Investigating Composite Fabric Impregnated with Non-Newtonian Fluid for Protective Clothing

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Abstract
Commercial high-performance fibre materials for body armour have very low surface friction and this has become an issue in the effectiveness of ballistic impact energy absorption. Also, the incidence of sports injuries in high contact sports is high. The severity of injuries of police and sportsman can be reduced by wearing enhanced protective clothing that have the ability to absorb the shocks. In this study, a type of non-Newtonian fluid has been developed. It becomes hardened upon a shock impact which was observed through a drop-on-weight test. The non-Newtonian fluid was successfully applied on to a traditional plain weave body armour fabric made of Twaron®. The treated fabric was studied by Scanning Electron Microscopy and a yarn pulling-out test. It shows that the force to pull out a yarn from the non-Newtonian fluid treated fabric is 4 times higher than that of the untreated one. The flexibility of the non-Newtonian polymer treated fabric remains unchanged. The polymer can be used for applications where impact protection can be a highly desirable property.

Keywords
Non-Newtonian fluid, shock absorbing, mechanical properties, protective clothing, sportswear

1. Introduction

Research work, both practical and theoretical, for the improvement of ballistic impact of body armour, as well as sportswear has been reported by many [1-6]. Various materials have been used for body armours. In modern body armour systems, fabrics still dominate, specially woven fabrics made of high performance polymer fibres with high tenacity such as Twaron®, Kevlar® and Dyneema®. Ceramic materials such as alumina and silicon carbide are traditionally used to stop high-energy threats such as rifle rounds [7]. Ceramics are placed in front of a composite rear face.

Twaron® and Kevlar® well known as a highly crystalline polymer, however their surface coefficient of friction is very low. To achieve improved ballistic performance of body armour made of Twaron® and Kevlar® fabric, it is necessary to find ways to overcome the lack of friction of the Twaron® and Kelvar®. A technique that combines yarns of high tensile strength, high modulus, and low coefficient of friction and yarns of high coefficient of friction has been used to improve the surface friction of Kevlar® fibres [8]. The disadvantage of this method is that the bulk properties of the Kevlar® fabric have been reduced, which will affect its protective performance.

In continuum mechanics, a Newtonian fluid is a fluid in which the viscous stresses arising from its flow, at every point, are linearly and proportional to the rate of change of its deformation over time [9]. In a non-Newtonian fluid, the relation between the shear stress and the shear rate

is different, and can even be time-dependent. In a non-Newtonian fluid the viscosity increases with the rate of shear strain [10]. The properties of non-Newtonian fluid are controlled by factors such as its component size, shape, and distribution.
Ballistic impact are normally tested according to tests standards. There are various ballistic impact test standards used by different countries. For example, a test standard issued by the US Department of Justice specifies the National Institute of Justice (NIJ) standard, which is also widely used across the US and Europe [9]. In this standard, body armour is classified into five types (IIA, II, IIIA, III, IV) by level of ballistic performance. For example, type III test involves firing of 7.62 mm NATO full metal jacket (FMJ) bullets (Figure 1) with a mass of 9.6 g and a velocity of 847 m/s ± 9.1 m/s.

Figure 1 7.62 mm full metal jacket (FMJ), steel jacked bullets [14]

Despite the effort made to study the ballistic performance of fabrics, limited reports can be found on the modification of fabrics using polymers such as non-Newtonian fluid with shock absorbing properties. The aim of this research is to develop a non-Newtonian fluid and study some of the mechanical properties that related to protective performance of the fabrics treated with non-Newtonian fluid to be compared with that of the untreated.

2. Manufacture of non-Newtonian polymer

Silica nanoparticles (n-SiO_2, *Sigma Aldrich* Fumed Silica powder 0.007μm) and Polyethylene glycol (PEG, *Sigma Aldrich* Poly(ethylene glycol) average mol wt 200) were used to produce a fluid with non-Newtonian characteristic. The former was used as Nano filler and the latter as carrier fluid. Ethanol was used as solvent to assist the disentanglement and dispersion of Nano powder within the polymeric matrix. Figure 2 shows the as received fumed silica Nano powder before dispersion.

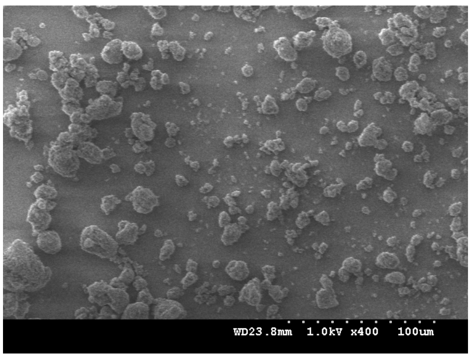


Figure 2 Fumed Silica powder (0.007μm)

100 portion and 50 portion (in volume) of diethyl ether and dichlorodimethylsilane respectively, were added into a 250 ml Erlenmeyer flask fitted with a rubber stopper. The mixture of the two chemicals was stirred with a stirring bar for 5 minutes. Then 100 portion (in volume) of water

was gradually added into the mixture to hydrolyse the silane. The speed of adding water was very slow, by dropwise, especially for the first 25 portions. During this process, hydrogen chloride (HCl) gas was produced and the heat generated by the chemical reaction will evaporate the ether away. A thermometer was used to monitor the temperature of the mixed chemicals. An ice water bath was used to cool the mixture when needed.

