Evaluation of silica aerogel-reinforced polyurethane foams for footwear applications

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Abstract

In this work, a simple way to create a nano-cellular structure within polyurethane (PU) foam was developed by the incorporation of silica aerogels, and the resultant foams were evaluated for footwear applications. To protect the brittle aerogels from breakage, the softness of PU foams was first tailored by changing the ratio of glycerol and polypropylene glycol (PPG). Different amounts of silica aerogels (0−15 wt%) were then loaded into a selected PU foam and analyzed in terms of compressive mechanical properties, shock attenuation performance, and thermal insulation. After incorporation of the aerogels, the compressive modulus, the compressive stress, and the deformation recovery of the foams improved, while the excellent flexibility was preserved. For simulated gait experiments, the shock attenuation capability of the foams was shown to increase with an increase in the aerogel content. These findings can probably be attributed to the improved elasticity of the solid phase and the changed morphology of the gaseous phase as observed from the SEM images. Moreover, the thermal insulation of the developed foams was also investigated, showing an increased trend with the aerogel content.

Keywords: polyurethane foam, silica aerogel, nano-cellular structure, shock attenuation, thermal insulation

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1. Introduction

A main challenge facing manufacturers in the current footwear industry is to improve footwear comfort, which is technically dependent on the combination of several factors, namely good fit, low weight, body protection, long-term durability, and internal thermal environments [1]. Wearing comfortable shoes can not only improve performance but also prevent injuries during human activities, such as running and jumping.

Based on the above considerations, elastomeric foams are usually used in footwear applications since they are lightweight, recover large deformations, absorb shock, and have excellent thermal insulation [2-4]. Brodsky [4] evaluated five different materials for footwear manufacture and found that the flexible foam materials exhibited good cushioning properties and pressure distribution, among which polyurethane (PU) foam performed best in pressure relief. However, the relatively short useful life of PU foams limits their application in the footwear field. Compared with PU elastomers, PU foams initially provide a better cushioning performance, but tend to deform gradually. After long-term use, the elastomers showed a slight loss in shock attenuation, whereas a considerable reduction was observed for the foams [5, 6]. In order to achieve good shock attenuation performance in footwear applications, good shock attenuation should be combined with elasticity and resistance to fatigue. For this reason, one design was developed that consisted of two layers: a PU elastomer layer and a PU foam layer [7]. The former provided mechanical properties to be resistant to compression, but it was heavier and harder than foams; the latter felt soft to foot contact and gave good shock attenuation. Nevertheless, the issue of the poor durability of PU foams is still not solved completely. There is a need to develop new PU foams that have the mechanical properties of a PU elastomer without compromising other properties, e.g. flexibility, cushioning property, thermal insulation, etc.

Another important factor for foot comfort is the thermal insulation of footwear. To a great extent, the thermal insulation of footwear is dependent on the volume of the air trapped inside. Therefore, many foam materials have been used as thermal insulators to take advantage of the excellent insulation feature of the air or other gases [8]. It was reported that some of the foam materials possessed comparable or slightly higher values in thermal conductivity compared to the gases, such as 0.04 W m^{-1} K^{-1} for polystyrene

foams and 0.03 W m^{-1} K^{-1} for rigid PU foams [9, 10]. However, if the internal cell size is reduced to the nano level, the foams will have a lower thermal conductivity than the relevant gas, due to the Knudsen effect that the heat conduction is restricted through the gaseous phase [11]. Potentially, these nano-cellular foams can be used as thermal insulators as their thermal insulation is better than existing insulation devices. Although many efforts have been made in optimizing the fabrication process of foams to decrease the cell size and increase the cell density, access to such nano-cellular structures via traditional ways is still complicated [12-14].

Silica aerogels are a class of nanoporous materials that exhibit many unique and favorable properties like high surface area, low density, low sound velocity, non-flammable, and high thermal insulation [15-17]. Kraner Zrim et al. [18] prepared the laminated silica aerogel fibrous matting composite and evaluated its suitability for protective footwear applications. Unfortunately, this study only investigated the thermal insulation and water vapor permeability of the composites. Since both the mechanical properties and the thermal insulation of the foams greatly depend on their cellular structures [19-21], in this work, nano-cellular structures were created inside the PU foams by the introduction of silica aerogels, with an aim of improving mechanical properties, cushion performance as well as thermal insulation. As shown in Fig. 1(a), the PU foams were fabricated using isophorone diisocyanate (IPDI), glycerol, polypropylene glycol (PPG), and water. In order to avoid too hard or too soft products with no shock attenuation, the flexibility of the PU foams was first tuned by controlling the ratio of the soft segment to the hard segment. Subsequently, an appropriate foam was selected and reinforced by silica aerogels, resulting in the introduction of nano-cellular structures (Fig. 1(b)). Based on the requirements for the footwear materials such as good mechanical properties, body protection against impact and cold environment, low shape change, and light weight [1], the feasibility of using the resultant foams for footwear applications were analyzed in terms of mechanical properties, shock attenuation, and thermal insulation.

