

Article

Shear-Thickening Composites for On-Demand Rebound Performance and Softness

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Abstract: For footwear insoles, high rebound performance is required in some instances such as for running, while softness for comfort is of higher importance during normal walking and standing to minimize high stress. Hence, materials with rebound performance in some scenarios and softness for other scenarios are desired. In this paper, we investigate rebound performance and hardness of composites made of a shear-thickening material and elastic foam. First, a hydrogel type of shear-thickening material (Slime) is characterized to investigate the influence of water content. After that, two particular shear-thickening hydrogels with better rebound performance (but not outstanding in the shear-thickening effect) are selected and integrated into the elastic foam to produce a composite insole. It is found that, as compared with the commercial elastic insole and commercial shear-thickening insole, softer and superior rebound performance can be achieved simultaneously only if the right shear-thickening material is used in the composite.

Keywords: shear-thickening effect; hydrogel; rebound performance; sole; insole; ethylene-vinyl acetate; energy recovery; energy recovery ratio

1. Introduction

Footwear serves as an essential garment designed to protect our feet from environmental adversities such as ground textures and temperature variation. Considering the unique shape of feet among individuals, podiatry seeks to adopt techniques to help increase comfort for users ranging from casual to performance orientated. The insole and lining are components of footwear directly in contact with the foot and they are crucial for providing the user comfort. Amongst various footwear designs available on the market, insoles are one component that can be customized to the individual's foot requirements. Aside from tailoring the shape of insoles for comfort enhancement, materials are influential for providing comfort for casual or performance use. Insoles that are material optimized possess the potential to fulfill performance-based demands with high rebound requirements or casual-based demands with softness needs.

Stimulus-responsive materials possess the inherent capability of changing their properties/shapes in the presence of the proper stimulus [1]. Certain unique fluids, classified as non-Newtonian fluids, can dramatically increase their viscosity with an increase in shear rate, with the phenomenon known as the shear-thickening effect. Many engineering applications based on this phenomenon have been identified and explored in previous studies [2–7].

Solid or quasi-solid shear-thickening materials/composites have been developed considering Newtonian fluids, which tend to flow easily and could be problematic in certain engineering applications [8,9]. D3O[®], which was invented by Phil Green and Richard Palmer in 1999, has probably been the most successful commercial shear-thickening product thus far [9]. This type of shear-thickening

material has been studied to be suitable for implementation as footwear insoles such as Enertor™ from the D3O Lab, as shown in Figure 1a, or as midsoles such as TAICHI 1.0 from the Peak Sport Products Co. Limited, since it is soft during low strain rates (e.g., walking) but instantly becomes much stiffer under impact loading (e.g., running) to provide high rebound force. While both of the above-mentioned are gum-like materials to the touch, MemorySil™ from adaptive rubber LLC is a rubber-like material.

