The use of shear thickening nanocomposites in impact resistant materials

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ACCEPTED FOR PUBLICATION IN ASME *Biomechanical Engineering*, Feb. 20, 2015

Abstract

The work presented here demonstrates using a novel, field-responsive nanocomposite based on shear thickening fluids (STFs) as responsive protective materials with superior damping and energy adsorption properties. Peak forces and accelerations measured using an instrumented Instron™ drop tower demonstrate that STF nanocomposite prototypes and impact foam taken from a commercial football helmet have similar performance for low kinetic energy impacts. However, tests with STF nanocomposite samples exhibit significantly reduced peak acceleration and peak force for impacts above 15 J. Thus, the STF containing nanocomposite material provides improved energy adsorption upon impact as compared to the commercial foam. These tests suggest that STF nanocomposite materials have promising potential as novel energy dissipating components in personal protective equipment.

Introduction

The motivation for this study is the desire to develop improved materials to provide protection against concussions and other impact-related injuries. Recently, sports related concussions have received significant attention as new research has emphasized the negative consequences of brain injuries on the long-term health of athletes.[1] It is estimated that between 1.6 and 3.8 million concussions occur annually in the United States across all sports, with football being a significant contributor.[2, 3] Moreover, longer term health impacts, like chronic traumatic encephalopathy (CTE) and early onset Alzheimer's, may not manifest until long after a athletic career has ended.[1, 4] A study of 261 sports related deaths from 1980-2009 also identified football as the most lethal sport studied for youth participants (under 21 years of age), accounting for 57% of the fatal injuries.[5] The majority of these deaths resulted from head and spine trauma, including helmet-to-helmet collisions. Helmet-to-helmet collisions have also been previously identified as the dominant concussion mechanism.[6] The potential health risks associated with playing football vary from acute traumatic brain injury to long-term degenerative conditions like CTE.[7 8] As a consequence, there is a need for novel protective materials that can respond more effectively to adsorb impact energy and mitigate transmission of impulse to the player. This work specifically studies a new type of field responsive material (shear thickening fluid - STFs) in laboratory impact tests where we quantify the peak force, peak acceleration, and calculate head injury criteria (HIC) values from the impact data. The major goal of this study is to explore the use of shear thickening fluids in impact resistant materials and evaluate their ability to mitigate the blunt impacts at levels comparable to those occurring in sports. The scope of this work is to compare commercial foam found in football helmets with combinations of foam and STF padding using material performance tests in laboratory.

We based our laboratory materials testing on the following studies of the risk of concussion, which can be quantified through the linear and angular acceleration of the brain as well as the duration time of the impact. The rate of injury is 5.56 per 1000 games or practices played for NCAA football players and the average player experiences 16.3 impacts per game for a final concussion incidence rate of 0.341 concussions per 1000 impacts.[9-11] Rowson and Duma note that a comparable number for the NFL is estimated as 0.286 concussions per 1000 impacts. [1213] Sub-concussive football impacts are reported as having peak acceleration of 26±20 g [11] and 60 ± 24 g [14] whereas concussive impacts are reported to result in peak accelerations of 105 ± 27 g[11] and 98 ± 28 g. [14] Viano also couples peak rotational acceleration (6432 ± 1813 g) with the linear acceleration to give the parameter space correlated to sustaining a concussion. Risk of injury is quantified using Equation 1, where risk of concussion R is expressed as a function of peak acceleration, labeled as x to be readily distinguishable from α, with units of g.[11]

$$R(x) = \frac{1}{1+e^{-(\alpha+\beta x)}} \qquad (1)$$

The regression coefficients for NCAA injury statistics are $\alpha = -9.805$ (no units) and $\beta = 0.051$ (g^{-1}). The coefficients for the NFL are $\alpha = -9.928$ and $\beta = -0.0497$ (g^{-1}). Peak acceleration alone does not necessarily give an accurate correlation to risk of injury because the length of time over which the impact occurs is also important. To decrease the linear and rotational acceleration to safer levels helmet technology would need to decrease the peak acceleration by increasing the duration of impact. A currently accepted laboratory metric to determine the performance of a helmet design to mitigate the risk of injury is the Head Injury Criterion or HIC.[15] The HIC is calculated using Equation 2 where t_2 and t_1 are the final and initial times respectively (the units of *a(t)* are in g). The maximum value for (t_2-t_1) that is commonly used is approximately 15 ms.

$$HIC = \left\{(t_2 - t_1) \left[\frac{1}{t_2 - t_1} \int_{t_1}^{t_2} a(t)dt\right]^{2.5}\right\} max \qquad (2)$$

This is an accepted criterion in sports medicine and the HIC limit for sustaining a concussion has been cited as 345±181, which had peak acceleration of 94±28 g.[14] This study found that no concussions occurred for the HIC range of 143±37 with a peak acceleration of 68±15 g. The probability of injury is a sigmoid function that has very low risk of injury near the concussion threshold but rises rapidly with comparatively small changes in peak acceleration.

