

SEGMENTED GEL COMPOSITES AND RIGID PANELS MANUFACTURED
THEREFROM
TECHNICAL FIELD

The present invention relates to the field of reinforced composites useful in a variety of industrial and domestic applications.

SUMMARY OF THE INVENTION

The present invention describes a novel reinforced gel composites and the process of manufacturing a fiber or open-cell foam reinforced gel composite comprising the steps of, providing a segmented fiber batting sheet or a segmented open-cell foam sheet, combining the sheet with a gel precursor, gelling the gel precursor in the combination to make a composite sheet, rolling the composite sheet; and drying the composite to make a fiber reinforced gel composite. Additionally, further steps of unrolling the dried composite, applying an adhesive to at least one face and preferably one major face of the composite and attaching it to another planar material may be carried out. Such planar material may be another composite made in the similar manner.

Additionally, a process of manufacturing a gel composite panel is described which comprises the steps of, providing a dried, segmented fiber-reinforced or open-cell foam reinforced gel composite sheet with at least two major surfaces and multiple segmented cross-sectional surfaces (preferably including partial cross-sectional surfaces where segments are not scored all the way through the thickness), applying an adhesive to at least one major surface of said composite; and attaching said composite to another dried, segmented gel composite.

Additionally, a process of manufacturing a reinforced gel composite is described which comprises the steps of, providing a segmented open cell foam sheet, combining the open-cell foam sheet with a gel precursor, gelling the precursor in the combination to make a composite, rolling the composite; and drying the composite to make a reinforced gel composite. The segmented fiber batting or the segmented open cell foam sheet of any of the preceding processes may have a facing layer or facing sheet attached to them. Such facing layers may comprise fibers. The fiber battings or non-wovens of the processes of the present invention may comprise non-continuous fibers or continuous filaments.

Additionally, the above described processes involve the step of incorporating additives into the composite selected from the group consisting of titanium dioxide, iron oxides, carbon black, graphite, aluminum hydroxide, phosphates, borates, metal silicates, metallocenes, molybdates, stannates, hydroxides, carbonates, zinc oxides, aluminum

oxides, antimony oxides, magnesium-zinc blends, magnesium-zinc-antimony blends, silicon carbide, molybdenum silicide, manganese oxides, iron titanium oxide, zirconium silicate, zirconium oxide, iron (II) oxide, iron (III) oxide, manganese dioxide, iron titanium oxide (ilmenite), chromium oxide and a combination thereof.

In additional embodiments, the above processes involve the step of adding at least a binder to the fibers or using a fibers or fiber systems comprising at least one binder. The processes of the present invention involve the use of segmented fiber battings or segmented open-cell foam sheet with at least one segment being rigid.

In additional embodiments, the processes of the present invention use as gel in the fiber reinforced gel composite, one or more material or derivatives thereof selected from the group consisting of zirconia, yttria, hafnia, alumina, titania, ceria, silica, polyacrylates, polystyrenes, polyacrylonitriles, polyurethanes, polyimides, polyfurfural alcohol, phenol furfuryl alcohol, melamine formaldehydes, resorcinol formaldehydes, cresol formaldehyde, phenol formaldehyde, polyvinyl alcohol dialdehyde, polycyanurates, polyacrylamides, various epoxies, agar, and agarose and combinations thereof. In additional embodiments, the open-cell foam sheet of the present invention comprises one or more materials or derivatives thereof selected from polyurethanes, isocyanate-based materials, polyisocyanurates, polyimides, polyvinyl chloride, Styrofoam, silicones, polyolefins, epoxies, urea-formaldehyde, later rubber, fluoropolymers and syntactic foams.

