NANO-MODIFIED THERMOPLASTIC PRE-FORMS FOR THE MANUFACTURING OF COMPOSITE STRUCTURES

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1 Introduction

Fiber reinforced thermoplastics (FRT) are characterized by their broad range of physical properties, a high automatisation potential and large scale production capability. The challenge by their production results from the high viscosity of the polymer matrix. Therefore, FRT are being mostly produced in a energy and time consuming two-stage process, where the consolidation of the pre-forms is separated from the molding step.

2 Goal of the research project

To increase the efficiency of the manufacturing process, innovative semi-impregnated thermoplastic pre-forms are being developed within the context of the research project "NanoOrgano – drapable pre-forms made from nano-modified hybrid yarns for the production of FRT". It is research collaboration between institutes and companies founded by the German Federal Ministry of Education and Research (BMBF). The development of hybrid pre-forms allows simultaneous consolidation and molding. In order to improve the mechanical properties of the composite, the thermoplastic component is being additionally modified by nano-particles.

3 Experimental works

Fig. 1 shows the technology chain of the project. The developed technology bases on the application of nano-modified semi-consolidated thermoplastic preforms. Due to the nano-modification of the thermoplastic matrix different mechanical properties, like impact and energy absorption, are improved.
Using the melt-spinning technology, the thermoplastic nano compound is further processed to continuous filament yarns. In a following process step the nano modified polyamide (PA) filaments are commingled with Aramide to hybrid yarn structures. The commingled yarns are further processed to woven and multi-axial warp-knitted fabrics with a surface weight of approx. 400 g/m². The manufactured fabrics represent semi-consolidated thermoplastic preforms with textile character. These can be easily draped into the desired form. After heating beyond the melting point of the thermoplastic component and applying of pressure, the pre-forms are molded to composite structural parts.

3.1 Nano-modified polyamide (PA6) yarns

The production of the nano-modified PA6 yarns includes two milestones of the project, namely the compounding of the nano-particles and the extrusion of the compounds to continuous filament yarns.

Production of nano compounds

Within the research project, different kinds of titanium dioxide particles (TiO_2) and barium sulfate ($BaSO_4$) particles, produced by the company Sachtleben Chemie GmbH, Duisburg, are applied. Within the experimental study on the dispersing behavior of nano particles in PA6 matrix, standard particle types, like Hombitec RM 300 (TiO_2, particle size 15 nm), Sachtoperse N20 ($BaSO_4$, particle size 20 nm) and HP ($BaSO_4$, particle size 20 nm) are used.
In order to find a relation between the number of extrusion steps and the deagglomeration quality, experimental test series with different number of extrusion steps were conducted. For these compounds, the distribution of the particles and the size of the agglomerates in the compounds are investigated by scanning electron microscopy (SEM) and analyzed by image analysis software. Additionally, the dispersion of the nano particle in the compounds was investigated by Microfocus-Computer-Tomograph (µCT) measurements. Both, SEM and µCT

have shown that, the count and the size of the agglomerates decrease with the higher extrusion degrees. The Young's modulus of the nano compounds remains almost constant within the varied extrusion cycles (Fig. 2). The improvement of the deagglomeration does not lead to an increase of the Young's Modulus. The Young's modulus of TiO_2-filled compounds is higher than that of $BaSO_4$-compounds, which could be explained due to a better particle-matrix interaction. The tensile strength of TiO_2-compounds and neat polyamide 6 has the same level and maintain constant over the conducted extrusion steps. For $BaSO_4$-compounds the tensile strength starts at a low level but increases with further extrusion steps in order to reach almost the same level of neat and TiO_2-filled PA 6 after seven extrusion steps (Fig. 2).

Filament extrusion

The nano-compounds were processed into filament yarns with different particle content. To meet the requirements on the future large scale production, a set of process parameter and an appropriate design of spin package were determined. Thus, a stable and cost efficient melt spinning process for the manufacturing of the nano modified filament yarns was achieved.

