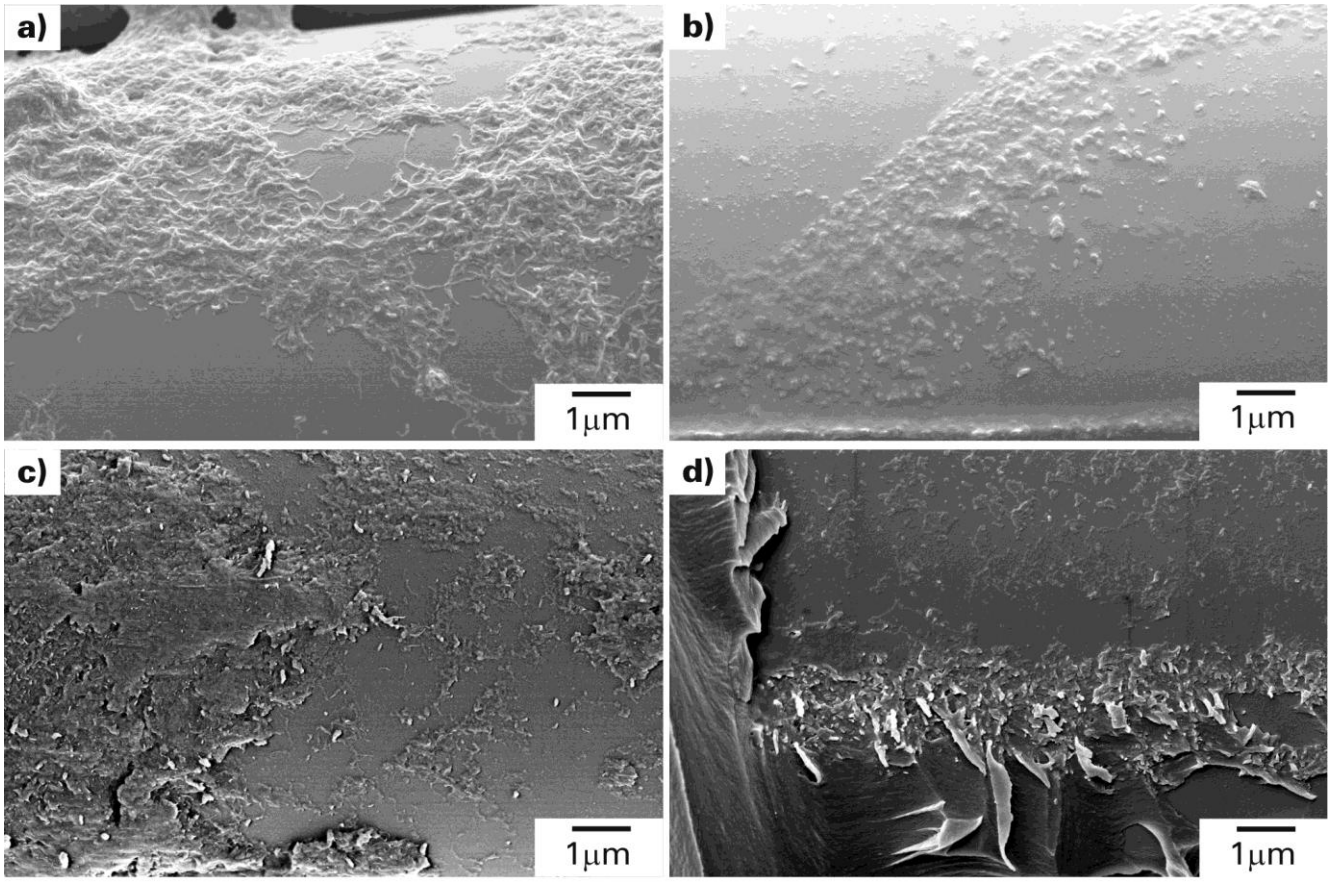

Fig. 1: SEM micrographs of GF surfaces containing nanoparticles. As-spun GF surfaces showing a) CNTs and b) TiO_2 particles embedded in the sizing layer. Fractured surfaces after SFPO illustrating the effect of c) CNTs and d) TiO_2 particles on the interfacial crack growth. Both kinds of nanoparticles result visibly in crack deflection changing the failure mechanism from predominantly adhesive to cohesive failure

