SPINCOM YARNS - FROM REINFORCEMENT TO FUNCTIONAL FIBRES

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Abstract
SpinCOM yarns were spun with three different polymeric matrices, namely Polypropylene, Polyamide and Polylactic Acid. Tailored sizings were applied and the resulting mechanical performance of unidirectional composites was evaluated and compared. Significant improvements in the fibre/matrix bonding were achieved by employed sizing chemistry. The consolidation behavior during isothermal moulding was investigated. Different fibre volume contents could be realized and resulting mechanical properties were tested.

1. Introduction

Thermoplastic polymer matrix composites offer advantages of short production cycle capabilities which make them feasible for high volume productions. In contrast to thermosetting composites, they exhibit better impact resistance, higher toughness, recyclability and in the case of polylactic acid (PLA) even biodegradability. However, fibre impregnation is more difficult due to the high melt viscosity of the thermoplastic matrix. Different impregnation techniques have been proposed and performed. One of the most promising routines is provided by SpinCOM yarns which are based on the principle of homogeneously distribution of continous matrix filaments and reinforcement glass filaments (GF) during melt spinning [1]. In contrast to other commingling techniques, such as air jet texturing, the reinforcement fibres are not damaged during commingling. Especially the homogeneous fibre/matrix distribution of online commingled yarns leads to short impregnation paths and low void contents reflected by the high mechanical performance of the thermoplastic composites.

Beside the ease of processing, SpinCOM yarns also offer the possibility to add additional functionalities such as conductivity to the composite [2]. This can be achieved either by modifying the matrix filaments or the glass fibre surface. Our approach focuses on the development of the sizing which is applied during the yarn spinning in order to promote adhesion strength between fibre and matrix. In contrast to traditional sizing systems we add nano particles such as CNTs yielding to additional functionalities in the latter composites. In the case of CNTs electrically conducting interphases can be achieved. The conductivity depends on the applied mechanical strain or thermal load. The conductivity change can then be used for Structural Health Monitoring (SHM) of such a composite [3] [4].

Biodegradable polymers like PLA have been often used in special non load bearing biomedical applications like tissue engineering or targeted release of active ingredients. In order to use PLA in orthopaedics for bone recovery it can be spun as online commingled yarns with silica based bioglass filaments to achieve the required high tensile strength and stiffness. For this purpose it is necessary to improve the adhesion strength between PLA and glass fibre to reach the properties of bone and to tailor the degradation behaviour upon healing. An appropriate modified sizing can be used in order to reach these encountering challenges and being biocompatible.

The objective of this work is to manufacture SpinCOM yarns with different polymeric matrices such as PP, PLA and PA. The influence of traditional sizing systems but also functional sizing systems will be discussed in terms of mechanical and electrical properties of the GF composites. Another important topic is to investigate the consolidation parameters during isothermal compression moulding in order to reduce the void content thus increasing mechanical performance. SpinCOM yarns with different fibre volume contents will be spun and the influence on the mechanical properties of the composites are investigated.

2. Experimental

2.1. Processing of SpinCOM yarns

The processing of SpinCOM yarns 1 differs significantly from other commingling techniques. Glass and polymer filaments are parallel spun and commingled while passing the sizing applicator. This approach combines different advantages towards traditional commingling techniques such as air texturing: The filament distribution homogeneity is reasonable high since commingling is done at a state where both, matrix and glass fibre yarns do not posses pronounced fibre integrity. The SpinCOM yarn integrity is later on achieved by applying a sizing. The mechanical load on the yarn during commingling is negligible low as compared to air jet texturing. Neither glass fibres are broken nor are polymer fibres are streched which results in high yarn strength and avoids thermal shrinkage during consolidation.

Depending on the matrix polymer different sizings were applied during the fibre spinning as shown in table 1.All sizings consisted of a silan and at least one polymeric filmformer. In order to investigate GF-matrix adhesion strength silan and polymeric filmformer were systemically changed.

2.2. Composite manufacturing

Filament winding of the SpinCOM yarns followed by isothermal compression moulding was used to manufacture unidirectional composites with a GF volume fractions between 42 and 61 %.

