



24th ABCM International Congress of Mechanical Engineering
December 3-8, 2017, Curitiba, PR, Brazil

COBEM-2017-1124

NANOTECHNOLOGY FOR PERSONAL PROTECTION SYSTEMS: THE NEW NANO-MODIFIED BULLET PROOF VEST DEVELOPMENT

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Abstract. *This paper deals with development of a new class of bullet proof vests where aramid fibers are impregnated with shear thickening fluids (STF) based on a combination of ethylene glycol two nanoparticles, i.e. nanosilica and calcium carbonate. This approach allow us to develop a mathematical model based on behind armor blunt trauma (BABT) condition. The ballistic tests were performed following NIJ 0101.06 standard using 9 mm Full Metal Jacket (FMJ) and 357 Magnum Jacketed Soft Point (JSP), with average mass of 8.0 g and 10.2 g, respectively. The average energy measured for each ammunition type used (9 mm and 357) was around 520 J and 980 J, respectively. The projectile penetration depth or the 19 layers/SFT system was 0.13 mm/g and 0.17 mm/g (9 mm and the magnum 357 ammunitions), while for the 32 layers aramid system without treatment was 0.13 mm/g and 0.16 mm/g, respectively. Therefore, the new bullet proof material with 19 layers impregnated with SFT proved to have the same ballistic protection of a 32 layers of aramid textiles with any treatment.*

Keywords: *nanotechnology, bullet proof vest, shear thickening fluid, ballistic tests, blunt trauma behind armor*

1. INTRODUCTION

Now-a-days in Brazil, security forces are regularly exposed to events where fire arms and outlaws are involved. Moreover, traditional bullet proof vest, commonly used by these security forces, have a life spam of five years and its replacement cost is high. Therefore, there is an urgent need to develop a new class of bullet proof vest. To achieve such goal some initial steps must be followed. The NIJ-0101.04 standard (NIJ, 2010) defines the maximum penetration value, which is around 44 mm for a class II-A, for a bullet vest certification. However, as described by Courtney and Courtney (2009), the projectile impact generates a localized and intense wave propagation which can cause serious damages to internal organs. Moreover, as commented by Wen et al. (2015)], vital organs such as liver or heart can be dilacerated by these pulse pressure waves. However, the traditional design is still based on the NIJ's penetration limit and the concept of the largest majority of fiber layers still undamaged. Most of the work done up to this date was focused on improving ballistic performance using shear thickening fluids (STF) by different impregnation techniques (Lee et al, 2003;Feng et al. 2014; Haris et al 2015, Laha & Majundar, 2016) . The problem of pressure wave propagation is neglected based on assumption of no perforation, but the recent growth of injuries due to non-perforation events is making this problem a critical issue.

Lee et a. (2003) dispersed nanosilica into polyethylene glycol (PEG) and the solution was introduced to aramid fibers. They called this mixture shear thickening fluid. It is a non-Newtonian fluid in which when under applied force acts as a solid. Their results were encouraging, and since then – 2003, different researchers followed the same idea.

Feng et al (2014), for example, employed the same idea of STF for impregnation of plain weave Kevlar fibers. They investigated the response of Kevlar + STF systems to quasi-static stab tests. The difference between Lee's and Feng's work is the silica scale-size. Lee's work employed nanosilica while Feng's research group employed submicron size and fumed silica. Feng's conclusions about the submicron silica were expected as it is a well-known fact that submicron particles are able to be embed in the filaments, thus enhancing mechanical coupling between fibers and particles, as compared with the Kevlar fabrics, due to their rigidity. Their conclusions regarding the fumed silica, however, was interesting. According to Feng et al (2014), the aggregates of fumed silica are more likely to accommodate loads through direct mechanical deformation under stress, resulting in reduced effect on fabric mobility. Fumed silica was also employed by Haris et al (2015). They dispersed fumed silica into polyethylene glycol using a combination of mechanical mixing and sonication. This procedure was more effective into the silica dispersion into PEG. The aramid fabrics were immersed into the STF diluted solution (the solution was diluted using ethanol) and the fibers were constantly rubbed to promote impregnation. The ethanol was later on removed by letting the fabrics inside an oven at 60C for 30 minutes. Their results revealed a decrease on normalized average peak pressure amplification by 39.4%, which is a good result. However, the amount of fumed silica incorporated into the fabrics was still low (they tested 20% w/w and 27.5% w/w), which lead to some specimen failure (perforation). To try to solve this problem, a different approach was investigated by Laha and Majumdar (2016). They employed layers of aramid fabrics with different weave patterns, i.e. plain weave, 3/1 twill, 2/2 twill, 5 end satin and 2/2 matt, all of them impregnated with 60% w/w STF. The silica size was on nanometer scale (100nm) and the impregnation process employed a Mathis lab Padder, with padding roller laid at horizontal direction. This procedure allowed them to a uniform impregnation even inside tows. They observed that in STF treated fabrics, regardless the weave pattern, the energy was absorbed not only by the primary yarns but also by the secondary yarns. The STF present between the yarns was able to engage the secondary yarns in energy absorption during impact. The same strategy was proposed by Majumdar et al (2014). They, however, were able to reach nanosilica concentrations up to 70% w/w. The Mathis lab Padder was again employed to force the nanosilica into the yarns. Srivastava et al (2011) when further, as they investigated the influence of padding pressure on STF impregnation process. By evaluating the yarn pull-out force, they try to predict the Kevlar + STF system response to impact. Unfortunately, they were not able to get good correlations even for low velocity impact. The problem is even more complex when high velocity impact is considered.