As the SFPO method is relatively labour intensive, investigations have been focussed on the 7 wt% film former samples. Although the presence of the nanoparticles in the sizings results in a significant change of the fracture pattern as becomes evident from figure 1, their effect on the quasi-static interfacial shear strength is relatively modest. However, the nanoparticles significantly affect the results of the single fibre pull-out test compared to the reference samples without CNTs or TiO_2. In Figure 3 a typical force-displacement curve of the single fibre pull-out test is shown. The evaluation of the fibre-matrix properties are commonly based on the F_{max} and F_{kink} values, respectively. With regard to F_{kink}, no differences to the reference samples were observed, thus it can be concluded that the investigated nanoparticles do not affect the critical stress necessary for the first debonding of the fibre/matrix interface. However, they affect the fracture mechanism by their presence within the interface as becomes evident from the higher dissipated energies during the fibre pull-out. Figure 4 shows a compilation of all values for "dissipated energies". The "dissipated energy during fibre pull-out" is the area below the force-displacement curve up to the F_{max}-value shown in figure 3.

The values for the dissipated energies during pull-out for a test series with different nanoparticle concentrations can be found in figure 4. It can be seen that the reference sample as well as the samples with a very high CNT content result in lowest dissipated energies, whereas the highest values are found for the intermediate CNT concentrations in the sizing. These results are not surprising, as for bulk nanocomposites similar tendencies have been reported. A possible explanation is that at very high CNTs concentrations the particles might act as spots for stress concentrations and can embrittle adjacent polymeric matrix.

The same applies for the TiO_2 samples. Best results are obtained for intermediate TiO_2 concentrations, whereas the reference and higher particle contents lower dissipated energy values. In contrast to the CNTs where already a low filler content such as 2.5 wt% relative to the solid content of the film former shows improvement, the TiO_2 samples require up to 10 wt% for optimum results.

3.3 Mechanical Properties of Unidirectional GF/Epoxy Composites

Besides the micromechanical SFPO, the differently sized GFs were used for preparation of unidirectional composites. During the preparation it became evident that the GFs sized with the lowest film former concentration (3 wt%) cannot be properly processed. Excessive fibre brakeage prevented the required exact fibre alignment for a unidirectional composite. As a result, only the 7 and 15 wt% film former samples were tested. In total, three different kinds of tests were performed in order to assess the effect of the nanoparticle enriched interphase on the mechanical properties of the composites. All results are shown in figure 5 as a function of particle and film former content, respectively.

For CNT containing samples with 7 wt% film

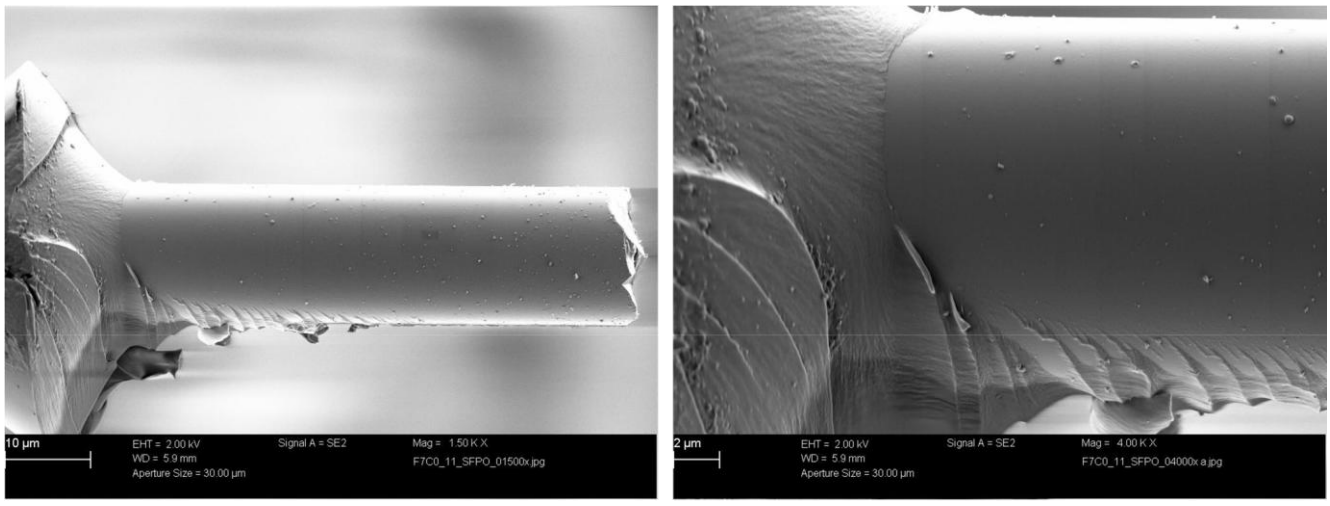

Fig. 2: Fractured surfaces after single fibre pull-out. Left: low magnification, right: higher magnification of the same fibre. Apart from a few areas with epoxy resin, the GF surface is mostly smooth