The processing parameters were varied in terms of time, temperature and pressure to optimize the consolidation and achieve low void contents. Polished cross sections of the GF laminates were used to determine the void content. Specimens for mechanical testing were cut out of the unidirectional plates using a rotating diamond saw. Compression shear tests (CST) [5], tensile tests (ISO 527-5), transverse tensile tests (ISO 527-4), as well as 4 point bending tests (DIN ISO 14125) were performed.

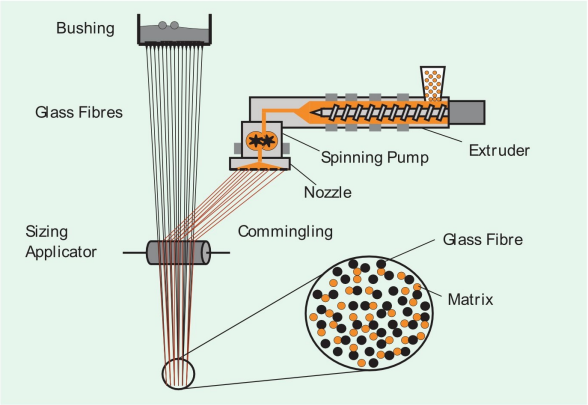

Figure 1. Principle of SpinCOM yarn processing

2.3. Design of experiments and statistical analysis

The chosen Box-Behnken design resulted in 15 experiments according to three levels and three factors. Besides the stepwise variation of the moulding pressure, time and temperature were changed and the resulting mechanical properties were used in order to determine consolidation quality. The statistical analysis of the experimental results was performed by analyzing the factorial design with a statistical software (Statgraphics, Centurion). By creating regression equations a model fit was obtained relating the results of the mechanical testing to main and secondary effects, respectively.

2.4. Mechanical testing

For mechanical testing, a universal test machine (Allround Line, Zwick Roell, Germany) with a contact strain extensometer (multiXtens, Zwick Roell, Germany) was utilized. The change in resistance of the CNT sized GF yarn during tensile testing was recorded simultaneous with the tensile loading using the a Keithley 6514 programmable electrometer.

3. Results and discussion

3.1. Influence of sizings in GF/PLA and GF/PA6.6 composites

For the GF/PLA composites, the epoxy film former (S1) based sizing as well as the chitosan-based sizing (S3) showed a significant increase of interphase strength being reflected in improved mechanical properties of the composites transverse to fibre direction, such as transverse tensile strength and compression shear strength (Figure 2a). Especially biodegradable chitosan-based sizing S3 will be selected for further component design and application. The stress-strain-curves of GF/PLA composites based on sized fibres S0 and S2 indicated significantly lower maximum values for stress and strain, which reveal poor stress transfer of the composites interphases.

For the GF/PA6.6 composites, the variations in terms of transverse tensile strength and compression shear strength (Figure 2b) are even more pronounced, ranging from 3 MPa (V5) up

Sizing	Sizing formulation	Matrix polymer
P0	3-Aminopropyl-triethoxysilane, polypropylene film former	PP
P1	3-Aminopropyl-triethoxysilane, polypropylene film former, CNT Dispersion	PP
V1	3-Aminopropyl-triethoxysilane, polyurethane film former	PA6.6
V2	3-Ureidopropyltrimethoxysilane, polyurethane film former	PA6.6
V3	3-Aminopropyl-triethoxysilane, polyurethane/polyacrylate film former	PA6.6
V4	3-Ureidopropyltrimethoxysilane, polyurethane/polyacrylate film former	PA6.6
V5	3-Aminopropyl-triethoxysilane, polyurethane/epoxy film former	PA6.6
V6	3-Ureidopropyltrimethoxysilane, polyurethane/epoxy film former	PA6.6
V7	3-Aminopropyl-triethoxysilane	PA6.6
S0	Bioresorbable finish	PLA
S1	2-Aminoethyl-3-aminopropyl-trimethoxysilane epoxy film former	PLA
S2	3-Ureidopropyltrimethoxysilane, polyurethane film former	PLA
S3	2-Aminoethyl-3-aminopropyl-trimethoxysilane, chitosan film former	PLA