Park et al (2015) employed STF and aramid fibers to create a protective flexible barrier (soft body amour) against high velocity impact project. The manufacturing process was similar to the one proposed by Lee et al (2003). Using a gas gun system, Park et al (2015) were able to reach velocities at ballistic range below 700 m/s. By using STF impregnated multi-layered aramid fabrics Park et al (2015) were able to provide the same ballistic protection with less fabrics. They were able to decrease the number of aramid layers in 37.5% without compromising the ballistic protection. As discussed by Harris et al (2015) the peak pressure is directly proportional to the number of layers, thus less number of layers will promote a decrease on peak pressure.

This paper deals with design and experimental tests of bullet proof vests make of aged Kevlar fibers and impregnated by shear thickening fluid (STF) made of a mix of nanosilica, CaCO₃ nanoparticles and ethylene glycol. To make the system more efficient, a new impregnation procedure based on an atomization technique associated to traditional infusion was developed.

2. MATERIALS AND EXPERIMENTS

Unlikely traditional techniques employed for aramid fabrics impregnation by STF, this research focused on development of a new class of non-Newtonian fluid. The new STF is a combination of two different nanoparticles, i.e. nanosilica and calcium carbonate (CaCO₃), dispersed into polyethylene glycol (PEG). The dispersion process was made using a combination of ultra-sonication at 20 KHZ and high shear mixing at 12000 RPM. The homogenization (sonication and high shear mixing) process was performed for 30 minutes. To be able to reach high impregnation rates a new impregnation procedure based on an atomization technique associated to an infusion process enhanced by an ultra-sonication at 42 KHZ was developed. The first step was the enhanced infusion process for 30 minutes followed by the atomization process for another 30 minutes. By applying these two techniques combined, the amount of inorganic nanoparticles inside and surrounding the external surfaces of each aramid layers reached values between 60 and 72 % in weight. These different impregnations, intra- and inter-layers, not only allowed the increase on STF content but it can also responsible for more energy dissipation. To be able to prove this hypothesis, a design of experiment matrix (Montgomery, 2014) was developed. The control samples were made of 18, 24 and 32 layers of Kevlar 29 fabric with areal density around 1.44 g/cm³ without any STF impregnation. The test samples have a combination of nanosilica and CaCO₃ nanoparticles varying from 0 to 100 wt. % at increments of 25 wt. %, i.e. 0/100, 25/75, 50/50, 75/25, 100/0. The ballistic tests were performed following NIJ standard (2010) using 9 mm Full Metal Jacket (FMJ) and 357 Magnum Jacketed Soft Point (JSP), with average mass of 8.0 g and 10.2 g, respectively. The average energy measured for each ammunition type used (9 mm and 357) was around 520 J and 980 J, respectively. A Roma Plastilina clay was selected to model the flesh response of the human body.

3. DATA ANALYSIS

The first phase of data analysis is based on spatial distribution of nanoparticles into the aramid fabrics. This analysis will allow us to understand the mechanisms behind the yarn/yarn and yarn/nanoparticle friction. As it can be observed in Figures 1A-C, nanosilica were able to infiltrate inside the yarns and between yarns. The same pattern can be observed for CaCO₃ (see Figures 2A-C). The nanoparticles content reached values around 72%.

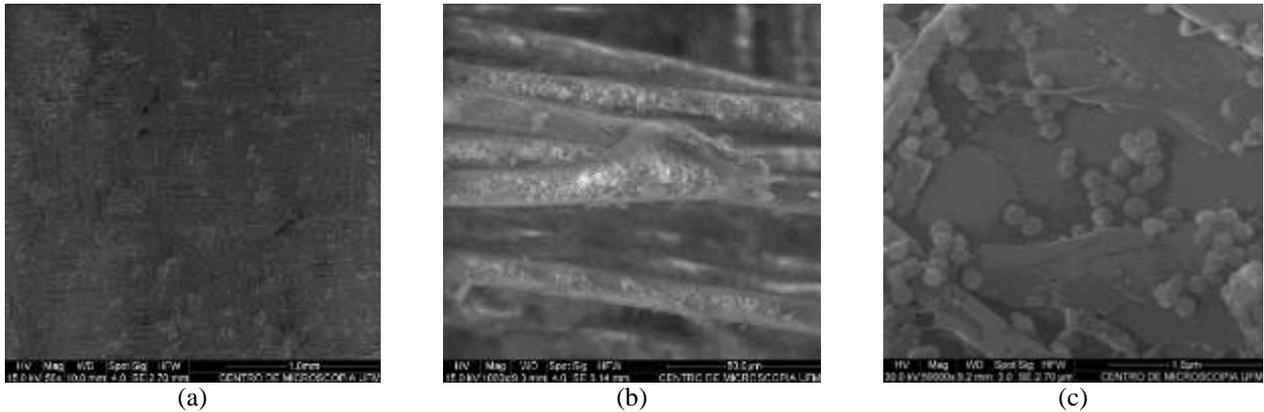


Figure 1- SEM observation of aramid fibers impregnated with nanosilica. (a) Surface fiber/nanosilicas; (b) fiber impregnation; (c) nanosilica dispersion.

