OVERJACKETING EXTRUSION OF UHMWPE MULTI-FILAMENT YARN 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 matrix reinforced with ultra-high molecular weight polyethylene (UHMWPE) woven fabric. The interfacial affinity of both polyolefins is enhanced by means of a plasma polymerization process that introduces a nanometer-scale polar functional layer on the surface of the filaments at a processing speed of 44 m/min. The activated UHMWPE yarn is then coated with a layer of the matrix material using an overjacketing extrusion process at a processing speed of up to 40 m/min in order to produce a hybrid yarn. The two processes do not result in any detrimental effect on the tensile strength and degree of crystallinity of the UHMWPE yarn. 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 a very good fiber-matrix interfacial interaction. Although the 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 very poor adhesive properties. 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 researches for almost 25 years. Thus, 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 of 0.70 (V_f). The composites had a longitudinal modulus and ultimate tensile strength of 74 GPa and 1300 MPa in the 0° direction, respectively. Nevertheless, the same properties in the 90° 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 composite tapes

consisting of UHMWPE fiber and 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.

Another approach that has attracted the attention of various research groups is the development of UHMWPE single polymer composites (SPCs). Cohen et al. [4] treated UHMWPE yarn with a tetralin solution containing 1.75% weight 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. The resulting composite material had tensile strength values of 1400 MPa in the longitudinal direction and 23 MPa in the transverse direction. 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].

In contrast to the previous work reported in the literature, the effort reported in the present paper attempts to develop 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 means of two processing technologies in the form of a plasma polymerization process that enhances the surface polarity of the UHMWPE material, followed by an overjacketing extrusion (OE) process which coats the UHMWPE yarn with a polymer that serves as matrix material in the finished composite part. The literature available in this regard is extremely limited. With respect to the continuous processing of an UHMWPE yarn, Teodoru et al. have carried out the plasma treatment of UHMWPE fibers with an argon dielectric barrier discharge with 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 [7]. Regarding OE, Won et al. [8] have reported on the sheathing of a Zylon® tubular braid with LDPE, where the original braid with a linear density of 48,000 denier was coated with 2.7 g/meter of the LDPE. An adaptation of the OE process has been used by van der Werff et al. in order to produce a three component extrudate composed of a PEEK core, a thermochromic liquid crystal middle layer and a polypropylene sheath which was applied at an overjacketing speed of 60 m/min [9].

2 MATERIALS AND METHODS

2.1 Materials

The UHMWPE material used in this work is a MirAcle® Minu γ yarn supplied by Dong Yang Mfg. Co., with a linear density of 16 g/km, density of 0.965 g/cm^3 [10], tensile strength of 2.5 ± 0.1 GPa and strain to break of 3.6 ± 0.2%. Additionally, a 3/1 twill Dyneema SK75 fabric with an area 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 in this work 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 [11]. The material is produced using Dow's post-metallocene polymerization technology, which enables the production of an isotactic copolymer with very narrow molecular weight distribution and broad melting range [12].

2.2 Material processing

Given that UHMWPE has a nonpolar surface which does not promote a strong adhesion to other

polymers, the as-received yarn was subjected to a plasma polymerization process in order to activate its surface by introducing an oxygen-functional layer on the surface of the filaments. For this purpose, a preliminary cleaning of the filaments was done in which the yarns were immersed in a hexane bath and passed through two continuous ovens at 60 °C before being wound at a speed of 9 m/min. Details of the equipment used are given elsewhere [13]. A spool of clean yarn was then placed in the plasma chamber of a continuous plasma-treating device developed and patented by Empa [14], which allowed to perform the plasma polymerization reaction while winding the yarn at a speed of 44 m/min. For the plasma polymerization to occur, the chamber is flooded with 6 standard cubic centimeter per minute (sccm) of ethylene (carrier gas) and 24 sccm of carbon dioxide (reactive gas) while the pressure in the chamber is maintained at approximately $1.3*10^{-1}$ mbar. The resulting exposure time of the UHMWPE yarn to the plasma polymerization process is in the order of 12 min, which leads to a coating thickness of approximately 55 ± 10 nm, as measured with a profilometer.