Recent research has shown that rate dependent responsiveness of shear thickening fluids (STFs) during deformation can be harnessed to engineer novel protective materials.[16-20] Shear thickening fluids are highly concentrated suspensions of colloids and/or nanoparticles in a low molecular weight fluid, which have temporarily high viscosity under stress.[21] The well-established dynamic structure formation of these fluids enables shear thickening fluids to have superior energy dissipation properties as compared to simple fluids and gels. These are *field-responsive* materials, i.e., they exhibit improved energy absorbing properties as impact force increases. This is in direct contrast to traditional materials, such as polyurethane and vinyl nitrile foams, which fail catastrophically when impacted at force levels in excess of the normally expected range. The mechanism responsible for the novel material response of STFs is well established and has been supported through experiments and Stokesian dynamics simulations.[22, 23] The size and volume fraction of particles in the STF formulation, along with the properties of the suspending medium, determines the severity of the thickening response as shear stress increases.[24, 25] Thus, the field-induced response of STF-containing composites can be engineered to yield optimal energy adsorption and impulse mitigation by tailoring the formulation for the specific application. Accurate rheology measurements for shear thickening fluids are critical for optimizing the response of these fluids, and hence STF-based nanocomposite devices, for a specific impact threat. The experimental results presented in the articles cited above can be used to help to guide STF formulation for specific applications depending on their characteristic or limiting forces, rates, and energies.

Based on this body of literature, we propose shear thickening fluids for use in personal protective equipment and in this work, perform laboratory tests to ascertain the performance of STF composites relative to polymer foams characteristic of those found in football helmets .[11, 26] The scope of this study is to examine the efficacy of STF nanocomposite materials in mitigating the peak force and peak acceleration during impact in controlled laboratory experiments. Thus, the materials have been tested outside of a helmet to determine their material and mechanical characteristics independent of the helmet device. The goal of this study was to directly compare the impact performance of commercial foam taken directly from a commercial helmet and STF nanocomposites for energies up to 30 J. We observe significant differences at higher impact energies that suggest potential benefits in using STF nanocomposites for absorbing blunt impacts in protective devices for sports and medical applications.

Materials and Methods

The shear thickening fluid (STF) used in these experiments was composed of 61% (by weight) Nanosil™ silica particles suspended in 200 g/mol poly(ethylene glycol) (PEG). The STF was prepared by combining the desired mass of silica particles (450±5 nm diameter) and Clariant poly(ethylene glycol) (PEG) with nominal molecular weight 200 g/mol. The silica nanoparticles were slowly added to the desired quantity of PEG in a Nalgene bottle. The mixture was then roll-mixed for 2 days to allow the particles to fully disperse. The gentle flow associated with a roll mixer is the best way to suspend particles as more intense mixing processes would cause the fluid to thicken, making dispersion more difficult. The 61 wt% Nanosil™ STF displays the same characteristic rheology as other STFs that have been reported in the literature.[29] The rheological properties of the STF were measured after roll mixing to ensure that each batch of STF was functionally identical. As shown in Figure 1, increasing the shear rate leads to large increases in the stress response of the material. Note that a standard, Newtonian fluid would show a linear relationship between stress and shear rate, whereas the STF shows a highly nonlinear response to the applied shear rate above the critical value for shear thickening. It is this high stress that increases dramatically with increasing rate of deformation that provides the beneficial field-response of STF containing nanocomposites. Referring to the material parameters shown in the inset figure, shear thinning was observed from 0.1 Pa to 31.6 Pa and the minimum viscosity was measured to be 8 Pa*s. Shear thickening occurs for stresses above τ_{crit} =31.6 Pa where the viscosity increases approximately two orders of magnitude from 8 Pa*s at τ_{crit} to 305 Pa*s at the highest shear stress tested. A small amount of hysteresis was observed between the forward and backward stress sweeps, between 100 and 1000 Pa. This will not significantly affect the shear thickening performance of the fluid. Importantly, the fluid can be sheared back and forth multiple times without any measurable change in performance. The properties of the STF were tuned so that the shear thickening response would be activated during significant impact but not during normal handling.

The samples for impact testing were constructed of polymer encapsulated STF nanocomposites either as a monolithic sample or layered with the commercial polymer foam such that the overall sample thickness was maintained at 33mm. The 33 mm thick commercial foam padding, which was obtained from a Riddell Revolution Speed football helmet, was selected as representative material present in current generation football helmets. The prototypes are identified by the thickness of the STF padding layer, as shown in Table 1, where the nomenclature indicates that the 8 mm prototype has an STF layer that is 8 mm thick and a Riddell foam layer that is 25 mm thick, while the 33 mm prototype is composed solely of the STF padding. In multicomponent samples the STF layer was the upper layer with impact onto this top layer. The STF padding is composed of a spacer fabric, obtained from Gehring