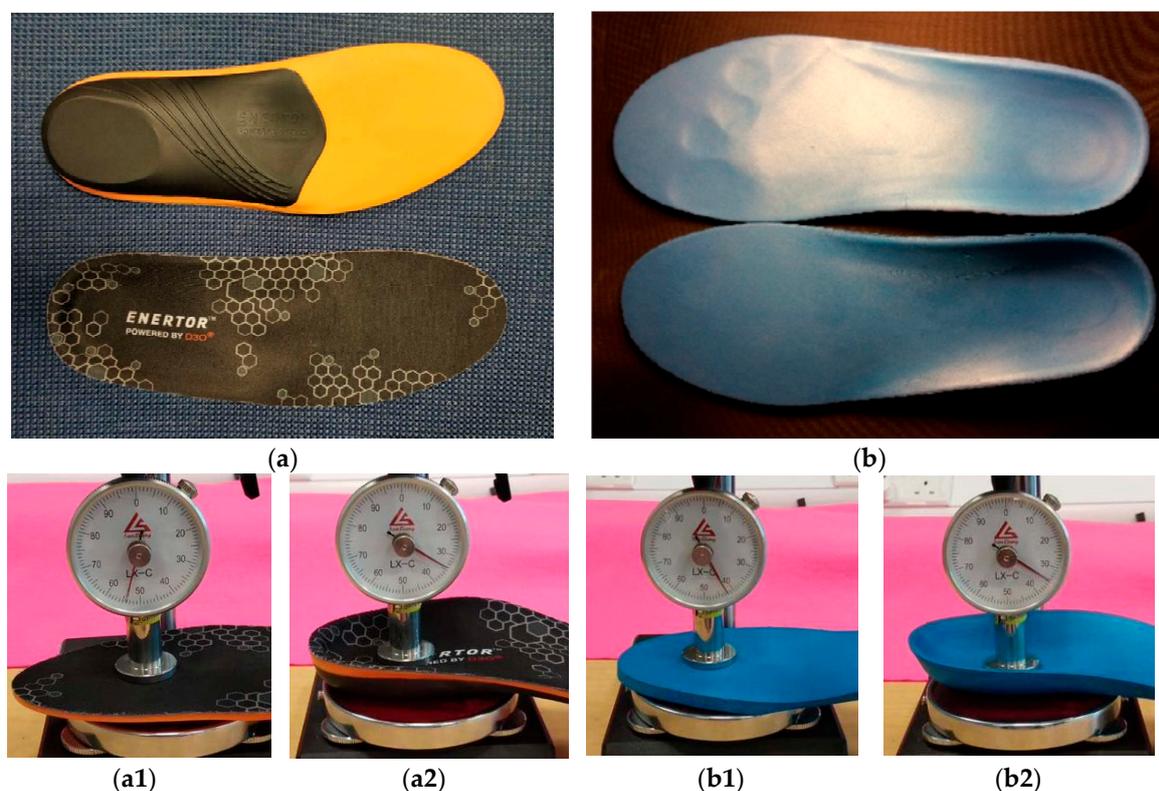


Figure 1. (a) Enertor™ D3O® insole (bottom side (the back is composite) and top side). Shore hardness (measured from top) 55C (forefoot area) (a1) and 37C (heel area) (a2); (b) Commercial ethylene-vinyl acetate (EVA) insole (uniform foam, (bottom) original and (top) after heating and stepping atop to fit/program) (reproduced from [10]). Shore hardness (measured from top) 42C (forefoot area) (b1) and 35C (heel area) (b2) (slight difference between the forefoot and heel should be due to the bottom of the heel is not a flat surface as the forefoot).

Enertor™, as shown in Figure 1a, is essentially a closed-cell polyurethane foam composite, in which polyborodimethylsiloxane (PBDMS) is dispersed through the foam matrix to provide the shear-thickening function [9]. Since ethylene-vinyl acetate (EVA) is preferred to polyurethane by the footwear industry (Figure 1b), TAICHI 1.0 is developed to utilize an EVA-based foam with another shear-thickening material involving P4U (brand name, from Shenzhen Suer Intelligent New Material Technology Co., Ltd., Shenzhen, China) used as a PBDMS replacement in the foam composite [11]. As compared with a typical commercial EVA insole, shown in Figure 1b, Enertor™, shown in Figure 1a, has a higher shore hardness durometer of 55C against 42C for commercial EVA at the insole's forefoot area (Figure 1a1,a2,b1,b2).

Additionally, some solution-state thermoplastic polymers or their composites and insufficiently cross-linked solid-state thermoset polymers possess a similar shear-thickening feature, but the shear-thickening effect is insignificant [12].

This paper intends to serve a two-fold purpose. First, an experimental investigation on the influence of water content in a particular shear-thickening hydrogel (Slime, refer to Section 2.1 for its details), in which the weight ratio between borax and polyvinyl alcohol (PVA) is fixed. Hydrogels with superior

rebound performance are identified via experimentally determined energy recovery ratio. This study adopts the use of Slime due to its easy accessibility and convenience to tailor its mechanical properties such as hardness and viscosity via manipulating only the water content. While the Slime is sensitive to water/moisture, and thus not ideal in many real applications without proper seal design, it shares most of the shear-thickening characteristics present in other shear-thickening materials. Secondly, two types of hydrogels with better rebound performance are identified and integrated into a commercially produced EVA insole to produce a shear-thickening composite. Subsequently, the composite insole rebound performance of the forefoot and heel is compared with the original EVA insole and a commercial shear-thickening insole (Enertor™). A few conclusions are obtained based on the experimental results.

2. Shear-Thickening Hydrogel (Slime): Fabrication and Characterization

2.1. Materials and Experimental

Slime (also called Flubber) refers to a particular borax hydrogel formed by crosslinking of PVA with a boron compound in water [13,14]. Slimes containing higher water content with a consistency similar to chum gum can flow under gravitational force and “self-heal”. Furthermore, it displays soft and ductile behavior and is easy to deform under low-speed stretching, however, upon high-speed stretching, it tends to display hard and brittle behavior and fracture at a small strain. The observed shear-thickening effect is more apparent when the water content is relatively higher. With a decrease in water content, Slime becomes increasingly difficult to flow under the gravitational force. Similar to many hydrogels, dried Slime intrinsically has the heating and water/moisture responsive shape memory effect (SME), i.e., it is able to recover its original shape only if a particular stimulus (e.g., heat and/or water/moisture) is applied [15–17]. The SME in a piece of dried Slime is demonstrated in Figure 2, in which (a) to (c) demonstrates the heating-responsive shape recovery in the first round of shape memory cycle, and (c) to (e) reveals the water/moisture-induced shape recovery in the second round of shape memory cycle.

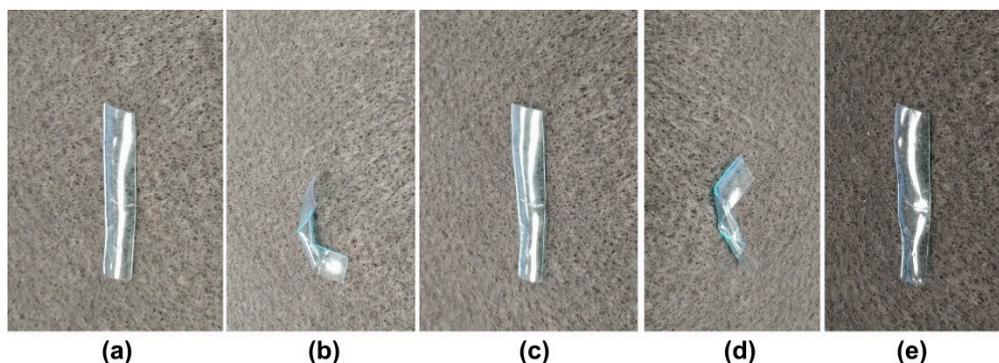


Figure 2. Shape memory effect (SME) in dried Slime. (a) Dried Slime; (b) After heating and twisting; (c) After heating for shape recovery; (d) After a second round of heating and twisting; (e) After wetting by water droplet, and then drying in air.

