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Novel approach for the development of ultra-light, fully-thermoplastic composites

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ABSTRACT

A novel approach for the development of ultra-light, fully-thermoplastic fiber reinforced composites is presented. The composite material consists of a polyolefin plastomer (POP) matrix reinforced with ultra-high molecular weight polyethylene (UHMWPE) fibers. The interfacial affinity of both polyolefins is enhanced by the deposition of a nanometer-scale polar functional plasma polymer film on the surface of the filaments within a reel-to-reel continuous process. The activated UHMWPE yarn is subsequently coated with a layer of the matrix material using a modified wire coating process in order to produce a hybrid yarn. The improved adhesion between the two materials is demonstrated by means of a specially developed yarn pull-out method that measures the UHMWPE–POP interfacial shear strength. The combination of the two techniques employed in the development of the hybrid yarn largely maintains tensile strength as well as the crystalline structure of the UHMWPE yarn as determined by wide angle X-ray diffraction. Alternate layers of woven hybrid yarn and woven pure UHMWPE yarn are then stacked and the lay-up is consolidated by hot compaction, resulting in a composite laminate with a fiber volume fraction of 0.54 and a density of 0.93 g/cm^3.

1. Introduction

The use of fiber-reinforced composite materials for light-weight structural applications requires an outstanding mechanical performance of the composite part. This is best achieved by using high performance continuous filaments aligned in the direction of mechanical loading, coupled with an excellent fiber–matrix interfacial interaction. Although the overall market share between thermoset and thermoplastic composites is somewhat balanced (approximately 60%–40%) [1], the field of light-weight structural composites is strongly dominated by carbon fiber–epoxy composites. Within the thermoplastic composites market, continuous fiber thermoplastics are also mostly reinforced with carbon fiber due to the fact that the UHMWPE fibers, the only thermoplastic fibers capable of competing with carbon fiber in terms of mechanical performance and light-weight, show poor adhesive properties and limited thermal resistance. The chemical composition of UHMWPE fibers results in an inert fiber surface that does not provide any polar functional groups for chemical interaction with a polymeric resin system.

The concept of making a fully thermoplastic composite reinforced with continuous UHMWPE fiber has lured researchers for almost 25 years. Marais and Feillard [2] reported in 1992 on the development of a unidirectional (UD) composite with a high density polyethylene (HDPE) matrix reinforced with UHMWPE fiber. For this purpose, a UD pre-impregnated material (prepreg) was prepared by wrapping a HDPE film around a mandrel, followed by the very tight wrapping of UHMWPE fiber on the film at elevated temperature in a process similar to filament winding. Laminates from the resulting prepreg were prepared by compression molding yielding composites with a fiber volume fraction (V_f) of 0.70. The composites had a longitudinal modulus and ultimate tensile strength of 74 GPa and 1300 MPa, respectively. Nevertheless, the same properties in the transverse direction were only 1.5 GPa and 10 MPa. A few years later, Hinrichsen et al. [3] reported on the development of a powder impregnation process for the production of unidirectional composite tapes consisting of UHMWPE fiber and a low density polyethylene (LDPE) matrix. Having a V_f of 0.62, the tapes showed an elastic modulus of 22 GPa and a tensile strength of 1100 MPa in the fiber direction. Nonetheless, as in the case of the work reported by Marais and Feillard, the transverse properties of the unidirectional composite tapes can be assumed to be exceptionally low due to the extremely poor fiber–matrix adhesion.

A method which has attracted the attention of various research groups in an attempt to overcome among other things the limitations

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imposed by a poor fiber–matrix adhesion is the development of UHMWPE single polymer composites (SPCs). Cohen et al. [4] treated UHMWPE yarn with a tetralin solution containing 1.75% w/w of UHMWPE powder. The coated yarn was wound onto a plate in order to generate UD layers which were subsequently compressed to make the SPC. Unfortunately, the resulting composite material still showed a tremendous degree of anisotropy, with tensile strength values of 1400 MPa in the longitudinal direction and 23 MPa in the transverse direction, illustrating an enormous lack of inter-fiber adhesion. Mosleh et al. manufactured UHMWPE SPCs by compression molding plain weave fabrics and powder. The resulting composites had a V_f of 0.60 and achieved a tensile strength of 300 MPa [5]. Similar values have been reported by Ward and Hine for the hot compaction of woven Dyneema® fabric which resulted in sheets with a tensile strength of 250 MPa and tensile modulus of 7 GPa [6]. However, the fabrication of SPCs by hot compaction entails the main disadvantage that the UHMWPE filaments may be subjected to partial melting, in detriment of their mechanical properties [6].

