

MULTILAYER COMPOSITES FOR APPLICATION IN BULLETPROOF VESTS

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Abstract

The quest for lighter and more flexible body armour solutions demands for the development of new materials or the application of existing materials not traditionally used in this field. An example is Shear Thickening Fluids (STFs), which have been the subject of research for the past two decades, but despite the results obtained so far, considering the potential adoption of STF for ballistic strength enhancement of fabrics, it has not yet been applied in practice. More recently, thermoplastic matrix composites have also been investigated. Taking into account the current state of the art, this study evaluates the low-velocity impact performance of composites using two different matrices: UHMWPE GUR[®] 5113 and Shear Thickening Fluid DIC701N, both reinforced with two types of Twaron[®] fabrics. It was demonstrated that the partial impregnation by the UHMWPE matrix provided higher energy absorption by allowing generate mechanisms contributing to its dissipation, such as fibre/matrix debonding, delamination, and fibre stretching. Excessive impregnation contributed to increase the composite's fragility and lower energy absorption. For a single layer of fabric, the absorbed energy was 37% higher for STF/fabric composite than for the neat fabric at the same areal density.

1. Introduction

Body armours capable of withstanding 7.62×51 mm FMJ (M80) projectiles or 7.62×63 mm FMJ (.30 AP) armour-piercing projectiles at velocities of approximately 847 m/s and 878 m/s, respectively, are usually designated as Multilayer Armour System-MAS and also classified according to NIJ Standard-0101.06 as Type III or IV, respectively. These armours, whether rigid or flexible, can be supplemented with ceramic plates based on aluminium oxide to increase protection capacity. Their first layers have enough hardness and compression resistance to destroy the projectile's penetration and absorb and dissipate part of its energy, causing its deformation and partial fragmentation but not avoiding lethal injuries. Subsequent layers are used to totally retain the projectile and its fragments and absorb and dissipate all kinetic energy associated with the post-impact shock wave. A third layer of a ductile material (e.g., aluminium) are sometimes added to total restrict the penetration of fragments that may eventually pass through the previous system [1 - 4].

Rigid armours typically consist of thermosetting matrix composites reinforced with high-performance fibre fabrics, such as para-aramid ones (Twaron[®], Kevlar[®], etc.), and may simultaneously contain neat fabrics. Flexible armours, on the other hand, are multilayer structures using the same high-performance fibre fabrics and ultra-high molecular weight polyethylene (UHMWPE) (Dyneema[®], Spectra[®], etc.) in the form of fabrics or flexible laminates. Fabrics may have a single weave (e.g., plain or satin), other weave styles or a combination of them.

The demand for lighter and more safety body armours requests the development and use of new materials or of other ones not traditionally applied in this field. An example of this is the Shear Thickening Fluids (STFs). They are non-Newtonian fluids whose viscosity drastically increases when the applied shear rate exceeds a critical value [5, 6]. They present the remarkable characteristic of return to their initial state when the applied stresses are removed and consist of a carrier liquid and rigid

colloidal particles. The most researched STF in the field of ballistics consist of silica particles, usually fumed, dispersed with volumetric concentrations not exceeding 55-65% in Polyethylene Glycol (PEG) or Polypropylene Glycol (PPG) [6]. Several studies demonstrate that ballistic fabrics impregnated with STFs enhance their performance [5, 7].

The use of thermoplastic matrix composites reinforced with high-performance fibre fabrics has also been under investigation. Compared to thermosetting resins, thermoplastics typically have less adhesion to fibres, contribution to increase their absorption of energy by allow them to reach maximum deformation [8]. Another important factor is the better distribution of the stresses generated during impact that results from the higher flexibility of the matrix, that allows their greater dispersion among fibres and the increase of the area involved in their dissipation. In fact, thermoplastics are much flexible than thermosetting resins, known for their rigidity and reduced deformation [9].