Textiles, into which the STF has been intercalated. A single layer of STF saturated spacer fabric is approximately 6 mm. Finally, the STF containing spacer fabric is encapsulated with Engage 8200, a poly (ethylene) copolymer (Dow Chemical). Encapsulation adds approximately 2mm to each STF sample and the values in Table 1 include this 2mm of polymer encapsulation film. STF pads thicker than 8 mm were assembled by combining multiple layers of spacer fabric until the desired thickness was achieved. The STF remains fluid throughout the entire life of the sample as the Engage 8200 encapsulation material contains the fluid and is robust during multiple impacts due to its elastomeric properties. All layer thicknesses were verified using a digital caliper and were accurate within ±1 mm of the target values. An example photograph of a 22mm STF pad is shown in Figure 2.

All of the impact testing performed in this study was conducted on the materials directly as opposed to being contained in a helmet assembly. The testing protocol as described below is designed to explore the material's performance during impact of the STF composites with the commercial foam as a reference material. An Instron Dynatup 9200 drop tower (USA) was used to evaluate the performance of each sample during impacts from heights ranging from 0.05 m to 1 m, where drop height and the resulting kinetic energy were the independent variables for this study. The instrument determines the displacement during impact (i.e., compression of the sample) using Newton's first law, the measured velocity at impact and the time-dependent force measurement. The impact head used for the drop tower experiments was a 0.0254 m diameter circular cylinder with a flat end. A thick steel plate was used as the backing material and each sample pad was clamped in place at the center of the plate. Each experiment was run in triplicate with three identical samples, as described in Table 1, being used for each experimental drop height. A single sample would experience 20 impacts across the range in 0.05 m height increments. The three resulting curves were then averaged to get mean values and relevant standard deviation of physical variables. The mass of the impact head was approximately 3 kg in total, which dropped from 1 meter has kinetic energy of 30 J which is the maximum energy possible for the apparatus.

Results

Force versus displacement curves are calculated by the instrument software from the time record of the force transducer and are reported in Figures 3 and 4. The optimal force versus displacement curve corresponding to the lowest stress intensity would be a step force-displacement curve, distributing the force evenly throughout the sample compression. In contrast, samples that exhibit a sharp force peak result in a much more intense impact and are undesirable from the standpoint of risk of concussion. Figure 3 shows results for a moderate impact energy, revealing that STF nanocomposite matches or surpasses the impact mitigation performance of commercial foam used in a typical football helmet. All of the STF containing samples have lower peak forces than the commercial foam for these experiments. The difference of the peak force between the commercial foam and the STF nanocomposite prototypes becomes much more apparent as the impact energy increases to 30 J, as shown in Figure 4. This is consistent with the expected response of the STF in the prototypes, where greater thickening and hence, energy absorption, is expected for higher impact energies (i.e., the harder the STF is hit, the more the fluid thickens and a greater difference can be observed). In contrast, the commercial foam develops a sharp force peak near maximum compression (note that all of the samples are all 33 mm in thickness initially), which suggests that the foam is essentially defeated by this impact energy and is more significantly compressed than the STF alternatives. This bottoming out leads to the bulk of the impact being absorbed over the last 5 mm of compression. In contrast, the force versus displacement curves for the STF nanocomposite prototypes all have lower peaks and are broader; meaning that the energy of the impact is absorbed over a greater distance within the sample such that the impact is less severe. STF containing samples do not "bottom-out" even at these very high energies and further compression is possible suggesting performance can be achieved even at higher impact energies.

As shown in Figure 4, the commercial foam bottoms-out and exhibits an extremely sharp force peak rising to 11 kN. The energy associated with the impact is absorbed across 5 mm or less and tearing of the sample at the point of impact was observed as a result of the foam being severely compressed. In contrast, even the replacement of 8 mm of commercial foam with 8mm of STF nanocomposite decreases the peak force below the threshold reported necessary for skull fracture (mean values are reported as 6.4 (1.1 std. dev.) kN and 11.9 (0.9 std. dev.) kN for quasistatic and dynamic loading respectively[30]). Further increasing the STF nanocomposite content significantly lowers the peak force further to approximately 3 kN. Comparing curves for the 22 mm and 33 mm STF nanocomposite pads reveals that they have similar peak force values, although the 33 mm STF pad allows for less deflection.

A conclusion to draw from the experimental data presented in Figures 3 & 4 is that the 22 mm STF nanocomposite pad material is the pad configuration that yields the best performance of those tested and that this configuration represents a very significant improvement over the existing technology at the impact energies tested using the methods presented here. We hypothesize that the 22 mm STF pad backed with 11 mm of commercial foam can better mitigate the higher impact energies than the 33 mm thick monolithic STF pad because the STF may become stiffer than desired during these impacts. Further research and development would be needed to determine the optimal configuration and STF rheological response for specific protective devices.