Table 1. Sizing formulations applied during the SpinCOM yarn processing

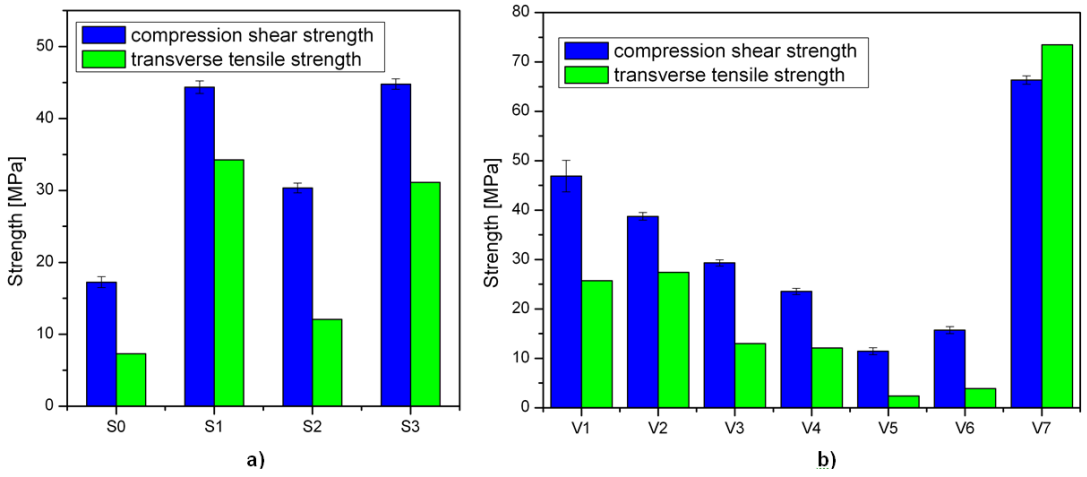

Figure 2. Mechanical performance for GF/PLA composites with different sizings S1 to S4 (a) and GF/PA6.6 composites with different sizings V1 to V7 (b)

to 73 MPa (V7). These findings are also reflected by the stress-strain curves (not shown here), which indicate a very early failure for poor interphase strength when polyurethane/polyacrylate film former (V3) applied, whereas both strength and strain increase significantly with improved interfacial interaction. SPinCOM yarns with 3-Aminopropyl-triethoxysilane sizing and without film former (V7) revealed the best transverse tensile strength. It indicates that all film formers used in the sizing formulations decreased tensile strength to a certain extent and did not

contribute to improved toughness. Further research is necessary to reveal the mechanisms influenced by local nanoscale interphase properties.

3.2. Influence of isothermal consolidation parameters onto the mechanical properties of SpinCOM based composites

The consolidation quality has a strong influence on the mechanical properties of a composites but also to the manufacturing costs [6]. In order to achieve low void contents within the composite is crucial to understand the influence of the consolidation parameters on the laminate quality. Transverse tensile testing and microscopy of polished cross sections were used to determine the laminate quality.

For the case of GF/PP composites only consolidation temperature and time have a significant influence on the transverse tensile strength as it can be seen in figure 3. By increasing the consolidation temperature the polymer becomes less viscous and fibre matrix wet out is improved. A homogenous temperature distribution during moulding is achieved by reasonable consolidation times. The consolidation pressure does not have a significant impact on the mechanical properties. This can be explained by the homogenious fibre matrix filament distribution within a SpinCOM yarn. The flow paths a very short thus no excessive pressure is required for complete fibre matrix wet out.

