

A rubber-based aerogelTechnical Field

The present invention relates to a rubber-based aerogel and a method of forming the same.

Background

About 17 million tons of tyres each year reach the end of their use life worldwide. Most of these end up in landfills or are discarded as untreated waste. As such, waste tyres pose a major environmental concern. To add to that, burning of tyres is also not a viable option since tyres burn very dirty in an incomplete combustion process, requiring further energy to clean resultant particulates. Recycling levels of tyres remain low as most rubber recycling processes are energy intensive. There is therefore a need for an improved use of waste rubber.

Summary of the invention

The present invention seeks to address these problems, and/or to provide an improved aerogel comprising rubber fibres.

According to a first aspect, the present invention provides a rubber-based aerogel comprising a porous network of cross-linked rubber fibres, wherein the rubber-based aerogel has a thermal conductivity of 0.030-0.050 W/m K.

The rubber fibres may be any suitable rubber fibre. According to a particular aspect, the rubber fibres comprised in the rubber-based aerogel may be obtained from tyres.

The cross-linked rubber fibres comprised in the rubber-based aerogel may be cross-linked with a suitable cross-linker. According to a particular aspect, the cross-linker may be a thermoplastic polymer. For example, the cross-linker may be selected from, but not limited to: polyvinyl alcohol (PVA), glutaraldehyde (GA), poly(methyl methacrylate) (PMMA), polyamides, polylactic acid (PLA), polyvinyl chloride (PVC), or a combination thereof. In particular, the cross-linker may be PVA. Even more in particular, the cross-linker may be a combination of PVA and GA.

According to a particular aspect, the rubber-based aerogel may have a density of 0.02-0.20 g/cm<sup>3</sup>.

According to another particular aspect, the rubber-based aerogel may have a compressive Young's modulus of  $\leq 5000$  kPa.

The rubber-based aerogel may be superhydrophobic. In particular, the rubber-based aerogel may have a contact angle of  $120$ - $160^\circ$ .

- 5 The rubber-based aerogel may have a high porosity. In particular, the rubber-based aerogel may have a porosity of  $\geq 80\%$ .

According to a second aspect of the present invention, there is provided a method of forming the rubber-based aerogel described above, the method comprising:

- 10
- hydrolysing rubber fibres to form hydrolysed rubber fibres, wherein the hydrolysing forms at least carboxylic groups on a surface of the hydrolysed rubber fibres;
  - cross-linking the hydrolysed rubber fibres with a cross-linker;
  - gelation of cross-linked rubber fibres; and
  - drying to form the rubber-based aerogel.

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In particular, the method of the present invention is a simple and easily scalable method.

20 According to a particular aspect, the cross-linker used in the cross-linking may be a thermoplastic polymer. In particular, the cross-linker may be selected from, but not limited to: polyvinyl alcohol (PVA), glutaraldehyde (GA), poly(methyl methacrylate) (PMMA), polyamides, polylactic acid (PLA), polyvinyl chloride (PVC), or a combination thereof. Even more in particular, the cross-linker may be PVA. The cross-linker may further comprise GA.

25 The drying may be by any suitable means. For example, the drying may comprise, but is not limited to: freeze-drying, ambient pressure drying, or a combination thereof.

The method may further comprise modifying the surface of the rubber-based aerogel. For example, the modifying may comprise any suitable type of modification of the surface. The modification may be by any suitable reagent. According to a particular aspect, the modifying may comprise treating the surface of the rubber-based aerogel  
30 with a silane-based compound, an amine-based compound, or a combination thereof.

In particular, the modifying may comprise treating the surface of the rubber-based aerogel with, but not limited to: methoxytrimethylsilane (MTMS), methyltriethoxysilane (MTEOS), methyl(triacetoxy)silane, ethyl(triacetoxy)silane, propyl(triacetoxy)silane, methyltris(methylethylketoxime)silane, vinyltris(methylethylketoxime)silane, 5 phenyltris(methylethylketoxime)silane, (3-aminopropyl)triethoxysilane (APTES), tetraethylenepentamine (TEPA), aminomethyl propanol (AMP), polyethylenimine (PEI), or a combination thereof.

#### Brief Description of the Drawings

In order that the invention may be fully understood and readily put into practical effect  
10 there shall now be described by way of non-limitative example only exemplary embodiments, the description being with reference to the accompanying illustrative drawings. In the drawings:

Figure 1 shows a schematic representation of the rubber-based aerogel formed according to embodiment of the present invention;

15 Figure 2 shows a method of forming the rubber-based aerogel according to one embodiment of the present invention;

Figure 3 shows a schematic representation of surface modification of the rubber-based aerogel by methoxytrimethylsilane (MTMS);

Figure 4 shows the SEM images of rubber-based aerogels fabricated with different  
20 recycled rubber fibre concentrations. Figure 4(a) shows an aerogel formed from 1 wt % recycled rubber fibres, Figure 4(b) shows an aerogel formed from 2 wt % recycled rubber fibres, Figure 4(c) shows an aerogel formed from 3 wt % recycled rubber fibres and Figure 4(d) shows an aerogel formed from 4 wt % recycled rubber fibres;

Figure 5 shows the TGA curves of the rubber-based aerogel with different recycled  
25 rubber fibre concentrations;

Figure 6 shows the sound absorption coefficient curves of rubber-based aerogels (11.2 mm thickness) at different recycled rubber fibre concentrations (3.0-5.0 wt %); and

Figure 7 shows the compressive strain–stress curves of rubber-based aerogels with different recycled rubber fibre concentrations.