Peak force (Figure 5) measurements during impacts ranging in energy from 1 to 30 J indicate that the STF containing pad reduces this metric compared to commercial foam alone. Figure 5 shows the peak force measured for the commercial foam and STF nanocomposite samples. The test results show comparably low peak forces up to approximately 12 J of impact energy. However, the commercial foam exceeds the lower limit of the average concussion zone at 17 J of impact energy and increases steadily up to approximately 10 kN during the experiments. The 8 mm STF nanocomposite prototype exhibits a peak force plateau from 20 to 25 kN, which then abruptly increases above 25 kN. This was the result of the sample being fully compressed during higher energy collision. This is identified from the force vs. displacement curve shown in Figure 3, where the 8 mm sample exhibits higher deformation than the 22 mm or 33 mm STF nanocomposite pads. Remarkably, the 22 mm and 33 mm pads maintain a peak force plateau well below 4 kN even up to 30 J of impact energy.

Discussion

We note that the material testing procedures employed are not a surrogate for the impacts experienced by a football player in a real world collision. Our impact head has a 1 inch diameter circular surface and focuses the kinetic energy over this relatively small area. These tests however do show that there are significant differences in material responses between a foam typical of that used in commercial protective equipment and the field-responsive STF padding, and further, that the optimal performance is likely to be achieved through hybridization of the two materials in a synergistically functional device. The peak force reduction achieved at high impact energies by incorporating STF composites into the test samples may be effective in providing improved protection to humans and to explore this we analyze our material performance test results within an accepted framework of protective material performance evaluation as follows.

The risk of injury for NCAA and NFL players during head impact can be correlated to the measured peak acceleration calculated from impact tests using the model in Equation 1.[11] This calculation does not correlate explicitly to a real world decrease in injury rates because the laboratory impact experiments described above were not conducted directly on helmets. However, this calculation serves to translate the raw peak force and acceleration data and gives a method to quantitatively compare the relative performance for the single pad impacts. Peak acceleration for the commercial foam increases monotonically over the test range of impact energies. Figure 6 shows that risk of injury exceeds 99% probability above 340 g, which was reached by the commercial foam at the 30 J impact energy. Thus, the range of impact energies probed during our laboratory materials testing protocol provides an adequately severe impact with which to evaluate both STF and foam materials. The 22 mm and 33 mm STF nanocomposite pads reach plateau values of approximately 100 g for the highest kinetic energy impacts tested experimentally. The corresponding risk of injury values from the model were 1.3% for the 22 mm STF nanocomposite pad and 0.6% for the 33 mm STF pad based on the peak acceleration values at 30 J. The peak acceleration of the 22 mm STF sample was 66% lower than the peak acceleration for the commercial foam. However, the functional decrease in risk of injury is greater than 66% because of the non-linear relationship between peak acceleration and risk of injury. The model, shown in Equation 1, shows that small reductions in peak acceleration in the range between approximately 100 and 300 g result in large decreases in risk of injury. Hence, a 66% reduction in peak acceleration can have an enormous effect on reducing the risk of injury, which the model quantifies as being a 97.7% decrease in the risk of injury. Although this number should not be interpreted as a prediction of material performance in a helmet device, it provides a important indication of the potential, substantial benefits of incorporating the STF nanocomposites into personal protective equipment for impact mitigation.

The model can show the general dependence of risk of injury on peak acceleration curve, which illustrates the clinical implications of the impact physics. Figure 6 shows that the calculated risk of injury is very low for the peak accelerations observed below 15 J of kinetic energy, less than 1% for all of the samples, except the commercial foam at 15 J, which is slightly higher. This shows that impacts from 0 to

15 J are low intensity and correspond to inherently low risk collisions. The material requirements to mitigate impacts in this regime are relatively low, so the commercial foam and STF-containing pads perform in a similar manner. The material requirements to mitigate impacts between 15 J and 30 J of kinetic energy are much higher, as is evidenced by the commercial foam being quickly overwhelmed as kinetic energy increases. The risk of injury according to Equation 1 quickly rises from 1% risk to 99% risk whereupon it plateaus. This shows that the impacts in this regime are too intense to be mitigated by the foam itself. It is important to note that the 8 mm STF sample ultimately rises to approximately the same risk of injury as the commercial foam as the kinetic energy approaches 30 J. The 22 mm and 33 mm STF samples plateau at lower risk of injury values than the commercial foam sample, showing that the reduction in peak acceleration is significant enough to yield a meaningful decrease in risk of injury. These results are intriguing as the rate of increase in calculated risk of injury with increasing impact energies increases only very slightly for the STF containing samples, which is consistent with the field-responsive shear thickening rheology shown in Figure 1. The STF material can dissipate progressively more energy the harder it is sheared, which is shown to translate into dramatically improved impact protection as calculated from our materials testing results.