The fibers in the fiber batting sheet, facing layer or the segmented fiber reinforced gel composites of the present invention comprise one or more materials selected from the group consisting of mineral wool, glass wool, rock wool, fiber glass, polyester, polyolefin terephthalates, poly(ethylene) naphthalate, polycarbonates and Rayon, Nylon, cotton based lycra (manufactured by DuPont), Carbon based fibers like graphite, precursors for carbon fibers like polyacrylonitrile(PAN), oxidized PAN, uncarbonized heat treated PAN such as the one manufactured by SGL carbon, fiberglass based material like S-glass, 901 glass, 902 glass, 475 glass, E-glass, silica based fibers like quartz, quartzel (manufactured by Saint-Gobain), Q-felt (manufactured by Johns Manville), Saffil (manufactured by Saffil), Durablanket (manufactured by Unifrax) and other silica fibers, Polyaramid fibers like Kevlar, Nomex, Sontera (all manufactured by DuPont) Conex (manufactured by Taijin), polyolefins like Tyvek (manufactured by DuPont), Dyneema (manufactured by DSM), Spectra (manufactured by Honeywell), other polypropylene fibers like Typar, Xavan (both manufactured by DuPont), fluoropolymers like PTFE with trade names as

Teflon (manufactured by DuPont), Goretex (manufactured by GORE), Silicon carbide fibers like Nicalon (manufactured by COI Ceramics), ceramic fibers like Nextel (manufactured by 3M), Acrylic polymers, fibers of wool, silk, hemp, leather, suede, PBO – Zylon fibers (manufactured by Tyobo), Liquid crystal material like Vectan (manufactured by Hoechst), Cambrelle fiber (manufactured by DuPont), Polyurethanes, polyamides, Wood fibers, Boron, Aluminum, Iron, Stainless Steel fibers and other thermoplastics like PEEK, PES, PEI, PEK, PPS and combinations thereof.

Additionally, the processes for making panels described in the present invention make use of one or more of the adhesives selected from the group consisting of potassium water glass, sodium water glass, cement and alkali-activated aluminosilicates, polyethylene, kapton, polyurethane, polyester, natural rubber, synthetic rubber, hypalon, plastic alloys, PTFE, polyvinyl halides, polyester, neoprene, acrylics, nitriles, EPDM, EP, viton, vinyls, vinyl-acetate, ethylene-vinyl acetate, styrene, styrene-acrylates styrene-butadienes, polyvinyl alcohol, polyvinylchloride, acrylamids, phenolics and combinations thereof. The thermal conductivity of the reinforced gel composites made from the above processes is less than 25 mW/mK at ambient conditions and preferably less than 16 mW/mK.

A segmented fiber reinforced or open-cell foam reinforced gel composite is described wherein the gel is continuous through the fiber in at least one segment and at least one gap exists between at least two adjoining segments. A gap as described here means there is a discontinuity in both the fiber and the gel of these adjoining segments. This gap need not be present all through the thickness and may be present partially through the thickness of the fiber reinforcement sheet, open-cell foam sheet or the resulting composite sheets.

Additionally, a rigid panel is described comprising at least two layers of fiber reinforced or open-cell foam reinforced gel composites wherein at least one layer comprises segmented reinforced gel composite with at least a gap in both fiber or open-cell foam and gel between at least two adjoining segments.

In an embodiment, the gel composites or the panels of the present invention further comprising fillers selected from the group consisting of titanium dioxide, iron oxides, carbon black, graphite, aluminum hydroxide, phosphates, borates, metal silicates, metallocenes, molybdates, stannates, hydroxides, carbonates, zinc oxides, aluminum oxides, antimony oxides, magnesium-zinc blends, magnesium-zinc-antimony blends, silicon carbide, molybdenum silicide, manganese oxides, iron titanium oxide, zirconium silicate, zirconium oxide, iron (II) oxide, iron (III) oxide, manganese dioxide, iron titanium oxide (ilmenite), chromium oxide and a combination thereof. In another

embodiment, the panels or composites of the present invention further comprise at least a binder in the fiber structure.