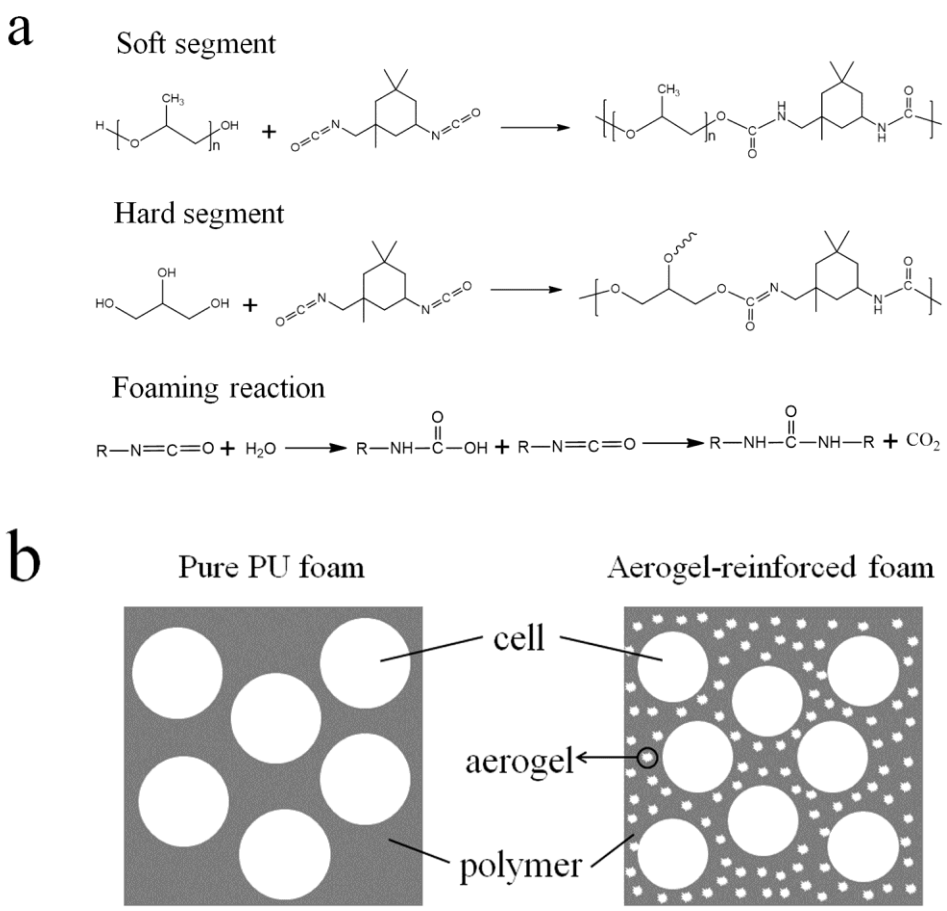

Fig. 1. (a) Reaction scheme of PU foams and (b) schematic structures of pure PU foam and aerogel-reinforced foam.

2. Materials and methods

2.1. Materials

Glycerol, PPG (average M_w = ~1000), and tin(II) 2-ethylhexanoate were purchased from Sigma-Aldrich (USA). Niax silicone L−580 was purchased from Momentive Performance Materials (USA). Isophorone diisocyanate (IPDI) was purchased from Tokyo Chemical Industry (Japan). Silica aerogel powder (particle size: 1−20 μm and pore diameter: 20 nm) was obtained from JIOS Aerogel (USA). All chemicals were used as received.