Here, Elmer’s clear glue was utilized for PVA and 20 Mule Team Borax Detergent Booster for borax. The inclusion of additional chemicals in these commercial products were meant to fine-tune certain performance characteristics for the targeted functions of these commercial products and not necessarily intended for the borax hydrogel investigated. Local tap water in Singapore was used without any further treatment. Seven different types of samples were prepared. In this study, the weight ratio between borax and PVA glue was kept as 7:10, while the amount of tap water varied from 10% to 70% in weight percentage. Herein, unless otherwise stated, the water content in % is meant for tap water in wt%. Refer to Table 1 for the ingredients for 500 g of each type of sample.

Table 1. Ingredients of seven types of samples (for 500 g).

Sample No.	Water (wt%)	Borax (g)	PVA Glue (g)	Tap Water (g)
1	10	185.3	264.7	50
2	20	164.7	235.3	100
3	30	144.4	205.9	150
4	40	123.5	176.5	200
5	50	102.9	147.1	250
6	60	82.4	117.6	300
7	70	61.8	88.2	350

For the preparation of hydrogel samples, first, the measured amount of borax was mixed with the required amount of tap water, and then stirred for good dissolving. Then, the predetermined amount of PVA glue was added to the mixture. The mixture was further stirred and rolled, if necessary, for one hour to ensure good homogeneity. Then, the resulted hydrogel was aged at a room temperature of about 20 °C and an atmospheric pressure of 758.00 mmHg, for 24 h, in dark, enclosed and sealed conditions to release the residual stress and to enhance homogeneity. Hydrogel samples of two geometrical dimensions, i.e., cylindrical (diameter 68 mm and height 20 mm) and in blocks (104 × 104 mm, 36 mm thick), were prepared and used for characterization.

For non-Newtonian fluids, their flow properties cannot be described by a single constant viscosity. For this hydrogel, when shear stress is applied, it thickens and becomes more viscous. The time taken for a 9.6 mm diameter steel ball (weight 4 g and density 7.8 g/cm³) to sink from the surface to the base (20 mm) of the hydrogel was measured using a digital stopwatch. Viscosity (η) was calculated according to [2] as:

$$\eta = \frac{2gr^2(\rho_2 - \rho_1)\left(1 - \frac{r}{R}\right)^{2.25}}{9v} \quad (1)$$

where g is 9.81 m/s², ρ_1 is the density of hydrogel, ρ_2 is the density of the sphere (7.8 g/cm³), v is the falling time over the fixed distance of 20 mm, r is the radius of the steel ball (4.8 mm), and R is the radius of the cylindrical hydrogel sample (34 mm).

Only the cylindrical samples with 50% tap water content or more were tested. For the hydrogels with less water content, i.e., 10% to 40% tap water, they were able to retain their shapes under gravitational force for long periods, and it would take a very long time for the ball to sink by using its weight. Thus, block-shaped samples of these hydrogels were tested for their stress versus strain relationship under quasi-static uniaxial compression. They were loaded with a deadweight of 250 g in the first loading step, and then the load was gradually increased with an increment of 100 g in each following step. Unloading was applied after about 1950 g was reached. The height change was recorded immediately after the required load was reached.

For the rebound test to evaluate the energy recovery, a 36 mm diameter spherical steel ball (weight 23 g) was dropped from a height of 100 cm onto the surface of the block-shaped samples. The rebound height (h) was measured from the highest point achieved by the sphere's lower surface from the first rebound. Thus, energy recovery ratio (in %) can be calculated according to Equation (2):

$$\text{Energy recovery ratio} = \frac{\text{Rebound height}}{\text{Drop height}} \times 100\% \quad (2)$$

where the drop height is 100 cm.

While a higher rebound height value suggests better energy recovery, the shear-thickening effect is meant for shear-induced significant strengthening, i.e., a striking increase in hardness. Except for the

loading/unloading tests, all other experiments were repeated a few times. Herein, the stress and strain are meant for the engineering stress and engineering strain.

2.2. Results and Analysis

In Figure 3, the relationship between the time to sink and water content of the hydrogels with 50%, 60%, and 70% tap water content are plotted. The results are consistent as the error bar is very small. Within the tap water content range 50%–70%, the sink time decreases rapidly, from about 22 min to less than one min. Subsequently, in Figure 4, the relationship between viscosity and tap water content is presented, which essentially shares the same trend as that of the relationship between the time to sink and water content in Figure 3. The drop in viscosity is about 50 times, from 16,115 to 334 Pa.s, when the tap water content is increased from 50% to 70%.

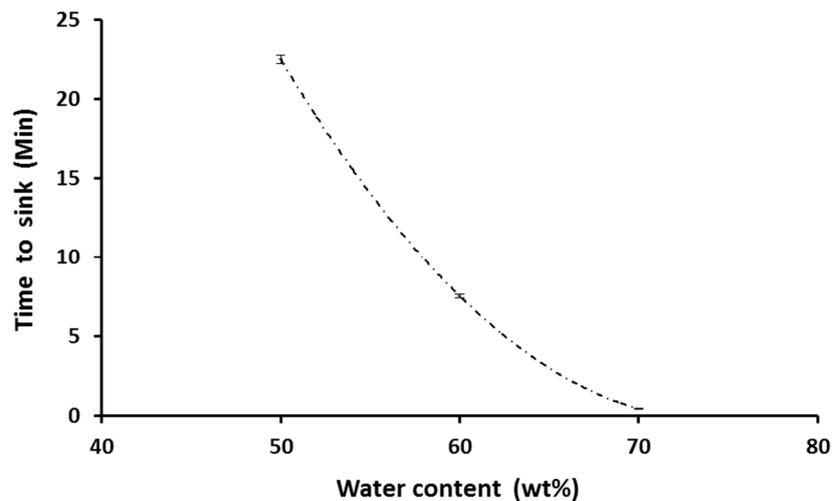


Figure 3. Influence of tap water content (in wt%) on steel ball sinking time.