former, a concentration of 5 wt% relative to the solid content of the film former yields to highest mechanical properties. In case of the transverse tensile strength one can speak of a statistically significant increase, however, for the Charpy impact and compression shear strength the standard deviations overlap. Thus, one has to be careful with the conclusions and only a trend of the mean values to higher strengths is found. However, these findings support the results of the SFPO experiments, indicating improved mechanical properties at intermediate CNT concentrations.

In principal, the same applies for the 15 wt% film former samples besides highest improvements are observed at 10 wt% relative to the solid content of the film former. Since these were also the highest CNT contents to be investigated no conclusions can be drawn, whether it is possible to even further increase the mechanical performance or not.

For the TiO_2 modified composites the influence due to the nanoparticles is not as dominant as for the CNT ones although higher filling contents are used. In case of 7 wt% film former no changes in terms of mechanical performance can be observed. Even though, there are hints that at 20 wt% TiO_2 improved performance can be obtained, the standard deviations overlap again. It is likely, that there is an effect due to TiO_2 since the SFPO also predicted one. In general, higher particle contents are required than predicted by the SFPO for best macromechanical results. Thus, optimum results could be assumed in the region above 20 wt% TiO_2 which was not investigated so far. This shift in nanofiller content can be related to the fact that mechanical testing of UDs involves different failure mechanisms than the SFPO-test.

In case of 15 wt% film former such behaviour cannot be observed. For higher TiO_2 contents the mechanical results starts to degrease, particularly transverse tensile strength and compression shear strength.

