Impact responses of an open-cell natural rubber foam impregnated with shear thickening fluid

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Abstract
This research aims to investigate the impact responses of an impact absorbing material prepared from natural rubber (NR). Shear thickening fluid (STF) was developed in order to improve compatibility, and impact response capability of a NR foam. The material was prepared by impregnating NR foam with STF (30 wt% nanosilica with 10 nm). The obtained material is soft under normal circumstances, but immediately stiff when undergoing sudden impact before softening again. The effects of foam densities (0.098, 0.15, 0.24 g/cm³), STF contents (10, 20, 30 vol%), and fluid filling techniques were investigated. Experimental results show that the absorbed force tends to increase by increasing the foam density and the fluid content. Impact absorption capability of the proposed STF (STFA)/NR foam is higher than that of the conventional STF (STF0)/NR foam. In other words, STFA can improve the impact responses of the material providing comparable results with the commercial kneepad, which has the dilatant behavior.

KEYWORDS
drop test, impact absorbing material, natural rubber, open cell foam, shear thickening fluid

1 | INTRODUCTION

Shear thickening fluids (STFs) are a class of non-Newtonian fluids, which exhibit an increase in an apparent viscosity when shear rate increases. Shear thickening mechanisms were proposed consisting of order–disorder transition, hydrocluster mechanism, and contact forces.[1–3] STFs can be prepared in the forms of colloidal suspension or silicone-based fluid. However, most research works in literature have focused their attention on the impact resistance improvement of the particle-based STF. Many researches focused on preparation techniques of protection materials. The STF, prepared by dispersing nanosilica into ethylene glycol, were applied in high performance fabrics such as Kevlar, aramid based Twaron, and ultra-high molecular weight polyethylene (UHMWPE) fabric.[4–8] Other particles were also been studied for STF preparation such as polystyrene ethyl acrylate (PSt-EA) particles in ethylene glycol (EG), carbon nanotubes and graphene nanoplatelets in polyethylene glycol (PEG200), and polymethylmethacrylate (PMMA) in glycerin-water mixture.[9–11]

The STF/foam composites were also investigated in several works. STF/Polyurethane (PU) foams were mostly
investigated for their mechanical, acoustic and thermal performances, and impact resistance performance of STF/PU foam cored sandwich composites were studied.\textsuperscript{[3,12,13]} Commercial products such as D3O, PORON XRD, and DEFLEXION which have dilatant behavior were explored their rheological and compression mechanical properties by References \textsuperscript{[14,15]}. The materials such as D3O and PORON XRD are made from closed-cell and open-cell urethane respectively, and DEFLEXION is made from closed-cell silicone foam. The fluid flow in the open-cell foam affects the stress response of the material due to fluid viscosity. On the other hand, the fluid (air) contribution in the closed-cell foam is dependent on the strain.\textsuperscript{[14]} In literatures, the energy absorbing materials were prepared from synthetic polymer fabric/foam impregnated or filled with dilatant fluid. There are very few works studying the improvement of the natural rubber (NR) by incorporating the dilatant fluid or STF. The main advantage of the material based NR is an environmentally-friendly renewable material.

This research aims to develop an impact absorbing material prepared from NR, in order to encourage the competition of Thailand in the global market as well as promote the manufacture of the value-added rubber products (product upgrading). The proposed particle-based STF has been developed in order to improve particles-rubber interaction, and impact response capability of pen-cell NR foam. The impact responses of the proposed material have been investigated by considering the effect of foam densities, STF amounts, and the effect of STF filling techniques. The efficiency of impact energy absorption has also been briefly compared with the commercial knee guard (D3O), which is made from synthesis rubber foam such as PU distributed with a borated silicone STF.\textsuperscript{[16–17]}

