INFLUENCE OF RESIDUAL THERMAL STRESS IN CARBON FIBER REINFORCED THERMOPLASTIC COMPOSITES ON THE FIBER-MATRIX INTERACTION EVALUATED BY SINGLE-FIBER PUSH-OUT TESTS

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Abstract
Cyclic thermal expansion and calorimetric measurements as well as single-fiber push-out tests performed with a flat-end indenter tip have been conducted on a unidirectional carbon fiber reinforced thermoplastic composite. The as-received composite is subject to process-induced residual thermal stress which is revealed by cyclic thermal expansion measurements. The residual thermal stress can be reduced by exposing the composite to temperatures above the glass transition temperature of the Polyphenylene sulfide matrix. This stress release proceeds without affecting the degree of crystallinity of Polyphenylene sulfide, as verified by differential scanning calorimetric measurements. The influence of residual thermal stress on the interfacial shear strength was investigated by single-fiber push-out tests. Reducing the amount of residual thermal stress causes a change in failure behavior from brittle to quasi-ductile while the interfacial shear strength remains unchanged.

1. Introduction

Thermoplastic composites (TPCs) are currently receiving considerable attention as promising material for applications in structural components in aeronautic and automotive industry. Besides extraordinary strength and modulus at low weight, their significance is mainly attributed to the time-saving production processes compared to thermoset composites [1,2]. Since consolidating and forming of TPCs requires temperatures in the melting range of the polymer, the heterogeneous material is subject to high thermal expansions resulting in residual thermal stress persisting in the matrix material [2-4]. The dominating source of residual thermal stress on microscopic level is the mismatch in coefficients of thermal expansion between fibers and thermoplastic matrix [2,3,5]. During cooling of the consolidated composite, the matrix is subject to higher volumetric shrinkage than the fiber, which results in radial compressive stress at the interface [5,6]. On a macroscopic scale, processing conditions like local gradient in cooling rate or temperature and the manufacturing process itself primarily determine the residual thermal stress state [2,4,7].

The objective of this work is to evaluate the influence of residual thermal stress on the interaction between fiber and matrix. For this purpose, a heat pressed composite made from carbon fibers and Polyphenylene sulfide (PPS) matrix material is annealed beyond the glass transition of the matrix to reduce the residual thermal stress inherently present in the untreated

state. By comparing two composite samples of differing thermal stress state, the influence of residual thermal stress on the interfacial shear strength τ_{is} is investigated.

Cyclic thermal expansion measurements performed with a pushrod dilatometer were conducted to identify the level of residual thermal stress incorporated in the matrix material. When the composite is heated beyond the glass transition temperature T_g of the matrix, irreversible contraction of the test specimens occurs during subsequent cooling. Since the initial crystallinity for both samples investigated is the same and the thermal treatment during the thermal expansion measurements does not influence the degree of crystallinity, as revealed by cyclic differential scanning calorimetry (DSC), this effect is ascribed to relaxation of process-induced residual thermal stress [7-9].

The mechanical performance of fiber reinforced composites is closely related to the interfacial bonding strength between fiber and matrix [10,11]. To directly evaluate this interfacial parameter single-fiber push-out tests were conducted [12,13]. A stress-based analysis is used to evaluate the interfacial shear strength [13-15]. The investigations demonstrate the importance of the thermal stress state on the mechanical performance of carbon fiber-reinforced thermoplastic composites.

2. Experimental

2.1. Material and sample preparation

The specimen investigated in the present study is an unidirectional carbon fiber-reinforced thermoplastic composite consisting of Torayca T700SC 12k carbon fibers and PPS matrix material (C/PPS). The unidirectional laminate was manufactured by a heat pressing process using an adjusted heat treatment cycle with 15 minutes dwell time at 320 °C, a heating rate of 15 K/min and a cooling rate of 10 K/min. In order to receive one further thermo-physical state of residual thermal stress, a larger piece of the untreated composite specimen was annealed at a temperature of 230 °C. The heating and cooling rates were set to 10 K/min.

For the thermal expansion measurements both specimens were cut by a precision low speed diamond saw (Isomet, Buehler) to nominal specimen dimensions of 25 mm x 2.0 mm x 2.0 mm with the principle axis of the fibers being transversal oriented to the length direction of the specimen. This alignment of the specimens allows for measuring the matrix influence on the linear thermal expansion behavior. In order to achieve maximum measurement accuracy, the two opposing front faces have to be plane-parallel to each other. This was reached by a polishing process.

For the micromechanical investigations thin slices of about 10 mm x 2.0 mm x 0.7 mm were cut by the diamond saw and thinned to a final thickness of about 45 µm by a two-sided lapping and polishing process (Precision Lapping and Polishing System PM5, Logitech Ltd.). Thus, plane-parallel sample surfaces were generated with minimal damage to the sample and with the fiber axis direction being parallel aligned to the thickness direction of the slices. In the next step, the thinned slices were placed on glass substrates with a groove of typically 50 µm in width. The setting by quartz wax ensured a close and stiff contact to the substrate.