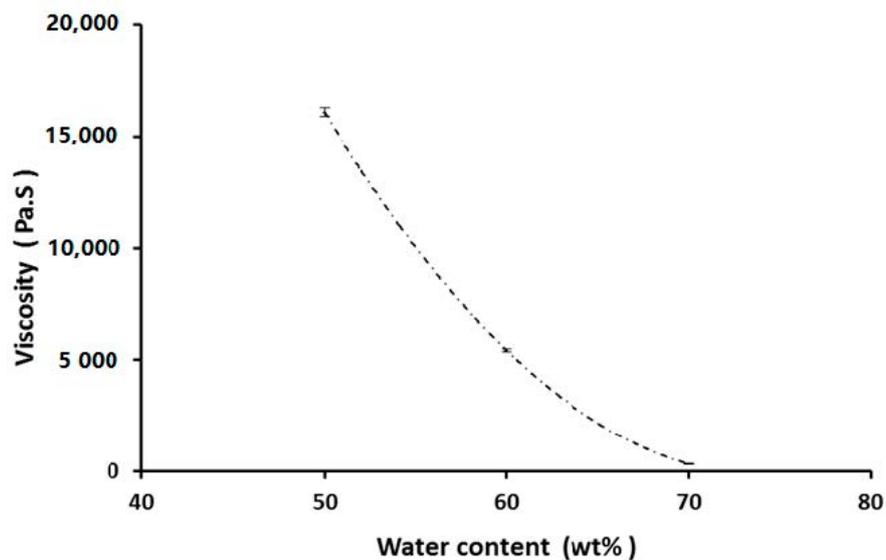


Figure 4. Influence of tap water content (wt%) on the viscosity of hydrogels.

Figure 5 (left) presents the stress versus strain relationship in loading/unloading in a step-by-step manner (quasi-static) for the hydrogels with a tap water content from 10% to 40%. It is apparent that these hydrogels are much softer than normal commercial EVA insoles [18], and with an increase in water content, the hydrogel softens under uniaxial compression (Figure 5, right).

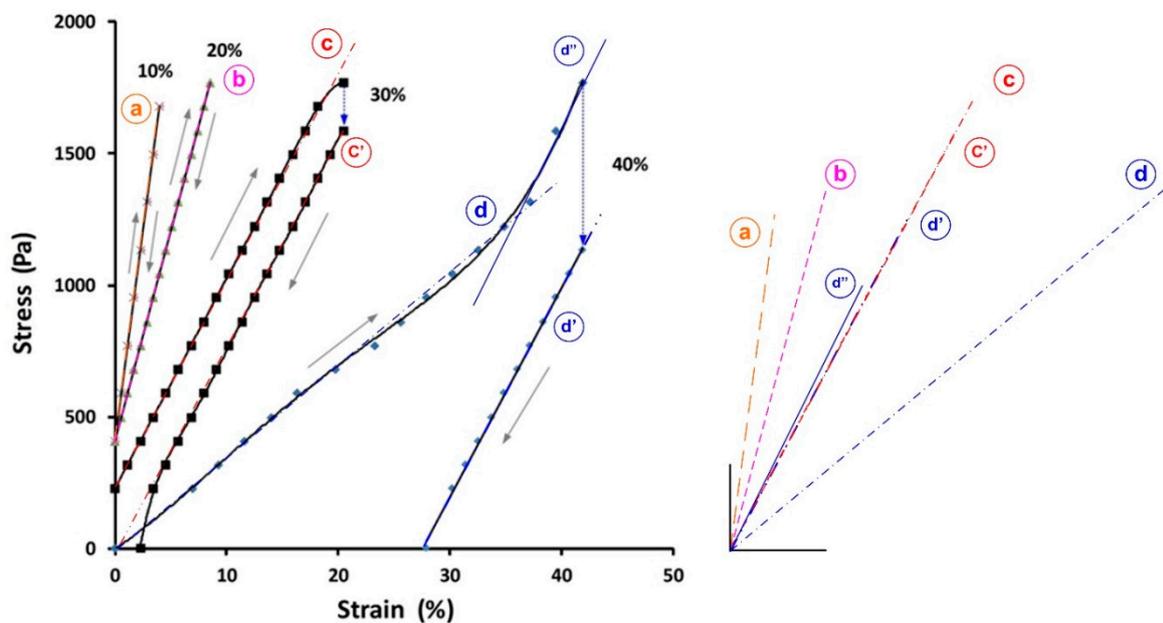


Figure 5. Stress versus strain relationships in a loading/unloading cycle (in a quasi-static manner) (left) (black lines are data fitting of the slopes) and comparison of the slopes in loading/unloading (right).

The hydrogels with 10% and 20% tap water content appear to be highly linear elastic after the applied load is over a limit. Before this limit is reached, the strain is negligible. It is also noticed that cracks tend to appear in these hydrogels, and these cracks cannot be easily self-healed.