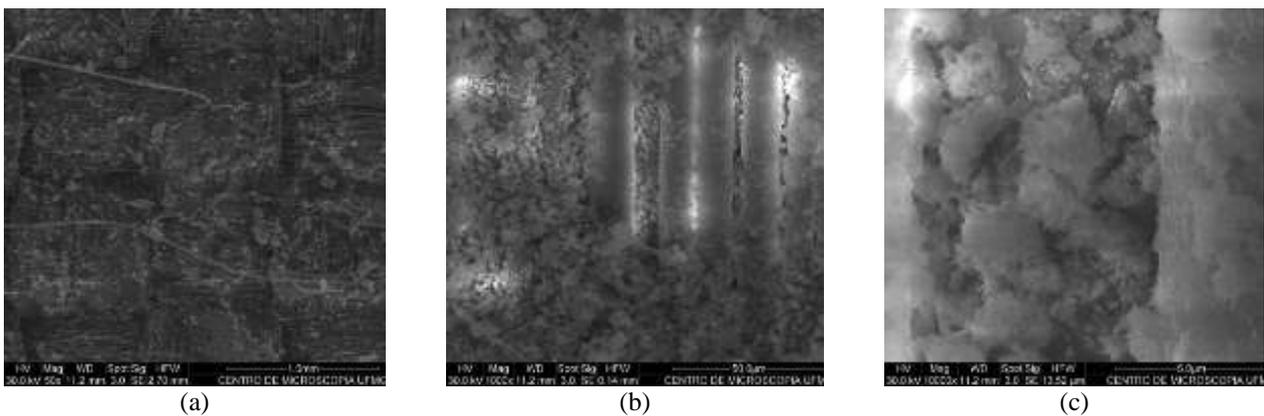


Figure 2- SEM observation of aramid fibers impregnated with CaCO₃. (a) Surface fiber/nanosilicas; (b) fiber impregnation; (c) CaCO₃ dispersion.

The ballistic tests were performed considering two phases. The first one was an exploratory phase where three different number of layers (18, 24 and 32) were employed and six different ratios between CaCO₃/nanosilica were tested (0/100, 25/75, 50/50, 75/25, 100/0). Table 1 summarizes the data obtained for each sub-group. Figures 3 through 8 show the front and back views for each sub-group (18, 24 and 32 layers). As it can be observed the STF provided an extra strength to the aramid layers. The dissipation energy mechanism was by increasing the friction between yarns and layers and by the fiber breakage.

Table 1 – Phase 1- Ballistic Test summary

Plate	Composition	Thickness [mm]	Ammo Type	Energy [J]	Indentation Depth [mm]	Perforated Layers	Plate Dept/Mass [mm/g]
P1	18 No STF	4.27	9mm	528.01	33.2	3	0.26
P2	18 No STF	4.21	.357	996.18	48.5	5	0.38
P3	18+STF3	5.39	9mm	513.93	39.0	8	0.21
P4	18+STF3	5.47	.357	1009.96	-	18	-
P5	18+STF4	5.52	9mm	517.43	37.0	0	0.21
P6	18+STF4	5.57	.357	1004.44	41.0	6	0.22
P7	18+STF5	5.67	9mm	523.59	39.0	9	0.19
P8	18+STF3	5.66	.357	1000.30	-	18	-
P9	18+STF6	5.75	9mm	525.36	36.5	6	0.22
P10	18+STF6	5.72	.357	964.82	-	18	-
P11	18+STF7	5.81	9mm	522.71	48.0	11	0.25
P12	18+STF7	5.85	.357	1011.35	-	18	-
P13	24 No STF	5.87	9mm	532.45	30.5	2	0.18
P14	24 No STF	5.53	.357	987.95	33.0	2	0.20
P15	24+STF3	7.11	9mm	545.88	35.1	7	0.13
P16	24+STF3	7.09	.357	1019.67	35.0	6	0.13
P17	24+STF4	7.39	9mm	550.39	32.0	10	0.12
P18	24+STF4	7.51	.357	1023.85	37.0	6	0.15
P19	24+STF5	7.86	9mm	517.43	34.5	11	0.13
P20	24+STF5	7.63	.357	1000.30	39.0	8	0.15
P21	24+STF6	7.92	9mm	525.36	34.0	14	0.13
P22	24+STF6	7.84	.357	970.24	43.5	12	0.16
P23	24+STF7	7.85	9mm	540.49	39.9	13	0.15
P24	24+STF7	7.91	.357	996.18	39.0	9	0.15
P25	32 No STF	7.77	9mm	517.43	27.0	2	0.12
P26	32 No STF	7.74	.357	939.30	30.0	2	0.13
P27	32+STF3	7.70	9mm	567.71	26.5	5	0.07
P28	32+STF3	7.84	.357	994.80	33.0	9	0.09
P29	32+STF4	7.83	9mm	544.98	29.7	12	0.08
P30	32+STF4	7.89	.357	994.80	32.0	8	0.09
P31	32+STF5	7.93	9mm	567.71	28.6	11	0.08
P32	32+STF5	7.96	.357	967.53	30.0	7	0.08
P33	32+STF6	7.95	9mm	565.87	27.0	11	0.08
P34	32+STF6	7.93	.357	955.38	33.0	7	0.10
P35	32+STF7	8.19	9mm	514.81	29.0	13	0.09
P36	32+STF3	8.05	.357	971.60	35.5	12	0.11