After completion of hydrolysing the silane, stirring of the mixture was stopped for 5 minutes. The aqueous layer was then separated and discarded using a separatory funnel. The residual acid/HCl in the ether layer was neutralised using 1 mol sodium carbonate solution; 750 portion of 1 mol sodium carbonate solution was used in total. The ether layer was washed three times. 25 portion of diethyl ether was added after first wash to compensate any solvent loss due to the heat generated by the chemical reaction. Finally, the ether layer was washed with 250 portion of water. The pH value of the discarded aqueous layer after washing the ether layer was examined using pH paper.

Followed by the above processes, anhydrous magnesium sulfate was added into the ether layer to get rid of any residual water. The mixture of ether layer and magnesium sulphate was left still for at least half an hour. Then the magnesium sulphate was separated using filter papers. The resulting solution was put into a warm water bath (50ºC) for 1.5 hrs to evaporate the ether and produce silicone oil.

The next stage was producing all-polymer non-Newtonian material polyborondimethylsiloxane (PBDMS) through cross-linking of the silicone oil. Firstly, silicone oil was poured into a thick wall 500 ml beaker and stirred using a stirring rod. Then 5%, 5% and 100% by weight of boric acid, Brij®93 (surfactant), and distilled water respectively, were added to the silicone oil. The mixture was stirred using a mechanical mixer for 10 minutes, and 20 kHz ultra-sonication technique (by BioLogics' Ultrasonic homogeniser) for 2 hrs at room temperature. The process of ultra-sonication removes potential air voids from the mixture resulting in a sticky viscous material. It was then kneaded by a spatula for 30 minutes to produce a homogeneous material. The mixture was stirred, then heated using an 180ºC oil bath for 1 hour. The mixture was further heated for 1 hour at 180ºC using an oven. After heating, the beaker was left to cool. The resulting polymer was collected by scraping using a spatula.

3. Drop on weight test to non-Newtonian polymer

The non-Newtonian characteristic of the polymer material developed in Section 2 was tested using two methods. In the first method, a stainless steel weight was placed on top of a rectangular brick made of developed material as shown in Figure 3. After 16 sec half length of the steel weight was submerged in the polymer. This shows that the polymer is very viscous at static condition. In the second test, the steel weight was dropped from a certain height (1 m) onto the polymer brick as shown in Figure 4. It can be seen that the steel weight was rebound immediately after it impacted onto the polymer brick. The arrowlines in Figure 4c-d show the movement paths of the steel weight at different stages of the impact process. There was no indentation on the surface of the polymer brick, immediately after the impact presented in Figure 5, showing a closer view of the polymer brick after being impacted by the steel weight. This shows that the impact strength of the polymer increased dramatically under the condition of shock impacting, the surface of polymer brick is hardly changed. We name the developed polymer material a 'non-Newtonian polymer'.

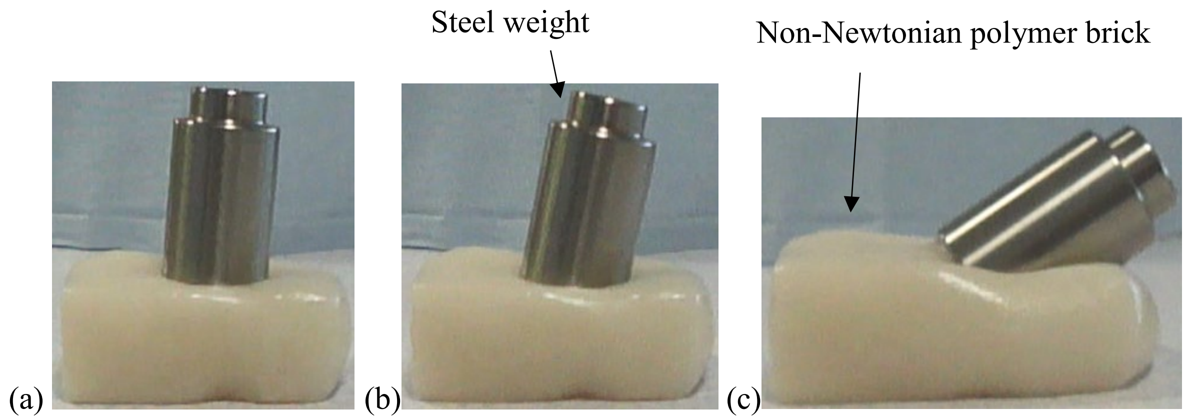


Figure 3 Indentation of non-Newtonian polymer by a steel weight at (a) starting point, (b) 4s and (c) 16s