2.2. Fabrication of polyurethane foams

Polyurethane foams were fabricated via a one-shot method according to the formulation listed in Table 1, in which each component amount was calculated based on one hundred parts of polyol by weight. The desired softness of the PU foams was achieved by controlling the PPG content, and an appropriate foam was then selected to evaluate the reinforcement effect of silica aerogels. The predetermined amounts of glycerol and PPG were mixed at different ratios to provide hydroxyl groups of 100:0, 80:20, 60:40, 40:60, and 20:80, followed by the addition of the surfactant (Niax silicone L−580), the blowing agent (distilled water), the catalyst (tin(II) 2-ethylhexanoate), and the filler (silica aerogel powder). Subsequently, the corresponding parts of IPDI (the NCO index was fixed at 1) were added and stirred for another 1 min at room temperature. Finally, the resultant mixture was immediately poured into a cubic open mould that was preheated to 50°C and allowed to foam for 5 min. The obtained PU foams were placed at room temperature for 48 h for further curing. The foams were named according to the number of OH groups from the glycerol and the PPG. For example, the sample PU40−60 represented 40% OH groups from glycerol and 60% OH groups from PPG.

Table 1. Formulation of the PU foams

Component	Role	Parts by weight
glycerol, PPG	OH group	100
Niax silicone L−580	surfactant	4
tin(II) 2-ethylhexanoate	catalyst	1
DI water	blowing agent	0.5
silica aerogel	filler	0−15
NCO index (IPDI)	NCO/OH	1

2.3. Density of foams

The density of the PU foam samples was calculated from the mass and volume of the samples according to ASTM D3574-17 standard. The samples were in cubic shape and their mass and dimension were measured using a digital balance and a caliper gauge, respectively.

2.4. Compression tests

The compressive properties of the PU foam samples were determined using an Instron 5567 testing machine according to the EN ISO3386-1 standard. All measurements were carried out at room temperature and 65% relative humidity with a crosshead speed of 1 mm/min. The circular specimens for compression tests had a dimension of 55 mm in diameter and 12 mm in thickness, and were compressed to 50% of their original thickness. At least three samples were tested for each batch, and the average values at break or 50% deformation were reported.

2.5. Compression set

The compression set of the PU foam samples were determined under constant force in air according to the ASTM D395 method A. All foam samples were cut into a cylindrical disk shape with a diameter of 29 mm and a thickness of 12.5 mm, and then assembled in a compression device. A compressive force of 200 N, corresponding to a pressure of 0.3 MPa, was applied to the tested samples. The deformation remained for 22 h at room temperature, and then the external force was removed. The deformed samples were left for another 1 h, and the thickness of the foams was then measured. The compression set was calculated using the following equation:

$$compression\ set\ (\%) = \frac{original\ thickness - final\ thickness}{original\ thickness} \times 100\% \quad (1)$$

2.6. Morphology

A small piece of each PU foam sample was cut using a knife and coated with gold. The cross-section morphologies of the prepared samples, including the cell size, the cell density, and the cell dispersion, were examined using a field emission scanning electron microscope (FE-SEM, JEOL, JSM-7600F).

2.7. Impact tests.

The shock attenuation of the PU foam samples was evaluated by dynamic impact tests. The tests were conducted on an impact machine with a twin wire flying arm (Cadex Inc). All foam samples were pre-conditioned at 23°C and 65% relative humidity prior to testing. A steel spherical impactor (5 kg in mass, 73 mm in radius) was dropped,

providing 5 Joule of impact energy on a foam sample (25 cm × 25 cm × 1.5 cm in dimension) placed on the load cell assembly. The transmitted force through the tested foams was collected from the load cell. Force *vs.* time curve, average peak force and peak acceleration of five repeated impacts were recorded.

2.8. Thermal insulation

The thermal conductivity of the PU foam samples was measured using a sweating guarded hotplate (Thermetrics) as per the ASTM D1518 standard. The foam specimens of 25 cm × 25 cm × 1 cm in dimension were tested under still air conditions after conditioning at 20°C and 65% relative humidity.

3. Results and discussion

3.1. Softness adjustment of PU foams

PU foams were fabricated via chemical reactions between different components, as shown in Fig. 1(a). The PU matrix was formed as a result of the reaction between the isocyanate groups from the IPDI and the hydroxyl groups from the glycerol and the PPG, while the foaming of the mixture was caused by carbon dioxide produced from the reaction of the isocyanate groups with the water. Foam softness is one of the critical parameters of footwear design for the purposes of comfort and protection. Foams that are too hard or too soft are inappropriate materials for the footwear design, as the former are incompressible and the latter "bottom-out" [7, 22]. As such, the flexibility of the PU foams in our system was adjusted by changing the ratio of the glycerol to the PPG, in which the PPG is responsible for the flexibility improvement due to its longer linear molecular chains relative to glycerol.