For the plates with 18 layers none of the 9 mm FMJ projectiles were able to perform a complete perforation. The STF effect can be noticed by the better performance of these plates, in other words, smaller deformations measured into the Plastilina witness clay. In this case, all samples had deformations below the NIJ limit (44 mm). The STF 4 samples had no layer perforated. For the impacts of .357 Magnum JSP projectiles, the untreated 18-layer plate was able to retain the projectile without drilling, but the depth value measured in the Plastilina exceeded the maximum value allowed by the NIJ standard of 44 mm, which may disqualify it for ballistic protection. Among STF treated plates, only that treated with STF4 (75% m / m calcium carbonate + 25% m / m active nanosilica) was able to retain the .357 Magnum JSP projectile and maintain the depth value within the value maximum allowed.

As the nanoparticles density are different and to be able to make a comparison between the ballistic response of each group the Plastilina indentation mark (depth) was normalized by the plate mass. Figure 9 shows the relative depth for the 24 layers group. As it can be noticed, all samples performed well – below the NIJ limit. However, the STF 6 combination under 357 Mangum projectile impact barely passed. This behavior can be accredited to formation of nanosilica clusters, which can be lead to stress concentrations regions.

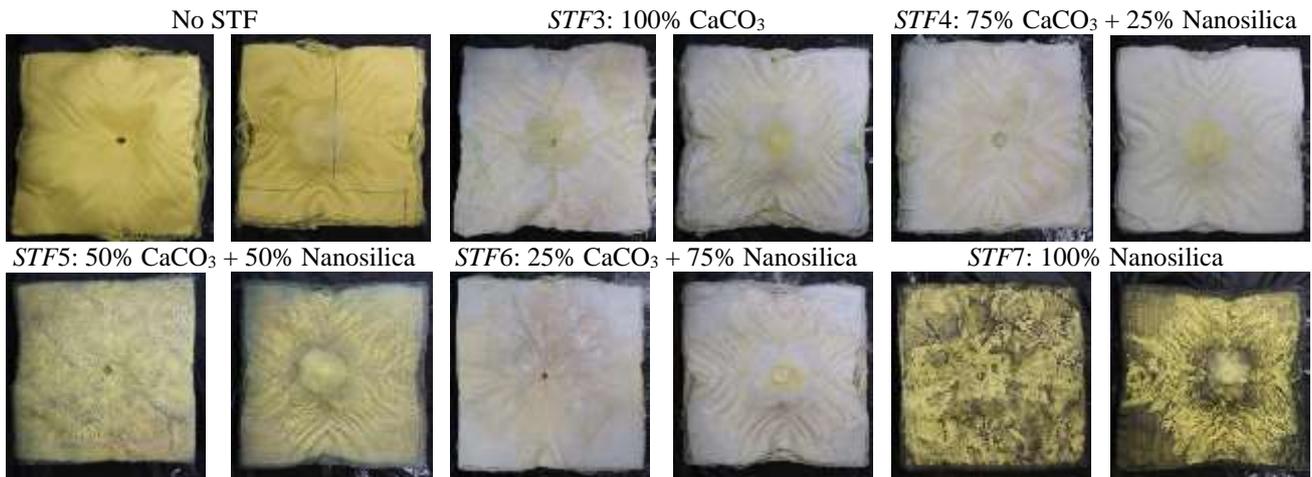


Figure 3. Front and Back views - 18 layers 9 mm projectile

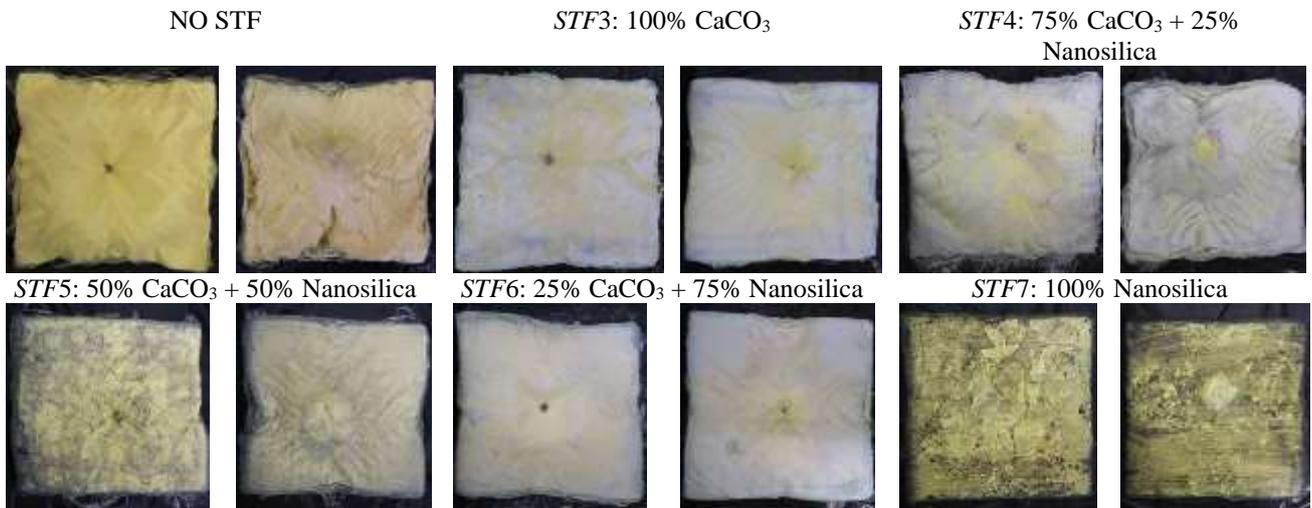


Figure 4. Front and Back views - 18 layers 357 magnum projectile