This work is motivated by the search for lighter and more flexible body armours while ensuring compliance with the requirements of NIJ Standard–0101.06 for Type III and IV armours. Such a long and phased work starts with the knowledge and selection of materials traditionally applied in this field and the selection and evaluation of materials whose properties make them candidates for these applications. Thus, two para-aramid fabrics, Twaron[®] CT 608 and PT 900, were selected for use as neat or reinforcement. For the matrix, the choice fell on a dilatant impregnation compound DIC701N (STF diluted in ethanol) developed by Polyanswer and UHMWPE, GUR[®] 5113, produced by Celanese. The choice of STF is due to its being a commercial product, specially developed to impregnate fabrics manually or through industrial spread coating processes. With the selection of UHMWPE, it is intended to combine the above-mentioned advantages of a thermoplastic matrix and also due to its excellent stress resistance and impact strength. This material will also act as a barrier against moisture, which significantly affects the mechanical properties of aramid fibres. In this study, composites resulting from the combination of the materials mentioned above were evaluated for low-velocity impact in order to acquired knowledge that will allow developed further studies on their application in body armours for withstand high-speed impact of projectiles.

2. Experimental

2.1. Materials

Two aramid fabrics from Teijin, Twaron[®] CT 608 and PT 900 were utilized in this study. The former is based on plain weaves with arial density of 123 g/m² and is composed of ultra-microfilament of para-aramid yarn Twaron 2642, featuring an effective linear density of 570 dtex and 1000 ultra-microfilaments per yarn, while PT 900 combines plain with satin weaves with arial density of 204.6 g/m² and is made from microfilaments of para-aramid yarn Twaron 2040, having an effective linear density of 960 dtex and 1000 microfilaments per yarn. According to the manufacturer, the latter combines the ballistic effectiveness of open satin weaves with the structural integrity of plain weaves. While the CT 608 yarns exhibits a strength at break of 148 N, tenacity at break of 2600 mN/tex, chord modulus of 100 GPa, and strain at break of 3.5%, the PT 900 yarns presents strength and tenacity at break of 225 N and 2350 mN/tex, respectively, chord modulus of 89 GPa, and strain at break of 3.45%.

As matrices were also used the UHMWPE GUR[®] 5113 from Celanese, having an average molecular weight of 3.7×10^6 g/mol, tensile modulus of 800 MPa, tensile stress at yield greater than 17 MPa and strain at break of 430% and the dilatant impregnation compound DIC701N provided by Polyanswer. This last compound, which is categorised as biobased material by the TUV Austria, comprises a shear thickening fluid (70% by weight) and ethanol (30% by weight). It is a suspension, based on a urethane chemical structure, having an unpolymerized urethane monomer liquid as continuous phase combined with a dispersed phase consisting on particles resulting from the polymerization process. Upon application onto fabrics, the effect of temperature evaporates the solvent, causing their effective impregnation or coating.

2.2. Preparation of composite laminates and STF coated fabrics

The composite laminates (CLs) were produced by compression moulding in two stages using a 500 kN Moore Press. In the first stage 6.8 g of UHMWPE granules were preheated for 4 minutes at a temperature of 260 °C, compressed at a pressure of 6,25 MPa for 4 minutes and, subsequently, demoulded at 130 °C after cooling with water to obtain a film presenting an average thickness of 0,28 mm. In the second stage, the final CL was processed by compressing a square of 140 x 140 mm aramid fabric between two of the UHMWPE films, with 150 x 150 mm, previously manufactured, as it is depicted in Figure 1a). The processing conditions were identical to those of the first stage, but with a pressure 13,62 MPa. In both stages, the materials were sandwiched between two 0.12 mm thick PTFE sheets to facilitate demoulding.