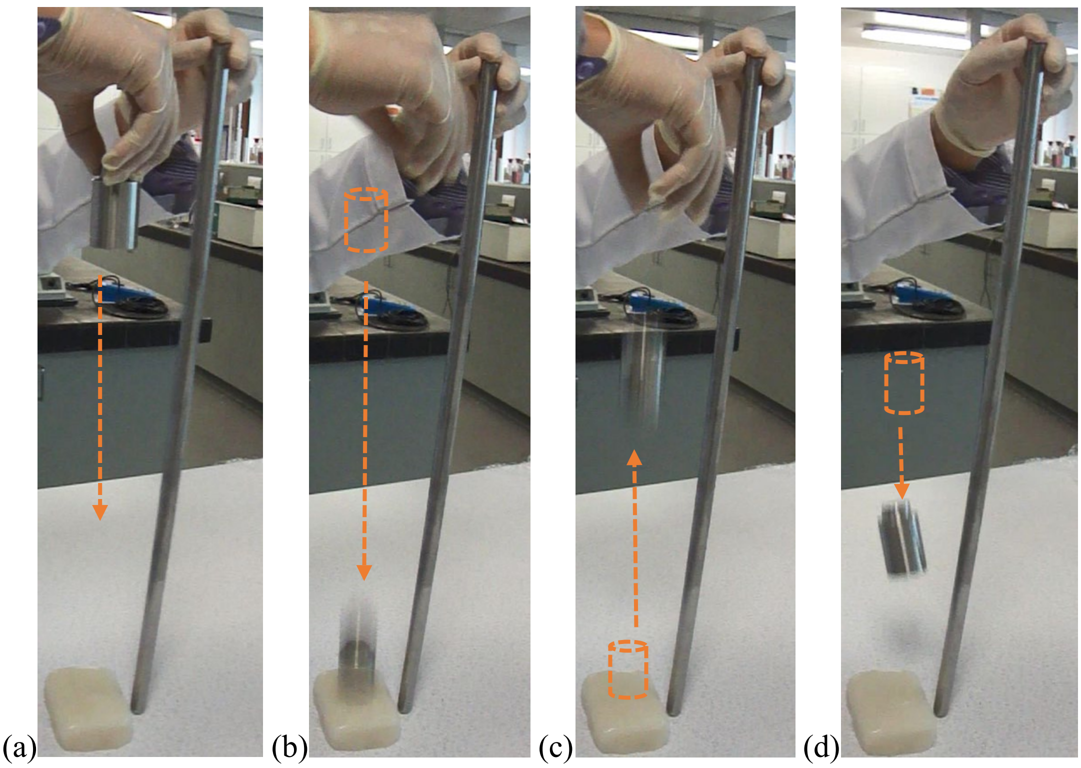


Figure 4 Drop on weight test of non-Newtonian polymer: (a) at 0s, (b) at 0.228s. (c) at 0.294s, and (d) at 0.399s

Figure 5 Drop on weight test of non-Newtonian polymer after impact – a closer view

4. Manufacture of fabric composite impregnated with non-Newtonian polymer

The silica based non-Newtonian polymer impregnated fabric composite (NNP-fabric) was produced using the non-Newtonian polymer created in section 2 and scoured Twaron® plain woven fabric supplied by Fothergill UK. The detailed parameters of the fabric are listed in Table 1. The non-Newtonian polymer was diluted using ethanol at 3:1 volume ratio of ethanol: non-Newtonian polymer. The diluted non-Newtonian polymer was poured into a plastic container, and the Twaron® fabrics in layers were soaked in the polymer fluid for 3 minutes as shown in Figure 6. Two steel rods were used to squeeze the excess polymer fluid. The fabrics were allowed to dry in the air for 48 hours at room temperature and humidity (23ºC, 46%) before further use. The weight increment of the composite fabric after drying was approximately 20%.

Table 1 Properties of Twaron® fabric

Fibre type	Weave structure	Yarn count, dtex		Yarn strength, N/cm		Yarn density, end (pick)/cm		Thickness, mm	Fabric weight, g/m^2
		warp	weft	warp	weft	warp	weft		
Twaron®	1/1	930		1000		8.5		0.28	165

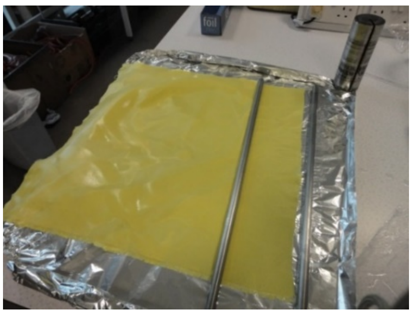
(a)  (b)  (c) 

Figure 6 (a) and (b) manufacture of composite fabric treated by silica based non-Newtonian polymer, and (c) drying of the composite fabric

The morphology of the composite fabric was studied using Scanning Electron Microscope (SEM). As shown in Figure 7, the surface of the Twaron® fabric, yarns and fibres were covered with the non-Newtonian polymer: (a) treated fabric with visible plain weave structure, (b) part of a yarn in the fabric, (c) some filaments in a yarn and (d) a single filament in a yarn.