In a following step, the plasma-treated material was subjected to an OE process. OE is an adaptation of the traditional wire coating process which allows to apply a polymeric coating on a textile yarn. For this purpose, an extruder feeds a thermoplastic polymer melt to the wire coating die as illustrated in Fig. 1. A steel capillary tube threaded vertically into the wire coating die serves as a guide for the UHMWPE yarn. The capillary tube also functions as a barrier between yarn and polymer melt inside the die. The end of the capillary tube is placed about 0.3 – 0.5 mm before the outlet of the wire coating die in order to mimic a pressure type tooling. As a result, the two materials are allowed to come in contact inside the die and the pressure exerted by the polymer mass is used as an aid to enhance the adhesion between the two materials. The processing conditions employed for the OE of MirAcle yarn with POP are detailed in Table 1.

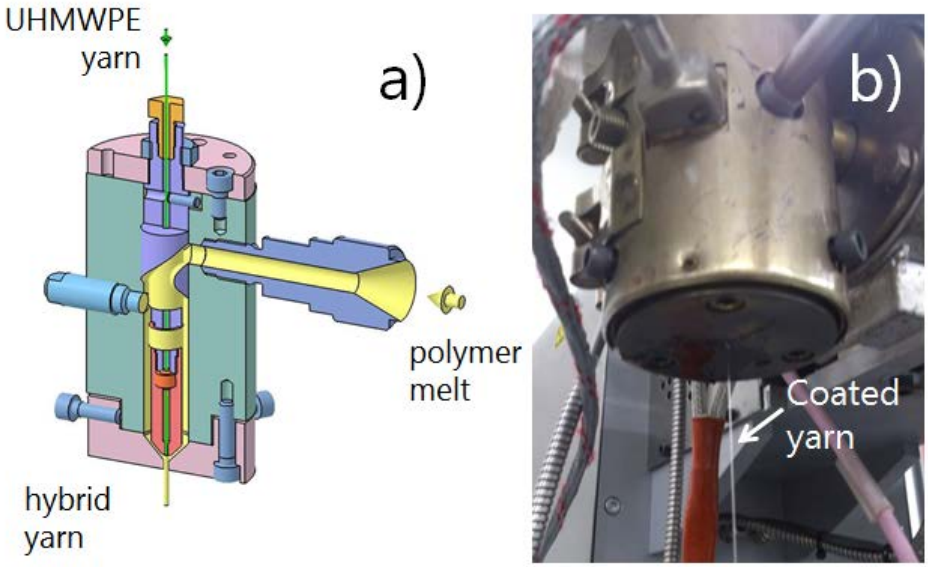

Figure 1: Schematic of wire coating die used for the OE (a), and actual view of die during the OE of a UHMWPE yarn (b).

The hybrid yarn obtained from the OE process was then woven into an 40 cm-wide fabric with a 4/1 twill structure by means of a sampling loom. The choice of weave structure is meant to minimize the number of crossings between warp and weft yarns. The woven fabric was then used to make composite laminates by hot compaction with a 50 t hydraulic press equipped with two sets of heating and cooling plates. A stack of 14.5 x 14.5 cm woven fabric layers with a predefined layup is placed inside a 15 x 15 cm steel frame with a thickness of 3 mm. The stack is then compressed following a predefined pressure ramp while maintaining a constant temperature of 120 °C. At the end of the hot

compaction process the frame and composite laminate are quickly transferred to the cooling plates, where the composite material is cooled down to room temperature while still being held under pressure. The composite laminates were subsequently cut with a water jet in order to produce specimens for mechanical characterization.

Temperature Profile (°C)					Melt pump rate (rpm)	Take-up speed (m/min)
T_1	T_2	T_3	Melt pump	Overjacketing die	20	15 – 40
155	155	155	155	145		

Table 1: Processing conditions of MirAcle yarn for OE with POP with a single screw extruder having three heating regions $T_1 – T_3$.

2.3 Mechanical characterization

Tensile testing of MirAcle yarns after different processing steps was performed with an Uster Tensorapid 3. A gage length of 250 mm, testing speed of 50 mm/min and clamping force of 450 N/cm^2 were used. A total of 20 specimens were tested for each yarn type.