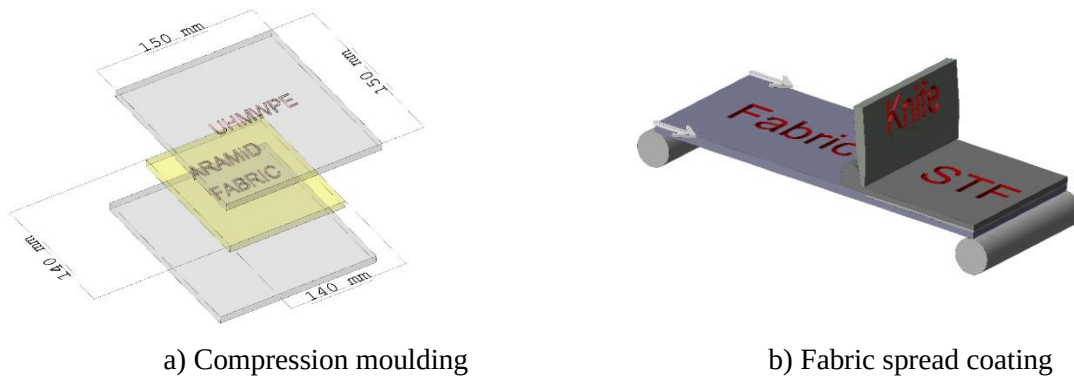


Figure 1. Production of composite laminates

STF coated fabrics (STFCFs) were prepared by spread coating technique with the knife-over-air method, as shown in Figure 1(b). In this process, the blade applies pressure to the upper surface of the fabric substrate, which is supported solely by tension between two rolls, promoting the penetration of the coating substance into the fabric and scraping off the excess, ensuring a uniform coat. Then, the coated fabric was made to pass through an oven to evaporate the solvent. The dilatant impregnation compound DIC701N used had a low surface tension and a dynamic viscosity of 1600 dPas, making it impossible to apply. Therefore, its viscosity was reduced to 140 dPas by adding 7.5 phr of isopropyl alcohol and 1.5 phr of levelling agent before application. The line speed was 8 m/min and the solvent evaporation was conducted in two phases: 1 minute and 30 seconds at 100 °C followed by 2 minutes at 180 °C. As the fluid penetration to the opposite face of fabric was challenging, owing to its viscosity and the dense weave of fabrics, the fabric was inverted to allow repeating the process on the other side.

Two types of composites laminates and STF coated fabrics were produced using the Twaron[®] CT 608 and PT 900 aramid fabrics. The add-on weight percentage, $x(\%)$, was calculated for each sample as:

$$x(\%) = \frac{PF - NF}{NF} \times 100 \quad (1)$$

where PF is the weight of laminate or coated fabric and NF is the weight of the neat fabric.

3. Testing and characterization

3.1. Characterisation of UHMWPE films

To analyse the effect of thermal stages on the structure and their mechanical properties, the UHMWPE films used in this work were subjected to Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR), Differential Scanning Calorimetry (DSC) and Tensile tests.

The structural changes of UHMWPE resulting from thermal stages were evaluated using a Perkin-Elmer FTIR 100 Spectrometer, equipped with a SPECAC Golden Gate ATR accessory. Its ATR-FTIR spectra

were obtained, at the wavenumber range of 600 to 4000 cm⁻¹, using a resolution of 4 cm⁻¹ and 16 scans, for the virgin material and after the first and second processing stages. Twelve samples were tested from each stage.

A Netzsch Heat Flux DSC 200 F3 was utilised to perform the thermal characterisation of samples of the virgin UHMWPE and after being submitted to the first and second processing stages. The samples underwent heating between 30 °C and 200°C at a scanning rate of 10°C/min. Prior to each scan, they were heated to 200°C, held at this temperature for 1 minute, and then cooled at a 20°C/min rate. Six samples were tested from each condition.

The UHMWPE films resulting from the first and second processing stages were tensile tested by using an universal mechanical testing machine Shimadzu AG-X. The tests were conducted according to ISO 527-3 standard, using an initial distance between grips of 100 mm, at a speed of 1 mm/s to measure the modulus of elasticity and at a speed of 50 mm/s to measure other properties. Ten samples from each processing stage were tested.

3.2. Characterisation of STF

3.2.1. Rheological analysis of STF

The steady-state rheological properties of STF were determined by using the ARES Rotational Strain-controlled rheometer from TA Instruments. Prior to characterization, the dilatant compound DIC701N was dried in a vacuum oven HERAEUS VT6025 at 100°C for 6 hours to evaporate the ethanol. Experimental setups employed a parallel plate geometry with two plates of 25 mm diameter separated by a 0.8 mm gap. Rheological experiments were conducted at two temperatures, i. e. 25 °C and 35 °C, with shear rates ranging from 10⁻⁵ s⁻¹ to 10² s⁻¹. A delay time before acquisition of 10 seconds, a measurement time of 5 seconds, and 10 points per decade, were used. Two samples were tested.