2 | EXPERIMENTAL SECTION

2.1 | Materials and methods

In this study, the materials used include 10 nm fumed silica oxide (commercial grade, Aerosil200), 200 g/mol polyethylene glycol (commercial grade, PEG200), and commercial ethanol (> 95% purity). The silica oxide is widely used for material reinforcement purposes, and it gives better dilatant responses than other materials.\textsuperscript{[7]} The PEG was selected as a liquid carrier due to its low volatility, thermal stability, and non-toxicity. Dilatant fluid or STF was prepared by dispersing 30 wt% silica particles in PEG200 using ultrasonic probe sonicator (Hielscher USP400S Germany, with 400 W and 24 kHz). Ethanol was used to reduce the apparent viscosity of the mixture. The additional chemical in STFA was added to improve the interaction of the particle and foam matrix. NR latex foam has been made from high ammonium NR latex (60\%TSC). All solid ingredients were prepared in dispersion form by ball-milling for 72 h. The ammonium in the latex has been initially reduced by continuously stirring at 120 rpm for 2–3 min before the specified ingredients have been mixed providing latex compound. The latex compound was matured at 60°C–120°C for 1–1.5 h depending on the thickness of the final product. The final foam density was controlled by initially determining the ratio of the compound mass to the mold volume. More information of the latex foam preparation could be found in Reference \textsuperscript{[18]}.

Open cell sponge or foam (Length × Width × Thickness = 8 × 8 × 1.5 cm) was initially made from NR latex with three different densities, 0.098, 0.15 and 0.24 g/cm\(^3\). Impact absorbing pad based NR was prepared by impregnating the NR foam with the dilatant fluid. Table 1 shows mechanical properties of the neat open cell foam, and Figure 1 shows the characteristic of the open cell foam (Thermo Fisher Scientific QUANTA400, SEM at ×50). The impact absorption property was investigated by considering effect of the prepared NR foam densities, the fluid types, and amounts, and effect of the filling techniques.

In this research, two types of the dilatant fluid were prepared by homogenizing nanoparticles without/with the additional chemical (for better quality) in the same carrier: the conventional silica colloidal (STF0), and the improved (STFA) fluids (patent/petty patent pending). The STF0 consists of only two components nanoparticles and PEG, and STFA contains three components, nanoparticles, PEG, and the additive chemical which enhance rubber-STF dispersion and interaction.

2.2 | Rheology and impact tests

Shear rheological measurements of STFs were obtained using an HAAKE\textsuperscript{TM} rheometer (HAAKE RheoWin

| Mechanical properties (units) | Neat NR foam |
|------------------------------|--------------|
| 100% modulus (MPa)           | 0.11 ± 0.02  |
| Tensile strength (MPa)       | 0.55 ± 0.05  |
| Tear resistance (N/mm\(^2\)) | 3.02 ± 0.15  |
| Hardness (Shore O)           | 5.00 ± 0.20  |
| Compressive strength (N/mm\(^2\)) | 255 ± 11.50 |
| Density (g/cm\(^3\))         | 0.25 ± 0.01  |
| Resilience (mm)              | 31.33 ± 0.57 |
software, version 4.63.0004) with parallel plate fixture with plate diameter 30 mm at room temperature. Rheological properties were tested at the Agro-Industry Development Center for Export (ADCET), Faculty of Agro-Industry, Prince of Songkla University.

Impact absorption testing was done by using a drop test machine with free falling impact mass. The drop test was achieved at Department of Mechanical Engineering, Prince of Songkla University with an impact mass 4.96 kg at a drop height 21.5 cm (resulting in a low initial impact force 7500 N or 10.3 J). Equations (1) and (2) are used to calculate impact energy and velocity ($v$).

\[ E_k = \frac{1}{2}mv^2 \approx E_p = mgh \]  
\[ v = \sqrt{2gh} \]

where, potential energy ($E_p$) is converted into kinetic energy ($E_k$) during an impact of a drop mass ($m$) onto the specimen with drop height, $h$. As a result of the free fall motion, friction is assumed to be zero in this case.