2.4 Thermal analysis

Degree of crystallinity determinations of the UHMWPE material after different processing steps were performed using a Mettler 822e differential scanning calorimeter (DSC). Specimens were prepared by carefully cutting a small amount of the yarn (1.0 – 2.5 mg) and placing it in an aluminum crucible. Chopping the UHMWPE fiber can be a challenge due to its cut resistance, but a pair of Super Knips® sharp pliers proved to be very efficient. The cut fibers should be carefully placed in the crucible, ensuring that the bottom of the crucible is entirely covered with filaments and that there are no filaments protruding out of the crucible after the lid has been pressed in place. In order to quantify the enthalpy of crystallization of the UHMWPE yarns, a heating ramp from 25 °C to 250 °C at a heating rate of 20 °C/min was employed. The degree of crystallinity was then calculated by dividing the crystallization enthalpy obtained experimentally by the literature value of 100% crystalline polyethylene (69 cal/g) [15].

2.5 Interfacial behavior

The adhesion between the UHMWPE yarn and the sheathing polymer has been quantified by means of a pull-out test. For this purpose, hybrid yarns produced by OE have been embedded in epoxy resin using a mold and fixture designed specifically to produce specimens suitable for pull-out testing. A series of hybrid yarns are positioned in the mold and, once all yarns are in place, epoxy resin is poured into the mold and allowed to cure. A typical cured specimen is shown in Fig. 2a. Given that the goal of the test is to quantify the adhesion between UHMWPE and the sheathing polymer, and not the adhesion between polymer and epoxy, the sheath of the free-standing yarns needs to be removed in order to be able to pull the UHMWPE yarn located in the core of the hybrid yarn. This is achieved by carefully slicing the polymer sheath with small scissors. The last step of the specimen preparation consists of slicing the epoxy block perpendicularly to the embedded hybrid yarns so that the length of embedded yarn is small enough that failure during mechanical testing actually occurs by pull-out of the embedded yarn, and not by tensile rupture of the free length of yarn. An epoxy block containing four hybrid yarns ready for pull-out testing is shown in Fig 2b. Pull-out experiments are performed by attaching the epoxy block to the lower clamp of a universal testing machine, while one of the lengths of free yarn is held by a specially developed fixture which allows holding single filaments and thin yarns (Fig 3). The experiments were performed on a Zwick Z100 testing machine with a 10 N load cell at a constant rate of extension of 5 mm/min.

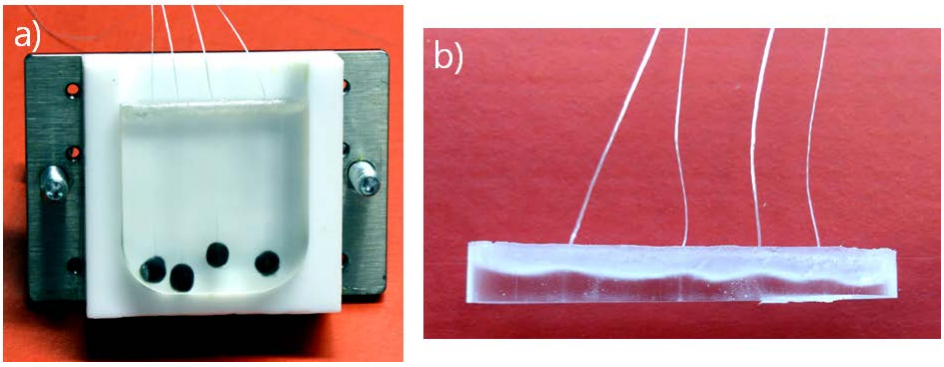

Figure 2: Specimens for the yarn pull-out test right after curing in the mold (a), and ready for testing after slicing the epoxy block (b). Each of the four specimens shown consists of a segment of hybrid yarn embedded in epoxy and a segment of free-standing UHMWPE yarn (the POP sheath has been removed).

