Original Article

Influence of silane coupling agent on shear thickening fluids (STF) for personal protection

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The present work studied the influence of silane coupling agent in non-Newtonian fluid, in the impact resistance, adhesion and flexibility results. The results of stab performance for Kevlar samples impregnated with silane agent showed results significantly higher than others samples non impregnated, such results are closely associated with the formation of siloxane bonds due to the coupling agent. The impact resistance properties of all samples were tested using drop tower testing, and the flexibility was tested beyond bending angle test. SEM and FTIR analyses were used to verify the chemicals compositions and to evaluate qualitatively the presence of nanoparticles samples. Abrasion test was realized to verify the influence of silane agent of the resistance adhesive of non-Newtonian fluid under samples. The Kevlar samples impregnated with STF and coupling silane presented best flexibility (angle of bending = 30.33°), a significant increase on the dissipation kinetic (penetration depth) in comparing to the others and resistance adhesive of non-Newtonian fluid under samples. Therefore, practically this property remained unalterable in relation to Kevlar samples with STF and Kevlar control.

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1. Introduction

A fluid is considered non-Newtonian when its viscosity is not constant at a given temperature and pressure [1–3]. Instead, the value depends on flow conditions such as the geometry, rate and shear time, and the kinematic history of the sample. The behavior of non-Newtonian fluid can be classified into three categories: viscoelastic fluids, time dependent and time independent. Non-Newtonian fluids non-time dependent are the field of this work. Those can be classified in Shear-thinning or pseudoplastics, viscoplastics, and shear-thickening (STF) [4]. STF’s are also known as dilatant materials and their apparent viscosity increases proportionally to the shear rate. This behavior can be explained as follows: when the fluid is at rest, the liquid present in it, is sufficient only to fill the voids. As the shear rate increases, the dense form of the solids breaks

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down and the material expands slightly causing an increase in the void. Therefore, the available liquid is no longer sufficient to lubricate the solid particles movement and the resulting solid-solid friction causes the stresses to increase rapidly, also increasing the apparent viscosity [5]. The properties of SFT's has been taken in several studies on their use as reinforcement of textile fibers applied to ballistic protection [6]. Wilson and Jacob also used silica nanoparticles and verified the formation of siloxane bonds during functionalization process, in addition to a significant improvement in the shear rigidity, penetration resistance and a slight increase in tensile strength. In spite of this advance, fiber/STF adhesion, as in the case of Kevlar®, was shown to be weak, requiring the use of a coupling agent that allows a better adhesion between organic and inorganic compounds. The silane compound is a type of coupling agent that can act on this adhesion because it increases the friction between the particles [7]. This work aims to study the influence of silane agent on shear thickening fluid (STF) under mechanical properties of the composite for ballistic protection.

2. Materials and methods

For all experiments was used Kevlar 29 high-performance woven fabrics, compound of Aramid (poly p-phenylene terephthalamide), taffeta 1 × 1 plain weave structure, 7 weft/cm and 7 warp/cm density, 375.0 ± 16 Tex count in both direction yarns, and 497 ± 25 g/m² weight, as shown in Fig. 1.

The methodology applied was that as described in literature, with some adaptations. Shear Thickening Fluid (STF) was prepared using 88% of ethanol, 6% of polyethylene glycol 300 (by ISOVAR) and 6% of silica in size of 7 nm (AEROSIL 300 by EVONICK), underweight in constant stirring on a magnetic stirrer during 40 min. Initially, the solution was prepared using alcohol 99% purity (by ATRIOM), nanosilica and coupling agent (3-Metacriloxipropiltrimetoxisilano by PROSIL) in 1.29% concentration by weight in a Becker under constant stirring on a magnetic stirrer during 20 min. Followed by addition of polyethylene glycol and stirring for further 30 min. Finally, the impregnation process was made in a foulard using 0.5 bar at room temperature. Thereafter, the impregnated samples were dried using an oven under 78 °C during 1 h.

Fig. 1 – (a) Kevlar woven samples used in the study and (b) shows the optic microscopy Kevlar® 29 woven structure.

2.1. Bending test

This test consists to deform the material at a midpoint (13 mm), causing a curvature or bending form on the surface without fracture occurrence. This test is usually employed to determine the flexibility of materials as shown in Fig. 2. At first, the sample tested (51 mm) was loaded with a mass of 20 g, in which it gave rise to an angle of curvature that in turn is mentioned in the literature as a measure of sample flexibility [8], higher the angle, it indicates more flexibility.

2.2. Drop tower test

It was carried out in objective to measure the stab resistance of the composite. Penetration tests were carried out using a 51” knife blade, based on NIJ-0115.00 [9], specifying the minimum performance requirements for a material resistant to attack by pointed and edged weapons [10]. The samples had been placed in multilayer foam as described in Fig. 3a. To perform the knife test, the knife blade S1” was assembled on a support, and then, loaded with a mass of 3.34 kg corresponding to 13 Joule Fig. 3b. The depth penetration in the sample was calculated leading to consider the length knife cut in the witness papers in each layer penetrated by the knife blade S1”.
2.3. Adhesion test (Martindale)

For adhesion test, were used a process similar to “Martindale” method ISO 12947. The tests were carried out, applying 2000 cycles of Lissajour movements, with 0,5 Kpa pressure on the samples (Kevlar control, Kevlar with STF and Kevlar with STF and coupling agent) [11]. However, the tests were stopped every 1000 cycles, in order to measure the adhesion. The adhesion of samples was calculated using a solution of methylene blue dye (1 g/L) and a micropipette (10 μl). Every stop, the samples were subjected to the apparatus shown in Fig. 4a, that consists in to qualify, by horizontal wettability (Fig. 4b) according to the adhesion of the STF under the fabric surface samples, after friction cycles. Therefore, it will have greater adhesion the sample that presents wettability with the presence of STF and coupling agent, as seen in Fig. 4c.