An alternative approach for the development of a fully thermoplastic composite can be found in the possibility to coat the reinforcing yarn with what eventually will serve as a thermoplastic matrix, thus generating a hybrid yarn which can then be used to make a fiber-reinforced composite structure by a hot compaction process in which the matrix polymer is consolidated in the molten state without partial degradation of the UHMWPE filaments. If the surface of the fibers composing the reinforcing yarn is previously activated, an enhanced adhesion between the matrix polymer applied as a coating and the reinforcing fiber can be ensured. Such a novel approach can be achieved for instance by means of a modification of the traditional wire and cable coating process. Wire coating (also known as overjacketing extrusion) is an extrusion operation in which a rigid wire is pulled through an extruded molten polymer contained in a die [7]. Depending on the type of die used, the achieved overjacketing is of a “pressure” or “tubing” type. In the pressure-type coating both materials are allowed to come into contact while still in the die, taking advantage of the pressure exerted by the polymer mass in order to enhance the interfacial adhesion between both materials. Alternatively, the tubing-type coating combines both materials at the outlet of the die, under atmospheric pressure [7]. Examples of the implementation of the wire coating process to coat fibrous materials can be found for instance in the work of Tao et al., who have employed a wire coating-type method in which a nylon filament was coated with rayon [8]. Another variation of the wire coating method has been used by van der Werff et al. in order to produce a three layered fiber composed of a PEEK filament as core, a thermochromic liquid crystal middle layer and a polypropylene sheath [9]. Won et al. [10] have reported on the sheathing of an entire Zylon® tubular braid with LDPE, where the original braid with a linear density of 48,000 denier was coated with 2700 g/km of the LDPE.

Although UHMWPE is a material that does not readily bond to other polymers, accounts on the improvement of its adhesive behavior by means of continuous plasma treatments are very scarce in the literature. Teodoru et al. have carried out the plasma treatment of UHMWPE fibers with an argon dielectric barrier discharge at a processing speed of 0.1 m/min. According to the authors, the continuous plasma treatment resulted in a significant improvement of the adhesive properties of the UHMWPE fibers due to the introduction of polar functional groups on the fiber's surface and the enhancement of its roughness, although no quantitative adhesive data were described [11].

In contrast to the previous work described in the literature, the study reported in the present paper investigates UHMWPE-based composite materials by means of the development of a novel semi-finished product which enables the production of ultra-light, fully-thermoplastic composites. The semi-finished product consists of a continuous UHMWPE-based hybrid yarn produced by way of two processing technologies. Plasma polymerization (after cleaning of the yarn) is used to deposit an adhesion-promoting polar functional film on the UHMWPE material [12]. This process is followed by an overjacketing extrusion which coats the UHMWPE yarn with a polymer that serves as matrix material in the finished composite part. The effect of the various preparation steps on the tensile and structural characteristics of the UHMWPE yarns and the mechanical properties of the final composite plates are discussed. The feasibility of employing continuous processes at yarn speeds in the order of 40 m/min to activate an inert fiber surface and adhere it to a polymer, leading to a four to fivefold improvement in interfacial interactions between both materials, is demonstrated for the first time.

2. Materials and methods

2.1. Materials

Two types of UHMWPE yarns have been used in this work: a MirAcle® Minu γ with a linear density of 16 g/km supplied by Dong Yang Textile Mfg. Co., and a Dyneema® SK75 having a linear density of 11 g/km supplied by DSM Dyneema. Additionally, a 3/1 twill Dyneema® SK75 fabric with an areal density of 180 g/m^2 was used together with woven hybrid yarn for the fabrication of composite laminates. The polymer used as sheathing material to produce the hybrid yarn is a polyolefin plastomer (POP) supplied by The Dow Chemical Company under the trade name of Versify® 4200. The plastomer has a density of 0.876 g/cm^3, melting temperature of 84 °C, glass transition temperature of -23 °C and a melt volume rate of 28 cm^3 in 10 min at 230 °C under a force of 2.16 kg. POP is a propylene–ethylene copolymer containing 80 to 95 weight % of propylene-derived units [13].

2.2. Yarn cleaning and plasma polymer deposition

The as-received yarn was subjected to a plasma polymer deposition process in order to activate its surface by introducing an oxygen-functional layer on the surface of the filaments [14]. Given that this plasma polymer film shall be deposited on a clean filament surface, a continuous dip washing was employed as a preliminary step. In this cleaning process, the yarns were immersed in a hexane bath and dried in two continuous ovens at 60 °C at a speed of 9 m/min. Manufacturing residuals are thus removed from the yarn surface in order to ensure that direct contact between the fiber surface and the deposited polymer film will occur. Details of the equipment used are given elsewhere [15]. A spool of clean yarn was then placed in the vacuum chamber of the in-house pilot plant device to perform a reel-to-reel plasma treatment, which allowed depositing the oxygen-containing functional plasma polymer film while winding the yarn at a speed of 44 m/min. For the plasma polymer deposition to occur, the gas flow in the chamber was 6 standard cubic centimeter per minute (sccm) of ethylene (polymerizing gas) and 24 sccm of carbon dioxide (reactive gas) while the pressure in the chamber was maintained at 0.13 mbar. The exposure time of the UHMWPE yarn to the plasma polymerization process leads to a coating thickness of approximately 55 ± 10 nm as measured by surface profilometry on flat reference samples. Due to the enhanced surface area of the yarn, a nano-scaled layer is thus deposited mainly on the outer filaments of the yarn structure.

2.3. Overjacketing extrusion

The plasma-treated material was subjected to an overjacketing extrusion (OE) process which allows to apply a polymeric coating to a textile yarn. For this purpose, a Rheomex OS single screw extruder ($D = 19$ mm, $L/D = 25$) feeds the polymer melt to a Haake OS melt pump which in turn supplies the polymer melt at a fixed throughput of 5.25 g/min to the wire coating die as illustrated in Fig. 1a. Given that the untwisted UHMWPE multifilament textile yarn lacks the rigidity of the metallic wire typically used in the conventional wire coating process, a steel capillary tube threaded vertically into the wire coating die serves as a guide for the UHMWPE yarn. The end of the capillary tube