Figure 6 shows that the same general trends apply to the HIC calculations based on the tests performed here. The commercial foam has a higher HIC value for intermediate and high energy impacts, and falls within the concussion zone as defined by Viano.[14] The 22 mm and 33 mm STF nanocomposite prototypes have HIC values that stay below the concussion zone across the entire range of experimental impact energies. The HIC value measured for the commercial foam at the highest impact energies is reduced by approximately 50% for the 22 mm and 33 mm STF-containing samples. As the HIC calculation emphasizes the time over which the impact energy is dissipated, this comparison shows that when duration of impact is taken into account the STF prototypes again mitigate the impact better than commercial foam alone.

Conclusions

The experimental data presented here demonstrates that field-responsive nanocomposites containing shear thickening fluids (STFs) dissipate more energy and thereby reduce the severity of impacts in a range of impact energies that are relevant to sports related injuries.[31] The experimental measurements show that peak force and peak acceleration are both reduced by 66% for the highest energy impact energy compared to an existing polymer foam technology employed in commercial devices. Published physiological studies correlating peak acceleration during impact to risk of injury suggest that replacing foam by STF intercalated fabric has the potential to significantly reduce the risk of injury, which is also evident in the HIC calculations based on the same data. The performance of the STF nanocomposites materials shows that they are very promising materials for protecting against blunt force trauma and may find efficacy as a novel field-responsive technology for mitigating sports-related concussions. However, further work is necessary to examine the inherent trade-offs in weight, cost, longevity and other important factors to commercial product performance, as well as to assess this field-responsive material's performance in actual product testing.

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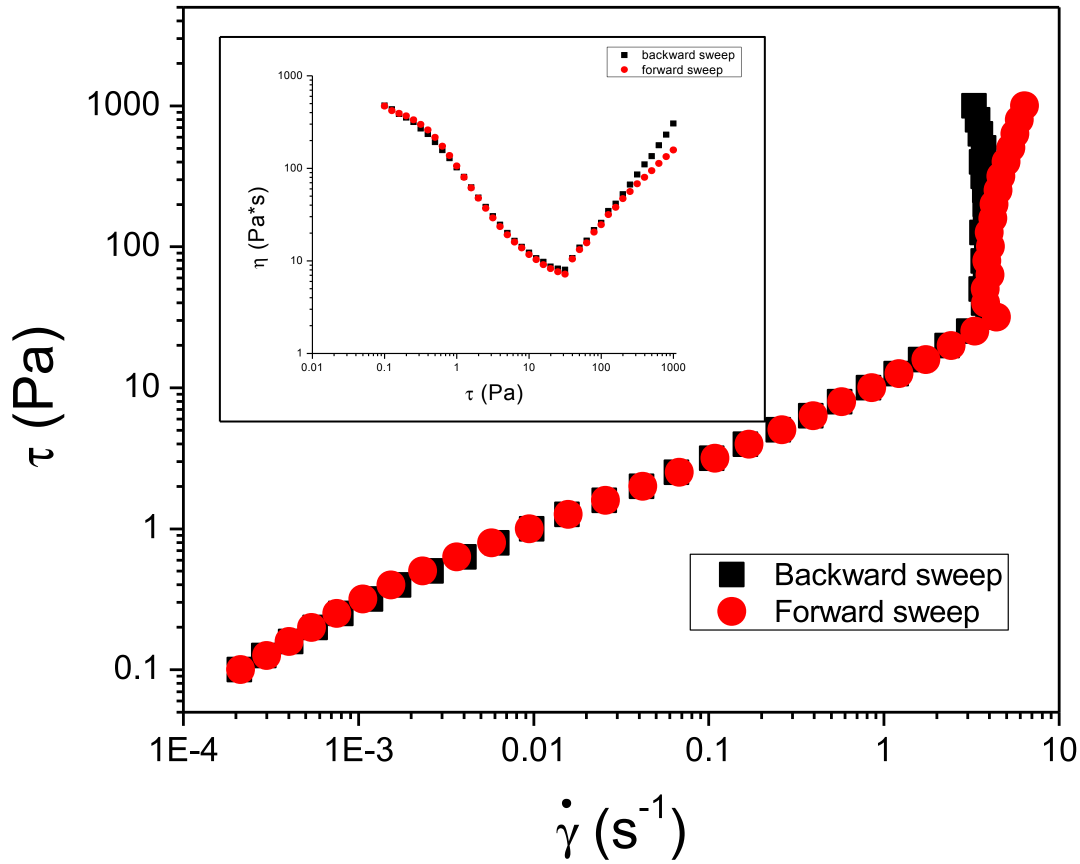

Figure 1: Shear stress vs. shear rate of 61% by weight suspension of Nanosil silica particles in PEG 200. The inset graph shows viscosity vs. shear stress. Note the abrupt increase in shear stress at the critical rate for shear thickening.

Figure 2: A prepared 22mm STF pad sample. The total sample thickness is 33 mm where 22 mm is the thickness of the STF portion of the sample and the remaining 11 mm is a polymer foam pad extracted from a Riddell Revolution Speed helmet. The spacer fabric is dark green and the STF itself is opaque white in appearance.