As shown in Table 2, the density of the resultant PU foams ranged in 0.147−0.405 g/cm^3 and increased as the PPG content increased. The increased density is related to a gradual increase in the total weight. In comparison with glycerol, PPG has a lower hydroxyl value and a higher molecular weight. Therefore, in order to retain the equivalent number of –OH groups for reacting with –NCO groups, the higher weight of PPG is required instead of that of glycerol.

Table 2. Density and mechanical properties of the resultant PU foams

Foam	Density (g/cm^3)	Compressive modulus (MPa)	Compressive stress (MPa)	Compressive strain at break (%)
PU 100−0	0.147 ± 0.008	1.343 ± 0.121	0.13 ± 0.02	8.9 ± 1.2
PU 80−20	0.216 ± 0.015	0.493 ± 0.025	0.76 ± 0.13	40.9 ± 3.1
PU 60−40	0.293 ± 0.018	0.252 ± 0.019	0.50 ± 0.02	–
PU 40−60	0.359 ± 0.014	0.131 ± 0.006	0.28 ± 0.03	–
PU 20−80	0.405 ± 0.024	0.107 ± 0.011	0.10 ± 0.02	–

"–"No clear collapse in the structure at 50% deformation.

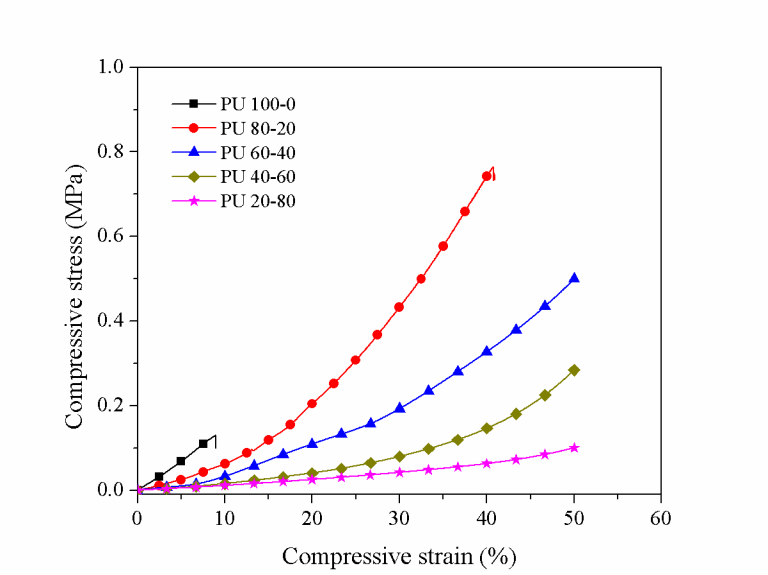

Fig. 2. Typical compressive stress−strain curves of PU foams with different ratios of glycerol to PPG.

The effect of PPG−to−glycerol ratios on the compressive mechanical properties of PU foams was investigated in uniaxial compression. The compressive stress-strain characteristics are displayed in Fig. 2 and the obtained data are summarized in Table 2. As expected, the IPDI/glycerol foam (PU 100-0) is the hardest sample, exhibiting maximal compressive modulus and compressive stress, but minimal compressive strain at break. It is obvious that, without PPG, the molecular chains formed by the reaction of IPDI with glycerol are rigid and incompressible, and a small deformation (8.9%) results

in the collapse of the foam structure. The addition of PPG has a softening effect on PU foams, which is reflected by an increase in the compressive strain at break and decreases in the compressive modulus and stress. As the PPG content increases, the compressive strain at break initially increases to 40.9% and then becomes more than 50.0%, whereas the compressive modulus and stress decrease gradually. These behaviors are caused by the two factors. One is that PPG has long molecular chains and, thus, provides the softness to the final foam product. The other is the result of the reduced crosslinks formed by the reaction between IPDI and glycerol when using PPG instead of glycerol.

3.2. Morphology of aerogel-reinforced foams

In general, micro/nano cells have a positive influence on mechanical properties and thermal insulation of foams [23, 24]. However, it is still complicated and difficult to create micro-/nano-cellular structures via traditional approaches [11]. This study developed a simple and environment-friendly way to introduce micro-/nano-cellular structures by the incorporation of silica aerogels. In this system, silica aerogels are expected to enhance the performance of the foam, while the flexible foam can protect the brittle aerogels from breakage. Based on the above softness analysis, the flexible PU 40-60 foam was selected and used to evaluate the effect of the aerogels on the PU foam properties regarding footwear applications.

