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Fiber-matrix interphase in applied short glass fiber composites determined by a nano-scratch method

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ABSTRACT

The fiber-matrix interphase in composites is defined as the intersection region between fibers and the matrix material. It shows altered matrix material properties. In dependency of the matrix material or the fiber coating, this phase is created by interdiffusion processes at the macromolecular scale driven by thermodynamic forces. Especially for FE simulations of composites and the validation of multi-scale material modeling approaches, the information about the existing interphase becomes important. Thus, the present study analyses the interphase in applied short glass fiber reinforced thermoplastics. For the identification of the interphase thickness, the nano-scratch method provides admissible results. This methodology is improved and adapted to the use in short fiber composite specimens. Thereby, the measured range of interphase thickness represents the inhomogeneity of the interphase. To assure that the measured interphase is not mainly constituted by the sizing of the glass fiber, incineration tests are performed additionally. The comparison of the interphase and the sizing thickness shows a significant thicker interphase.

1. Introduction and motivation

Short fiber reinforced thermoplastic composites are used in manifold industrial applications. Particularly, different light-weight applications in the automotive or aviation industry are using the benefit of the combination between a low density thermoplastic matrix and stiff short glass fibers. At macroscopic scale, the fibers are responsible for an increasing Young's modulus, representative for a higher stiffness, and a higher strength. Below the macroscopic scale, the fibers transfer and carry the loads in the composite. Thus, the thermoplastic matrix defines the geometrical fiber position and transmits the load into the fibers. To achieve these functions, an optimized fiber-matrix bonding is indispensable. For this purpose, between 1963 and 1966 a glass fiber coating (also described as sizing) based on silane coupling agents is developed [1]. In the continuing research progress, special chemical compounds as sizing systems for thermoplastic resins are established [2,3]. A detailed characterization of the constituents in glass fiber sizings as well as their role in the occurring chemical reactions is given by Petersen [4] and Thomason [5].

In 1983, Drzal et al. [6] studied the adhesion between fiber sizings and either the epoxy matrix materials or the graphite fibers. They developed that on both contact surfaces of the fiber sizing, the bulk material properties of matrix and fiber have changed in a specific range. The entire phase, containing the modified matrix material, the fiber sizing and the modified fiber material is denominated as “interphase” [6]. The identification of an interphase in glass fiber reinforced, semi-crystalline thermoplastics is also reported by different authors [7–10]. The content of semi-crystalline structures in the observed interphase leads to the equivalent description as “trans crystalline region” (TCR) [7,11]. In the last decade, detailed explanations for the development of the interphase between coated fibers and a polymer matrix are given [12–16]. The authors explain the interphase formation by interdiffusion processes at a macromolecular scale driven by thermodynamic forces.

Different experimental methods are applied to determine the specific chemical and physical properties of the composite's interphase. Using Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance Spectroscopy (NMR) or X-ray photoelectron spectroscopy (XPS), the effects between fiber, sizing and matrix are studied on the chemical molecular level [17–19]. Dynamic Mechanical Analysis (DMA), Raman Spectroscopy Stress

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Field Analysis, Differential Scanning Calorimetry (DSC) and Atomic Force Microscopy (AFM) are applied to identify physical properties like the stress distribution or a gradient modulus profile over the interphase thickness [20–23]. In the context of these investigations, the determination of the interphase thickness plays a major role. Several authors have studied the dimension of the interphase region. They identified an interphase thickness between a value of 0.03 μm and 3 μm, depending on the fiber fraction and matrix material [22,23]. For composites with identical fiber-polymer constitution, a deviation of the measured thickness by the factor of 4 is observed [24]. This outcome proves the influence of the applied measurement techniques on the value of the interphase thickness. The measured interphase thickness decrease progressively by using more precise experimental techniques [25]. In the last two decades a new method based on nano-indentation is presented aiming for an improved interphase thickness measurement. Nano-indentation, originally designed for the investigation of mechanical properties in thin films, is applied by Hodzic et al. to characterize polymer-glass interphases [26]. To identify the interphase thickness without the influence of the indenter tip over a continuous path, the nano-scratch technique is introduced [26–28]. Thereby, the indenter scratches the sample surface from the matrix to the fiber with a constant normal force. In several applications, this procedure is validated for the characterization of interphases below the micrometer scale [25,29].