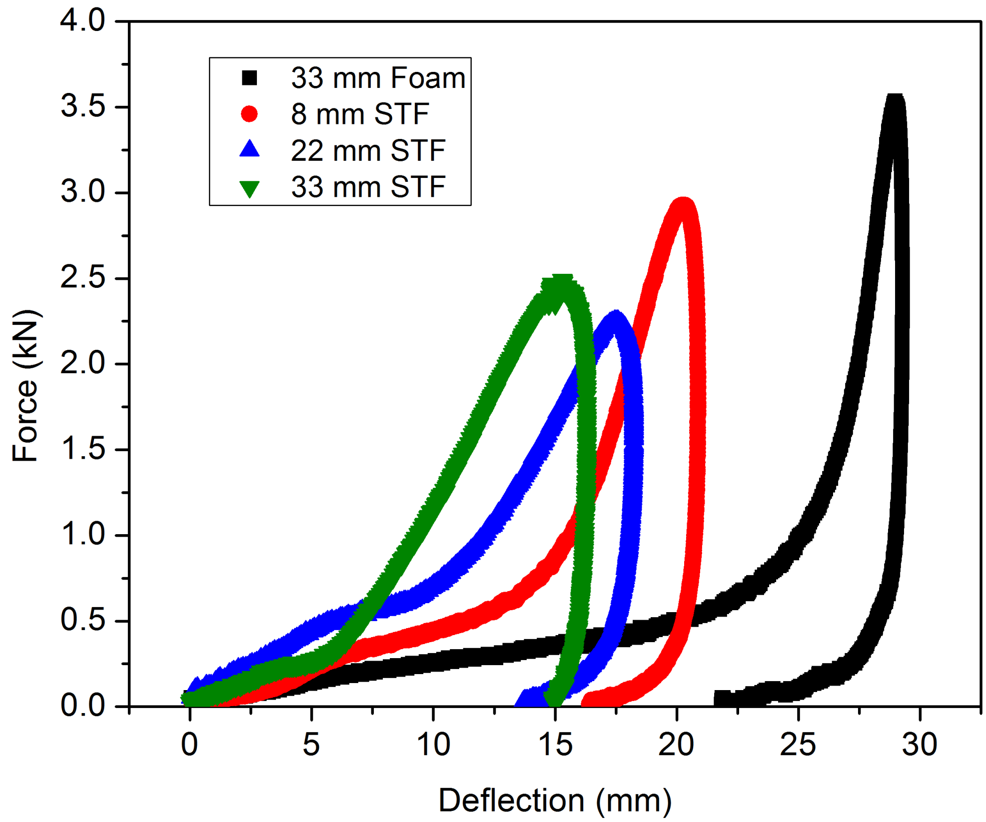

Figure 3: Representative force vs. deflection for commercial foam and 3 prototypes for 15 J impact. Total thickness for all pads is 33 mm.