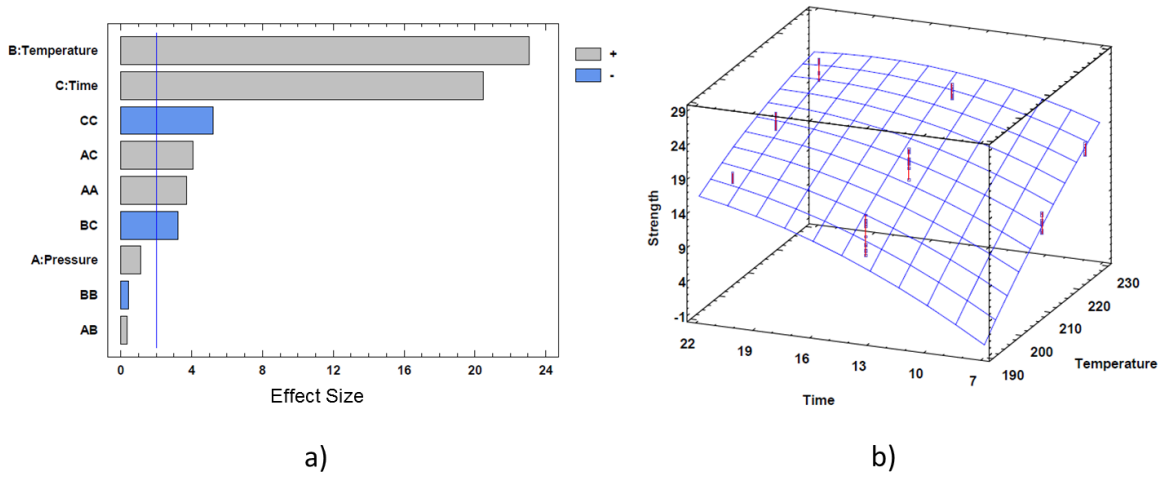

Figure 3. a) Pareto chart for the main and secondary effects and b) influence of time and temperature on the transverse strength

3.3. Influence of the fibre volume content in GF/PP composites

The fibre volume content of SpinCOM yarns can be tailored by the spinning pump settings during the polymer yarn spinning process. Therefore it is possible to tailor Young's modulus, tensile strength and strain to failure(Figure 4) of the unidirectional composites by changing the FVC of the SpinCOM yarn. The parameters for the isothermal consolidation process were set to T= 225 $°C$, t = 14 min and p = 1.5 MPa throughout the variation of the fibre volume content. The fibre/matrix distribution homogeneity was very good and not effected by the fibre volume variation.

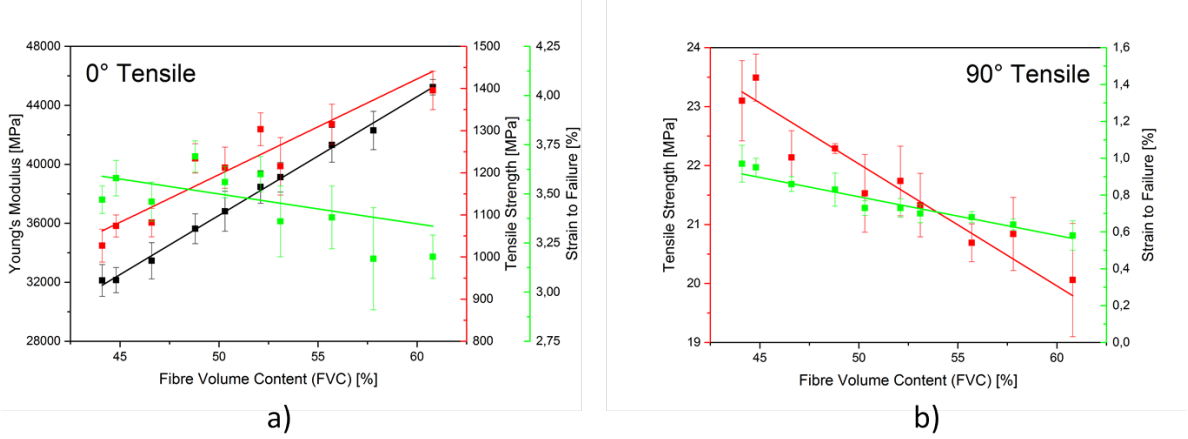

Figure 4. a) Mechanical properties along the direction of the fibres (0 °) and b) perpendicular (90 °) for GF/PP composites

Young's modulus and tensile strength can be improved by increasing FVC while strain to failure is decreasing longitudinal to the fibre direction. For the transverse mechanical properties both, strength and strain to failure a decreasing while FVC is increasing.