The distribution of the nano-particles in the cross-section of the filaments was investigated optically. The filament yarns were embedded in epoxy resin. Using a micro-tome device, thin sections of the sample were produced and analyzed by transmission electron microscopy (TEM). Fig. 3 shows a characteristic cross-section of nano-modified PA-filament. Using the digital image processing, it was shown that, more than 90 % of the available agglomerates in the filament cross-sections are smaller than 100 nm (see Fig. 4). This is a clear evidence for the good dispersion and particle distribution within the manufactured filament yarns.

The influence of the nano-particles and their concentration on the physical properties of the filament yarns was investigated by thermal gravimetric analyses (TGA) and differential scanning calorimetry (DSC). The influence of the nano particles on the mechanical properties of the yarns, like tensile-strength and the breaking-strain, was investigated in tensile stress tests according to DIN 53834.

Typical results of the DSC analysis are shown in Fig. 5. The DSC test cycle includes two heating and one cooling steps. Using this method, not only the effects of the nano-modification but also the structural properties as a function of the stress conducted crystallization during the extrusion process are analyzed. The first heating step gives some conclusions about the thermal and mechanical treatment within the spinning process. As Fig. 5 and Tab.1 show, the nano modification of the polymer leads to shifting of the α- and γ-peaks to higher temperatures. The higher particle concentration leads to lower enthalpy deviations ΔH_f and thus to lower crystallization degrees W_C. Within the cooling step, the particle modification leads to slight increase of the crystallization temperature T_C. This is proportional to the concentration of the nano particles and it is accompanied by lower enthalpy of transition. The second heating step allows conclusions concerning the properties of the polymers in direct relation to the concentration of the nano particles. As it can be seen in the Tab. 1, the nano modification leads to shifting of the temperature peaks. This shifting is proportional to the nano particle content in the fibers. Further, higher crystallization degree was measured with the increasing of the particle concentration.

According to DIN 53834, tensile stress tests are accomplished on the nano modified filament yarns. A relation between the yarn strength and the content of TiO_2 particle in PA6 is shown in Fig. 6. As it can be seen there, the tensile strength of the yarns decreases proportional to the particle concentration.

Investigation of the thermoplastic shrinkage and the tribological properties of the nano-modified filament yarns provide some promising results. It was shown that, the friction coefficient of the nano-modified yarns is lower than those of the reference yarn. This can be beneficial concerning the processing behavior of the yarns in the further textile chain. As it can be seen in Fig. 7, PA6 yarns with nano-particles shrink less than the reference yarn at temperatures close to the melting point. Thus, an improvement of the consolidation behavior and further of the mechanical properties of the composite are expected.

3.2 Manufacturing of textile pre-forms

Within the context of the research project nano-modified hybrid yarns and textile pre-forms were produced. These were further molded to composite parts in order to investigate the influence of the na-

no-particles on the mechanical properties of the thermoplastic composite.

A promising approach in the manufacturing of thermoplastic composites provides the application of commingling yarns. These are hybrid yarns consisting of high strength fibers, as reinforcement, and thermoplastic filaments, which form the thermoplastic matrix after the consolidation.

A key point in the production of hybrid yarns is the distribution quality of the fiber components within the cross-section of the commingling yarns (Fig. 8). Within the presented research, the influence of the relevant process parameter on the yarn quality was investigated. Using digital image processing a coefficient for the uniformity of the component distribution was calculated and used for the comparison of the different yarns structures.

With the parameter set providing the best yarn quality, textile woven fabrics and bi-axial warp knitted fabrics were manufactured (Fig. 9).

3.3 Consolidation and composite properties

In order to investigate the mechanical properties of the nano modified thermoplastic composites, the semi-impregnated textile preforms were molded to plates. The molding temperature was 250 °C. The molding pressure was varied in the range from 20 to 50 bar. Using the semi-consolidated preforms composite plates and complex 3D structures, a ballistic helmet, were produced (Fig. 10).