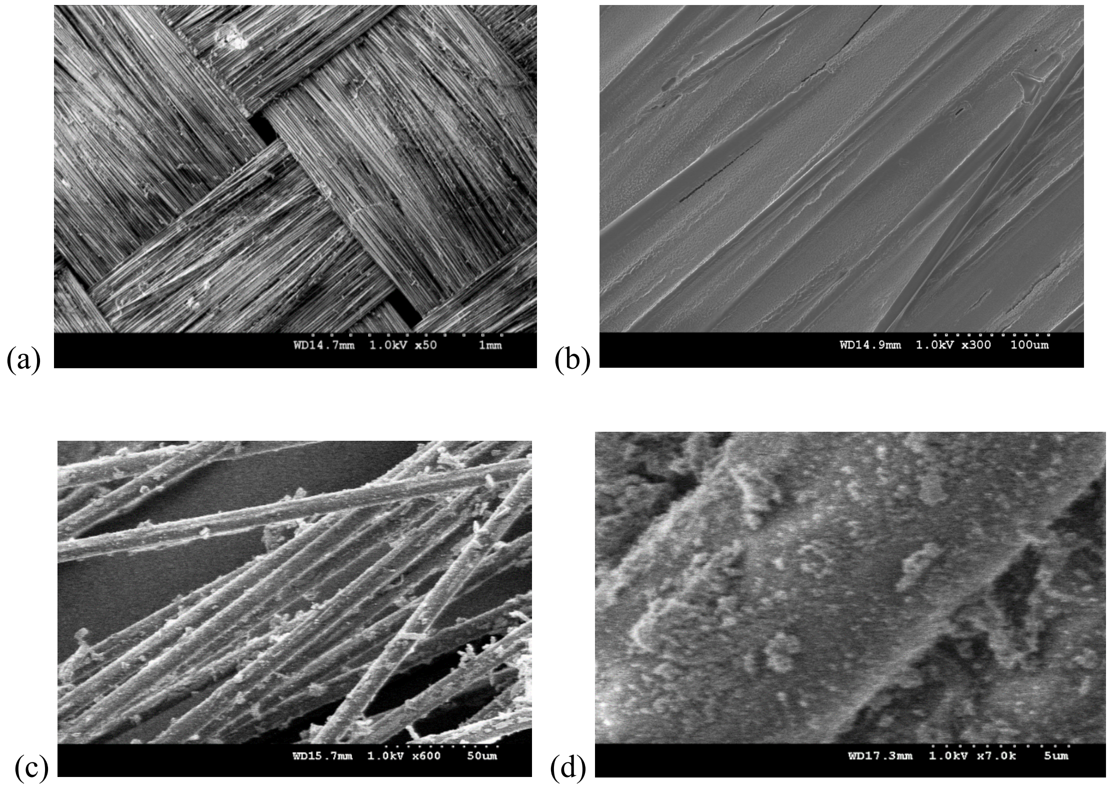
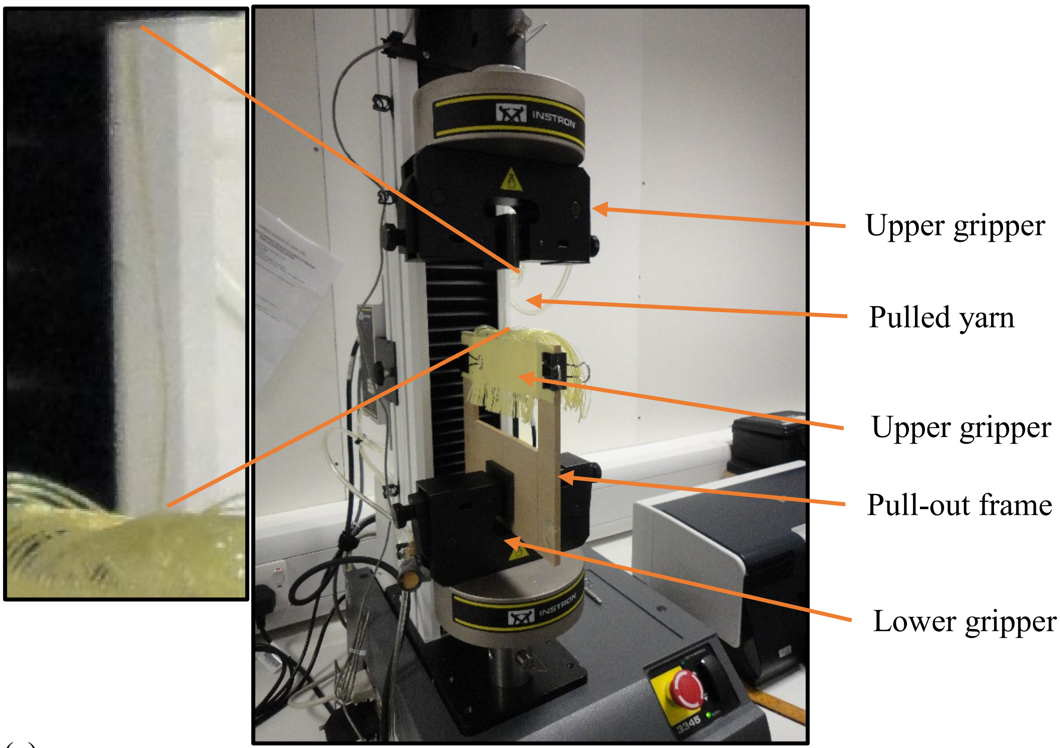


Figure 7 The morphology of silica based composite fabric impregnated with non-Newtonian polymer under different magnifications

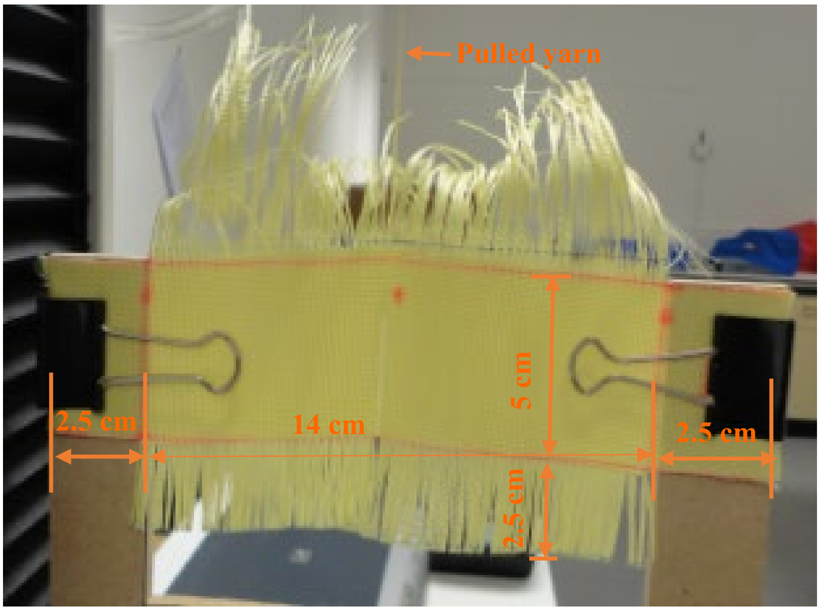
5. Yarn pulling out test

The Instron tensile tester Model 3345 was employed for this experiment. The composite fabric (NNP-fabric) produced in section 4 and the original scoured Twaron® fabric were tested. In order to study the effect of environmental factors such as moisture on the performance of the treated and untreated fabrics, a water bath was used to soak the treated and untreated fabrics for 24 hours. Thus there were a total of four types of fabric samples in this yarn pulling-out test: (1) dry fabric, (2) dry fabric treated with silica based non-Newtonian polymer, (3) soaked fabric and (4) soaked non-Newtonian polymer treated fabric.