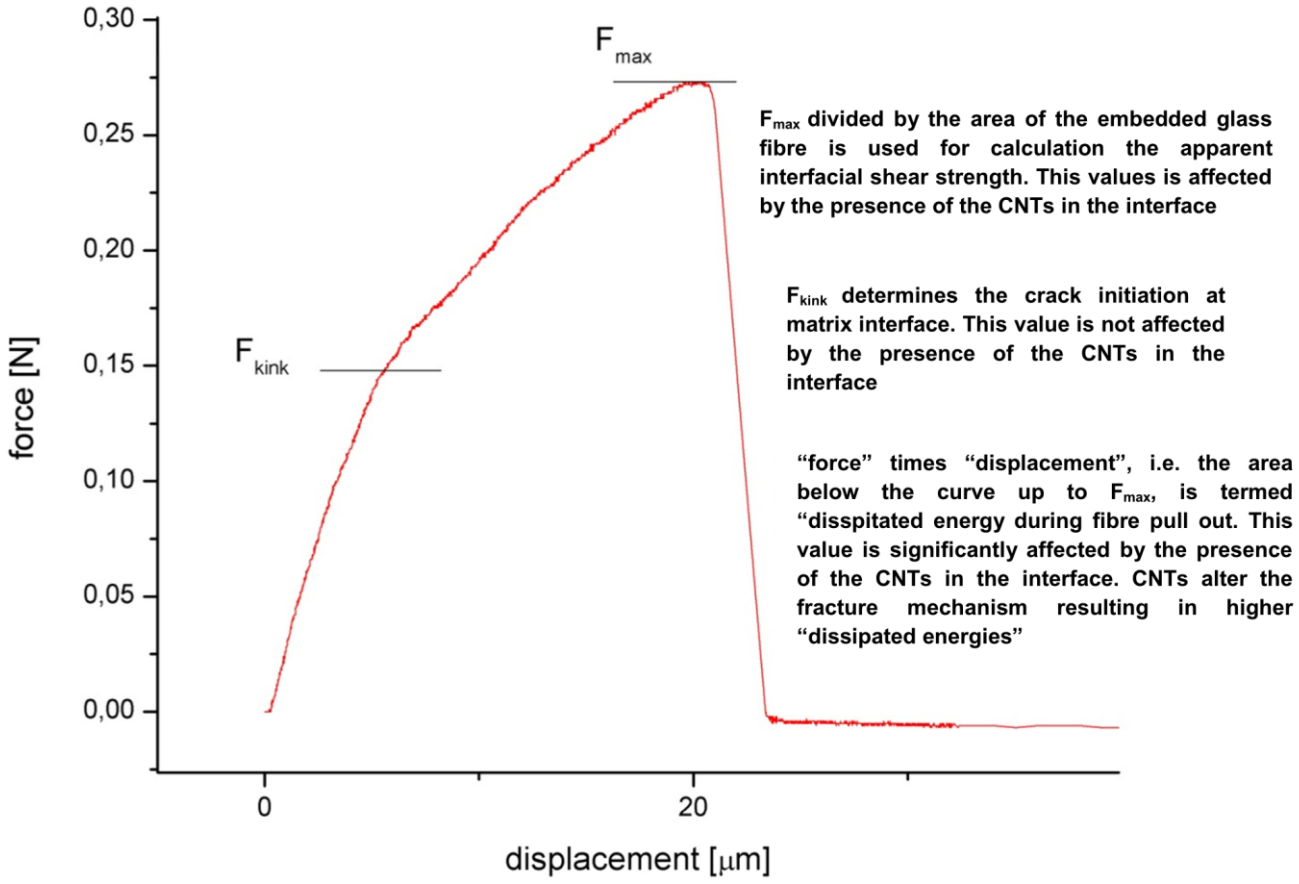

Fig.3: Typical force-displacement curve of a single fibre pull-out test

4 Conclusions

Based on the SEM images of the as-spun GF, the application of the nanoparticle-filled GF sizings results in a nanostructured surface of the GF. Although the surface coverage is not always homogeneous, the nanoparticles are finely dispersed and no signs of precipitation due to interactions with the other sizing constituents are observed.

The SEM fracture patterns after single fibre pull-out test show that the nanoparticles in the interface affect the fracture mechanism of the composites significantly, changing it from a predominantly adhesive failure to a more cohesive failure mechanism. The effect of crack deflection during crack propagation is reflected in the increased values for the dissipated energy during single fibre pull-out test. Those values indicate that for intermediate particle contents in the sizing the energy necessary to reach the maximum force in the single fibre pull-out test has increased to a certain extent. Similarly to this, an increase of the apparent interfacial shear strength is observed in the CNT sized GF composites. An identical trend as found for the micromechanical testing of the single fibre model composites was revealed for the unidirectional composites.

Although increased dissipated energy values are measured for the TiO_2 systems no increase in macromechanical performance was observed at contents up to 20 wt% relative to the solid content of the film former. For the 15 wt% film former samples even decreased mechanical performance was detected.

Taking the extremely low composite CNT concentration of approximately 0.028 wt% (*75 wt%* GF * *7 wt%* film former * *5 wt%* CNTs) into account, the interface modification of GF/epoxy composites using CNT-modified sizing is an effective strategy in order to influence composites mechanical properties.

For future studies, a further analysis of the sizing on the fatigue properties of the modified interphases is of great interest. Especially the SEM images indicate that the nanoparticles affect the crack growth during interface failure. Consequently, the interface debonding could be possibly slowed down during fatigue loading.

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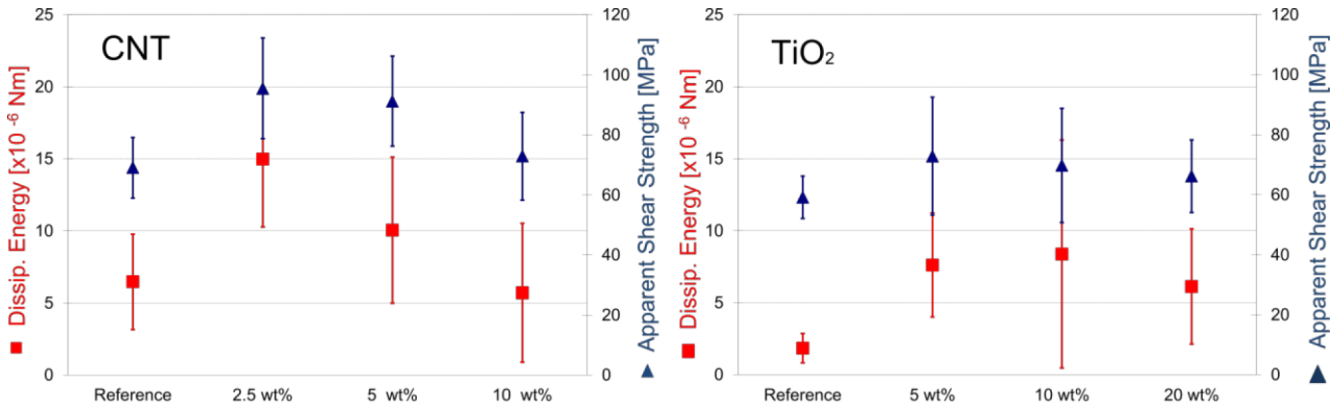

Fig. 4: Dissipated energy and apparent interfacial shear strength after fibre pull-out. The tested GF have the identical sizing formulation being only different with respect to the nanoparticle content. The weight content of the nanoparticles is relative to the solid content of the film former.