For the hydrogel with 30% tap water, this limit is found at a lower compressive stress level. Upon further loading, the stress versus strain curve appears to be linear until in the last loading step, where apparent softening appears. In the following process of unloading from about 20% strain, which is reached at the maximum load, the stress versus strain relationship is linear until the applied load is fully removed in the last unloading step. A small amount of residual strain is observed, and a small gap between the loading and unloading curves is also observed. The slopes in loading (c) and unloading (c') are about the same (refer to Figure 5, right). It appears that in the early unloading stage, the strain largely remains the same. It suggests a kind of friction-like energy dissipation inside of the material.

The hydrogel with 40% tap water starts to deform from the beginning of loading in a quasi-linear manner, and hardening starts from about 35% strain. In the unloading process, there is no apparent change in strain at the beginning, which is the same as that in the hydrogel with 30% tap water, but this unloading range is much larger in this hydrogel. The later unloading curve is more or less linear, and a significant amount of residual strain is observed. The comparison of the slopes in unloading shows that the hydrogels with 30% tap water and 40% tap water are about the same.

It can be concluded that, with the increase in water content, the hydrogel changes from hard and elastic to soft and viscous. The gap between loading and unloading curves, which indicates a kind of energy dissipation, increases with an increase in water content. If the tap water content is 50% or more, referring to the relationship between the sinking time and water content in Figure 3, “plastic” flow becomes more and more dominant.

The decrease in the load limit to initiate remarkable deformation upon compression appears to be associated with the water content. The hydrogen bonding between the borate ions and PVA chains may be weakened with an increase in water content, so that internal sliding starts at a lower stress level and the hydrogel appears to be softer. However, once over compressed, strain hardening occurs. It suggests that with a decrease in water content, the hydrogel becomes similar to Bingham fluid [12]. The hardened hydrogel does not soften upon unloading, which results in remarkable residual strain in the hydrogel with 40% tap water.

The energy recovery ratio (in %) as a function of tap water content is plotted in Figure 6. For the particular setup in the current rebound test, the maximum energy recovery, about 30%, seemingly appears in the hydrogels with about 20% tap water content. As mentioned above, with an increase in water content, the response of the hydrogel shifts from hard and elastic to soft and viscous. While the shear-thickening effect is meant for significant hardening under impact loading, which appears to be more apparent in these hydrogels with more water, in terms of energy recovery measured by the rebound performance, relatively harder hydrogels (i.e., with less water), but still much softer than the EVA sole, appear to be better. Hence, for the intended application of this study, we should select the shear-thickening materials that have better rebound performance, instead of remarkable shear-thickening effect.

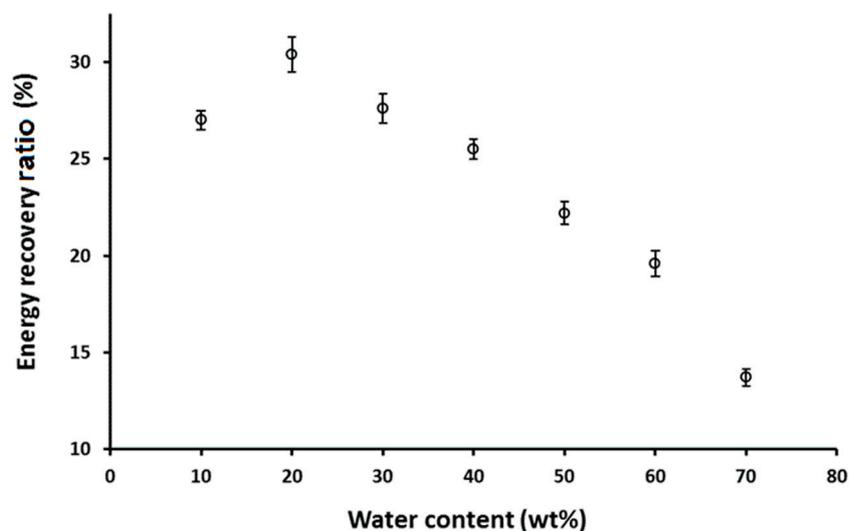


Figure 6. Energy recovery ratio (in %) as a function of tap water content (in wt%).

2.3. Shear-Thickening Composites

Hydrogels with a 25% and 37% water content were employed in the investigation of integration with EVA insoles and were prepared in the same approach as mentioned in Section 2.1. These two samples were selected for further testing since harder hydrogels with 20% water content or less tend to crack upon compression, which has self-healing difficulties due to low water content while softer hydrogels with 40% water content or more possess unsatisfactory energy recovery even with a striking change in hardness against impacts.

Figure 7a shows the shape and dimensions of the designed insole. The insole is designed to have a surrounding ring of EVA, which can be trimmed to tailor-fit various foot sizes and shapes or bent around the foot curvature to form a foam cage within the shoe lining and provide enhanced protection. There is 10 mm diameter through holes at the insole middle area to enable unconstrained stretching at high temperatures for exploiting the SME properties of EVA to achieve comfort fitting purposes [18,19]. Figure 7b shows an as-fabricated elastic EVA sole produced by Dong Guan Bid Ace Co. Ltd. with the density of the fabricated EVA sole at about 105 kg/m^3 . Since the density of EVA is between 926 and 950 kg/m^3 , the porosity ratio of the EVA sole is about 90%. The Shore hardness for the insole's forefoot area is measured to be around 45C while the heel area is about 50C.