Figure 8 shows the test setup of the yarn pulling-out test, where 5 kN load cell and vertical loading frame were used. Figure 8 (b) shows the dimension of the fabric sample that was fixed on a wood frame before placing on the Instron for pulling out for the extended yarns (pulled yarns indicated in Figure (b)). The yarn pulling-out speed was set as 10 mm/min. Data including yarn displacement and pulling-out force during the yarn pulling period were recorded.



(a)



(b)

Figure 8 Experimental test setup of yarn pull-out test: (a) overview and (b) fabric sample

Figure 9 shows typical load-displacement curve during yarn pulling-out experiment. The load indicates the resistance to the yarn pulled from fabric samples. Three distinct regions can be observed. In region I, no movement of the pulled yarn against orthogonal interlaced yarns is observed, i.e. only static force is involved in resisting the yarn being pulled. A peak force can be observed at the end of region I after which in region II movement of the pulled yarn is observed. At this stage, dynamic/kinetic friction replaced the static friction force in holding back the pulled yarn. A plateau region of vibration of the pulling force is observed until the free edge of the pulled yarn starts to get in touch with its interlaced yarns. From this point, the number of yarns interlaced with the pulled yarn start to decrease. At the end of region III, it shows that the pulled yarn is entirely pulled out of the fabric. Similar findings were observed by Nilakantan and Gillespie [13].

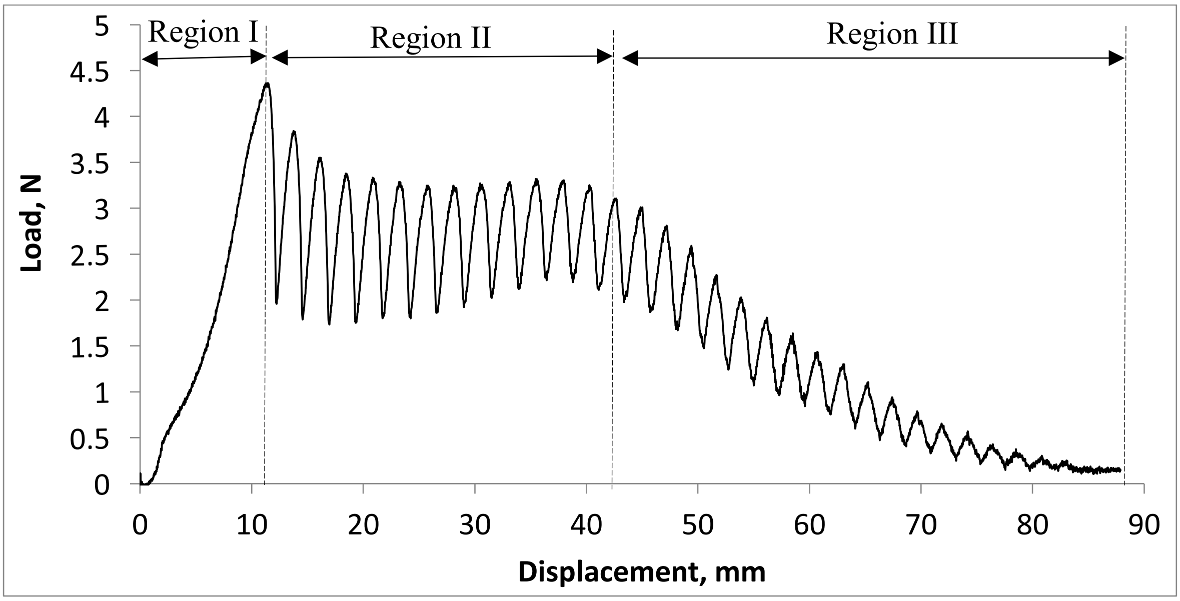


Figure 9 Typical load-displacement curve during yarn pull-out testing

Figure 10 provides a comparison of the load–extension curves for pulling yarns out from fabrics untreated and treated with the developed silica based non-Newtonian polymer. It can be seen that the initial slope of the curve for the treated fabric is steeper than that of the untreated. This indicates that the initial load needed for pulling a yarn from the fabric is higher for the non-Newtonian polymer treated fabric than the untreated fabric. It can be seen that the yarn pulling out force for the treated fabric is much higher than that in the untreated fabric. The peak load in treated fabric was 4 times higher than that in the untreated fabric. This is believed to be caused by the additional non-Newtonian polymer layer on the treated fabric surface, which restricted the movement of the fibres and yarns. A much higher load is required to overcome the resistance from the adjacent fibres and yarns and the covered polymer layer to pull out a yarn from the treated fabric than the untreated. It also can be seen that the forces to pull out a yarn from the treated fabric are higher than the untreated one during the whole yarn pulling-out process. Moreover, the increased friction among fibres and yarns produces a greater cohesive force between the yarns and fibres; a larger amount of energy will be required during fabric tensile stressing, as a result, the tensile strength of the treated yarns and fabrics may be increased.