In another embodiment, the segmented fiber batting or segmented open cell foam sheets of the panels or composites of the present invention have a facing layer or sheet attached. The face sheet layer may comprise fibers. The fiber battings of the present invention may comprise non-continuous fibers or continuous filaments or a combination thereof. In an embodiment, the facing sheet has reasonable water vapor permeability for practical applications while not allowing liquid water to pass through. In another embodiment, the facing sheet allows both water and water vapor to pass through. In yet another embodiment, facing sheet does not substantially let either liquid water or water vapor to pass through.

Additionally, the panels or composites of the present invention may further comprise additives selected from the group consisting of titanium dioxide, iron oxides, carbon black, graphite, aluminum hydroxide, phosphates, borates, metal silicates, metallocenes, molybdates, stannates, hydroxides, carbonates, zinc oxides, aluminum oxides, antimony oxides, magnesium-zinc blends, magnesium-zinc-antimony blends, silicon carbide, molybdenum silicide, manganese oxides, iron titanium oxide, zirconium silicate, zirconium oxide, iron (II) oxide, iron (III) oxide, manganese dioxide, iron titanium oxide (ilmenite), chromium oxide or a combination thereof.

Additionally, the panels or composites of the present invention may further comprise at least a binder in the fibers or use a fiber comprising at least one binder. The binder may be or organic or inorganic in nature or of a hybrid material. In an embodiment, at least a segment of the segmented fiber batting may be rigid in the preceding panel or composites.

Additionally, the panels or composites of the present invention have components that are made from the gel precursors of zirconia, yttria, hafnia, alumina, titania, ceria, silica, polyacrylates, polystyrenes, polyacrylonitriles, polyurethanes, polyimides, polyfurfural alcohol, phenol furfuryl alcohol, melamine formaldehydes, resorcinol formaldehydes, cresol formaldehyde, phenol formaldehyde, polyvinyl alcohol dialdehyde, polycyanurates, polyacrylamides, various epoxies, agar, cellulose and agarose and combinations thereof.

Additionally, the fibers in the panels or composites of the present invention are selected from the group consisting of mineral wool, glass wool, fiber glass, polyester, polyolefin terephthalates, poly(ethylene) naphthalate, polycarbonates and Rayon, Nylon, cotton based lycra (manufactured by DuPont), Carbon based fibers like graphite,

precursors for carbon fibers like polyacrylonitrile(PAN), oxidized PAN, uncarbonized heat treated PAN such as the one manufactured by SGL carbon, fiberglass based material like S-glass, 901 glass, 902 glass, 475 glass, E-glass, silica based fibers like quartz, quartzel (manufactured by Saint-Gobain), Q-felt (manufactured by Johns Manville), Saffil (manufactured by Saffil), Durablanket (manufactured by Unifrax) and other silica fibers, Polyaramid fibers like Kevlar, Nomex, Sontera (all manufactured by DuPont) Conex (manufactured by Taijin), polyolefins like Tyvek (manufactured by DuPont), Dyneema (manufactured by DSM), Spectra (manufactured by Honeywell), other polypropylene fibers like Typar, Xavan (both manufactured by DuPont), fluoropolymers like PTFE with trade names as Teflon(manufactured by DuPont), Goretex (manufactured by GORE), Silicon carbide fibers like Nicalon (manufactured by COI Ceramics), ceramic fibers like Nextel (manufactured by 3M), Acrylic polymers, fibers of wool, silk, hemp, leather, suede, PBO – Zylon fibers (manufactured by Tyobo), Liquid crystal material like Vectan (manufactured by Hoechst), Cambrelle fiber (manufactured by DuPont), Polyurethanes, polyamides, Wood fibers, Boron, Aluminum, Iron, Stainless Steel fibers and other thermoplastics like PEEK, PES, PEI, PEK, PPS and combinations thereof.