As is well known, the properties of foam products are greatly related to the morphology of the foams, such as their cell shape, cell size, and cell dispersion [19-21]. Therefore, the morphology variation of the foams before and after incorporation of silica aerogels was first studied using a SEM technique. As presented in Fig. 3, all foams exhibited a closed-cell structure, and the cells were relatively regular spheres. In comparison with pure PU foam, the aerogel-reinforced foams showed the morphologies with smaller cell sizes, higher cell densities, and better cell dispersion under the constant amount of the blowing agent (water), which is due to the dramatic rise in the flow viscosity of the precursor mixture after incorporation of aerogels. As will be discussed later, these morphology variations, as well as the introduction of nano-cellular structures, played an important role in the mechanical performance, shock attenuation, and thermal insulation of the foams.

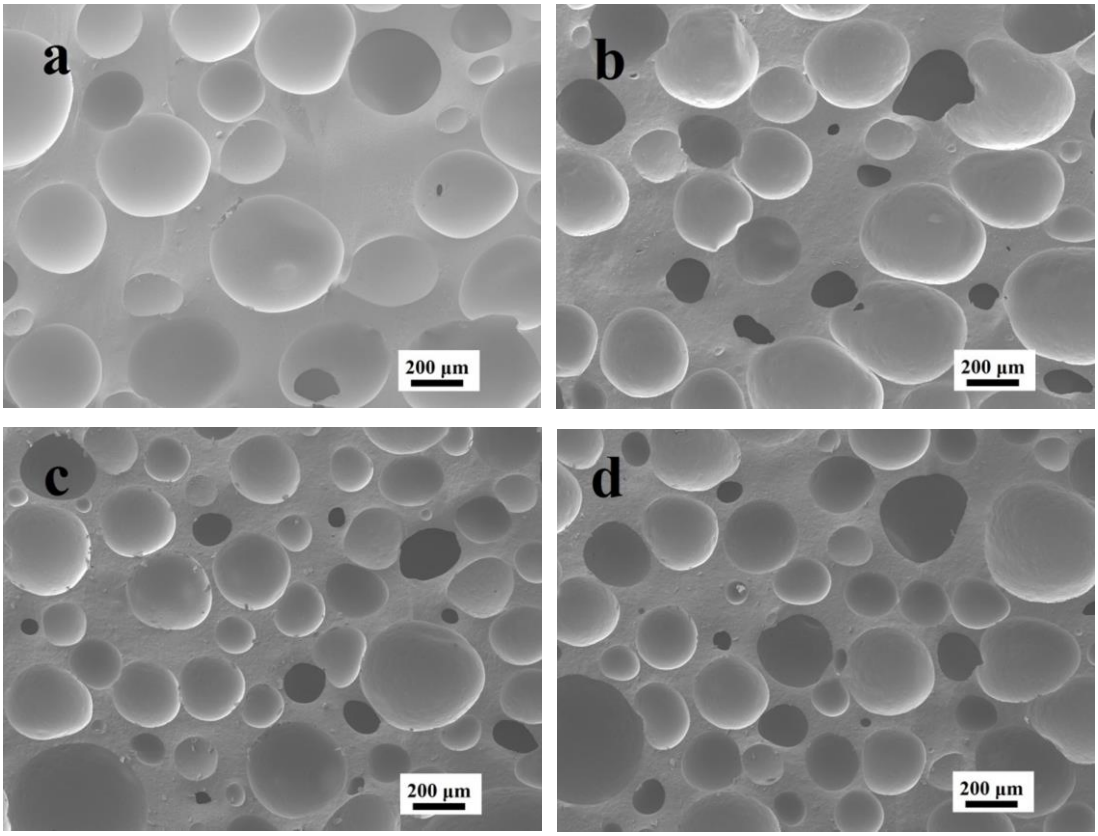

Fig. 3. SEM images of PU foams with aerogel contents of (a) 0 wt%, (b) 5 wt%, (c) 10 wt%, and (d) 15 wt%.

Table 3. Physical properties of the PU 40-60 foams reinforced with silica aerogels.