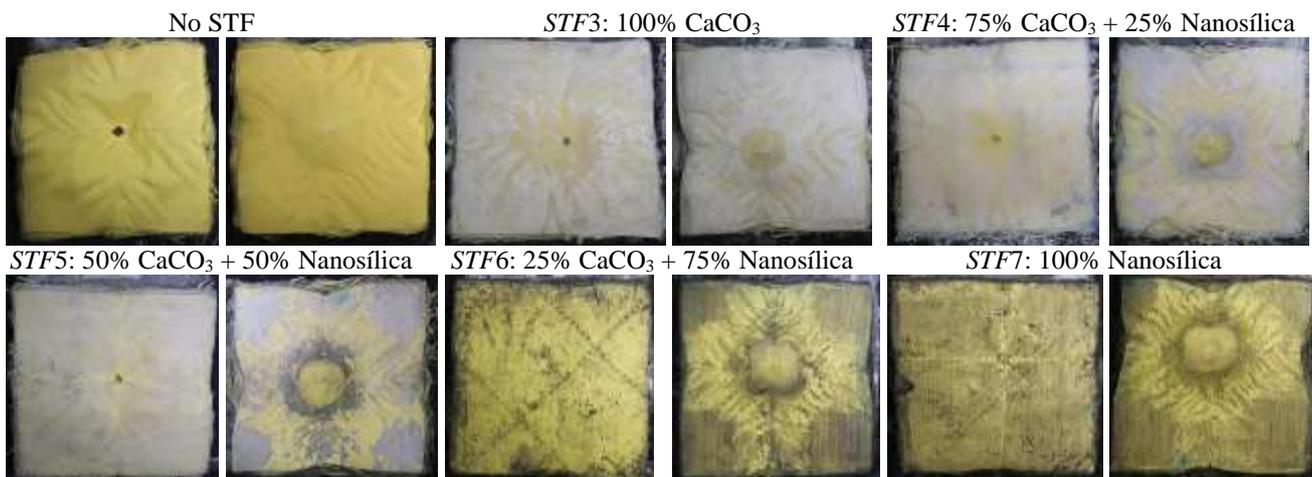


Figure 5. Front and Back views - 24 layers 9 mm FMJ projectile

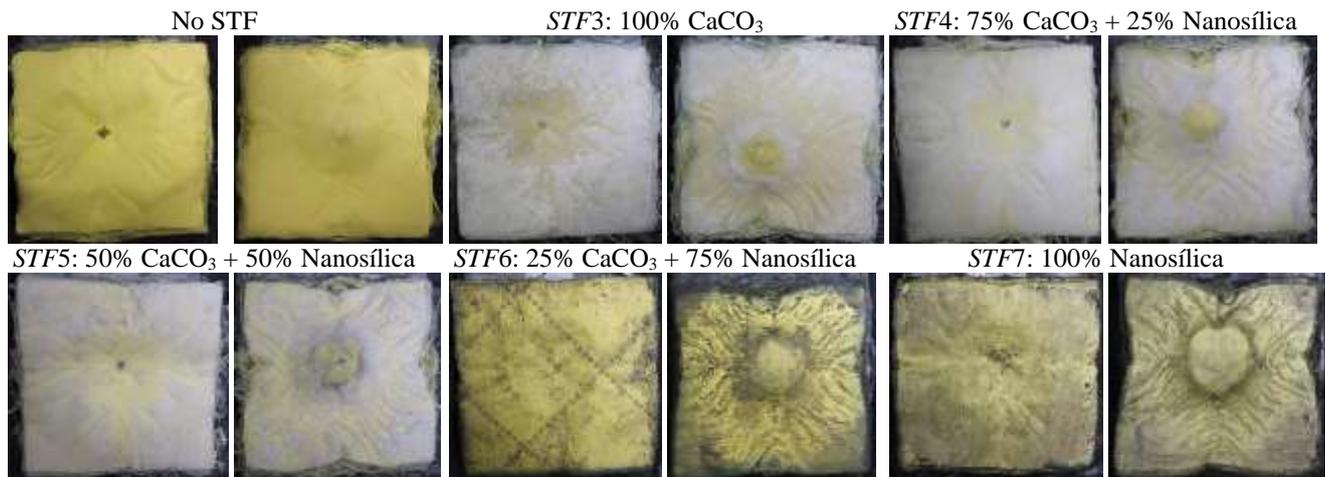


Figure 6. Front and Back views - 24 layers 357 magnum projectile

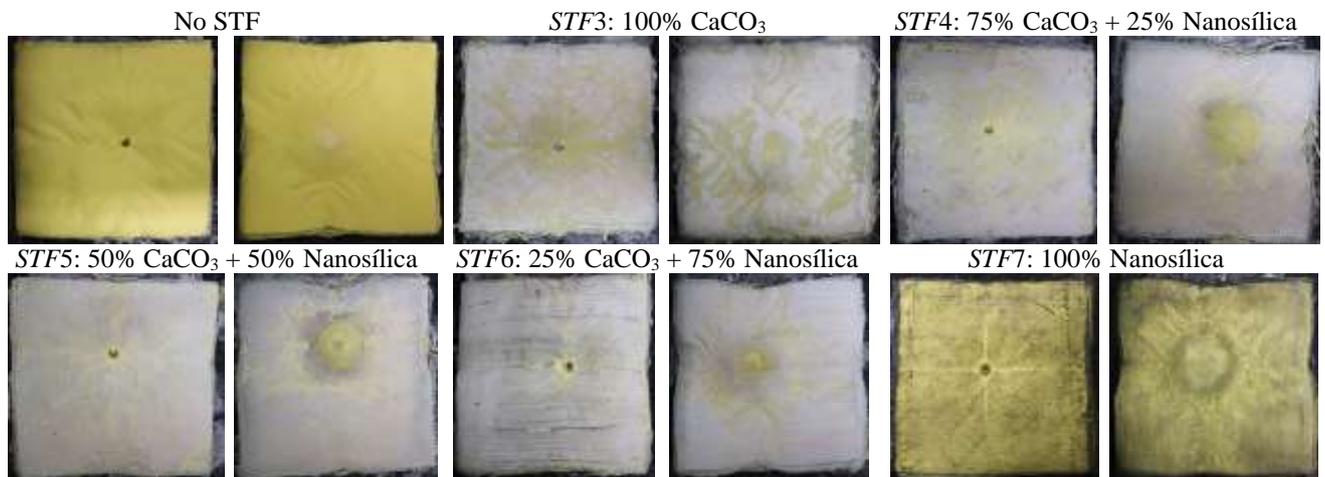


Figure 7. Front and Back views – 32 layers 9 mm FMJ

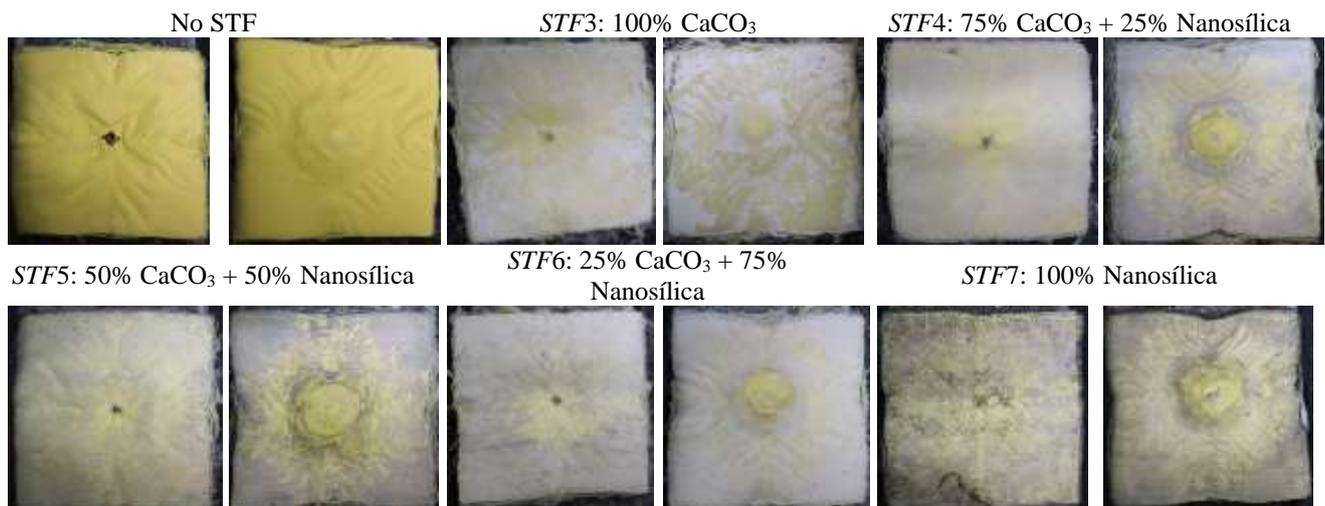


Figure 8. Front and Back views - 32 layers 357 magnum projectile

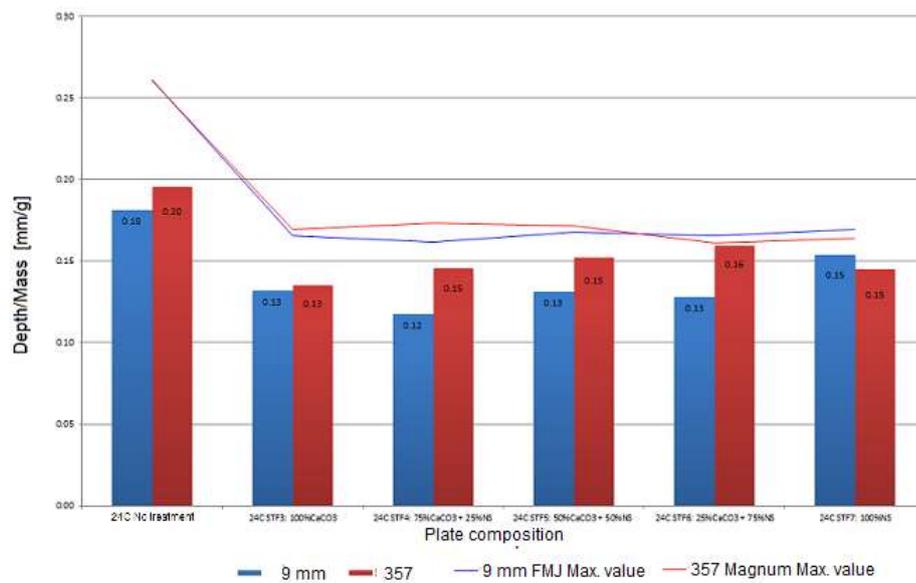
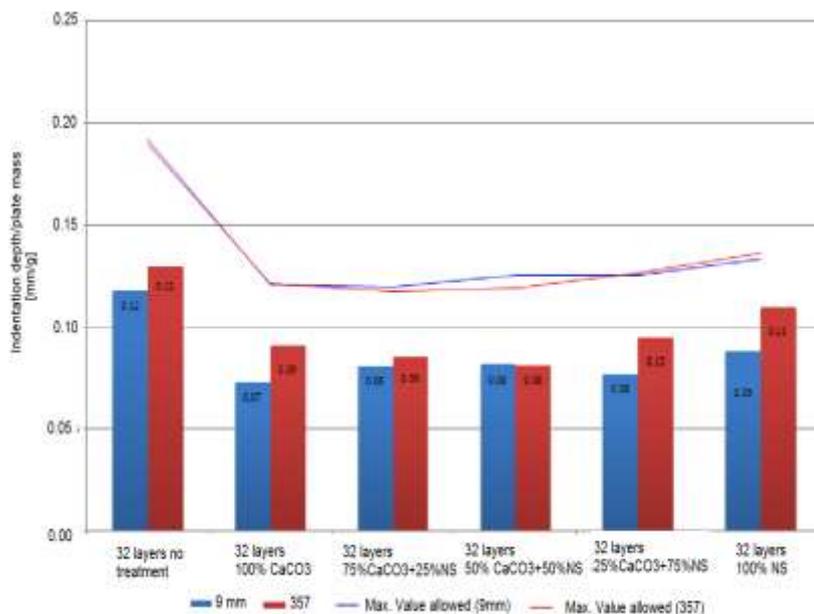
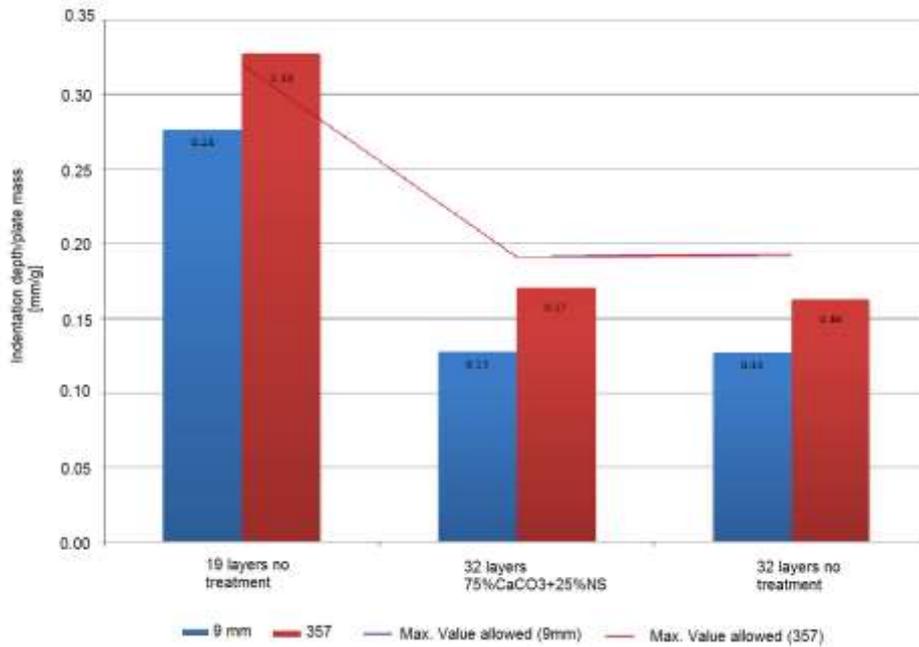