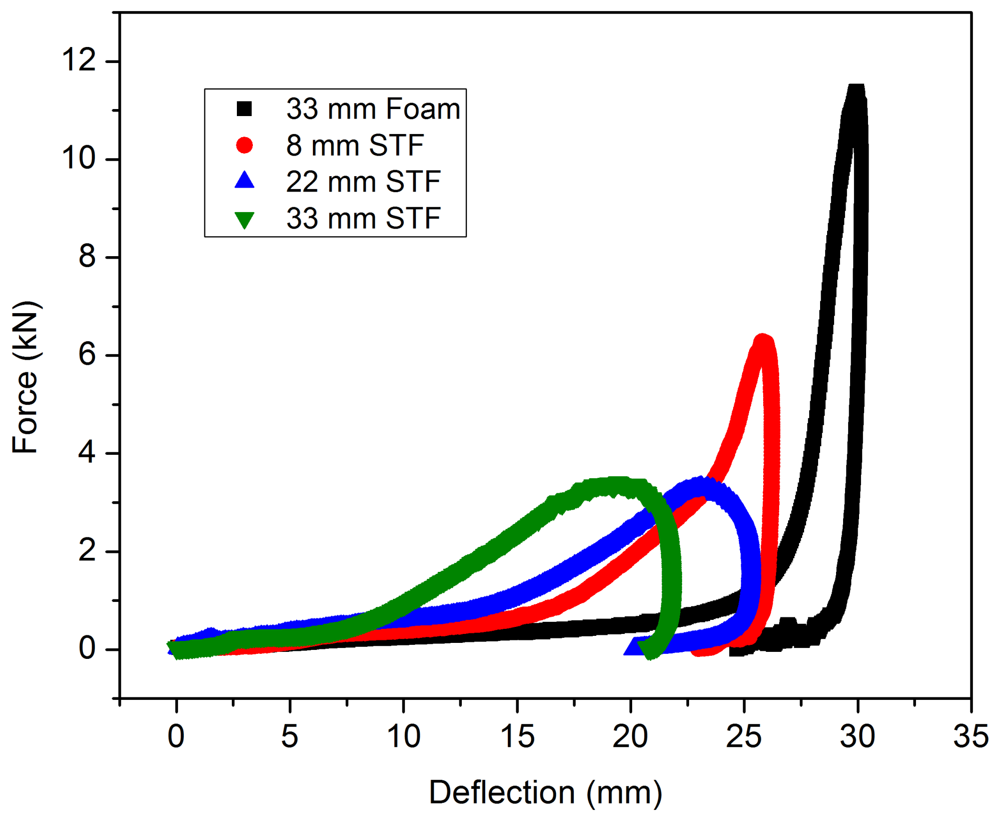

Figure 4: Representative force vs. deflection for commercial foam and 3 prototypes for 30 J impact. Total thickness for all pads is 33 mm.

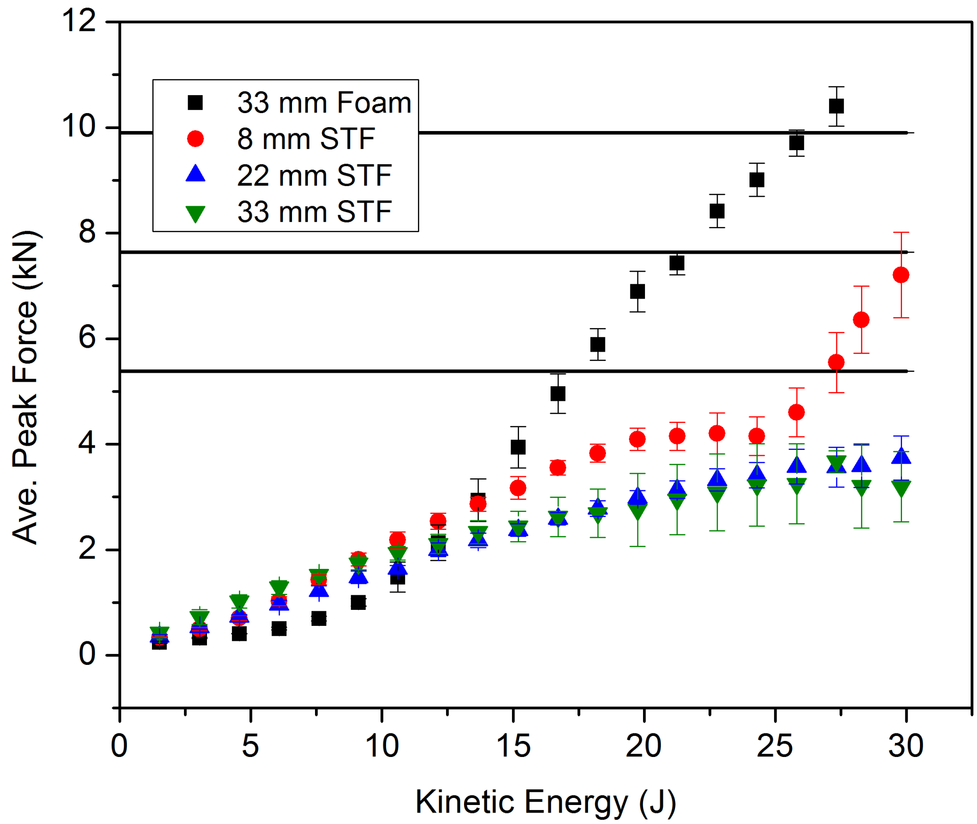

Figure 5: Average peak force vs. kinetic energy. The middle line represents the mean force required for sustaining a concussion while the upper and lower lines show the standard deviation limits. The criteria for the average concussion zone are taken from Viano 2005. [14]