The composite behavior of the new material is being currently investigated. The first test series show that, the ballistic properties of the thermoplastic composites are comparable with those of the thermo set composite, which is currently used in that application area. However, further investigations are needed, to determine the influence of the nano particle of the performance of the composite structure.

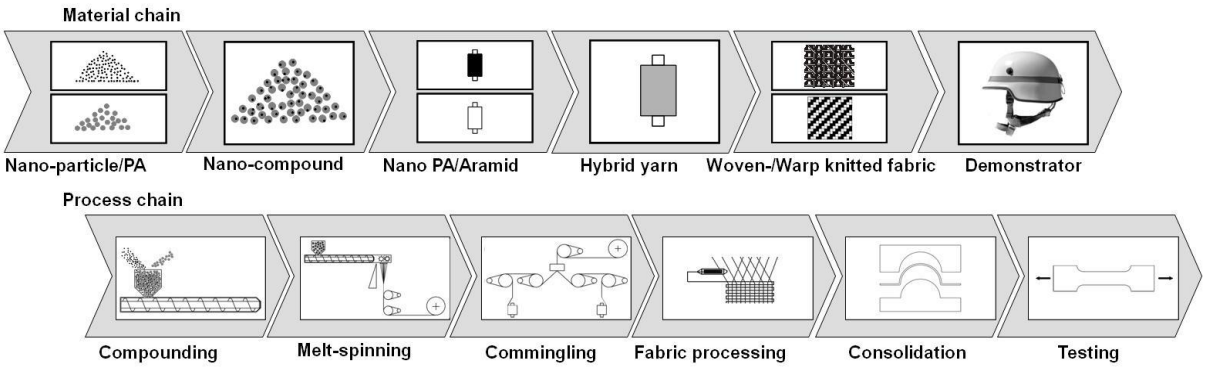

Fig. 1: Material- and process-chain of the research project

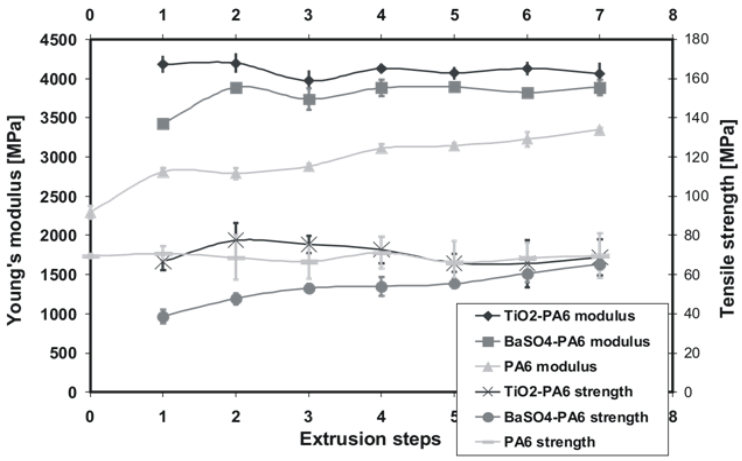

Fig. 2: Mechanical properties of the compounds

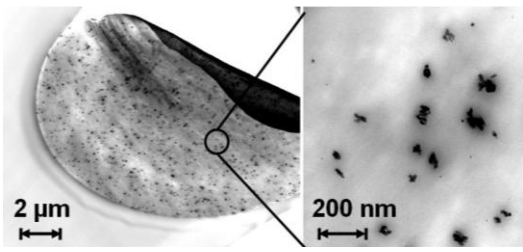