Additionally, the panels of the present invention include adhesives selected from the group consisting of potassium water glass, sodium water glass, cement and alkali-activated aluminosilicates, polyethylene, kapton, polyurethane, polyester, natural rubber, synthetic rubber, hypalon, plastic alloys, PTFE, polyvinyl halides, polyester, neoprene, acrylics, nitriles, EPDM, EP, viton, vinyls, vinyl-acetate, ethylene-vinyl acetate, styrene, styrene-acrylates styrene-butadienes, polyvinyl alcohol, polyvinylchloride, acrylamids, phenolics and combinations thereof. In an embodiment, the panels or composites of the present invention have an apparent thermal conductivity of less than 25 mW/mK at ambient conditions.

BRIEF SUMMARY OF THE DRAWINGS

Figure 1. illustrates aerogel composite produced using a rotary-glass non-woven as-is (without segmentation).

Figure 2. illustrates schematic depicting the manufacture of aerogel composites using scored non-woven products with increased rigidity.

Figure 3. illustrates a comparison of the dried gel composites produced with non-segmented glass wool sheet (above) and with segmented glass wool sheet (below).

Figure 4. illustrates segmented wet gel composite and the segmented dry gel composite.

Figure 5. illustrates panelization of segmented aerogel/fiber composite into Board stock.

Figure 6. illustrates- manufacturing of rigid panels starting from segmented fiber-reinforcement sheets and gel precursors.

Figure 7. illustrates an alternative embodiment of the fiber reinforcement where there is a gradual change in segment sizes along the length of the fiber reinforcement

DETAILED DESCRIPTION OF THE INVENTION

The present invention involves manufacturing of rolled insulation products based on aerogels and aerogel-like materials. Aerogels, which exhibit extremely low density, high surface area, good optical, thermal, and acoustic properties, have been explored for various applications. However, aerogels have inherent drawbacks such as weakness and brittleness. Various types of reinforcements may be used to add strength, flexibility and other important properties to aerogels. Fiber reinforced aerogel composites may be made from adding loose fibers or non-woven fiber sheets to the gel precursors, gelling the combination to make a gel sheet, aging the gel sheet and drying the formed gel sheet.

Aerogels, which exhibit extremely low density, high surface area, good optical, thermal, and acoustic properties, have been used previously to try to address this need and other needs for which their properties could be advantageous. However, aerogels have inherent drawbacks such as weakness and brittleness. Notably, when making highly transparent and hydrophobic aerogels, brittleness becomes much more acute, and thus they are more difficult to handle, and require long cycle times for fluid drying in order to avoid cracking.

The weakness and brittleness of low density aerogels can particularly have a negative impact on production scale-up and limit large scale manufacturing. Additionally, aerogels with lower densities may have the best transparency, but also exhibit higher thermal conductivity and thus, exhibit worse insulation performance.

The fragile structure of an aerogel (low density and high porosity) also poses several difficulties in conforming to irregular surfaces, or maintaining integrity in dynamic conditions such as when sandwiched between glass and different thermal expansion coefficients between glass and aerogel results in compressive forces. So, flexibility, compressibility, integrity, durability, strength, and resistance to sintering, dusting and cracking are all areas for potential improvement in aerogels and aerogel composites.

A number of attempts have been made to improve aerogels and aerogel composites to address these problems and take fuller advantage of their remarkable properties as materials. Some patents describe attempts to make composites with foams and particulate aerogels, for example, EP0489319, and US Patent Nos. 6,136,216; 5,691,392; 6,040,375; and 6,068,882.

Others, for example, US Patent Nos. 4,966,919; 5,037,859; 5,972,254; 5,973,015; and 6,087,407; and US Patent Application Publication No. 2002 / 0094426 describe other aerogel or aerogel composites with or without foams. Some, such as US Patent Application Publication No. 2005 / 0192367 and US Patent Application Serial No. 11 / 392,925 describe transparent aerogels or aerogel composites.