### Detailed Description

As explained above, there is a need to reduce accumulation of rubber waste, particularly tyre waste, to reduce its detrimental impact to the environment.

A material which has unique properties is an aerogel. Aerogels generally have low density, high porosity, low thermal conductivity and large surface areas. Aerogels have been applied in many fields due to its unique properties. One of the most common aerogels is silica aerogel. However, silica aerogels are very fragile.

In general terms, the present invention relates to rubber-based aerogels made from rubber fibres, particularly recycled rubber fibres. The rubber-based aerogels according to the present invention have superior properties. For example, the rubber-based aerogels of the present invention are super-hydrophobic, have a very low thermal conductivity and demonstrate good sound adsorption, good oil absorption, high thermal stability and a high flexibility. Therefore, the rubber-based aerogels may be used in a variety of applications such as, but not limited to, heat and sound insulation and oil spill cleaning.

According to a first aspect, the present invention provides a rubber-based aerogel comprising a porous network of cross-linked rubber fibres. In particular, the rubber fibres comprised in the rubber-based aerogel may be obtained from tyres, such as worn out and used rubber tyres. Rubber fibres are cheap and abundant. Accordingly, the cost of the aerogel may be reduced due to the ease of obtaining the raw materials.

For the purposes of the present invention, reference to rubber fibres may be taken to refer to rubber-based fibres, rubber-based powders, or a combination thereof. The rubber fibres may also comprise recycled rubber fibres. In particular, rubber-based fibres may comprise a mixture of Nylon 6®, Nylon 6,6®, Dacron®. In particular, rubber-based powders may comprise natural rubber, synthetic rubber, carbon black, or a combination thereof. Natural rubber may comprise polyisoprene. Synthetic rubber may comprise butadiene rubber, styrene butadiene rubber, or a combination thereof.

The rubber-based aerogel may comprise a suitable amount of rubber fibres. For example, the rubber-based aerogel may comprise 1-20 wt % rubber fibres. In particular, the aerogel may comprise 1-10 wt %, 2-8 wt %, 3-7 wt %, 4-6 wt % rubber fibres. Even more in particular, the aerogel may comprise 1-5 wt % rubber fibres.

The rubber fibres comprised in the rubber-based aerogel may have a suitable diameter. For example, the average diameter of the rubber fibres comprised in the rubber-based aerogel may be  $\leq 100 \mu\text{m}$ . In particular, the average diameter of the rubber fibres may be  $\leq 50 \mu\text{m}$ ,  $1\text{-}45 \mu\text{m}$ ,  $5\text{-}40 \mu\text{m}$ ,  $10\text{-}35 \mu\text{m}$ ,  $15\text{-}30 \mu\text{m}$ ,  $17\text{-}25 \mu\text{m}$ ,  $20\text{-}22 \mu\text{m}$ . Even more in particular, the average diameter may be  $30\text{-}50 \mu\text{m}$ .

The rubber-based aerogel may have a high porosity. For example, the porosity of the rubber-based aerogel may be  $\geq 80\%$ . In particular, the porosity of the rubber-based aerogel may be  $84\text{-}98\%$ ,  $85\text{-}97\%$ ,  $87\text{-}96\%$ ,  $88\text{-}95\%$ ,  $90\text{-}94\%$ ,  $92\text{-}93\%$ . Even more in particular, the porosity may be  $85\text{-}97\%$ .

10 The rubber-based aerogel may have low thermal conductivity and a high noise reduction coefficient due to its highly porous network. In particular, the trapped air within the highly porous aerogel may contribute to its very low thermal conductivity and high noise reduction coefficient. For the purposes of the present invention, thermal conductivity may be defined as the measure of the rubber-based aerogel to conduct  
15 heat. The thermal conductivity of the rubber-based aerogels of the present invention are lower compared to rubber fibres and comparable to conventional heat insulation materials such as polymer foams, wool and insulation boards.

According to a particular aspect, the thermal conductivity of the rubber-based aerogel may be  $0.020\text{-}0.050 \text{ W/m K}$ . For example, the thermal conductivity of the rubber-based  
20 aerogel may be  $0.030\text{-}0.050 \text{ W/m K}$ . In particular, the thermal conductivity of the rubber-based aerogel may be  $0.033\text{-}0.049 \text{ W/m K}$ ,  $0.034\text{-}0.047 \text{ W/m K}$ ,  $0.035\text{-}0.046 \text{ W/m K}$ ,  $0.036\text{-}0.045$ ,  $0.037\text{-}0.042 \text{ W/m K}$ ,  $0.038\text{-}0.040 \text{ W/m K}$ . Even more in particular, the thermal conductivity of the rubber-based aerogel may be  $0.035\text{-}0.049 \text{ W/m K}$ . Therefore, the rubber-based aerogels may be suitable for use in thermal insulation.