Aerogel content (wt%)	Density (g/cm^3)	Compressive modulus (MPa)	Compressive stress (MPa)	Residual deformation (%)	Compression set (%)
0	0.359 ± 0.014	0.131 ± 0.006	0.28 ± 0.03	21.5 ± 2.7	7.5 ± 1.2
5	0.336 ± 0.021	0.254 ± 0.011	0.44 ± 0.07	5.3 ± 1.3	1.7 ± 0.2
10	0.325 ± 0.018	0.518 ± 0.027	0.60 ± 0.07	3.4 ± 1.1	1.0 ± 0.0
15	0.317 ± 0.013	0.588 ± 0.024	0.68 ± 0.05	2.1 ± 0.8	0.0 ± 0.0

3.3. Compressive mechanical properties of aerogel-reinforced foams

After incorporation of silica aerogels, the density of the foams was found to slightly decrease depending on the increased aerogel contents (Table 3), which is attributed to a

super low density of the aerogels. The reduction in the density is helpful to design lightweight footwear, and thus reduce the energy demands of activities.

The compressive performance of the PU foams reinforced with silica aerogels was evaluated under loading-unloading cycles, as presented in Fig. 4 and Table 3. It is evident that the incorporation of the aerogels preserved the excellent softness of the PU foam, with a strain at break of more than 50%, regardless of the aerogel loading. The compressive modulus and stress of the resultant foams were observed to increase reasonably with the increasing amount of aerogels. These improvements can be explained in the aspects of the polymer properties and the morphology variations of the cells. In the case of the former, owing to the relatively higher bending rigidity of silica aerogels compared with the flexible PU foam [25], the use of the silica aerogels as fillers endows the PU material with an improved elasticity. The morphology variations of the foams also have an influence on mechanical properties [26]. Smaller and better-dispersed cells and higher cell density lead to a more uniform pressure distribution when a force is applied on the foam, as observed and discussed in the section on the morphology analysis.

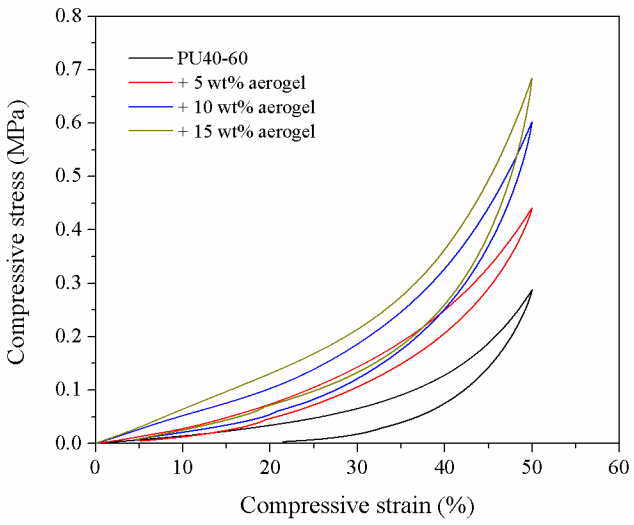

Fig. 4. Typical compressive stress-strain curves of aerogel-reinforced PU foams under a loading-unloading cycle.

The ability of the foams to return to their original shape was evaluated in terms of the instant shape recovery and the compression set. As shown in Table 3, the foams

reinforced with silica aerogels showed much better instant shape recovery from the applied deformation than pure PU foam. At the end of a loading-unloading cycle, the foams had less residual deformation with increasing silica aerogels and demonstrated only a residual deformation of 2.1% when loading 15 wt% aerogels, which was much lower than that of pure PU foam (21.5%). In combination with the complete shape recovery of all foams after free standing for 1 h, these findings suggest that the addition of the aerogels can effectively reduce the relaxation time, which will improve the foam performance under continuous loading-unloading cycles. The compression set testing was also performed to determine the retention of shape and elastic properties after prolonged compressive stress. Compared with the compression set of 7.5% for pure PU foam, the foams with aerogels had lower compression set values, especially for the 15 wt% aerogel loading where the compression set was completely removed (Table 3). The internal cells and the elasticity of polymer walls allowed the foam to deform under force. As long as the cells and the polymer structures did not collapse under force, the foam tended to regain its original shape on removal of force. Therefore, lower compression set values were observed for the aerogel-reinforced foams due to the improved elasticity of the solid phase and more uniform pressure distribution after introduction of aerogels. In addition, the shape recovery of the aerogel-reinforced foams also implies that, to some extent, the flexible foam is able to protect the aerogels from the physical breakage.

3.4. Shock attenuation of aerogel-reinforced foams

During weight-bearing activities such as walking, jumping, and running, some of energy can be absorbed by the bending and buckling of the cell walls of an elastic foam, and the rest is returned to the skeletal system upon the deformation recovery of the foam [27]. Therefore, for any specific amount of impact energy, higher energy absorption ability of the material will lead to less energy being transferred to the human body, consequently reducing the risk of injury. The impact tests used in this work were performed to achieve a dynamic analysis on the shock attenuation capability of the foams at the heel-strike.