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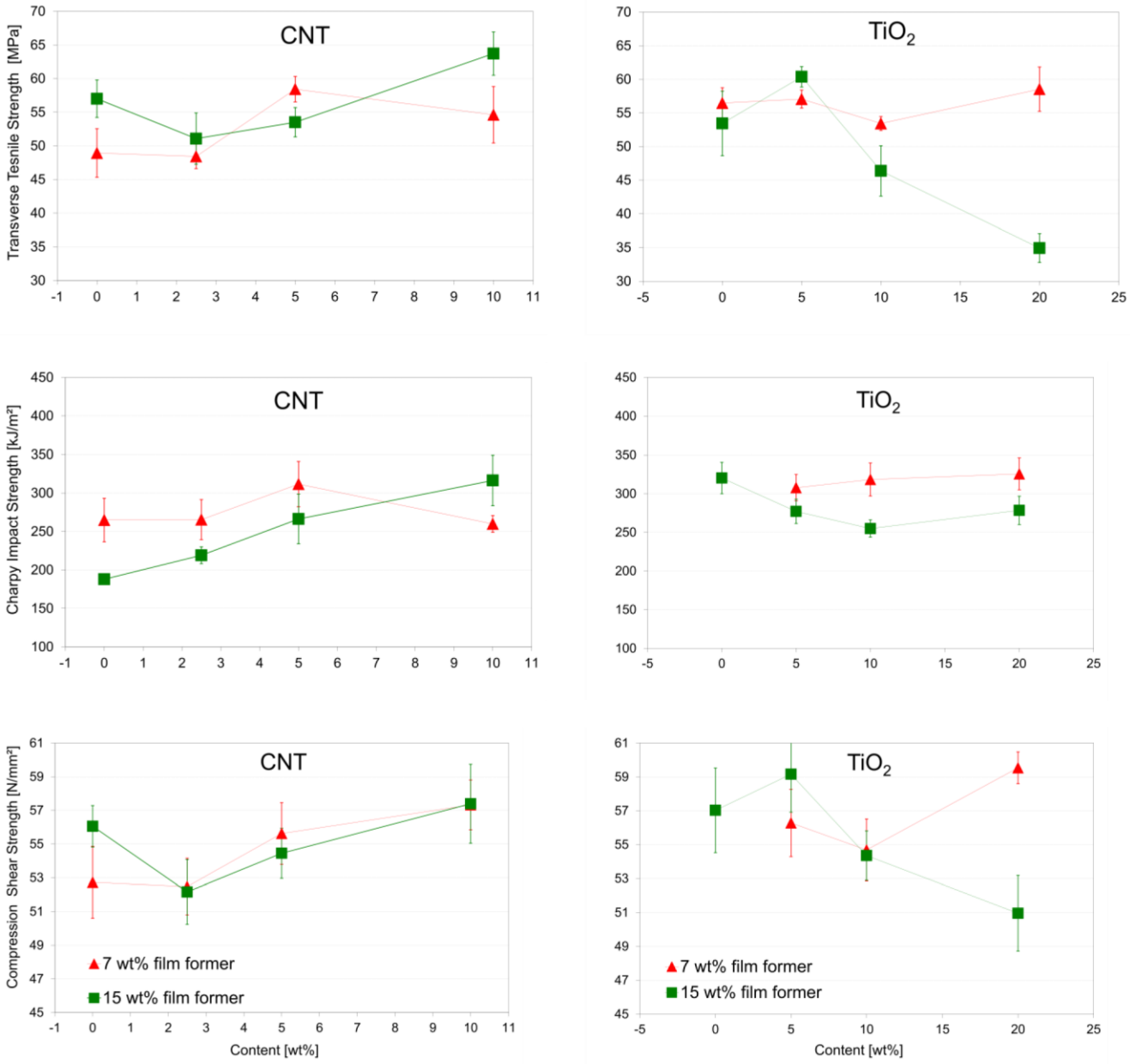

Fig. 5: Transverse tensile strength (top), Charpy impact strength (middle) and compression shear strength (bottom) of unidirectional composites depending on the film former and particle content. On the left side sizings with CNTs and on the right side with TiO_2 particles, respectively.