2.2. Cyclic thermal expansion and calorimetric measurements

Measurements of the thermal expansion behavior were carried out in a horizontal pushrod dilatometer (DIL 402C, Netzsch GmbH). The measurements were conducted using a cyclic temperature profile with a heating rate of 5 K/min up to 260 °C and instantaneous cooling to room temperature at 10 K/min, repeated three times. The normal feeding load of the pushrod was constantly set to 0.25 N. For both states of residual thermal stress at least three of the columnar samples have been analyzed. A differential scanning calorimeter (204F1 Phoenix, Netzsch GmbH) was used to detect changes of the crystallinity of the PPS matrix. The cyclic measurement comprises a temperature profile with heating up to 320 °C and cooling down to 0 °C with a constant rate of 10 K/min, repeated two times.

2.3. Single-fiber push-out test

The single-fiber push-out tests were performed with an Universal Nanomechanical Tester (Asmec GmbH), which allows displacement-controlled measurements in normal direction with an accuracy of 1nm. In lateral direction, the positioning accuracy of the indenter tip is 1µm. In the present study the push-out tests were performed with a flat-end indenter tip [15,16] of cylindrical shape. The push-out tests were conducted using a standard loading schedule, comprising a continuous loading of the fiber until complete interfacial debonding occurs. The loading rate was set to 50 nm/s. The individually tested fibers were chosen randomly irrespective of the local fiber volume content surrounding the measurement position. A number of at least 25 fibers of comparable cross-section area were tested for each push-out sample. Based on this random selection, the measured results are supposed to represent the interfacial shear strength and failure behavior of the whole sample.

3. Results and discussion

3.1. Thermo-physical investigation

In Figure 1, the change in length of two specimens in differing thermal stress states as function of temperature is shown over a number of three heating cycles. During initial heating of a specimen in the as-received state (C/PPS-0) up to the final temperature of 260 °C, the sample length increases with a reduced gradient around the glass transition temperature of 88 °C as quantified by dynamic mechanical analysis. While cooling down to room temperature, the specimen reveals a significant contraction in length. The subsequent heating cycles correspond to the first cooling curve. Thus, an irreversible length contraction happens during the first cycle. The specimen annealed at 230°C (C/PPS-230) shows no reduced gradient around T_g and experiences higher thermal expansion. However, compared to C/PPS-0 the irreversible contraction in length is reduced by a factor of four.

According to literature [7-9], the obtained irreversible thermal expansion is attributed to the relaxation of process-induces residual thermal stress. By annealing the untreated composite at temperatures beyond T_g, the amount of residual thermal stress is reduced. We attribute this to molecular reorientations within the amorphous phase of PPS.

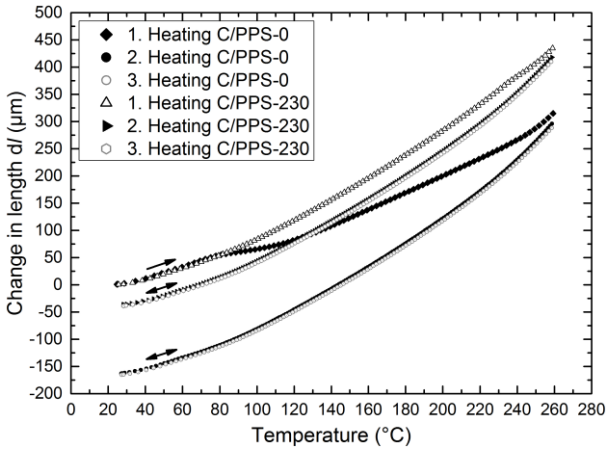

Figure 1. Change in length as a function of temperature for specimens in the two states of residual thermal stress.

The influence of changes in crystallinity of PPS on the thermal expansion behavior can be excluded, which is verified by cyclic differential scanning calorimetric measurements (Figure 2). During the heat pressing process full crystallization took place on the slow cooling from the melt. Thus, no crystallization is expected during the annealing of the composite. This is confirmed by the first cycles of the DSC signal of C/PPS-0 and C/PPS-230, which are identical and only show an endothermal melting and an exothermal crystallization peak without evidence of further crystallization. Also during the thermal expansion measurement no changes in crystallization occur. This is confirmed by the second cycles of the DSC measurements, which are completely identical to the first measurement cycles of the untreated and annealed specimens, respectively.