25 For the purposes of the present invention, noise reduction coefficient may be defined as the arithmetic average of the absorption coefficients for a specific material and mounting condition determined at the octave band center frequencies of 250, 500, 1000 and 2000 Hz. The noise reduction coefficient of the rubber-based aerogels of the present invention may be higher compared to conventional sound insulation materials  
30 such as cork, wool or any foams.

According to a particular aspect, the noise reduction coefficient (NRC) of the rubber-based aerogel may be 0.3 - 0.8 at a sound frequency range of 100-6300 Hz. In particular, noise reduction coefficient of the rubber-based aerogel may be 0.32-0.78, 0.38-0.76, 0.42-0.75, 0.50-0.70, 0.55-0.65, 0.56-0.60. Given the high NRC, the rubber-based aerogel may be suitable for use in sound insulation.

The rubber-based aerogel may have a low density of 0.02-0.20 g/cm<sup>3</sup>. In particular, the density of the aerogel may be 0.03-0.15 g/cm<sup>3</sup>, 0.04-0.14 g/cm<sup>3</sup>, 0.05-0.13 g/cm<sup>3</sup>, 0.06-0.12 g/cm<sup>3</sup>, 0.07-0.10 g/cm<sup>3</sup>, 0.08-0.09 g/cm<sup>3</sup>.

The rubber-based aerogel may have a compressive Young's modulus of  $\leq 5000$  kPa. Compressive Young's modulus may be defined as a measure of the stiffness of a solid material. For example, the compressive Young's modulus may be  $\leq 2500$  kPa,  $\leq 1000$  kPa,  $\leq 500$  kPa,  $\leq 460$  kPa. In particular, the compressive Young's modulus of the rubber-based aerogel may be 3-458 kPa, 3.5-450 kPa, 5-400 kPa, 10-200 kPa, 15-100 kPa, 25-75 kPa, 30-70 kPa, 35-60 kPa, 40-55 kPa, 45-50 kPa. The rubber-based aerogel may be able to spring back to its original shape instead of being plastically deformed after being compressed. In particular, the rubber-based aerogel may return to approximately 95% of its initial volume following compression. Accordingly, the rubber-based aerogel of the present invention is durable for repeated use.

The rubber-based aerogel may be superhydrophobic. In particular, the rubber-based aerogel may have a contact angle of 120-160°. In particular, the rubber-based aerogel may have a contact angle of 125-135°. Even more in particular, the contact angle may be 129-134°. According to a particular aspect, the water contact angle may increase when the fibre concentration comprised in the rubber-based aerogel increases. This is because the aerogel surface may be denser due to the addition of more rubber fibres within the aerogel. The superhydrophobicity of the rubber-based aerogel may be attributed to the stability of stability of the non-polar methyl groups from surface modification of the rubber-based aerogel. In particular, the surface modification may comprise replacement of the polar hydroxyl groups with non-polar methyl groups (R-CH<sub>3</sub>).

According to a particular aspect, the cross-linked recycled rubber fibres comprised in the rubber-based aerogel may be cross-linked with a suitable cross-linker to form the

rubber-based aerogel. The cross-linker may be a thermoplastic polymer. For example, the cross-linker may be selected from, but not limited to: polyvinyl alcohol (PVA), glutaraldehyde (GA), poly(methyl methacrylate) (PMMA), polyamides, polylactic acid (PLA), polyvinyl chloride (PVC), or a combination thereof.

- 5 According to a particular embodiment, the cross-linker may be PVA. In particular, the cross-linker may be a combination of PVA and GA. In particular, carboxyl and hydroxyl groups may be created on the surface of the rubber fibres following a pre-treatment. The rubber fibres may comprise various polymer fibres. The hydroxyl groups of the various polymer fibres comprised in the rubber fibres and the PVA added during the
- 10 preparation of the rubber-based aerogel may form hydrogen bonds. This is in addition to the hydrogen bonds that may form between the various polymer fibres. The carboxyl groups on the surface of the rubber fibres may also react directly with hydroxyl groups of PVA to form ester bonds. The GA may enhance the bonding between the PVA and the modified rubber fibres. In particular, the GA may give good attachment of PVA on
- 15 the modified rubber fibres because it has two aldehyde groups and may react with different chemical groups simultaneously. For example, one aldehyde group of GA may react with hydroxyl group of the modified rubber fibres to give a hemiacetal. The hemiacetal, having another aldehyde group on the other end, may further react with the hydroxyl groups of PVA to form acetyl bonds. Accordingly, PVA may form strong cross-
- 20 linking with rubber fibres due to their compatibility to form strong chemical and physical cross-linking. An example of the cross-linking of rubber fibres by PVA and GA is as shown in Figure 1.

According to a second aspect of the present invention, there is provided a method of forming the rubber-based aerogel described above, the method comprising:

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- hydrolysing recycled rubber fibres to form hydrolysed rubber fibres, wherein the hydrolysing forms at least carboxylic groups on a surface of the hydrolysed rubber fibres;
  - cross-linking the hydrolysed rubber fibres with a cross-linker;
  - gelation of cross-linked rubber fibres; and
- 30
- drying to form the rubber-based aerogel.

In particular, the method of the present invention is a simple and easily scalable method. Further the method of the present invention is safe as it avoids use of any toxic chemicals.

The rubber fibres used in the method may comprise any suitable rubber fibre. The  
5 rubber fibres may be as defined above. The rubber fibres used in the method of the present invention may be obtained from any suitable source. For example, the rubber fibres may be from waste rubber tyres.