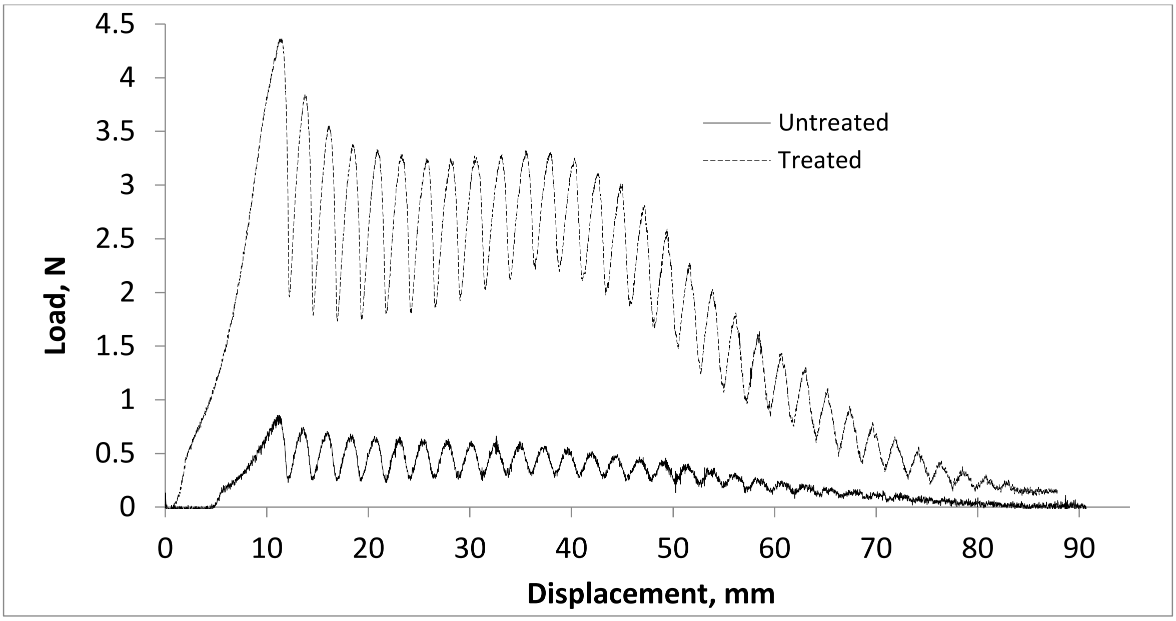


Figure 10 Displacement-load curves of untreated fabric and fabric treated with silica based non-Newtonian polymer

It has also been observed that the superiority of treated fabric over untreated fabric in yarn pulling-out test is not affect by 24 hrs water bath treatment, as shown in Figure 11.

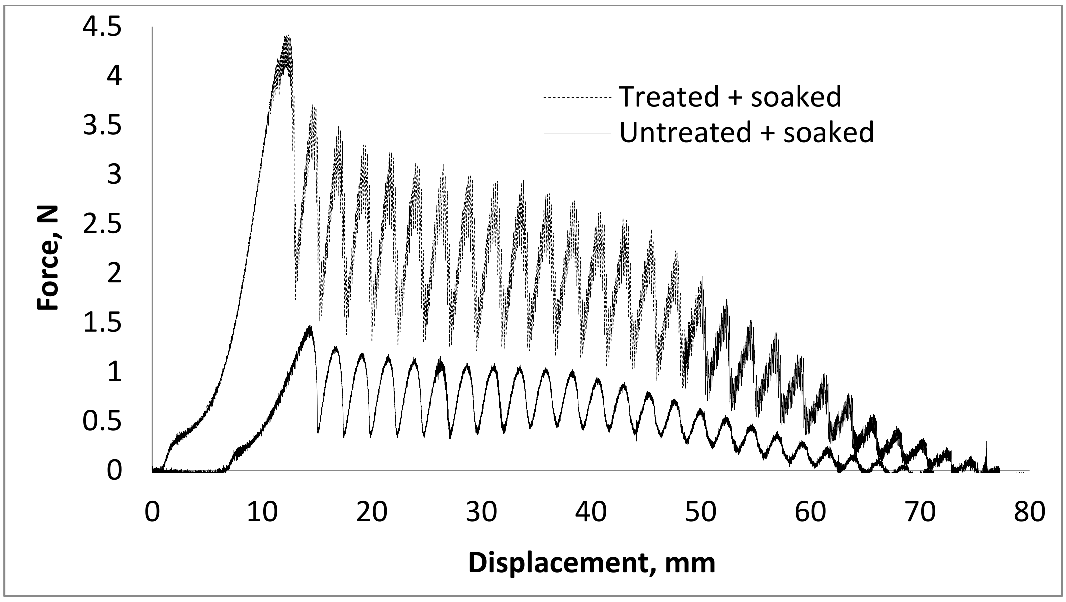


Figure 11 Displacement-load curves of fabric and fabric treated with silica based non-Newtonian polymer after 24 hours water bath treatment

Zhang and Sun [14] have studied the yarn pulling-out behaviour from woven fabrics and found that the yarn pulling-out force has a positive correlation to the impact performance: fabric with higher pulling-out force performed better in ballistic impact tests. Due to the experimental limitations, confirmatory ballistic test has not been conducted. However, according to Zhang and Sun's findings, it can be concluded that the ballistic impact performance of Twaron® fabric would be improved by post-treatment using non-Newtonian polymer, even considering the 20%

weight added to the treated fabric. Further experimentation should comparatively assess the protective performance of treated fabric matches that of non-treated fabric for the same mass, and whether treated fabric yields equivalent or improved protective performance for reduced mass.