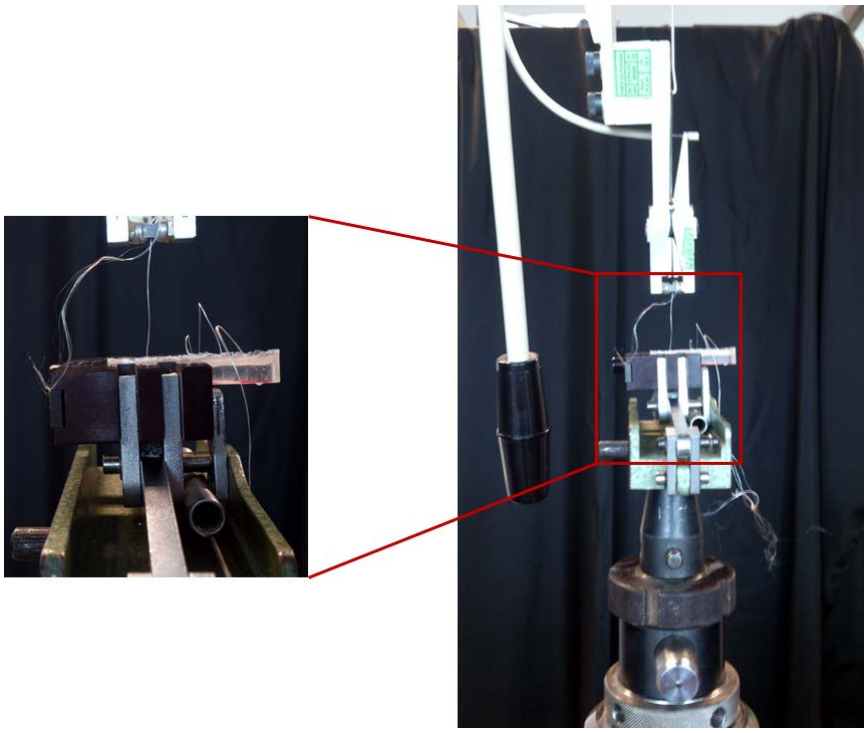

Figure 3: Fixture configuration for pull-out test with a universal testing machine.

3 RESULTS

3.1 Effect of plasma polymerization on POP-UHMWPE interfacial properties

MirAcle and POP are both polyolefin materials with inert, non-polar chemical structures which will form a relatively weak interface when combined without further treatment to form a fiber-reinforced composite. Therefore, a plasma polymerization of the MirAcle yarn was undertaken in order to improve its adhesion to POP. The yarn pull-out test has been used to quantify the adhesion between MirAcle and POP, where the average interfacial shear strength (τ) is calculated as a function of maximum pull-out force (F), perimeter of the MirAcle yarn in the polymer sheath (C) and embedded length (l) as shown in Eq. (1).

$$\tau = F / (C * l) \quad (1)$$

Pull-out testing of as-received MirAcle results in an average MirAcle-POP interfacial shear strength value of 0.5 ± 0.1 MPa. The bottom view of a pull-out specimen after testing can be seen in Figure 4a. The micrograph clearly shows the void left behind after the MirAcle yarn was pulled out of the POP sheath. When the experiment was repeated with the plasma polymerized MirAcle, the adhesion between MirAcle and POP turned out to be higher than the adhesion between POP and the surrounding epoxy. As a result, the entire hybrid yarn was pulled-out from the epoxy in which it was embedded (Figure 4b). Substitution of epoxy with acrylic resin did not improve the situation. Teodoru et al. have reported a similar situation, in which it was not possible to perform a pull-out test with UHMWPE fibers after they were treated with an argon dielectric barrier discharge [7]. In order to be able to quantify the actual improvement in interfacial properties of the UHMWPE yarn due to plasma polymerization, OE with a copolyamide (CoPA) typically used in hot melt applications was performed. Because of the presence of amide groups, the CoPA sheath is able to establish a strong bond with the surrounding epoxy resin. Experiments with as-received and plasma polymerized MirAcle yarn showed that after plasma polymerization the adhesion between UHMWPE and CoPA is 5 times higher than the measured value for the as-received material. This is in line with results stated by Devaux and Cazé, who measured the interfacial shear strength between a Spectra® UHMWPE fiber and LDPE matrix by means of a modified pull-out test. The as-received UHMWPE fiber was chemically treated with an oxidizing aqueous solution of potassium dichromate and sulfuric acid. Measurements indicated that the chemical treatment led to a fourfold increase in the adhesion between UHMWPE and LDPE. The improved adhesion was ascribed by the authors to the elimination of the superficial weak boundary layer, and the increase of surface roughness [16].