3 | RESULTS AND DISCUSSION

3.1 | Rheological properties of STFs

The dilatant fluids or STFs were prepared by dispersing the fumed silica in PEG200. Both types of the STFs contained 30 wt% silica particles in different liquid carrier components. The dilatant fluid, STF0, which was made from sole PEG200 (with dynamic viscosity 60–67 mPa.s at 20°C), has a much higher apparent viscosity than the proposed fluid, STFA, as seen in Figure 2A. The maximum apparent viscosities of STF0 and STFA were \( \approx 110 \) and 8 Pa.s, respectively. The liquid PEG200 has a kinematic viscosity of 42–47 cSt, while the liquid medium for STFA has much lower. Although both fluids have the same weight percentage of the silica loading. Both fluids showed similar trends of their rheological properties. The initial shear thinning was observed, and the shear thickening was followed. This phenomenon can be explained by order–disorder transition and hydroclustering or contact rheology models.\(^{[1,19–21]}\)

At low shear rates, both STF0 and STFA exhibit shear thinning due to entropic forces or changes in viscous forces as particle structure rearrange in layers.\(^{[19]}\) At the beginning of shear thickening, the colloidal particles are driven to exit these layers by hydrodynamic force resulting in the physical contact or clustering between the nanoparticles.\(^{[1,20,21]}\) The contacted particles generate the contact extended network at a high shear rate. After the critical stress, STF0 exhibits discontinuous shear thickening (DST), which shear stress suddenly jumps with increasing shear rate. But STFA exhibits continuous shear thickening (CST), which shear stress smoothly increases (Figure 2B).

3.2 | Impact responses of NR foam pads with STF

Impact absorbing specimens were prepared by impregnating NR foam with the dilatant fluid (30% by volume of the foam specimen). Three types of the specimen were

**FIGURE 1** Cellular morphology of a natural rubber latex foam
compared including neat foam (blank, without STF), foams impregnated with STF0 and STFA. Three-drop tests were made in each specimen with the different positions of the specimen. In this study, the commercial kneepad (D3O) was also considered. Effects of NR foam density (0.098, 0.15, and 0.24 g/cm³) and the STF amount (10, 20, and 30 vol.%) on absorbed force were investigated as seen in Figures 3 and 4, respectively.

Figure 3 shows the effect of different densities of the prepared open cell foam on the average impact responses. The drop-weight (4.96 kg) impact testing was repeated three times on each specimen. The error bars have been plotted using the SD of those results. Considering the first drop, the absorbed force tends to increase by increasing the NR foam density in case of NR with STF. The results show that the performances of NR with STF0 and NR with STFA are insignificant different in case of foam density 0.098 and 0.15 g/cm³. In the case of a foam density 0.098 g/cm³, the absorbed force of NR with STF0 and with STFA are in range of 3800–4400 N and 3600–4300 N, respectively. However, It is found that the energy absorption of the specimen with STFA are higher than one with STF0 considering at foam density of 0.24 g/cm³, with absorbed force 3800–4400 N and 4200–4900 N for NR with STF0 and NR with STFA, respectively. This might be because the STF0 material may be hardly distributed in the foam with a high density as a result of its higher apparent viscosity. A large agglomeration of nanoparticles within the NR foam with STF0 was observed as shown in Figure 5B. Furthermore, the additional chemical in STFA has more interaction with the NR network at the higher foam density. This might promote a higher chance for nanoparticles contact each other.

**FIGURE 2** Rheological analysis for shear thickening fluid (STF) (30 wt% silica particles)

**FIGURE 3** Effect of foam density on absorption efficiency of natural rubber (NR) foam (30 vol% STF)

**FIGURE 4** Effect of STF amount (vol%) on absorption efficiency of natural rubber (NR) foam
other within the fluid. In other words, the STFA has no significant benefit if the foam has too high of void concentration.

Figure 4 shows the effect of different dilatant fluid amount (percentage by volume) on the average impact responses. The NR foams had size of 8 cm × 8 cm × 1.5 cm (Length × Width × Thickness) or total volume of 96 cm³, three different specimens then were impregnated with the fluid (STF0 or STFA) amount of 9.6, 19.2, and 28.8 ml (10, 20, and 30 vol%, respectively). As shown in Table 2, the absorbed force tends to increase by increasing the amount of the dilatant fluid. However, the performances have insignificant differences in cases of 20 and 30 vol% STF. The experimental errors shown in Figure 4 were calculated by using data shown in Table 2. It is found that the errors or SD values were high as the result of wide range of those absorbed forces caused by continuous three drop tests. However, in all cases, the NR with STFA gave higher absorbed forces than NR with STF0.