6. Bending property related to fabric flexibility

Apart from yarn pulling-out resistance which is an important property to be assessed, the flexibility of the non-Newtonian polymer treated fabric, as body armour material, is also important to be considered. Bending Rigidity of a fabric can be used to reflect the flexibility of a fabric, and Bending Hysteresis can be used to indicate the recovery ability of the fabric after being bent.

Kawabata Evaluation System bending tester (KES-FB2) was used in this experiment. Square fabric samples each with 20 x 20 cm were prepared for this test. The test allows to evaluate non-linear elastic, friction and viscous behaviour of a fabric. It can record directly the evolution of bending moment (M) against curvature (K= -2.5 ~ +2.5 cm^{-1}) during a bending cycle. The effective dimension of the tested fabric sample is 20 cm long and 1cm wide (along bending direction). The samples were clamped between a fixed and a moving clamps vertically to prevent the effect of gravitational force, the moving clamp rotates around the fixed one during the testing period shown in Figure 12. The characteristic values obtained by the measurement are bending rigidity per unit length B and bending moment of hysteresis per unit length 2HB.

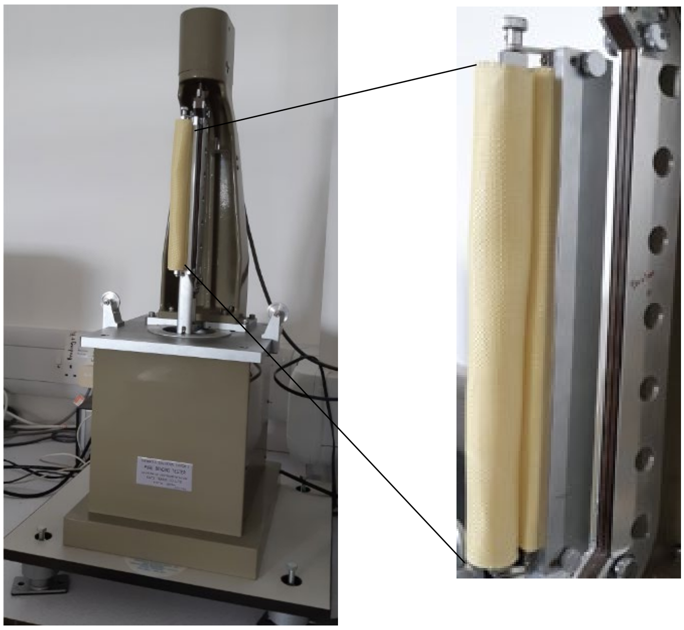


Figure 12 working principle and the experimental set of bending test

Figure 13 shows the bending moment against curvature curves of both fabrics untreated and treated by the developed non-Newtonian polymer. Bending stiffness B is the mean of the two slopes where one is the gradient of the approximate straight line of the curve when tested fabric sample is bent on its forward travelling and the other is the gradient of the other approximate straight line when the fabric is bent on its returning to its original position. It can be calculated by Equation (1). Higher B indicates greater resistance to bending motion. Bending Hysteresis 2HB is measured by taking the hysteresis width of the curve. Bending hysteresis indicates the ability of a fabric to recover the original state after being bent; the smaller the value of bending hysteresis the better the bending recovery ability of the fabric. It is expressed in equation (2).

$$B = \frac{B_f+B_b}{2} = \frac{\tan\alpha_f+\tan\alpha_b}{2} = \frac{1}{2}\left(\frac{A_f-B_f}{1.5-0.5} + \frac{A_b-B_b}{1.5-0.5}\right) = \frac{A_f-B_f+A_b-B_f}{2} \qquad (1)$$

$$2HB = \frac{HB_f+HB_b}{2} \qquad (2)$$

where B_f and B_b are the forward and backward bending stiffness of the test specimen respectively. Af, Bf, Ab, Bb are the forward and backward bending moment values at curvatures of 0.5 and 1.5 respectively.

Fabric bending property depends on the bending resistance properties of fibres, yarns, fabric structure and post-finishing process of a fabric and it increases with the increase of fabric weight and thickness. The frictions between fibres and yarns also affect the bending property. The increased weight and thickness of Twaron® fabric impregnated with non-Newtonian polymer causes increased bending rigidity on one hand, the increased interactions of fibres and yarns by the non-Newtonian polymer in the treated fabric increased the resilience of fibres and yarns during bending process, resulting in the decreased bending rigidity and bending hysteresis on the other hand. The change of bending rigidity and bending hysteresis is very marginal for the fabrics between Twaron® fabrics untreated and treated by non-Newtonian polymer.