Any suitable amount of rubber fibres may be used in the method of the present invention. For example, the amount of rubber fibres used in the method of the present  
10 invention may be 1-20 wt % based on the total weight of the rubber-based aerogel. For example, the amount of rubber fibres may be: 1-10 wt %, 2-8 wt %, 3-7 wt %, 4-6 wt % based on the total weight of the rubber-based aerogel. Even more in particular, the aerogel may comprise 1-5 wt % rubber fibres.

The method may further comprise pre-treating the rubber fibres prior to the hydrolysing.  
15 The pre-treating may comprise blending the rubber fibres into finer rubber fibres and/or to separate residual rubber from the rubber fibres.

The pre-treating may further comprise drying the rubber fibres for a suitable period of time following the blending. The drying may be under ambient conditions.

The hydrolysing may comprise adding a suitable reagent. For example, the reagent  
20 may be, an acid, base, aldehyde, ketone, or a mixture thereof. In particular, the reagent may be, but not limited to, acetone. The hydrolysing may yield carboxyl and hydroxyl groups.

The method may further comprise sonicating the hydrolysed rubber fibres following the hydrolysing. The sonicating may be for a pre-determined period of time. The sonicating  
25 may ensure that the reagent added for the hydrolysing is distributed uniformly in the reaction media.

The cross-linking may be under suitable conditions. For example, the cross-linking may be for a suitable period of time and at a suitable temperature. According to a particular aspect, the cross-linking may be for 1-24 hours. In particular, the cross-linking may be  
30 for 1-18 hours, 2-15 hours, 3-12 hours, 4-10 hours, 5-8 hours, 6-7 hours. Even more in

particular, the cross-linking may be for 1-5 hours. According to another particular aspect, the cross-linking may be at a temperature of 50-200°C. In particular, the cross-linking may be at a temperature of 60-190°C, 80-150°C, 90-120°C, 100-110°C. Even more in particular, the cross-linking temperature may be 80-120°C.

- 5 The cross-linker used in the cross-linking may be any suitable cross-linker. According to a particular aspect, the cross-linker used in the cross-linking may be a thermoplastic polymer. In particular, the cross-linker may be selected from, but not limited to: polyvinyl alcohol (PVA), glutaraldehyde (GA), poly(methyl methacrylate) (PMMA), polyamides, polylactic acid (PLA), polyvinyl chloride (PVC), or a combination thereof.
- 10 Even more in particular, the cross-linker may be PVA. The cross-linker may further comprise GA.

- The method may further comprise sonicating the cross-linked rubber fibres. The sonicating may be for a pre-determined period of time. The sonicating may ensure that the cross-linker added for the cross-linking is distributed uniformly in the reaction media
- 15 and air bubbles are removed.

- The gelation may comprise aging the cross-linked rubber fibres. The gelation may be for a suitable period of time under suitable conditions. According to a particular aspect, the gelation may comprise aging the cross-linked rubber fibres by freezing the cross-linked recycled rubber fibres. The freezing may be in a refrigerator or in nitrogen liquid.
- 20 The freezing may be at a suitable temperature. The gelation may be for 1-24 hours. In particular, the gelation may be for 2-18 hours, 5-15 hours, 7-12 hours, 8-10 hours. Even more in particular, the gelation may be for 10-24 hours.

- The drying may be by any suitable means. According to a particular aspect, the drying may comprise freeze-drying, ambient pressure drying, or a combination thereof. The drying may be under suitable conditions such as in vacuum. The drying may be for a
- 25 suitable period of time. For example, the drying may be for 10-48 hours. In particular, the drying may be for 12-45 hours, 15-42 hours, 18-40 hours, 20-36 hours, 24-32 hours, 28-30 hours. Even more in particular, the drying may be for 10-15 hours.

- According to a particular aspect, the method may further comprise sonicating the mixture prior to the drying.
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The method may further comprise modifying the surface of the rubber-based aerogel. For example, the modifying may comprise any suitable type of modification of the surface. The modification may be by any suitable reagent. According to a particular aspect, the modifying may comprise treating the surface of the rubber-based aerogel with a silane-based compound or an amine-based compound. In particular, the modifying may comprise treating the surface of the rubber-based aerogel with, but not limited to: methoxytrimethylsilane (MTMS), methyltriethoxysilane (MTEOS), methyl(triacetoxy)silane, ethyl(triacetoxy)silane, propyl(triacetoxy)silane, methyltris(methylethylketoxime)silane, vinyltris(methylethylketoxime)silane, phenyltris(methylethylketoxime)silane, (3-aminopropyl)tiethoxysilane (APTES), tetraethylenepentamine (TEPA), aminomethyl propanol (AMP), polyethylenimine (PEI), or a combination thereof. The modifying may be under suitable conditions.

For example, the modifying may be for a suitable period of time and at a suitable temperature. For example, the modifying may be for 1-48 hours. In particular, the modifying may be for 18-36 hours. Even more in particular, the modifying may be for about 24 hours. The modifying may be at a temperature of 50-200°C. In particular, the modifying may be at a temperature of 50-180°C, 70-150°C, 75-125°C, 80-120°C, 90-110°C, 95-100°C. Even more in particular, the temperature may be about 80-120°C, particularly 70°C.