Fig. 3 – (a) Multilayer foam representation and (b) drop tower test.

Fig. 4 – Adhesion test illustration. (a) Apparatus (b) horizontal wettability (c) wettability image.

Fig. 5 – Increase mass of the samples after impregnation.
Fig. 6 – SEM analyses for the samples studied. (a) Kevlar control; (b) Kevlar with STF; and (c) Kevlar with STF and coupling agent.

Fig. 7 – FTIR results for unmodified STF (Kevlar control).
greater stability throughout the cycles (the wettability of each sample was calculated using a photography and the software Image J as shown on Fig. 4c).

3. Results and discussions

Results obtained for samples with STF and coupling agent shows higher increase of mass on surface in comparison to others, as shown on Fig. 5. This evidenced that the use of silane agent favours the greater quantitative efficiency of non-Newtonian fluid in the samples.

The samples were analysed by SEM as shown on Fig. 6. The results show higher concentration of silica on surface on the samples with STF and coupling agent when in comparison to others.

Fig. 7 shows obtained FTIR curves for pure Kevlar control sample without any treatment, while the curves shown in Figs. 8 and 9 show high energy transmittance peaks, especially for the sample modified with non-Newtonian fluid STF and coupling agent silane (Fig. 9) respectively. The increase of siloxane bands and the presence of new functional groups were perceptible for both samples studied.

As shown in Fig. 9, the peaks shown at 1720 and 1637 cm\(^{-1}\) are attributed to carbon stretch vibrations C=O and vinyl stretch vibrations C=C, respectively, indicating high frequency bonds belonging to the silane bond groups [12–14]. The peaks shown at 2957 cm\(^{-1}\) and 2894 cm\(^{-1}\) correspond to bands of stretching vibrations of alkyl groups (CH\(_2\) and CH\(_3\)) which can be attributed to polyethylene glycol and silane agent. These peaks occur due to the functionalization of the silica particles and indicate the formation of new bonds [15,16].

The peak between 1073 cm\(^{-1}\) at 1380 cm\(^{-1}\) represents siloxane (Si–O–Si and Si–OC vibrations) which occurring naturally on silica. The samples modified with silane agent showed waves number on a larger scale and with greater intensity, indicating stronger links [17,18]. Thus, Kevlar samples with STF and silane agent, exhibited high siloxane binding peak, as shown in Fig. 9, promoting a significant increase in siloxane bonds and higher concentrations when in presence of higher amount of nanoparticles in the sample as shown in Fig. 6c, in addition, adhesion (Fig. 10) and best flexibility (Fig. 11) results, as well as depth of penetration results as shown in Fig. 12.

The wettability analysis shows that the more STF fluid on the surface sample is the more wettable. This analysis was carried out according to the different cycles in the martindale (1000 and 2000 cycles), in order to observe if Kevlar control, Kevlar with STF and Kevlar with STF + coupling silane presented a difference in FTS adhesion on the surface fabric. Curves shown on Fig. 10 show that the samples with STF and coupling agent showed higher adhesion of the STF on fiber surface when in comparison to others. The increase in the number of strong siloxane chemical bonds due to addition of the silane agent promoted a significant increase in adhesion,
this is directly associated to the durability and efficiency of surface modification.

Results for bending and drop tower tests were taken and shown in Figs. 11 and 12, respectively. The Fig. 12, shows clearly the samples of Kevlar with STF presented low flexibility (angle of bending = 20°) in comparing to the others (Kevlar control and Kevlar with STF and coupling silane), it shows clearly that the coupling agent stabilized the flexibility samples. The Fig. 12 shows the penetration depth test results for all samples studied the flexibility of the sampled samples was modified Kevlar control, Kevlar with STF and Kevlar with STF + coupling silane. Thus, the bending angle of the Kevlar with STF + coupling silane samples was higher when compared to the Kevlar with STF sample. Showing that the Kevlar sample with STF + coupling silane Kevlar control were more flexible than Kevlar with STF.

According to the results taken, we could conclude that the Kevlar with STF and coupling silane showed significantly less penetration depth (mm) than those Kevlar control (49%) and Kevlar with STF (32%) samples. This can be explained because the sample that presents the use of silane agent, has a greater distribution of impact kinetic energy, dissipating it layer by layer in a gradual behavior. This also shows that upon receiving the impact the sample dissipates the energy over the layers, propagating the smallest portion of the impact to the ballistic panel user, as shown in Fig. 12. The depth of penetra-

Fig. 10 – Adhesion test (Martindale) for all samples studied.

Fig. 11 – Bending for all samples studied.
tion of drop tower test as a function of layers of witness paper. It was obtained that all the samples impregnated with STF (Kevlar control, Kevlar with STF and Kevlar with STF + coupling silane) were compared with the standard sample. In this way, they exhibited significant penetration depth performance and in the behavior of absorption and dissipation (layer to layer of witness paper) of impact energy.

4. Conclusions

In this study, STF was prepared using submicron SiO₂ particles spherical of silica dispersed into Polyethylene Glycol (PEG) and prepared with the addition silane agent. The silane coupling agent addition provided strength increase in the shear thickening response. It reveals improvement in the impact energy absorption, significant increase in adhesion, promotes an increase in the number of chemical bonds, as well as, higher peaks, indicating stronger bonds of siloxane, thereby reducing penetration depth, increasing the flexibility in relation to the other samples (Kevlar control and Kevlar with STF). This demonstrates that the use of Silane Coupling agent promotes greater improvement of performance of ballistic penetration resistance of personal protective composites panels.

Conflicts of interest

The authors declare no conflicts of interest.

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REFERENCES