Within the context of embodiments of the present invention “aerogels” or “aerogel materials” along with their respective singular forms, refer to gels containing air as a dispersion medium in a broad sense, including without limitation, gels dried using supercritical fluids, fluids at subcritical conditions, dried at slightly elevated pressures, at elevated temperatures, dried using freeze drying techniques and combinations thereof; and gels dried with supercritical fluids in a narrow sense. The chemical composition of aerogels can be inorganic, organic (including polymers) or hybrid organic-inorganic. Inorganic aerogels may be based on Silica, Titania, Zirconia, Alumina, Hafnia, Yttria, Ceria, Carbides and Nitrides. Organic aerogels can be based on compounds including but are not limited to: urethanes, resorcinol formaldehydes, polyimide, polyacrylates, chitosan, polymethylmethacrylate, members of the acrylate family of oligomers, trialkoxysilyl terminated polydimethylsiloxane, polyoxyalkylene, polyurethane, polybutadiene, melamine-formaldehyde, phenol-furfural, a member of the polyether family of materials or combinations thereof. Examples of organic-inorganic hybrid aerogels include, but are not limited to: silica-PMMA, silica-chitosan, silica-polyether or possibly a combination of the aforementioned organic and inorganic compounds. Published US patent applications 2005/0192367 and 2005/0192366 teach extensively of such hybrid organic-inorganic materials and are hereby incorporated by reference in their entirety.

Aerogels applicable to the present invention include such aerogels which are reinforced by a fibrous structure. Such reinforcements provide strength and flexibility to the aerogel structure. US patents 6068882, 6087407, 6770584, 5124101, 5973015, 6479416, 5789075, 5866027, 5786059, 5972254, 4363738, 4447345, PCT application WO9627726, U.S. patent applications 20020094426, 2003077438, Japanese patent JP8034678, U.K. Patent GB1205572 teach some of the aerogel materials that may be practiced with the embodiments of the present invention. These documents are incorporated herein by reference to teach the methods of manufacturing such flexible aerogel materials, at least in part. Flexible aerogel materials can also have form factors that are blankets or thin strips. Although many of the embodiments of the present invention are focused towards coating aerogel composites, they can also be used to coat other forms of aerogels.

Fiber reinforcement when applied appropriately results in flexible aerogel materials. Such flexibility in aerogel materials is desirable in a variety of applications where said aerogel materials can be drop-in-replacements for the existing materials. However, flexibility sometimes may also result in certain damage to the aerogel structure. Though it may not affect other critical properties of aerogel materials, it can present a nuisance to physical handling. The present invention, in many of its embodiments provides methods to minimize the effects of such damage and further prevent any such damaged material from dislodging from the material matrix. Hence, any consequential mechanical handling issues related to aerogel particulate materials on the surface of such aerogel material are avoided and substantially reduced by the methods of the present invention. In some embodiments, the present invention provides for manufacturing rigid composites and panels.

It has been shown that the retrofit of existing homes, buildings and structures with insulation possessing high thermal resistance can significantly reduce energy consumption and corresponding CO₂ emissions. There has thus been a strong desire to develop aerogel-based insulation materials for the building and construction market. For applications not involving cavity wall and/or lofted attic insulation, a preferred product for this market is rigid panels. For instance, many interior or exterior retrofits of buildings involve the installation of non-flexible board stock such as mineral wool or EPS foam. Over the past decade, there has been a renewed interest in producing rigid panels with thermal insulation materials with greater R-values than that currently on the market. High performance aerogel-based insulation has been of particular interest. Fiber reinforced aerogel insulation is currently commercially available in high volume as a flexible durable composite blanket at thicknesses not exceeding 10mm. Multiple plies of these materials are typically laminated with adhesives to produce a rigid board of greater thickness. Because flexible aerogel based insulation is necessarily produced as a rolled-good, it may possess a certain degree of winding defects in the form of buckles, undulations and/or thickness variations and as such extensive process and quality control needs to be employed to manage these issues. The presence of these defects makes the lamination of flexible aerogel materials into rigid board stock a challenge. Individual layers of aerogel insulation with surface defects result in an incomplete surface bond due to the inability to attain full surface mating of each individual ply during the lamination process. Panels produced in such a fashion may contain a large number of voids and defects that not only affect mechanical strength but also overall thermal performance. There thus exists a strong need to eliminate the surface defects of these materials that are due mainly to the stresses imposed by winding and unwinding, stresses typically associated with the manufacture of rolled goods. The winding and unwinding