According to a particular embodiment, the method of the present invention may comprise forming the rubber-based aerogel according to method described above, wherein the drying comprises freeze-drying. An example of the method is schematically shown in Figure 2. The method may comprise hydrolysing the rubber fibres with acetone to produce carboxyl and hydroxyl groups on the surface of the rubber fibres. In this way, the rubber fibres may be disentangled. Subsequently, the rubber fibres are dipped in a mixture of acetone, PVA and GA. The use of PVA and GA as a cross-linker is advantageous because PVA is an inexpensive polymer which is water soluble, biocompatible and biodegradable. GA further increases the strength of the aerogel formed from the method. The mixture may then be sonicated to ensure homogeneity. In particular, the mixture may be sonicated for about 20 minutes at 80°C. The cross-linking may be carried out at a temperature of about 85°C for about 3 hours. Following the cross-linking, the cross-linked rubber fibres may be sonicated for homogenization

and removal of bubbles. The cross-linked rubber fibres may be placed in a refrigerator for a period of time, such as 1-20 hours and at a suitable temperature, such as about -18°C, to freeze and promote gelation of the rubber fibres. The frozen rubber fibres may then be freeze-dried for a period of time at a suitable temperature, such as 48 hours at  
5 -70°C, to prevent shrinkage and collapse of the rubber-based aerogel. Freeze-drying may be a cost effective method for mass production of the rubber-based aerogel.

The rubber-based aerogel may optionally be surface modified. For example, the rubber-based aerogel may be surface modified by coating MTMS on the surface of the rubber-based aerogel.

10 In particular, the method of the present invention is a simple and easily scalable method. Further, the method of the present invention is safe. The method of the present invention may use recycled rubber fibres. Accordingly, the method of the present invention enables the use of recycled rubber fibres to form an eco-friendly aerogel, thereby enabling use of the rubber from waste rubber tyres. This helps in  
15 reducing tyre waste while forming an aerogel with many functional uses in various applications.

Whilst the foregoing description has described exemplary embodiments, it will be understood by those skilled in the technology concerned that many variations may be made without departing from the present invention.

20 Having now generally described the invention, the same will be more readily understood through reference to the following examples which are provided by way of illustration, and are not intended to be limiting.

### EXAMPLE

25

#### *Materials*

Waste rubber tyre fibres (WRTFs) were purchased from Tires to Green Recycling, LLC and had a mixture of Nylon 6,6, Nylon 6, and Dacron with approximate ratio of 40:25:35. The as-purchased WRTFs had diameter of approximately 30-50 µm.  
30 Acetone, Polyvinyl alcohol (PVA, MW 89,000-98,000 g/mol), glutaraldehyde (GA, 25%

in water) and methoxytrimethylsilane (MTMS) were all purchased from Sigma-Aldrich Chemical Co. All the reagents were used without further purification.

#### *Fabrication method of rubber-based aerogels*

A schematic representation of the method is shown in Figure 2. In particular, raw  
5 WRTFs were first blended into finer fibres, as well as to separate the residual rubber from the fibres. The WRTF (30-50  $\mu\text{m}$  diameter and about 1-1.8 cm length) were then soaked in pure acetone at a fixed ratio of 1 g fibre:10 ml pure acetone to promote partial hydrolysis reaction, yielding carboxyl (ethylene glycol) and hydroxyl (terephthalic acid) groups. The fibres were dipped and swelled in acetone/PVA/GA/H<sub>2</sub>O mixture to  
10 promote cross-linking.

The mixture was then sonicated for 400 W, 80°C for 20 minutes to ensure homogeneity. The mixture was then cured at 85°C for 3 hours before being gelated in the refrigerator and then freeze-dried to prevent shrinkage and collapse from water surface tension.

15 The WRTF concentrations were varied from 1 to 5 wt. %. The mixture of treated recycled WRTFs (1.0 g), PVA solution (10 mL, 0.05 g/mL), GA solution (50  $\mu\text{L}$ , 25%) and H<sub>2</sub>O (80 mL) was sonicated together at 400W for 20 minutes using a Hielscher Ultrasound Technology UIP2000hdT sonicator. The cross-linking reaction was carried out in an oven at 80°C for three hours. Thereafter, the mixture was frozen in the  
20 refrigerator at -18°C overnight and the resulting frozen sample was freeze-dried using a Toption TPV -50F vacuum freeze dryer at a condenser temperature of -70°C and 0.1 mBar for two days to produce the rubber-based aerogels.

#### *Surface modification*

The rubber-based aerogels were then placed in an airtight container. A few small open  
25 glass vials, depending on the number of aerogels to be coated, containing MTMS were added into the container. Then the container was sealed and heated in an oven at 70°C for 24 hours for the silanation reaction to proceed. A schematic representation of the silanation reaction is shown in Figure 3. Thereafter, excess MTMS was removed and, the coated sample was placed in a vacuum oven until the pressure reached 0.03  
30 mbar for one hour.

### Characterisation

The structure and morphology of the aerogels were investigated using a field-emission scanning electron microscope (FE-SEM) (Model S-4300 Hitachi, Japan). Before the samples were studied, they were carefully divided into smaller samples and coated with a thin film of gold for 90 seconds at 20 mA using a sputter coater (Cressington 108auto, Cressington Scientific Instruments Ltd., Watford, UK) to enhance its surface sensitivity to electron beams. The gold-coated samples were then transferred into the vacuum chamber of the FE-SEM and viewed at an acceleration voltage of 11kV.