Fig. 5 shows the typical curves of the transmitted force as a function of time for pure and aerogel-reinforced foams. The transmitted force exhibited a similar curve to a real

gait, and thus the force returned to the human body, i.e. the transmitted force, can be directly observed. It is evident from the transmitted force changes that aerogel-reinforced foams outperform pure PU foam in the shock attenuation capability, showing lower transmitted force and longer buffering time.

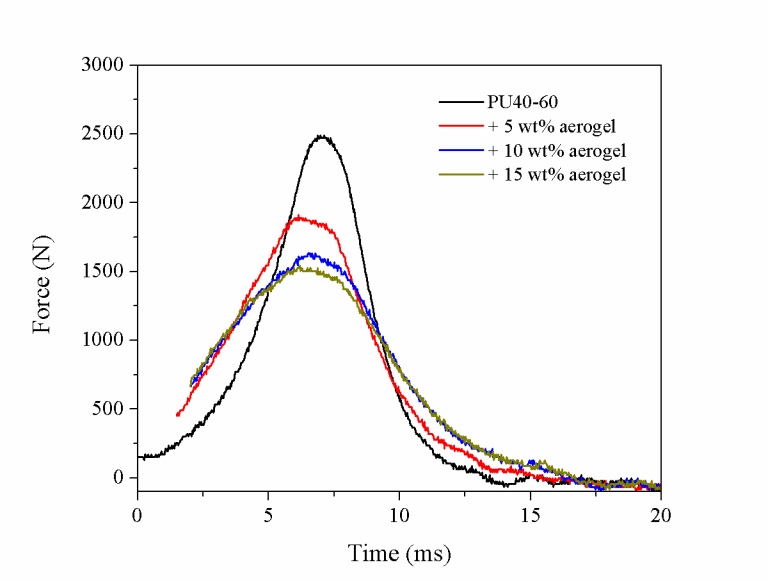

Fig. 5. Typical transmitted force *vs.* time curves for pure and aerogel-reinforced foams.

Peak force and peak acceleration are usually considered to be the two important parameters that reflect the shock attenuation of a material. These two parameters were measured and shown in Table 4. It can be observed that the peak force and the peak acceleration exhibit the same trend: decreasing with an increase in the aerogel content. When the aerogel content increases from 0 wt% to 15 wt%, the peak force and the peak acceleration decrease by 37.3% and 35.7%, respectively. Under a given impact energy of 5 Joule, lower values in the two parameters are indicative of the better impact absorption capacity of the foams and less energy being returned to the foot, indicating that the addition of the aerogels aids in the impact dissipation. The enhanced shock attenuation of the aerogel-reinforced foams can be explained in the same manner as for the compressive mechanical properties of the aerogel-reinforced foams. In the case of the solid phase, the aerogels improve the mechanical properties of the polymer. On the other hand, the morphology variations, e.g. smaller cell size, better cell dispersion, and introduction of

nano-cellular structures, contribute to a uniform pressure distribution and an better stress dissipation [28].

Table 4. Peak force and peak acceleration for pure and aerogel-reinforced foams under a 5 Joule impact.

Aerogel content (wt%)	Peak force (N)	% reduction in peak force	Peak acceleration (G)	% reduction in peak acceleration
0	2470 ± 22	—	46.2 ± 0.5	—
5	1919 ± 14	22.3 ± 0.6	35.8 ± 0.2	22.5 ± 0.4
10	1654 ± 22	33.0 ± 0.9	32.2 ± 0.8	30.3 ± 1.7
15	1547 ± 5	37.3 ± 0.2	29.7 ± 0.1	35.7 ± 0.2

3.5. Thermal insulation of aerogel-reinforced foams

Aside from mechanical properties and shock attenuation capacity, the thermal conductivity of foams is another crucial factor that has to be considered in the footwear application for cold environments. The thermal conduction within foam materials is mainly composed of the conductions via the gaseous and solid phases [29]. Since the thermal conductivity of the polymer is much higher than that of the gas (e.g. air, gaseous CO_2) [11], it may be a more effective way to improve the thermal insulation of the foam by reducing the thermal conductivity of the solid phase other than the gaseous phase. In this work, the thermal conduction via the solid phase was reduced by the introduction of the aerogels that have the lowest measured thermal conductivity [11, 30, 31]. The nano-cellular structures of the aerogels were thus introduced into the foam, leading to lower thermal conductivity due to the Knudsen effect that the heat conduction is limited via confined gaseous phases.