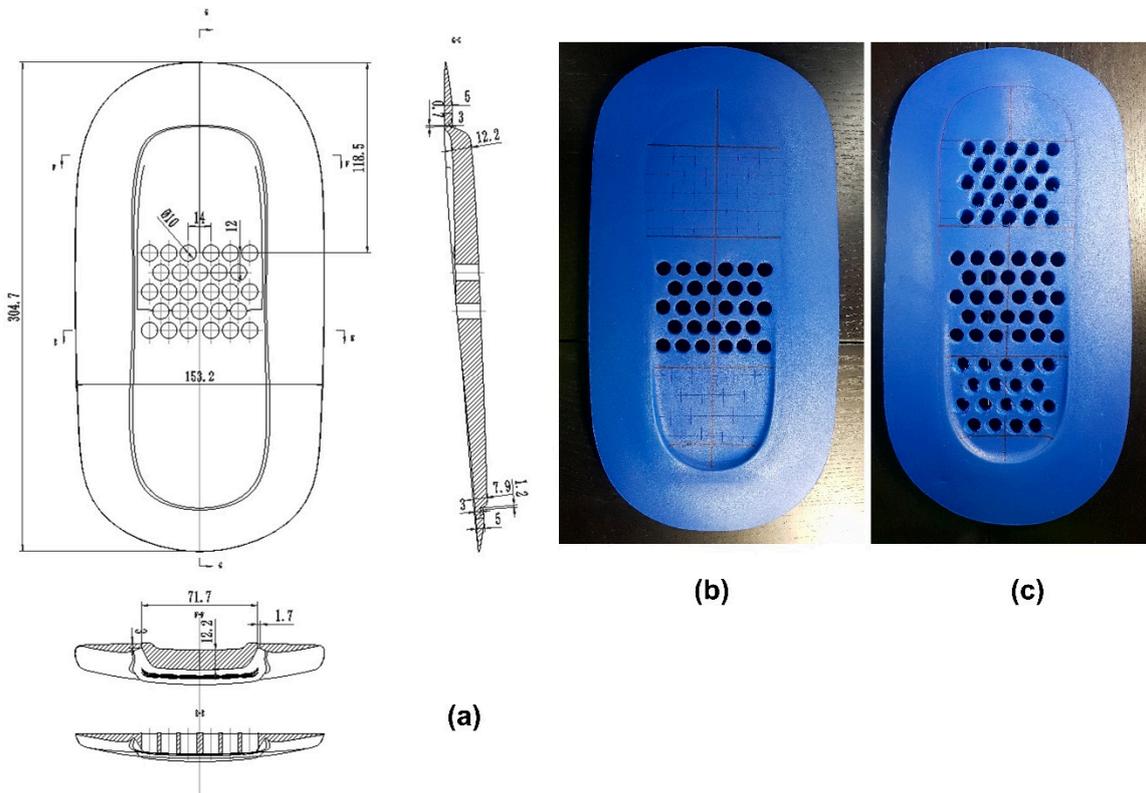


Figure 7. The EVA insole. (a) Details of insole design; (b) As-fabricated sole. Shore hardness is 45C for the forefoot area and 50C for the heel area; (c) After modification with additional 10 mm diameter holes (for filling of shear-thickening hydrogel).

Without the surrounding ring, as shown in Figure 8, the middle portion of the insole with an array of holes can be easily stretched at around 55 °C, which is the glass transition temperature of the EVA material. After cooling the insole back to room temperature, the length of the middle area increases from 60 to 75 mm. The length extension of the insole can be mostly remedied upon heating to above 55 °C, again using a hair dryer [18]. Additional 10 mm diameter through holes at the insole forefoot and heel areas were produced by drilling to fill the hydrogel material, as shown in Figure 7c for the location of the holes.

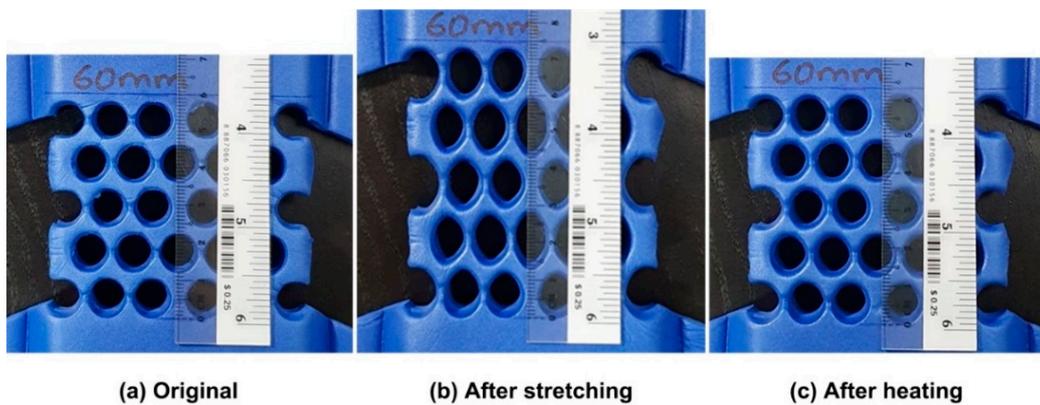


Figure 8. SME (enlarged view of the insole middle area with an array of holes and surrounding ring removed). (a) Original; (b) After heating and stretching; (c) After heating for shape recovery.