Porosity ( $\phi$ ) is the measure of void spaces in a material and may be expressed as a percentage of the volume of voids over the total volume. Given that the samples were made with a 2:1 weight ratio of WRTF to PVA, and using the densities of the rubber aerogel ( $\rho_a$ ), the WRTF fibres ( $\rho_f = 1.21 \text{ g/cm}^3$ ) and PVA ( $\rho_p = 1.19 \text{ g/cm}^3$ ), the rubber aerogel porosity was determined by:

$$\Phi = (1 - \rho_a / (0.666\rho_f + 0.334\rho_p)) \quad (1).$$

The hydrophobicity of the aerogel samples were investigated by conducting a water contact angle test on the surface of the samples. A VCA Optima goniometer (AST Products Inc., USA) was used for this test. The machine was controlled by a software built-in function where 2.5  $\mu\text{L}$  of water is dispensed from the syringe every time. Using the software, the water contact angle may be measured automatically. The measurement was repeated at different surface positions of the samples and an average was taken.

The thermal conductivity of the aerogel was determined by a C-Therm TCi Thermal Conductivity Analyzer (C-Therm Technologies, Canada), which applied a modified transient plane source method under ambient conditions. The Thermal Gravimetric Analysis (TGA) tests were performed by a TA Instruments Q500 Thermogravimetric Analyzer to study the thermal stability of the aerogels. The specimen was heated from room temperature to 800°C at a rate of 10°C/minute in air.

To investigate the acoustic insulation properties of the aerogels, the samples were subjected to testing with an SW422 and SW477 Impedance Tube to measure their

acoustic absorption coefficients. The results were obtained using the transfer function method, also called the two-microphone method.

The oil absorptivity was measured by allowing a cut piece of aerogel to absorb motor oil from a petri dish filled with water and motor oil. The oil absorptivity was then calculated by taking the amount of oil absorbed divided by the weight of the piece of aerogel. Firstly, a petri dish filled with some water was zeroed. Then, an appropriate amount of motor oil was added into the petri dish, noting the weight of the oil ( $m_i$ ). A small, cut sample of aerogel was then weighed separately to obtain the mass of the aerogel ( $m_a$ ), and then placed in the petri dish where it was stirred for one minute to absorb the oil. The stirring (including tossing and turning) was to get the aerogel fully coated with oil. After one minute, the aerogel was removed, and the leftover mass of the oil ( $m_f$ ) was measured. The absorption capacity,  $Q$ , was thus calculated with the following formula:

$$Q = (m_f - m_i) / m_a \quad (2).$$

The compressive Young's modulus ( $E$ ) of the rubber aerogels was obtained by subjecting the samples to a compressive test using a load frame machine (Series 5500, Instron, Massachusetts, USA); test specimens were subjected to a loadcell of 1000 N at a constant loading rate of 1 mm/min.

#### *Morphologies and structures of rubber aerogels*

The obtained rubber-based aerogels were very flexible. A schematic of the formation mechanism between the WRTF fibres and the cross-linkers used is shown in Figure 1. The reaction mechanism is as follows.

The addition of PVA during the preparation of the WRTF (consisting of nylon 6; nylon 6,6 and PET fibres) gel solution results in the formation of hydrogen bonds between the hydroxyl groups of the various polymer fibres in WRTF and PVA chains, as seen in Figure 1. This is in addition to the hydrogen bonds that form between the various polymer fibres. PVA is also involved in the formation of ester bonds between the carboxyl groups of the various polymer chains in WRTF and the oxide group of PVA chains, which may be formed after curing. Further, the GA contributed to the formation

of acetal bridges between the oxide groups of the various polymer and PVA chains which further reinforces the WRTF-PVA matrix.

The SEM images of the rubber-based aerogels of the different fibre concentrations (1.0 - 4.0 wt %) are shown in Figure 4. The rubber-based aerogel formed had an open porous network structure, indicating that the WRTFs successfully formed a three-dimensional porous network. The PVA/GA cross-linkers diffused and reacted with the WRTF surface to form acetal and ester bonds to generate porous WRTF structure. It was observed that there is a uniform distribution of PVA in the WRTF matrix and good bonding of PVA on the WRTF surface. The PVA strands are observed to form more frequently around the intersections of the WRTFs at lower fibre concentrations. This may be due to the expansion of the WRTFs to fill the gel solution uniformly during curing. Greater stresses may be induced on the PVA to maintain the bonds between WRTFs, as the voids are larger at lower fibre concentrations with less fibre to fill up the same volume. The density and porosity of the rubber aerogels are summarized in Table 1.