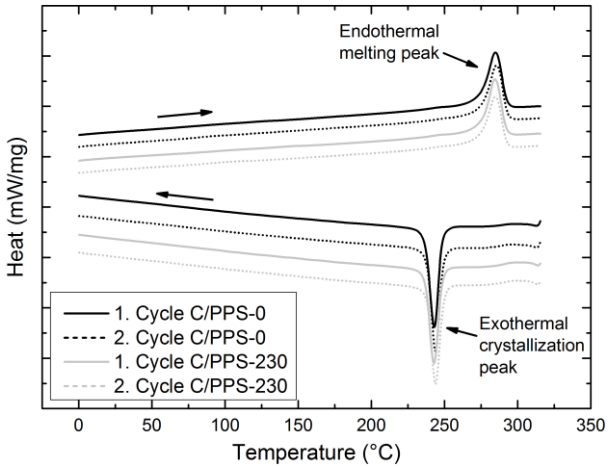

Figure 2. Typical DSC curves of the two specimens in the two states of residual thermal stress.

3.2. Micromechanical investigation

To investigate the influence of residual thermal stress on the interfacial mechanical properties, single-fiber push-out tests were conducted on the specimens of differing thermal stress state. In Figure 3, a representative load-displacement curve of a push-out test performed with standard loading schedule is shown for each specimen type. For specimen C/PPS-0, initial indenter displacement up to 300 nm leads to a linear increase in load. For lager indenter displacement, the slope decreases until peak load. After the peak, the load decreases abruptly over a short displacement range resulting in a final load drop. This drop indicates failure of the fiber-matrix bonding and push-out of the fiber. The onset of interface failure occurs at

54±5 mN and 0.8±0.1 µm, respectively. Since the obtained push-out curve is characteristic for brittle matrix composites [6,14,15] the failure behavior of C/PPS-0 is termed as brittle failure in the following. For the annealed specimen C/PPS-230, both peak load and onset of interface failure are shifted to much higher displacement values. The final debonding occurs at an increased indenter displacement of 1.8±0.3 µm but at a comparable load of 50±6 mN. The shape of the curve suggests progressive failure of the bonding between fiber and matrix Due to the extended range of damage progression, the failure behavior is termed as quasi-ductile in the following. We conclude that residual thermal stress has a significant influence on the push-out behavior. For the investigated specimens, reducing the level of residual thermal stress induces a change in failure behavior from brittle to quasi-ductile failure.

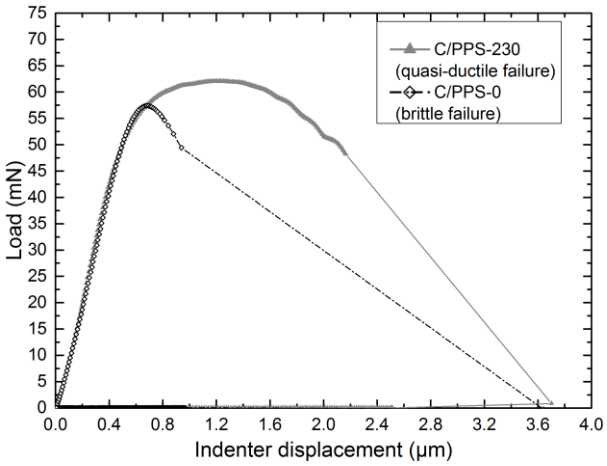

Figure 3. Representative load-displacement curves of single-fiber push-out tests conducted on the two specimens of differing residual thermal stress.

For the evaluation of the interfacial shear strength according to Marshall [13], the load at push-out is normalized to the crack surface. The thicknesses of the push-out slices amount to 44.9±1.1 µm and 44.1±0.7 µm for C/PPS-0 and C/PPS-230, respectively. The diameter of the fibers tested amounts to 6.6±0.2 µm. For the untreated specimen with brittle failure behavior, the evaluation gives an interfacial shear strength of 55.6±5.6 MPa. For the annealed specimen revealing quasi-ductile failure behavior a shear strength of 54.5±4.3 MPa is obtained. Taking into account the standard deviation we can conclude that the interfacial shear strength remains unchanged although the failure behavior changes from brittle to quasi-ductile. Therefore, the numerical value appears to be of limited significance for interpretation and evaluation of the interfacial mechanical performance of composite materials. This statement is supported by the fact, that the applied evaluation method is dependent on assumptions regarding the stress distribution along the interface [15] and neglects plastic deformation of the matrix.

4. Conclusion

The influence of residual thermal stress on the interaction between carbon fiber and PPS matrix has been investigated. Cyclic thermal expansion measurements have been conducted on two specimens in differing thermal stress states to identify the level of residual thermal stress. These measurements have revealed that the process-induced residual thermal stress can be reduced by annealing the untreated composite at temperatures beyond the glass transition of the matrix. The reduction of residual thermal stress proceeds without affecting the degree of crystallinity of PPS, as verified by differential scanning calorimetric measurements. The micromechanical investigations by means of single-fiber push-out tests revealed that the

residual thermal stress has a significant influence on the push-out behavior. Reducing the amount of residual thermal stress causes a change in failure behavior of the fiber-matrix bonding from brittle to quasi-ductile failure. Since the interfacial shear strength is the same in both states of residual thermal stress we suppose this material parameter to be of limited significance.

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