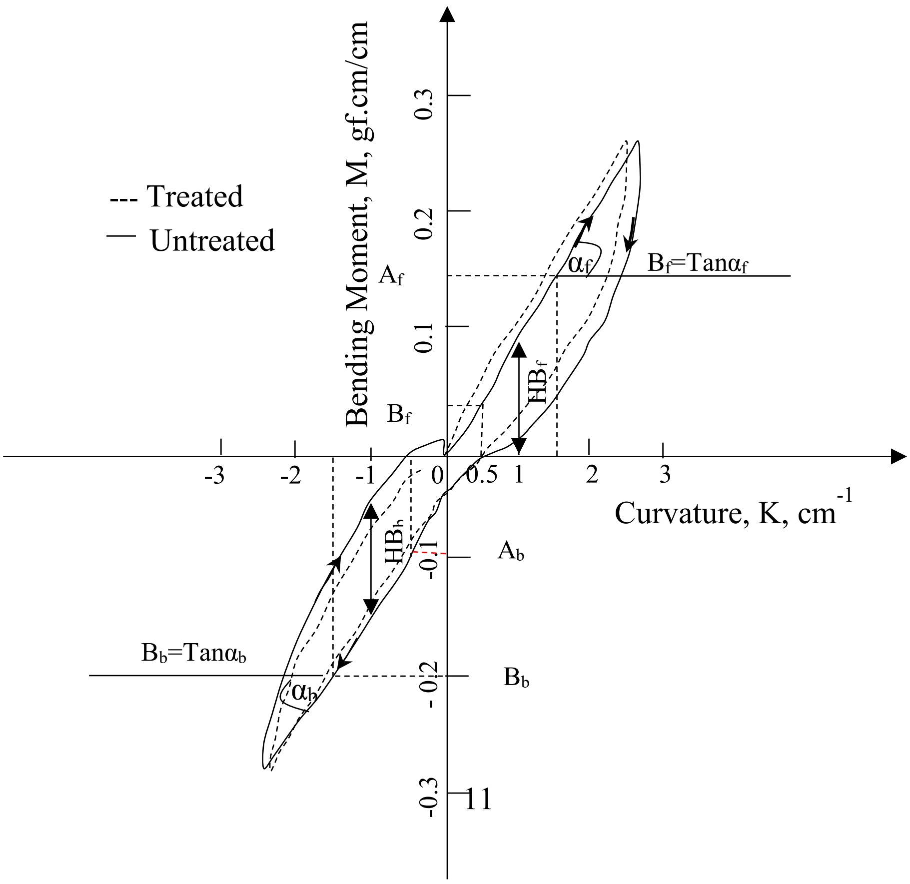


Figure 13 Bending test showing the difference between the treated and untreated fabrics

7. Conclusions

A non-Newtonian polymer has been developed to be used to improve the protective performance of traditional plain woven Twaron® fabric as a body armour material. The non-Newtonian polymer shows good shock impact absorbing performance revealed by a drop on weight test. Coating of silica based non-Newtonian polymer on Twaron® fabric has been achieved and a novel fabric composite was developed.

The inter-yarn friction force in Twaron® fabric treated with the non-Newtonian polymer is improved compared to that of the untreated fabric. It can be inferred that the yarn gripping effect of the treated fabric is higher too. The flexibility of Twaron® fabric treated with non-Newtonian polymer has not been changed. The use of the treated new composite fabric would bring great benefit not only to protective performance to weight ratio of conventional body armours made of high-performance fibres, but also potentially to mitigate behind armour blunt trauma during ballistic impacts due to the enhanced yarn-yarn stability in the treated composite fabric reflected by the yarn pulling-out test.

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References
[1] Jenningsa RM., Malbonb C, Brocka F, Harrissonc S, Carrb DJ. A preliminary study into injuries due to non-perforating ballistic impacts into soft body armour over the spine, Inj. 2018; 49:1251–1257.
[2] Edwardsa TD, Baina ED, Colea ST, Freeneyb RM, Hallsc VA, Ivancika J, Lenharta JL, Napadenskya E, Yua JH, Zhengc JQ, Mrozeka RA. Mechanical properties of silicone based composites as a temperature insensitive ballistic backing material for quantifying back face deformation, Forensic Sci. Int., 2018; 285:1-12.
[3] Sun D, Chen X and Wells G. Engineering and analysis of gripping fabrics for improved ballistic performance, J. Comp. Mater. 2014; 48(11): 1355-1364
[4] Sun D, Chen X, Lewis E and Wells G. Finite element simulation of projectile perforation through a ballistic fabric, Text. Res. J., 2013; 83 (14):68-78.
[5] Ge Z, Hu, H, Innovative three-dimensional fabric structure with negative poisson's ratio for composite reinforcement, Text. Res. J., 2013, 83 (5), 543-550.
[6] Wang C, Roy A, Chen Z, Silberschmidt V, Braided textile composites for sports protection: energy absorption and delamination in impact modelling, Mater Des., 2017, 136, 258-269.
[7] Medvedovski E. Ballistic performance of armour ceramics: Influence of design and structure, Ceram. Int. 2010, 36: 2103–2115.
[8] Hogenboom EHM and Bruinink P. Combinations of polymer filaments or yarns having a low coefficient of friction and filaments or yarns having a high coefficient of Friction, and use thereof. 1991; Patent 5035111, USA.
[9] Batchelor GK. An Introduction to Fluid Dynamics. Cambridge Mathematical Library series, Cambridge University Press. 2000.

[10] Mahfuz H, Clements F, Rangari V, Dhanak V, and Beamson G. Enhanced stab resistance of armor composites with functionalized silica nanoparticles, J. Appl. Phys. 2009, 105 (6): 064307-064314.
[11] U.S. Department of Justice. Ballistic Resistance of Body Armor NIJ Standard-0101.06, Washington. 2003.
[12] Midsouth Shooters. https://www.midsouthshooterssupply.com/item/00129xm80c/7point62x51mm-nato-mil-spec-149-grain-fmj-20-rounds, 2018.
[13] Nilakantan G, Gillespie JW. Yarn pull-out behaviour of plain woven Twaron fabrics: effect of yarn sizing, pull-out rate, and fabric pre-tension, Compos. Struct. 2013; 101: 215-224.
[14] Zhang D and Sun CT. Testing and modelling of yarn pull-out in plain woven Twaron fabrics. Compos. Part A **2009**, 40: 1863–1869.