| Sample name | WRTF:PVA ratio | Fibre conc. (wt. %) | Density (g/cm <sup>3</sup> ) | Porosity, $\phi_{avg}$ (%) | Thermal conductivity, (W/m k) |
|-------------|----------------|---------------------|------------------------------|----------------------------|-------------------------------|
| WRTFA1a     | 1:1            | 2.0                 | 0.070 ± 0.003                | 93.1 ± 0.5                 | 0.049 ± 0.001                 |
| WRTFA1b     | 3:1            | 2.0                 | 0.057 ± 0.003                | 93.8 ± 0.8                 | 0.047 ± 0.003                 |
| WRTFA1c     | 4:1            | 2.0                 | 0.052 ± 0.003                | 94.2 ± 1.8                 | 0.046 ± 0.001                 |
| RB01        | 2:1            | 1.0                 | 0.035 ± 0.003                | 97.1 ± 0.2                 | 0.035 ± 0.001                 |
| RB02        | 2:1            | 2.0                 | 0.052 ± 0.004                | 95.7 ± 0.3                 | 0.038 ± 0.001                 |
| RB03        | 2:1            | 3.0                 | 0.087 ± 0.004                | 92.8 ± 0.3                 | 0.042 ± 0.001                 |
| RB04        | 2:1            | 4.0                 | 0.134 ± 0.003                | 88.9 ± 0.2                 | 0.045 ± 0.001                 |
| RB05        | 2:1            | 5.0                 | 0.145 ± 0.003                | 88.0 ± 0.2                 | 0.047 ± 0.001                 |

**Table 1: Density, porosity and thermal conductivity of rubber-based aerogels**

The high porosities ( $\phi_{avg}$  = 88.0 - 97.1%) and low densities ( $\rho_a$  = 0.035 - 0.145 g/cm<sup>3</sup>) of the rubber-based aerogels may be attributed significantly to the sizeable voids, as observed in the SEM images. It can be observed that the density of the rubber aerogels is directly proportional to the fibre concentration. This is because despite the increase in the WRTF concentration, the volume of the sample remains the same.

Increasing the fibre concentration results in a greater mass of matter being packed within the same volume. Consequently, the porosity of the sample decreases with increasing fibre concentration.

It can also be observed that the density of the rubber-based aerogels are inversely proportional to the WRTF:PVA ratio. This is because with increasing WRTF:PVA ratio, less PVA is added into the sample. This results in a smaller mass of matter being packed within the same volume. Consequently, the porosity of the sample increases with increasing WRTF:PVA ratio.

#### *Hydrophobicity of rubber aerogels*

The rubber aerogels without MTMS coating were hydrophilic because the PVA cross linker used was hydrophilic. For oil spill cleaning application, the rubber aerogels were modified from hydrophilic to hydrophobic by modifying the surface of the rubber-based aerogels. In particular, a coating of MTMS formed silane groups on the rubber-based aerogel surface. The water contact angles on the external surfaces and cross-sections of the MTMS-coated rubber-based aerogels were 134.4° and 133.1°, respectively. This indicates that the hydrophobic coating successfully covered the whole aerogel network.

The water contact angle on the external surface was slightly higher than on the cross-section, due to the greater accessibility of the external surface. The rubber-based aerogels were exposed freely to the normal ambient conditions up to two months, to examine the hydrophobic stability and structure stability. The super-hydrophobic properties were maintained with water contact angles of 126.8° - 131.0°. The contact angle values are summarized in Table 2 below.

| Sample name | MTMS treatment | Water Contact Angle (°) | Properties of Rubber aerogels |
|-------------|----------------|-------------------------|-------------------------------|
| RB01        | Yes            | 129.20 ± 2.70           | Super-hydrophobic             |
| RB02        | Yes            | 133.10 ± 3.50           | Super-hydrophobic             |
| RB03        | Yes            | 134.40 ± 2.30           | Super-hydrophobic             |
| RB04        | No             | 0                       | Super-hydrophilic             |
| RB05        | No             | 0                       | Super-hydrophilic             |

**Table 2: Water contact angle of rubber aerogels with different WRT fibre concentrations**

*Thermal conductivity of rubber-based aerogels*

The thermal conductivity of the developed rubber-based aerogels at room temperature of 25°C was measured by a C-Therm TCi system, as summarized in Table 1 above.

5 The rubber-based aerogels exhibited ultra-low thermal conductivities ( $k_{\text{avg}} = 0.035 - 0.049 \text{ W/m K}$ ), which is very comparable with conventional insulation materials such as foams and wools ( $k = 0.020 - 0.055 \text{ W/m K}$ ). The thermal conductivities of air, PVA, Nylon 6,6, Nylon 6, and PET at room temperature are  $0.026 \text{ W/m K}$ ,  $0.31 \text{ W/m K}$ ,  $0.24 - 0.28 \text{ W/m K}$ ,  $0.24 - 0.28 \text{ W/m K}$ , and  $0.14 - 0.40 \text{ W/m K}$ , respectively. However, the  
10 thermal conductivity of the formed rubber-based aerogel is very lower than the individual components of the fibres from which the rubber-based aerogel is formed. The ultra-low thermal conductivities of the rubber-based aerogels may be because of the highly porous structures with  $\phi_{\text{avg}} = 88.0 - 97.1 \%$ . In particular, the aerogel pores effectively limit conductive and convective heat transport, and in view of the low  
15 density, the 3D solid network provides only limited pathways for heat to pass through.

It can be observed that the thermal conductivity of the rubber-based aerogels increased with increasing WRTF concentrations ( $1.0 - 5.0 \text{ wt. } \%$ ). This may be due to the presence of more WRTFs at higher WRTF concentrations that fills up the same fixed volume, resulting in lower porosities where the total volume of the voids within the  
20 aerogel structures is smaller. Consequently, with less air trapped in the voids, the thermal conductivity of the rubber-based aerogels may be increased.