The SEM micrographs of the neat NR foam, NR foam with STF0, and NR foam with STFA at 250x enlargement are shown in Figure 5. Both fluids can fill the gas and spaces within the foam matrix, Figure 5B,C. During the impact, the impact energy is dissipated throughout the foam matrix by cell-wall bending, buckling, deformation, and collapse. The impact responses of foams strongly depend on initial polymeric foam properties and its relative density. Viscosity and shear thickening efficiency of the nanoparticle-based STFs are influenced by hydrodynamic lubrication forces between nanoparticles. In the case of STF0, lubrication breaks down and frictional forces between particles play an important role for energy absorption capability.

However, STFA was developed to enhance both NR network cross-linking and particle motion. Its impact resistance is improved compared with the rubber foam with the conventional STF0. The silica particles in the specimen with STF0 were obviously agglomerated, Figure 5B, while the nanoparticles distribution of STFA over the foam was well, as seen in Figure 5C, due to much lower fluid viscosity.

3.3 | Comparison to commercial kneepad

In this section, impact responses of kneepad prototypes made from NR foam filled or impregnated with STFA

FIGURE 5 SEM micrographs (250x enlargement) of (A) neat natural rubber (NR) foam with average pore size <200 micron, (B) NR foam with STF0, and (C) NR foam with STFA (30 vol% STF)
were investigated and compared with the commercial kneepad (D3O), Figure 6B. Three commercial impact protective materials have also been compared using their rheological and compression mechanical properties by Reference [14]. The kneepad mold, Figure 6A was made from polylactic acid (PLA) by three-dimensional (3D) printer. “Blank” refers to the NR foam without STF, Figure 6C. “NRF” refers to the NR foam which was filled 20 g of dilatant fluid (or 6.6 vol% of the specimen) into the empty room (space volume of 20 cm$^3$) inside the specimen (the specimen has volume of 230 cm$^3$ and the STFA has density of 1.32 g/cm$^3$). “NRI” refers to the NR foam which was impregnated with 12 vol% fluid throughout the specimen. The rubber compound formula and related processing could not be discussed here since of the patent/petty patent pending.

Impact absorption test was done by using a drop test machine with a free falling impact mass. Initial impact force or energy were 7500 N or 10.3 J. Figure 7 shows the impact responses of four different kneepad specimens. The results show that both specimens made from NR foam with STFA (NRF and NRI) have comparable energy absorption capabilities with the D3O commercial kneepad which has the dilatant behavior. Then, this can be concluded that STFA can be applied to the NR foam by either filling or impregnating techniques.

### 4 | CONCLUSIONS

This research aims to develop an impact absorbing material prepared from NR. The proposed shear thickening fluid (STFA) has been developed in order to improve compatibility, and impact response capability of NR foam. Although maximum apparent viscosity and shear stress of STFA have lower than those of ST0, the impact absorption capability of STFA/NR foam was higher than of STF0/NR foam. The STFA appears low viscosity but the fluid still shows the dilatant behavior. The function

| Samples       | 10 vol% |          | 20 vol% |          | 30 vol% |          |
|---------------|---------|----------|---------|----------|---------|----------|
|               | First   | Second   | Third   | First    | Second  | Third    |
| NR + STF0     | 2650    | 2240     | 2040    | 4080     | 3820    | 3570     |
| NR + STFA     | 3110    | 2500     | 2240    | 4430     | 4080    | 3980     |

**FIGURE 6** Kneepad prototypes with thickness 3 cm (A) kneepad mold, (B) Commercial kneepad (D3O) ($\approx 0.41$ g/cm$^3$)$^{[14]}$ and (C) Kneepad made from NR ($\approx 0.4$ g/cm$^3$)

**FIGURE 7** Impact responses of kneepad prototypes
of the additional chemical in STFA is to interact with the matrix network of the NR foam, and to promote higher chance for nanoparticles to contact each other within the fluid when compared with STF0. Drop test results also show that the STFA can improve the impact responses of the NR foam providing comparable results with the commercial kneepad which has dilatant behavior. The main advantages of the proposed material are an environmentally friendly renewable material. In addition, it can be produced with comparable impact absorbing properties at significantly lower cost than the available commercial dilatant-behavior material, since it is made from NR which is the main products of THAILAND.

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