3.3. Characterisation of Materials by drop weight impact tests

Low-velocity dynamic drop weight impact tests were conducted on neat fabrics (NFs), STFCEs and CLs, according to ISO 6603-2 standard, using a drop impact tester CEAST Fractovis Plus. The samples, measuring 140×140 mm, were positioned and securely tighten with a clamping force of 10 kN between two circular jaws with eight teeth, each with a depth and width of 1 mm machined on the upper part, fitting perfectly into eight grooves made on the lower part, having the width and depth of 2 mm and 1 mm, respectively. The drop weight impact test set-up comprised a hemispherical impactor with a tip diameter of 20 mm and a impact mass of 25.044 kg. A drop height of 1000 mm was used, resulting in an impact velocity and total impact energy of 4.429 m/s and 245.6 J, respectively.

Due to the different areal densities of the tested samples, the energy absorbed by the STFCEs and CLs was normalized regardless of their areal density, using the following equation:

$$E_n = \frac{E_a}{(1 + \frac{x\%}{100})} \quad (2)$$

where E_n is the nomalized absorved energy (J), E_a is the absolute absorved energy (J) and $x\%$ the add-on percentage.

4. Results and Discussion

4.1. Characterisation of UHMWPE films

4.1.1. ATR-FTIR spectra of UHMWPE

ATR-FTIR spectra obtained from the virgin UHMWPE and films prepared by hot compression molding, after the 1st and 2nd thermal stages, are presented in Figure 2. The spectra of the three samples are

similar, indicating that the transformation process did not cause significant structural changes in the material.

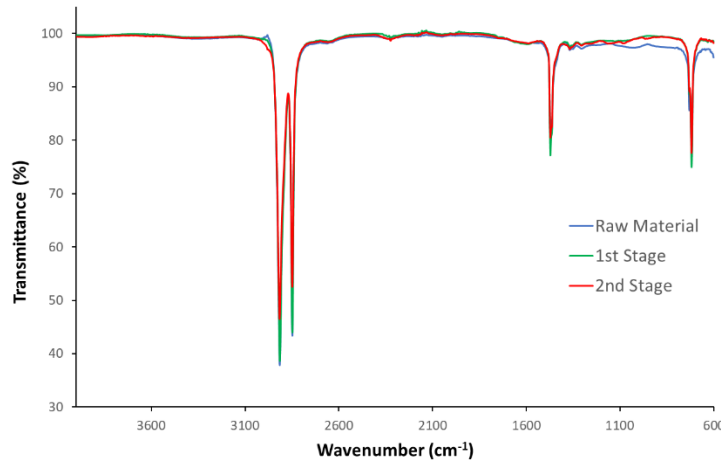


Figure 2. Spectra of UHMWPE raw material and films from 1st and 2nd stages.

4.1.2. Thermal characterization of UHMWPE

Figure 3 depicts DSC curves for the three studied conditions, samples of the virgin material and resulting from the first and second processing stages. As no broadening of the melting peaks between the samples is observed, it may be concluded that no thermo-oxidative degradation occurred during processing.

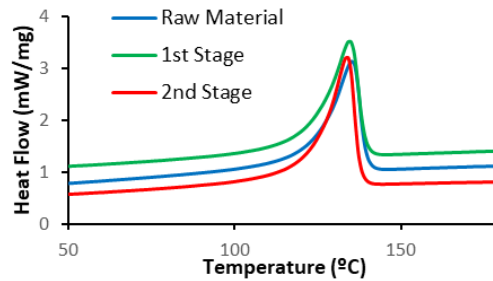


Figure 3. DSC curves of UHMWPE raw material and films from 1st and 2nd processing stages.

Furthermore, average values for the onset and peak melting temperatures and melting enthalpy of $122,04 \pm 0,45$ °C, $135,67 \pm 0,5$ °C and $186,70 \pm 1,2$ J/g, respectively, were obtained. These results do not show significant variations, indicating that the material is thermally stable under the temperature/time conditions experienced during the processing stages.