Fig. 3: Nano-particles in PA fiber

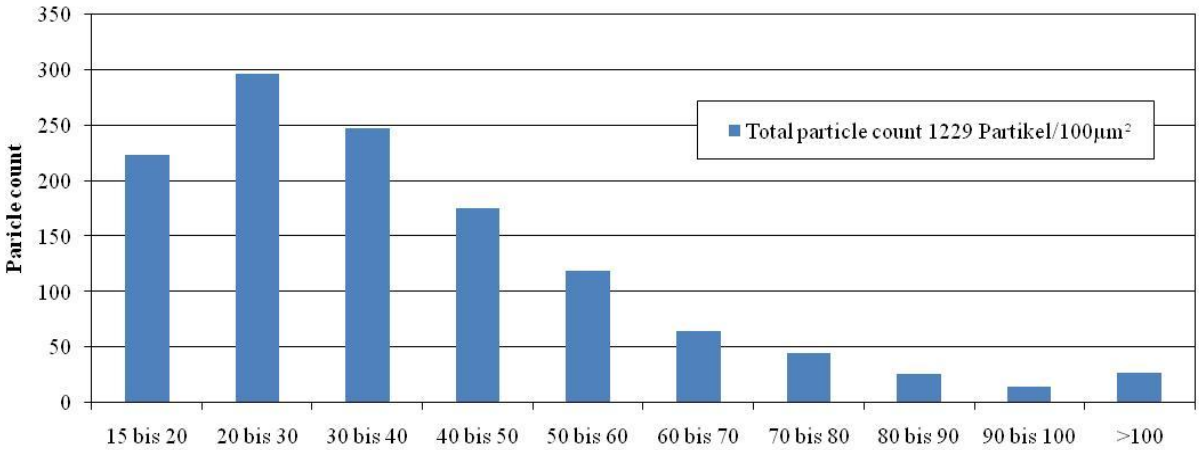

Fig. 4: Quality of the particle distribution

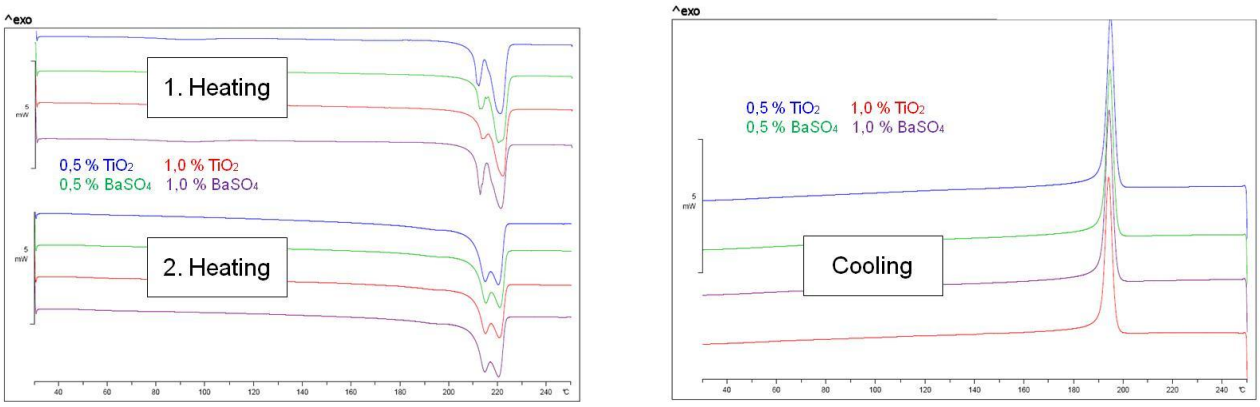

Fig. 5: Characteristic DSC-curves of nano-modified PA 6 filament yarns

Tab 1: Results of the DSC analysis

Step	Characteristic	Ref.	0,5% TiO_2	1,0% TiO_2	0,5% $BaSO_4$	1,0% $BaSO_4$
1. Heating	Peak 1 T_α [°C]	211,5	212,1	212,4	212,1	212,6
	Peak 2 T_γ [°C]	220,2	220,5	220,7	220,4	220,8
	Enthalpy of transition ΔH_f [J/g]	69,1	65,2	64,5	67,6	66,0
	Crystallization degree W_c [%]	30	28,3	28,0	29,4	28,7
Cool-ing	Crystallization temp. T_C [°C]	194,8	195,2	195,4	195,6	195,9