The thermal conductivity of the rubber-based aerogels also decreased with increasing WRTF:PVA ratio due to the presence of less PVA while the WRTF concentration remained constant. With less PVA in the rubber-based aerogels, the average thermal  
25 conductivity decreased due to the increase in the porosity, and the low thermal conductivity of air.

*Thermal stability of rubber-based aerogels*

For fire safety, practical thermal insulation materials must have high thermal stability. As there are no significant effects of the WRTF:PVA ratio on the thermal conductivity of  
30 the rubber-based aerogels, thermogravimetric analysis (TGA) tests were performed, to

evaluate the thermal stability of the rubber-based aerogels with the different WRTF concentrations. The results are as shown in Figure 5.

It can be observed that between 25°C and 200°C, there is a weight loss of approximately 2-4 wt %, due to removal of absorbed atmospheric moisture. This was followed by a weight loss of about 70 wt % between the temperatures of 200°C to 500°C, due to the oxidation decomposition of the WRTFs, the formation of carbonaceous products, and a large mass loss of the residual substances. Between 500°C and 800°C, there was a small drop in the sample weight, due to the oxidation of the charred residue. With increasing WRTF concentration, the percentage weight loss of the rubber aerogel increased as well. This is because the WRTFs account for an increasing majority of the weight by percentage as the concentration increases. Based on a 50% weight loss, rubber-based aerogels are stable up to 450°C.

#### *Sound absorption of rubber-based aerogels*

The acoustic insulation capabilities of the rubber-based aerogels were investigated using SW422 and SW477 Impedance Tube to accurately measure the acoustic absorption coefficients. It can be seen in Figure 6 that, among the WRTF concentrations investigated, the 11.2-mm thick rubber aerogel with a WRTF concentration of 4.0 wt % exhibited the best sound insulation. An increase in the WRTF concentration, and hence greater number of the WRTFs per unit area, led to an increase on fibre-to-fibre contact area, in the tortuosity as well as in the fibre entanglements. As a result, there was greater energy loss by the propagated sound waves due to increasing surface friction and also internal frictional losses caused by a high number of internal reflections, and thus the level of sound absorption increased. The rubber aerogel RB04 having 4.0 wt % outperformed the commercial foam absorber, particularly at 2000-3000 Hz, with a Noise Reduction Coefficient (NRC) of 0.41, approximately 10% better in terms of acoustic than that of the commercial foam absorber Basmel® (NRC = 0.34). Further, the rubber aerogel having 5 wt % rubber fibres and a thickness of 30 mm had a NRC of 0.56 (results not shown). This was 1.6 times better than the commercial foam absorber Basmel®, particularly at 2000-3000 Hz.

#### *Mechanical properties of rubber-based aerogels*

The mechanical properties of the developed rubber-based aerogels are also important for thermal and sound insulation applications. The compressive strain-stress curves and Young's modulus of the rubber aerogels are presented in Figure 7 and Table 3, respectively.

5

| Sample name | WRTF:PVA ratio | Average compressive E (kPa) |
|-------------|----------------|-----------------------------|
| RB01        | 2:1            | 3.85 ± 0.04                 |
| RB02        | 2:1            | 13.56 ± 0.11                |
| RB03        | 2:1            | 41.22 ± 1.28                |
| RB04        | 2:1            | 98.62 ± 3.34                |
| RB05        | 2:1            | 458.12 ± 0.44               |

10

**Table 3: Compressive Young's modulus of the rubber aerogels**

With rubber fibre concentration increasing from 1.0 wt % to 5.0 wt %, the Young's modulus of the rubber-based aerogels improved by 119 times. This is due to a larger amount and a better distribution of the WRTFs in the rubber-based aerogels. Particularly, the rubber aerogel RB05 with 5.0 wt. % of the WRTFs has a Young's modulus of 458.12 kPa, much larger than the common commercial Styrofoam and in the range of the silica aerogels (0.1-10 MPa). The mechanical properties of the rubber-based aerogels are affected by the physical properties of the aerogel, such as the aerogel's density and the WRTF mass density. The compressed rubber aerogels spring back to their original shape instead of being deformed plastically, demonstrating good durability.

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#### *Oil absorption of rubber aerogels*

The oil absorption capacities of the rubber-based aerogels are presented in Table 4.

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| Sample name | WRTF:PVA ratio | Oil absorption capacity (g/g) |
|-------------|----------------|-------------------------------|
| RB01        | 2:1            | 24.95 ± 0.36                  |
| RB02        | 2:1            | 13.76 ± 0.41                  |
| RB03        | 2:1            | 6.23 ± 0.13                   |
| RB04        | 2:1            | 4.45 ± 0.16                   |
| RB05        | 2:1            | 3.88 ± 0.19                   |

**Table 4: Oil absorption capacities of the rubber aerogels**

The oil spill was absorbed completely inside the rubber-based aerogel within a few minutes. It can also be seen from Table 4 that the oil absorption capacity of the rubber-based aerogel up to about 25 g/g is very competitive to the commercial polypropylene and polyurethane sorbents.