4.1.3. Mechanical properties of UHMWPE.

Table 1 presents the results of tensile tests on UHMWPE films resulting from the 1st and 2nd processing stages. It may be observed that similar values of moduli (E) and yield stresses (σ_y) were obtained in both cases, which are slightly lower than those reported by the manufacturer. However, a much higher variability of results was obtained for the strain at break (ϵ_b), which also showed to be much lower for the samples from the 1st processing stage. Such behaviour may be associated to the better homogenisation that was achieved in the material after the 2nd processing stage, where it was made to pass through one more heating and compression step. The differences between the obtained results and those reported by the manufacturer may be explained by the distinct processing technologies (injection and compression moulding) used in to produce specimens.

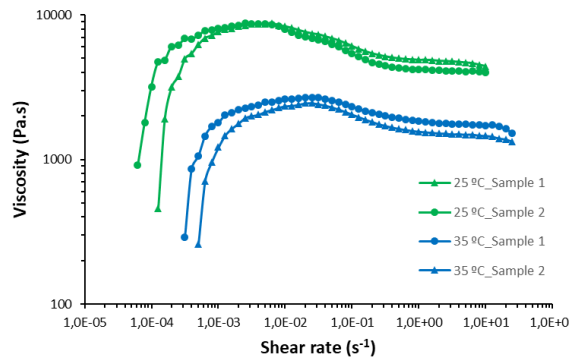
Table 1. Tensile testing of UHMWPE

Processing stage	E (MPa)		σ_y (MPa)		ϵ_b (%)	
	Average	SD	Average	SD	Average	SD
1st Stage	749.90	39.68	17.93	0.68	16.62	4.8
2nd Stage	755.04	41.02	17.73	0.55	57.04	49.57

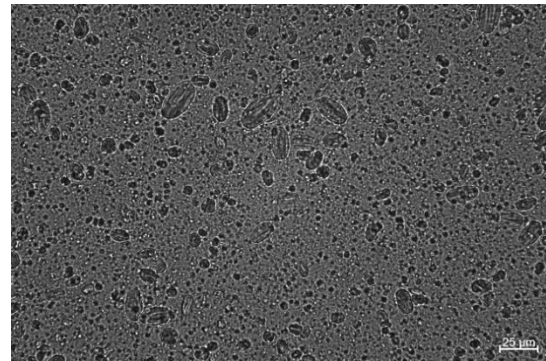
4.2. Characterisation of STF

4.2.1. Rheological behaviour of STF

The flow curves presented in Figure 4 a) confirm the non-Newtonian behaviour of the STF at the two temperatures studied. As expected, the STF samples have shown a viscosity decrease with the increase of temperature. For the temperatures studied, a slightly decrease of viscosity was observed across a wide range of shear rates after reaching the peak, but maintaining high values relative to the detected thickening within this range. This behaviour might have been generated by a broad distribution of particle sizes, as can be seen in microscope caption shown in Figure 4 b) and suggests that the material may exhibit good performance in energy absorption during impact, as demonstrated elsewhere [10]. It is noticeable that thickening behaviour occurred at low shear rates, which may also be associated with the high concentration and wide distribution of particle sizes, some of which have anisotropic shapes, facilitating frictional contact between them and providing a strong shear thickening effect [11, 12].



a) STF rheological curves



b) Optical microscope bright-field image of STF

Figure 4. Flow curves of STF.

4.3. Low-velocity impact results

Drop-weight impact tests were performed in both aramid fabrics used in this work, CT 608 and PT 900, using single and four stacked layers in its neat form and impregnated with the two different matrices studied (UHMWPE, STF) to manufacture the composite laminates above-designated as CL and STFCL. Table 2 summarises the results of total absorbed energy both in absolute and normalised terms (considering the add-on weight in percentage, see Eq. 1). As may be seen the use of UHMWPE as matrix leads to a much higher increase of composite weight (greater add-on of CL) than STF. Even though it's not easy, this phenomenon may be partially improved through the use of thinner UHMWPE films.

For CT 608, the use of UHMWPE as matrix always led to a decrease in absolute absorbed energy. It is important to note that the effect of the number of layers on the increase of the absolute energy absorption is more pronounced in NFs than CLs, which increased of 295.5% against 72%, respectively. The reduction of energy absorption in CLs compared to NFs is likely associated with the degree of impregnation, which, during impact, prevents the fibres from reaching maximum deformation, leading to a quasi-brittle failure.