Especially for realistic material modeling of composites, it is important to know the quantitative interphase weight and volume fraction of the entire composite. It enables to predict realistically the mechanical and failure behavior of technical components by simulation runs. In industry, short glass fiber composites produced by injection molding are dominating the field of composite materials since decades [30]. Nevertheless, the analysis of injection molded short fiber composite specimen in terms of an interphase existence or the application of nano-scratch is sparely documented in literature [31–33]. Thereby the authors mention, that it is not possible to record the load–displacement response of a single fiber nano-scratch due to a poor resolution driven by an huge material pile-up [31]. In consequence the evaluation of the interphase thickness of one single fiber is not possible. Additionally, the scratch is performed in a non-perpendicular direction to the fiber surface in the cutting plane [32]. This leads to the identification of an interphase with disproportional higher thickness [33] corresponding to the values mentioned above [22,23]. The injection molding process used for the fabrication of the specimens is thereby not correlated with the measured interphase properties. However, the heat development during the injection of melted polymer should influence the thermodynamic forces and interdiffusion processes which are responsible for the interphase creation. Until now, the impact of the injection molding process on the creation of an interphase is not known. In this context the importance of the fiber sizing on the developing interphase has to be reconsidered as well.

The present study is focused on the investigation of injection molded short glass fiber reinforced Polybutylene terephthalate (PBT). For the realistic prediction of mechanical material behavior, the fraction of an interphase on the entire composite is investigated. Therefore, the interphase thickness must be determined. Actually, the interphase thickness in injection molded composites with a thermoplastic matrix is not available from previous studies. For this background, the thickness of the formed interphase in a PBT short fiber composite is identified. The presented literature review shows, that nano-scratching is a possible tool to determine the interphase thickness with adequate accuracy. For the application of nano-scratching in this study, unidirectional short fiber composite specimens are developed and produced. The applied methodology of nano-scratch differs from the so far published principles. Instead of using a constant normal scratch force, a constant indent depth over the scratch path is applied. This leads to several advantages as less material pile-up and the independency of the indenter geometry from the interphase thickness measurement. Thereby, an estimation of the interphase global percentage in short fiber composites can be made. The results are compared with the approximated fiber sizing using incineration of short glass fibers.

As reported in several studies, the interphase shows an inhomogeneous distribution over the analyzed region [33–36]. Still, it is not analyzed how the use of a semi crystalline thermoplastic matrix affects the homogeneity of the interphase. For this reason, the present study evaluates the homogeneity of the interphase thickness in case of the PBT.

2. Material

A Polybutylene terephthalate reinforced with 20 weight percent of short glass fibers (PBT-GF20) is chosen in this study. This composite is provided in form of granulate by the company Celanese® and is distributed under the brand “Celanex® 2300 GV1/20”. It represents a material, which is used in manifold technical parts [37]. The general material properties provided by Celanese® are summarized in Table 1.

The PBT matrix material is a semi-crystalline thermoplastic polymer. The processed E-glass fibers show typical material properties, as reported previously [38]. However, specific data for the applied fiber sizing is not available. In general, the sizing consist of 80–90 wt.% film former, 5–10 wt.% silane coupling agents and 5–10 wt.% auxiliary agents (lubricants, antistatics) [4,39,40]. Based on the summary of Hartman et al. [41], Table 2 shows an overview of glass fiber sizing chemistry. The typical material nomenclature as well as the function of each constituent in glass fiber sizings is presented. The thickness of the fiber sizing depends on the fiber diameter, because the size is expressed in weight percent of the fiber. In the present case, coated fibers with a diameter of 14 μm are investigated. The density of the fiber sizing can be approximated to 1000 kg/m^3 [4].

3. Experimental methods

3.1. Fabrication of the composite specimen

In recent studies, a new specimen geometry for the biaxial mechanical characterization of short fiber reinforced thermoplastics is introduced [38,42]. The main feature of the specimen is a unidirectional fiber orientation in the measurement section. By unidirectional fiber orientation, the orientation of short fibers in one direction is understood. This is not to confound with laminates made of one or more unidirectional layers in endless fiber reinforced composites. The unidirectional fiber orientation in the present specimen can be explained with the high velocity of melt flow, which is induced by the sprue type and the decreasing cross-section of flow channel in the specimen geometry. Optical

Table 1
General material properties of the applied PBT-GF20.

Property	Value	Unit
Density	1450	kg/m^3
Tensile modulus	7400	MPa
Tensile stress at break	125	MPa
Tensile strain at break	3	%
Melting temperature	225	°C