Figure 9. Depth/mass ratio for the 24 layers group

Figure 10A shows a summary of the results obtained for the 32 layers group. As it can be observed all results were below the maximum values allowed by the NIJ standard. Notice that the 75 wt. % CaCO_3 + 25 wt. % nanosilica (NS) was the combination with the best performance. Although the results seem to be good, the increase on weight is a critical factor and make the wave propagation a major problem. The equivalent in weight to 32 layers with no treatment is 19 layers with 75/25 ratio (CaCO_3/NS). This condition was considered the phase two of our analysis. As it can be seen in Figure 10B, the 32 layers with no treatment and the 19 layers 75/25 samples had the same ballistic performance. One hypothesis for such good performance can be explained by a combination of some factors. The first one is the decrease on peak pressure, as commented by Haris et al [6], the number of layers is directly proportional to the peak pressure. The second factor is the yarn/yarn friction caused by the NS/ CaCO_3 interlayer and the STF non-Newtonian response at intra-layers.



(a)



(b)
 Figure 10. Ballistic performance results. (a) 32 layers; (b) 32 layers x 19 layers

Based on these experimental results a model based on Behind Armor Blunt Trauma (BABT) was proposed. Figure 11 shows the model proposed. This model allowed us to compute the specific work done by the projectile into the body, which is another way to evaluate BABT. By evaluating the pressure wave transmitted through the body armor to the body, it is possible to predict possible organs internal damage, a life threatening condition.

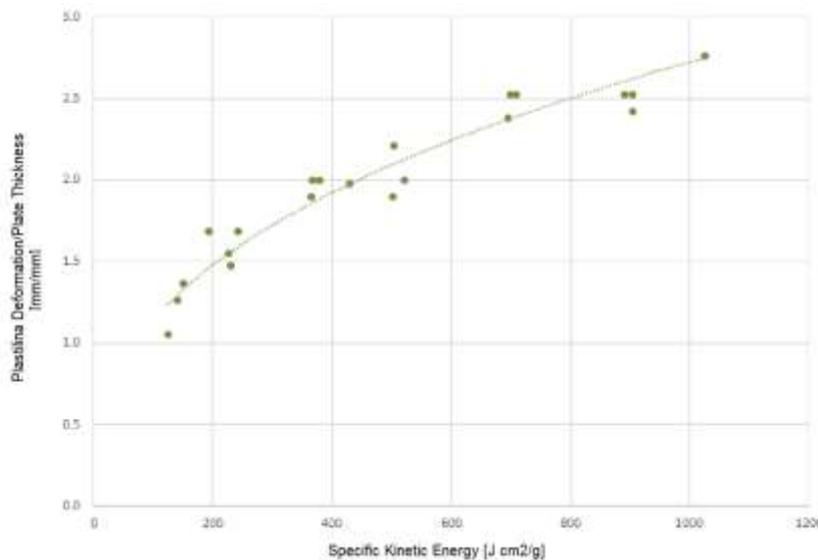


Figure 11. Proposed model to BABT

According to the model predictions, the 19 layers + STF (75/25) was capable to produce a smaller BABT than 32 layers without treatment with same ballistic protection

4. CONCLUSIONS

The STF was a combination of nanosilica and calcium carbonate nanocrystals, combined with polyethylene glycol. The STF assimilation process into aramid fibers has been accomplished through a combination of ultrasonic dispersion and airbrush, especially developed for this study. Two types of ammunition were considered, i.e. 9mm Full Metal Jacket (FMJ) and .357 Magnum Jacketed Soft Point (JSP). The results demonstrated an enhancement close to 25% in ballistic penetration resistance, due combined performance of aramid fabrics impregnated with STF and the epoxy

system. Furthermore, considering only the addition of STF to the aramid fabrics through the improved dispersion technique, an increase on performance close to 41% in ballistic performance was achieved. A normalized equation was proposed, which allows a comparative study between the effect of using non Newtonian fluids and the chest cavity trauma made by high speed projectiles.

5. ACKNOWLEDGMENTS

The authors would like to acknowledge the financial support provided by the Brazilian Research Council (CNPq) under grant 304646/2014-8 and the Air Force Office of Scientific Research (AFOSR) grant FA9550-14-1-0377. We also would like to acknowledge the technical support provided by the UFMG's Center for Micro-Analysis and the Minas Gerais State Foundation for Research (FAPEMIG).

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