The use of PT 900 as UHMWPE reinforcement results in an increase in absorbed energy compared to the neat fabrics. However, considering the same areal density, this improvement is advantageous only when 4 layers are used, where total impact energy absorption is observed.

Table 2 UHMWPE and STF add-on and impact energy absorption by NF, CL and STF CF

Material	Add-on (%)		Energy Absorption (J)			
			Absolute		Normalised	
	1 layer	4 layers	1 layer	4 layers	1 layer	4 layers
CT608 NF	-	-	31	122,6	31	122,6
CT608 STF CF	48,8	48,8	63,1	244,5 ⁽¹⁾	42,4	164,3 ⁽¹⁾
CT608 CL	342-351	225-256	17,7	30,5	4	9
PT900 NF	-	-	14,6	70,2	14,6	70,2
PT900 STF CF	48,9	48,9	29,7	245,4 ⁽¹⁾	20	164,8 ⁽¹⁾
PT900 CL	203-213	148-153	20,3	244,9 ⁽¹⁾	6,6	98,6 ⁽¹⁾

(1) Not perforated samples (absorbed energy corresponds to the maximum available one)

The better impact behaviour observed in the CLs using PT 900 instead of CT 608 fabrics, seems to be due to the lesser fibre impregnation promoted by UHMWPE, which leads to the development of energy absorption mechanisms such as fabric/matrix debonding, stretching of primary yarns and involvement of secondary yarns, and also delamination and matrix cracking when several layers are used. This happens because the PT 900 consists on the combination of plain and satin weaves, which makes it thicker and having greater thickness variation leading to a much higher difficulties in the impregnation made by compression.

However, other factors must be taken into account, such as: Considering the higher areal density of PT 900 relatively to CT608, it was expected that the former, in its neat form, would absorb more energy but, as it may be seen in Table 2, the opposite occurred. This seems to be due to its lower structural integrity, resulting from the combination of two types of weaves. This characteristic appears advantageous when the UHMWPE was used, because it's kind of weaving combined with a partial impregnation provided greater freedom of movement of yarns, allowing them to deform more before breaking, and consequently absorb more energy. Anyway, because PT 900 fabric has bigger yarns in diameter it also withstands higher efforts at break.

Composites using STF as matrix demonstrated to have better impact resistance than the neat aramid fibres themselves in all cases. This may be explained by the shear thickening effect that restricts fibre movement and promotes energy propagation among them, significantly increasing the area involved in energy absorption and dissipation. Simultaneously, as it is not a rigid matrix, it allows fibres to reach high deformations before failure, maximizing energy absorption. For both studied fabrics, even using a single layer, the normalized absorbed energy of STF CF is 37% higher than that of NF.

It should be noticed that the absolute and normalised absorbed energy determined for the 4 layered composites PT 900 CL, PT 900 STF CF, and CT 608 STF CF, which were not perforated, correspond to maxima energy available in the testing equipment setup (245,6 J) and, thus, they can't be directly compared against each other.

5. Conclusions

This study evaluates the low-velocity impact performance of composites using two different matrices: UHMWPE GUR[®] 5113 and Shear Thickening Fluid DIC701N reinforced with two types of aramid fabrics, Twaron[®] CT 608 and PT 900. CT 608 Composite laminates (CL) exhibited a drastic reduction in absolute energy absorption when compared to neat fabrics (NF). The PT 900 CLs absorbed higher

absolute energy than NFs. However, after normalising the absorbed energy for the same areal density, this improvement is only visible on the four layer reinforced composites, being more than 40,5% higher than the one determined on NFs. The better behaviour observed on PT 900 CLs, when compared to CT 608 CLs, is mainly due to the lesser impregnation of fibres by UHMWPE, which provides energy absorption mechanisms, such as fabric/matrix debonding, stretching of primary yarns, and involvement of secondary yarns. These effects, presented by the single layer fabric reinforced composites, become very pronounced on four layer ones, where delamination and matrix fracture are also visible, and a greater area of the laminate is involved in energy absorption.

The STF matrix proved to be an excellent enhancer of impact strength of fabric. For both fabrics analysed, even when only a single layer is evaluated, the normalised absorbed energy of the composites with this matrix is approximately 37% higher when compared to the neat fabrics.

Acknowledgments

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