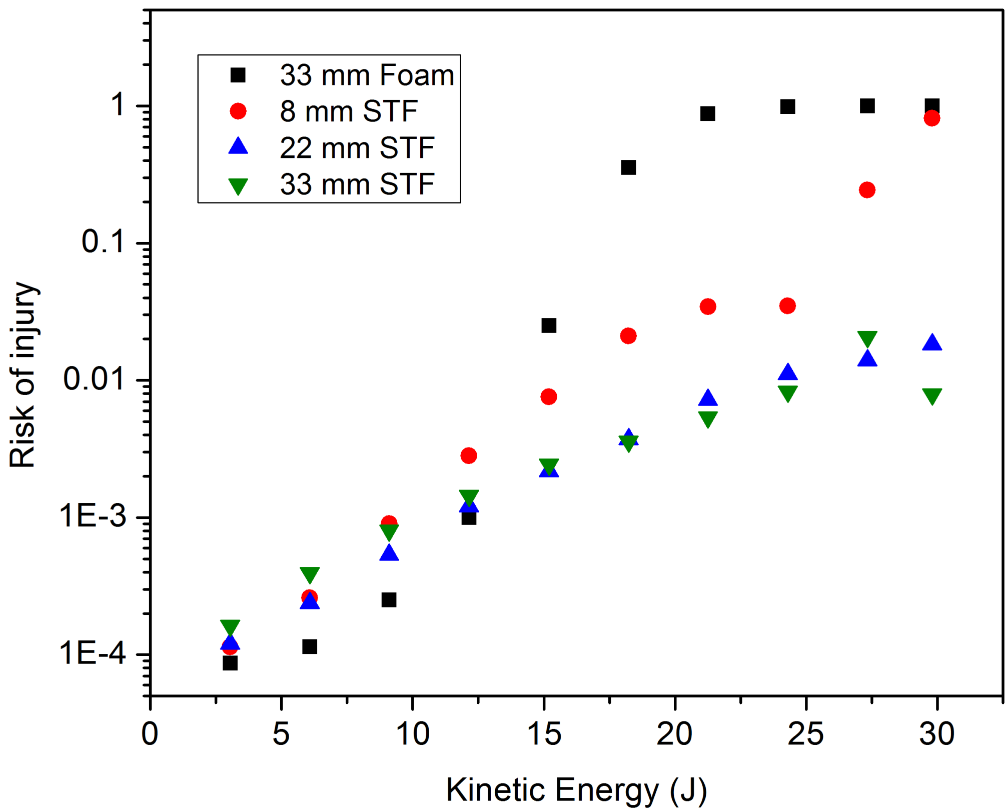

Figure 6: Probability of injury versus kinetic energy for commercial foam and 3 STF nanocomposite prototypes. Risk of injury calculated from Equation 1 using NCAA coefficients.

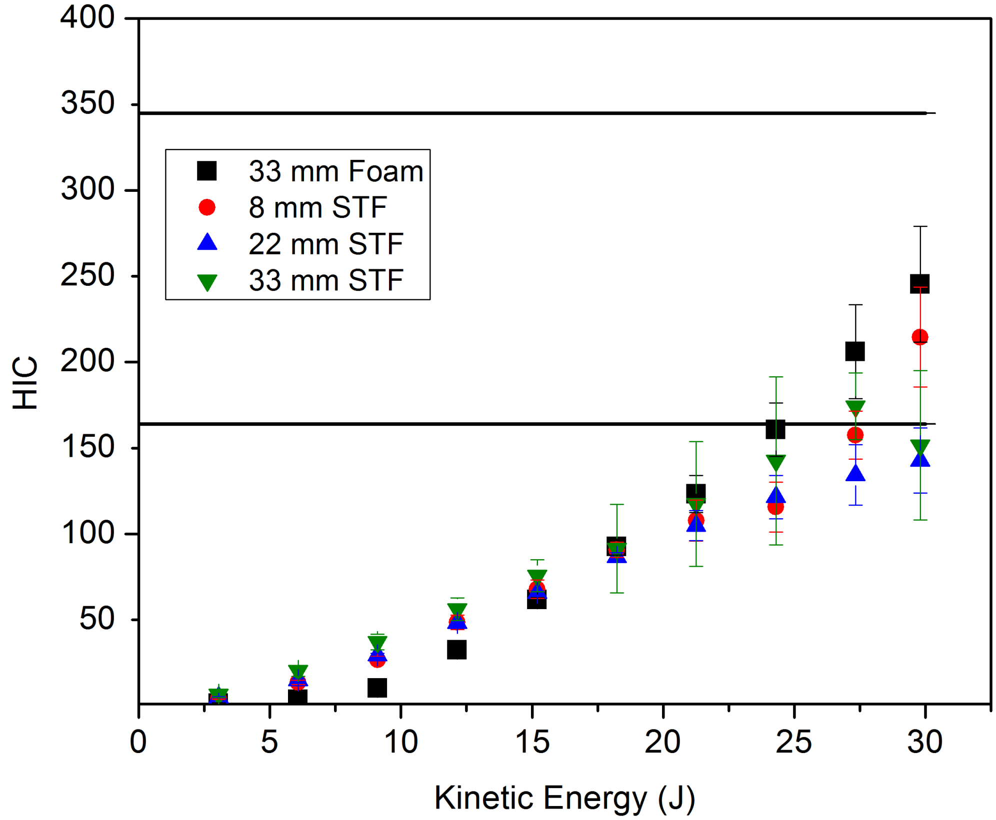

Figure 7: Average HIC vs. kinetic energy for commercial foam and 3 prototypes. The upper solid line represents the average HIC required for sustaining a concussion while the lower line shows the standard deviation lower limit. The criteria for the average concussion zone are taken from Viano 2005. [14]

Table 1. Sample composition by layer thickness.

Sample Name	STF layer thickness (mm)	Foam thickness (mm)	Total thickness (mm)
33 mm Foam	0	33	33
8 mm STF	8	25	33
22 mm STF	22	11	33
33 mm STF	33	0	33