Fig. 6 shows the thermal conductivity of the foams with the aerogel contents of 0−15 wt%. The loading of the aerogels into the foams was proved to be an effective way to reduce the thermal conductivity. The more aerogels that were loaded, the lower thermal conductivity the foams exhibited. In the investigated range of aerogel contents, the 15 wt% aerogels exhibit the lowest thermal conductivity, decreasing by 45% compared with pure PU foam. The reduction in the thermal conductivity is mainly attributed to the super-low

thermal conductivity of the aerogels. The incorporation of the aerogels successfully established nano-cellular structures in the solid phase, which more effectively limited the heat conduction than the micro- and macro-porous structures [11]. Furthermore, the decreased thermal conductivity is also related to the decreased cell size and the increased cell density after the addition of the aerogels into the foam [32, 33].

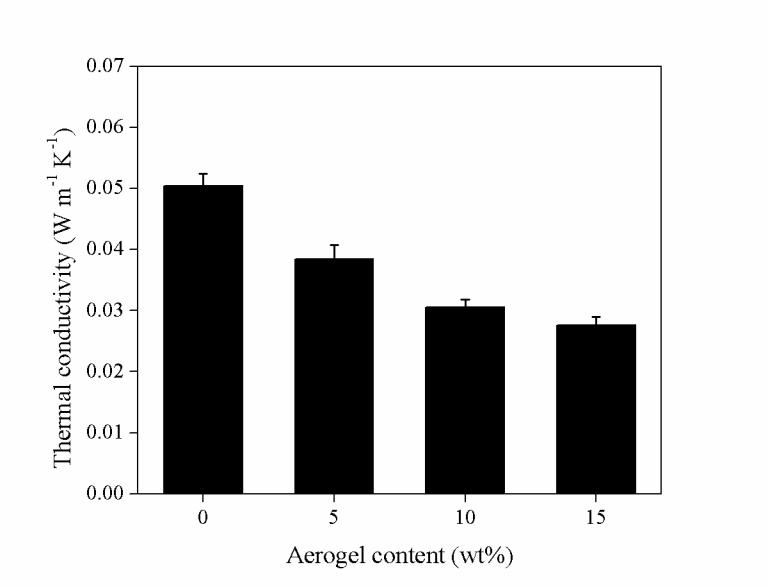

Fig. 6. Thermal conductivity for PU foams reinforced with 0-15 wt% aerogels.

4. Conclusions

With the purpose of determining the feasibility of silica aerogel-reinforced foams for footwear applications, the softness of PU foams was tuned to meet the footwear requirements and protect the brittle silica aerogels. The increase in the PPG content, which acted as the soft segments in our system, can effectively enhance the softness of the foams. Different amounts of silica aerogels as fillers were successfully loaded into a selected PU foam and their effects on mechanical properties, shock attenuation, and thermal insulation of the foam were investigated. The morphological analysis revealed that the incorporation of silica aerogels results in decreased cell size, increased cell density, and better cell dispersion. As the aerogel content increased, the compressive modulus and the compressive stress progressively increased, while the excellent flexibility of the foams was preserved. The addition of the aerogels also resulted in the improved instant deformation recovery and the reduced compression set. For the impact

tests simulating real gaits, the obtained results showed that the shock attenuation ability of the foams increased with an increase in the aerogel content. The enhancements in the compressive mechanical properties and the shock attenuation performance by the incorporation of aerogels can be attributed to the two factors. One is that the aerogels can improve the elasticity of the solid phase. The other one is that the changed morphologies of the gaseous phase (i.e. the decreased cell size, the increased cell density, and the nano-cellular structures) allow a more uniform pressure distribution and facilitate stress dissipation. In addition, considering the application of footwear for cold environments, the thermal insulation of the developed aerogel-reinforced foams was studied. It was found that the loading of the aerogels into the foams was effective in improving the thermal insulation, resulting in a 45% decrease in the thermal conductivity when the 15 wt% aerogels are loaded. The improved thermal insulation is related to the construction of the nano-cellular structure in the solid phase and the variations in the gaseous phase. Based on the above analyses of their compressive mechanical properties, shock attenuation performance, and thermal insulation, we conclude that aerogel-reinforced PU foams have a great potential in footwear applications.

Acknowledgements

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Conflict of Interest

The authors declare no conflicts of interest.

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