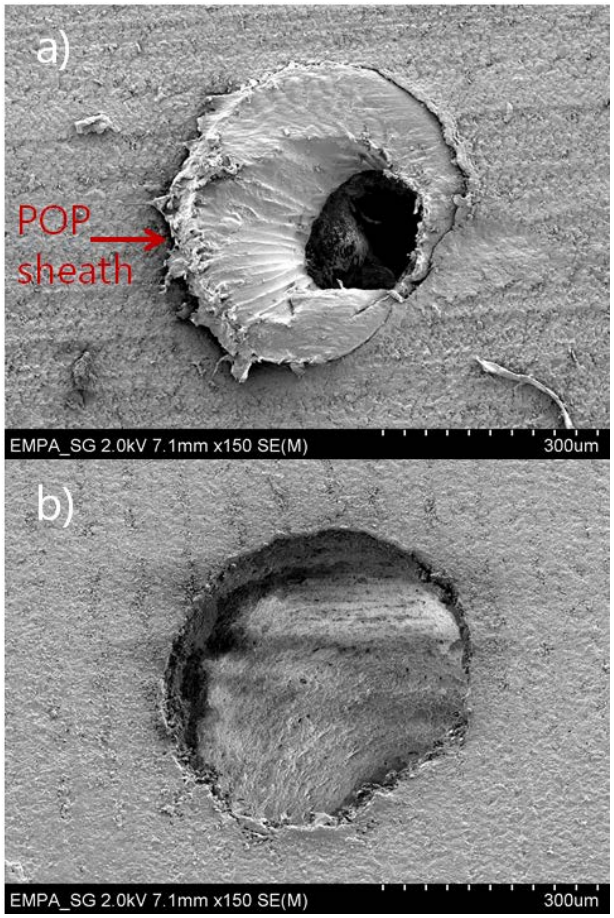

Figure 4: Micrographs of pull-out tests: pull-out between as-received MirAcle yarn and POP (a), and between hybrid yarn containing plasma polymerized MirAcle, and epoxy (b).

3.2 Effect of processing conditions on yarn properties

POP, with its broad melting range and low melting point, proved to be very flexible in terms of processing conditions, allowing to perform the OE with die temperatures ranging from 125 to 145 °C, and take-up speeds between 15 and 40 m/min. Within this processing window (maintaining the melt pump rate constant), the amount of sheath material applied to the UHMWPE yarn is only a function of take-up speed, irrespective of die temperature. The observed proportionality between amount of sheath material and take-up speed is depicted in Fig. 5 for a melt pump rate of 20 rpm and a pump capacity of 0.3 cm^3 per revolution.

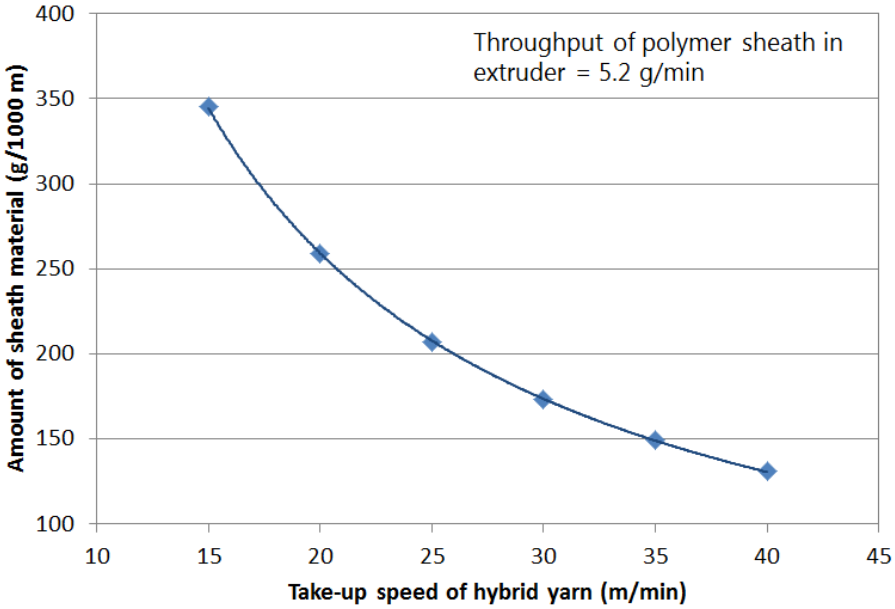

Figure 5: Effect of hybrid yarn take-up speed on resulting linear density of applied sheath (overjacketing die temperature 125-145 °C, melt pump rate of 20 rpm and pump capacity of 0.3 cm^3 per revolution).