The drilled holes within the insole were filled with Slime hydrogel and a two-dimensional (2D) highly stretchable elastic cloth was used to cover the top and bottom surfaces of the insole to securely house the hydrogel inside. Two insole samples were manufactured for further testing, which involved the utilization of 25% and 37% water content Slime hydrogel. Figure 9 shows the stress versus strain relationships of the 2D elastic cloth in uniaxial stretching along two directions on the cloth surface. One side of the elastic cloth was coated with a very thin layer of commercial thermoplastic polyurethane TPU 265 which worked as melting glue to firmly bond the elastic cloth and EVA insole together, while preventing the hydrogel from leaking through the elastic cloth and water in the hydrogel from evaporation [20].

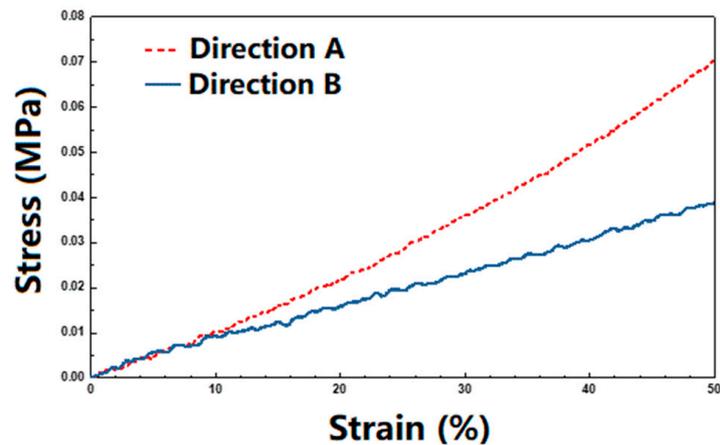


Figure 9. Typical stress versus strain relationships of 1 mm thick commercial two-dimensional (2D) elastic cloth in uniaxial tension along two directions at a strain rate of $10^{-3}/s$.

Figure 10 presents the top view of the two modified EVA insoles, where the surrounding rings were partially cut out such that the residual flaps can easily fold up to bond with the shoe upper in the next development stage of shape memory shoes. Since the standalone hydrogel is much softer than the EVA insole (refer to [18] for the mechanical behavior of typical EVA insole), the modified EVA hybrid insole integrated with hydrogel is expected to be softer than the original EVA sole.

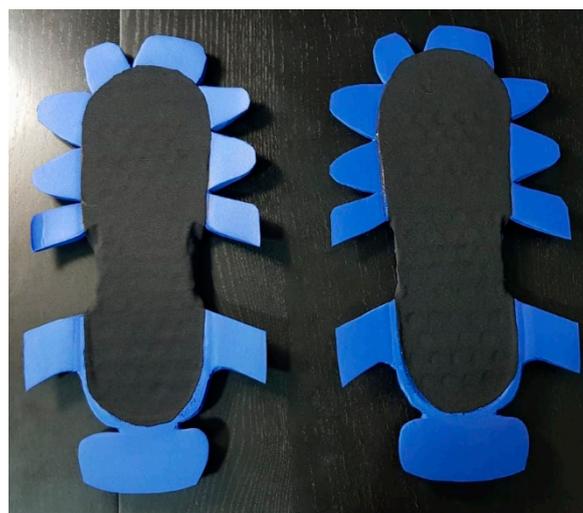


Figure 10. Modified EVA soles with surrounding ring partially removed.

2.4. Rebound Performance and Comparison

The setup of the rebound performance test is illustrated in Figure 11. The tested insole was firmly stuck to the ground using a strong double-sided tape with a piece of ruler vertically placed near the tested insole. A video camera was used to record the whole process including the release of cylinder mass onto the test insole and the subsequent rebounds. A stainless-steel cylinder mass weighing 222.4 g of 30 mm diameter and 40 mm length was released from a distance H of approximately 300 mm above the top surface of the insole to hit the forefoot or heel area. Since the 30 mm diameter of the cylinder mass is far larger than the 10 mm diameter of the drilled holes, the contact area for a normal direction impact consists of one or more hydrogel filled holes and the enclosing EVA material when the bottom surface of the cylinder mass impacts the top surface of the modified EVA insole. The maximum rebound height H' was obtained from the video recording via frame-by-frame analysis of the cylinder mass trajectory. Since a variation of falling trajectories is expected, only the results of tests in which the bottom side of the steel cylinder vertically hit the top surface of the sole are valid and included in the analysis.

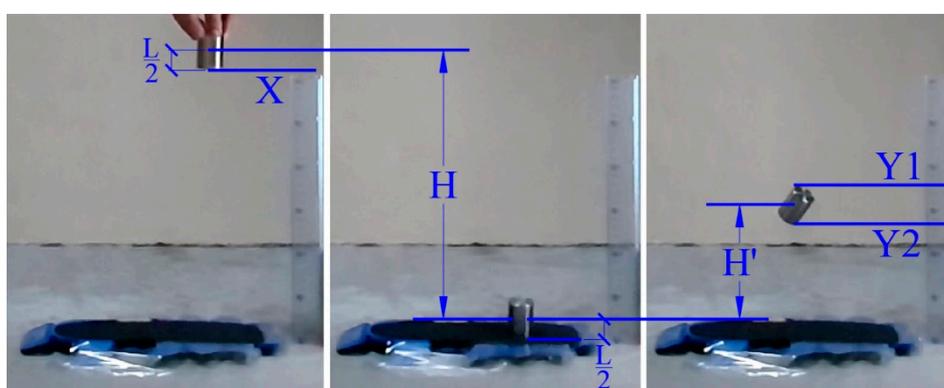


Figure 11. Illustration of rebound test. (Left) Pre-release of cylindrical steel mass; (middle) Normal direction impact; (right) At maximum rebound height.