3.4. Structural Health Monitoring (SHM) using conductive SpinCOM yarns

In order to investigate the principal behaviour of an embedded CNT modified SpinCOM yarn within a unidirectional composite, tensile tests in the fiber direction until ultimate load were conducted. Figure 5 gives a typical stress-strain curve and related resistance change signal. The stress strain curve is almost linear until failure. There are only marginal kinks prior to failure which can be attributed to individual fibre breakage. The stress strain curve does not give reliable information on the health of the structure. At low strain levels the change in resistance is fairly small. By increasing the strain, the resistance slope becomes steeper up to the strain level where the first fibre fails. From there on, the resistance changes dramatically until the entire composite fails. By using the resistance change signal, it is possible to visualize both the interface strain and interface failure accompanied by glass filament breakages within a brittle unidirectional GF/PP composite.

For large CNT concentrations, the resistance is less but the sensitivity also decreases. The same applies for the sizing thickness. The increase of the sizing thickness yields a decreased resistance and sensitivity. Even for the coated GF with the least sensitivity, it is still possible to monitor the failure propagation. With respect to the relatively low resistance, it can be used as a reliable alternative to the high resistance yarns with CNT concentrations closer the percolation threshold versus the concentrations used in the present investigation.

4. Conclusion

The successful spinning of GF hybrid yarns with different matrix polymers and the high mechanical properties of the resulting unidirectional composites demonstrate the potential of this technology for the manufacturing of secondary and primary structural components. Especially

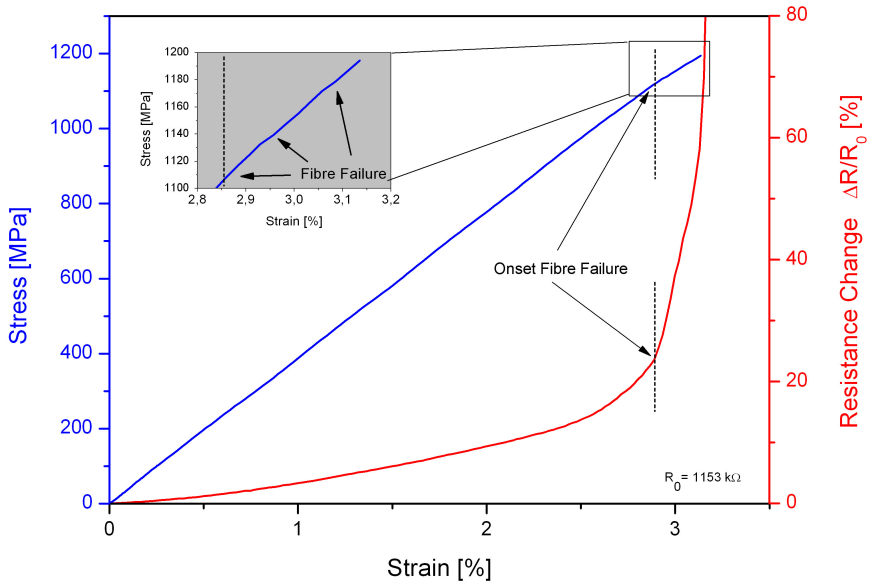

Figure 5. Stress-strain curve and simultaneous resistance change for a unidirectional composite containing a CNT coated yarn with 5 wt% CNTs relative to the film former and an average sizing thickness of 470 *nm*

the influence of tailored interphases onto the bonding between glass fibre and matrix was shown to significantly improve the interphase adhesion strength of the GF/Polymer composites. Optimized temperature and time parameters during the consolidation of SpinCOM yarns resulted in high mechanical performance as well as high fibre distribution homogeneity for various fibre volume contents.

5. Acknowledgements

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