The mechanical characteristics and degree of crystallinity of the MirAcle yarn as a function of processing step are summarized in Table 2. It can be observed that the plasma polymerization and OE steps do not appear to have a significant influence on the tensile strength of the material. In contrast, the strain to break is increased 25% after plasma polymerization. The increase in strain to break is accompanied by an increase in the material's toughness while the OE step results in a small increase in the material's crystallinity from 78 to 84%. It is known that the high-tenacity UHMWPE Dyneema fiber has a crystallinity of almost 90% [17]. Therefore, the molecular organization of MirAcle in the as-received state appears to have the potential to be improved and the OE process seems to serve as an annealing treatment that enhances the crystallinity of the material.

Treatment	Strength (GPa)	Strain to break (%)	Toughness (MPa)	Crystallinity (%)
As-received	2.5 ± 0.1	3.6 ± 0.2	50.2	78
After plasma polymerization	2.4 ± 0.1	4.5 ± 0.3	57.2	78
After OE	2.6 ± 0.1	4.3 ± 0.2	54.5	84

Table 2: Selected properties of MirAcle yarn as a function of processing step.

3.3 Fabrication of composite laminates

Composite laminates were produced by hot compaction. In order to increase the V_f of the final laminates, layers of woven hybrid yarn were stacked with layers of commercially available Dyneema fabric in an alternate fashion so as to construct a lay-up with a total of 16 layers (8 layers of woven hybrid yarn and 8 layers of Dyneema fabric). The Dyneema fabric was subjected to a plasma polymerization process similar to the one employed for the MirAcle yarn in order to enhance its adhesion to the POP matrix. The different hot compaction processes followed the steps described in Table 3. The hot press was maintained at a temperature of 120 °C and the fabric lay-up was placed between two steel plates inside a 15 x 15 cm steel frame, resulting in a final laminate thickness of 3 mm. An example of the resulting fully thermoplastic composite laminates is illustrated in Fig. 6. The theoretical V_f of the parts is 0.54, which corresponds to a laminate density of 0.93 g/cm3. The determination of the physical and mechanical properties of the composites is currently under way and will be disclosed at the conference.

Process step	Residence time (s)	Laminate 1 (Lay-up with 16 layers)	Laminate 2 (Lay-up with 16 layers)	Laminate 3 (Lay-up with 20 layers)
1	60	Preheating to 120 °C		
2	120	Hot compaction, 0.2 t		
3	30	Hot compaction, 1 t	Hot compaction, 2 t	
4	30	Hot compaction, 4 t	Hot compaction, 5 t	
5	30	Hot compaction, 8 t	Hot compaction, 10 t	
6	5	Transfer to cooling plates		
7	30	Cooling to 50 °C, 8 t	Cooling to 50 °C, 10 t	
8	-	Removal from cooling plates and extraction from steel frame		

Table 3: Processing steps for the hot compaction of fully thermoplastic plates.

Figure 6: Hot compacted fully thermoplastic composite plate.

4 CONCLUSIONS

Yarn pull-out tests have shown the efficiency of the plasma polymerization process in enhancing the adhesive characteristics of the UHMWPE yarn – POP matrix interface, enabling the development

of a polyolefin-based fiber reinforced composite. It has been shown that, maintaining all extrusion parameters constant, the amount of sheath material applied to the hybrid yarn during OE is exclusively a function of the hybrid yarn's take-up speed, although the maximum take-up speed is limited by the ability of the polymer melt to "follow" the moving UHMWPE yarn. The relatively high processing speed achieved both in the plasma and OE processes (about 40 m/min) opens a possibility for the adoption of these methods in a semi-industrial scale. Hot compaction of the developed hybrid yarn has proven to be feasible and the determination of the mechanical properties of the final laminates will help in assessing further improvements in the described methodology.

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