The energy recovery ratio (in %) is calculated by,

$$\text{Energy recovery ratio} = \frac{H'}{H} \times 100\%. \quad (3)$$

In addition to the original EVA insole and two modified insoles containing 25% and 37% water content hydrogels, respectively, a commercial shear-thickening insole Enerator™ from D3O Lab, as shown in Figure 1, was also tested for comparison.

In Figure 12, the energy recovery ratios (in %) of the original EVA insole, EVA modified insoles with two types of hydrogels containing 25% and 37% water content, and D3O insole are compared for both the forefoot and heel areas. For the testing conditions applied in the current investigation, the rebound performance of EVA modified insole with hydrogel (25%) is outstanding among all the tested materials. The average energy recovery ratio for both its forefoot and heel area is over 40%, well above that of the original EVA sole, EVA sole modified with hydrogel (37%), and D3O insole. Regarding Figure 6, the rebound performance of the EVA modified insole with hydrogel (25%) is superior to the pure hydrogel, whose rebound performance was at best 30%. Comparing between the original EVA insole and the D3O insole, it can be observed that the rebound performance of the original EVA insole forefoot area outperforms that of the D3O insole, but its heel area rebound performance is inferior to the D3O insole. After applying modification with a hydrogel of 37% water content, the rebound performance of the forefoot area slightly declines but still outperforms the D3O insole, while the rebound performance of the heel area has significant improvements, and therefore is superior

to the D3O insole. It suggests the importance of shear-thickening material selection with optimized compositions tailored to achieve the best performance for the composite.

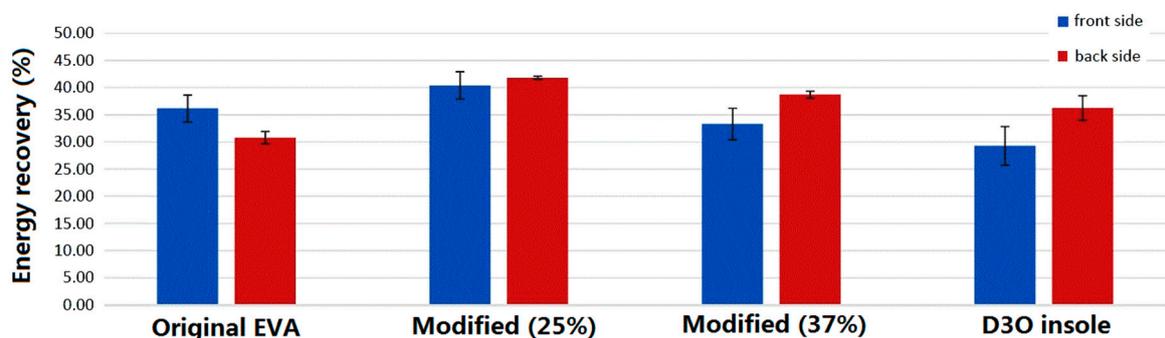


Figure 12. Comparison of energy recovery ratio (in %) in blue for forefoot area and red for heel area.

With the current approach of modification via filling of holes with shear-thickening hydrogel, the modified EVA insole with shear-thickening composite is softer than the original EVA sole and is mostly able to keep the original elasticity under slow speed loading. However, the partial replacement of EVA foam with hydrogel is at the expense of increased weight. Furthermore, it is problematic to preserve the water content in hydrogel, and hence there could be longevity concerns for the insole application despite potential performance advantages. Commercial shear-thickening insoles, such as TAICHI 1.0 and EnertorTM, are foam composites with high porosity ratios, and the embedded shear-thickening materials are not sensitive to water/moisture. Despite these challenges that could be explored in future studies, the experimental investigation reported here demonstrates that the energy recovery ratio is the key parameter in the selection of the shear-thickening material to achieve enhanced rebound performance of the composite that outperforms the elastic foam and shear-thickening material, while being softer than the elastic foam.

3. Conclusions

The influence of water content is investigated in a shear-thickening hydrogel, namely Slime. It was found that hydrogels with higher water content have a striking shear-thickening effect, while hydrogels with relatively lower water content have better energy recovery, which is very important in this application, and still have the capability of self-healing. With a decrease in water content, the hydrogel becomes a kind of Bingham fluid. Although it is revealed experimentally via the rebound experiment under defined testing conditions, the trend should be generic. This study provides guidelines for the selection of non-hydrogel shear-thickening material to replace Slime in the next step.

Two types of shear-thickening hydrogels with 25 wt% and 37 wt% water content experimentally determined to possess superior energy recovery were selected to modify a commercially produced elastic EVA insole to become shear-thickening composites. We found under the particular testing conditions applied in the rebound experiment, that the EVA insole modified with a hydrogel containing 25% water content was outstanding in terms of rebound performance and was superior to the original EVA insole, EVA insole modified with a hydrogel containing 37% water content, commercial D3O insole, and even the hydrogel itself. While the shear-thickening effect of hydrogel containing 25% water content does not appear striking, its capability in energy recovery is excellent, while being still softer than the EVA insole. It appears that higher energy recovery ratio, but not the striking shear-thickening effect, is the important parameter to ensure the best rebound performance of the composites. The particular structure of the shear-thickening composite might be an additional reason for its better performance than that of the commercial D3O insole. Further investigation is required for verification.

This study successfully demonstrates that softer and better rebound performance can be achieved simultaneously in shear-thickening composites, only if the right shear-thickening material is selected.

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