	Enthalpy of transition ΔH_f [J/g]	73,7	71,6	71,1	71,3	70,7
2. Heating	Peak 1 T_α [°C]	214,4	214,9	215,8	214,0	214,5
	Peak 2 T_γ [°C]	219,9	220,1	220,8	220,3	221,6
	Enthalpy of transition ΔH_f [J/g]	72,4	73,3	74,1	73,8	74,4
	Crystallization degree W_c [%]	31,5	31,9	32,2	32,1	32,3

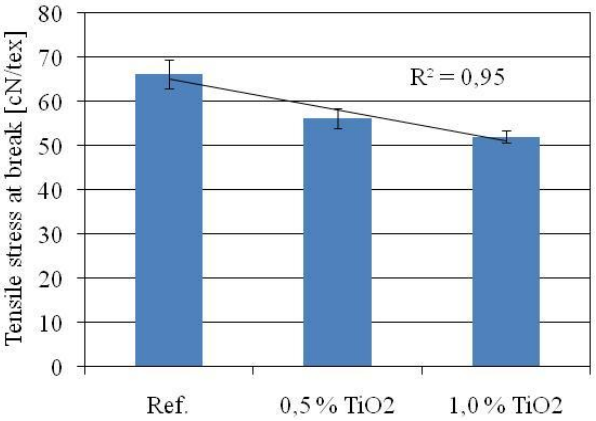

Fig. 6: Tensile properties of the filament yarns

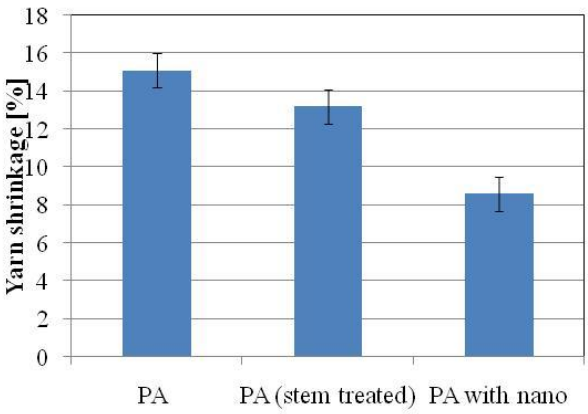

Fig. 7: Thermoplastic shrinkage of the yarns

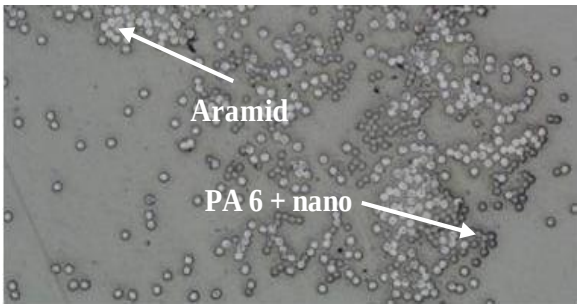

Fig. 8 Fiber distribution in commingling yarn

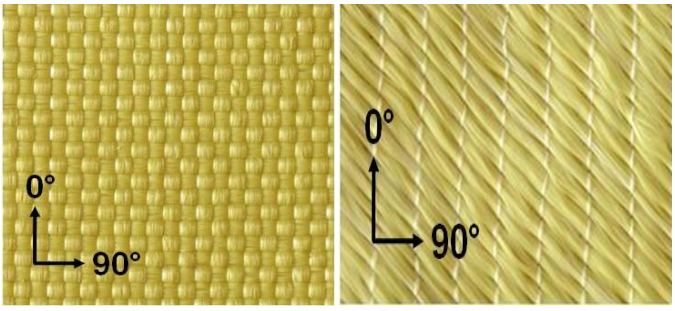

Fig. 9: Textile thermoplastic preforms

Fig. 9: Aramide/nano modified PA6 composite structures