process associated with the production of flexible composite aerogel insulation also presents challenges for the use of rigid fibrous based materials as reinforcement for these composites. Fibrous materials with high binder content and/or materials that are rigid cannot sustain the winding/unwinding process of rolled-good manufacture without sustaining copious amounts of defects in the form of delaminations, buckles and/or tears. Due to substantially improved economics, there is a strong desire to enable the use of lower cost fibrous reinforcements with high binder content for the production of flexible aerogel insulation. To date, these types of reinforcement materials are too rigid to be wound around a mandrel with a small radius without imparting non-conformities in the presence of folds, tears and delaminations. As such, there is a need to develop a process that could enable the winding and subsequent aerogel processing of such material without imparting the damage associated with winding. For the purposes of this patent application, a rigid panel means a panel of practical installable surface area (from 0.1 to 10 m²) with the ability to hold its own weight without bending to the extent that it interferes in the practical handling and installation of the panel. While one can make rigid panels by attaching non-rigid planar material to another rigid material, the rigid panel as defined above excludes such attached combinations and the rigid panels of the present invention focuses on one or more gel-composite layers attached through adhesives or otherwise being rigid as described above.

The present invention also describes an efficient method to manufacture flat-panel aerogel-based boards using low-cost fibrous substrates or open-cell foam substrates with increased rigidity. Such substrates are not normally amenable to standard processing in a cylindrical vessel for the various processes involved in manufacturing gel composites in rolled good form. Efficient utilization of vessels necessitates the manufacture of fiber reinforced aerogel materials in rolled good form in order to maximize the volume of a cylindrical vessel and reduce the fixed costs associated with production. As such, the fiber reinforcements used to reinforce aerogels need to have sufficient flexibility to sustain winding and unwinding. Materials with excess rigidity and/or materials with high binder content do not normally process well and typically result in the manufacture of aerogel composites with excessive defects in the form of folds, buckles, delaminations and tears (**Error! Reference source not found.1**). The final product formed using such rigid reinforcements is thus not amenable to the production of flat-panel board stock, a preferred product form for building and construction applications. The excessive amount of defects in such products diminishes thermal performance, material integrity and severely complicates any fabrication process.

We have discovered that the longitudinal segmentation (across the width of the blanket) of rigid non-woven fiber reinforcement or open-cell foam reinforcement enables sufficient flexibility so that the product can be wound/unwound with minimal delamination or buckling. In another embodiment, a facing sheet is integrated on one side of the blanket to provide additional tensile strength. Segmented non-woven blankets may be prepared by various methods including scoring the non-woven partially across its thickness, attaching separate segments to a face sheet, thus creating a segmented sheet connected together by the face sheet, scoring the non-woven sheet all the way and attaching a face sheet or any other practical ways known in the art. The terms segmentation and scoring are used interchangeably in this document to refer to the process of making segmented sheets in which segments are held together by a face sheet. Alternatively, the scoring (cutting) is performed for less than the thickness of the sheets such that the segmented sheet is still in one piece and held together by the portions through the thickness not cut by the scoring process. Certain scored non-woven sheets are available in the market. An example is a mineral wool non-woven, Isoroll MW from Isolparma S.r.l. The segmented non-woven sheet is carried by a face sheet/veil through the fiber-reinforced aerogel composite production process and the subsequent fabrication of rigid panel – see schematic in **Error! Reference source not found.**s 2 and 6. The non-woven fiber reinforcement can be efficiently wound in a cylindrical form and any gel-infused sheets manufactured therefrom may be unwound into a flat board-like shape with little to no damage. This allows for the efficient casting of a wet gel/fiber composite using a flat conveyor belt and the winding of the final wet-gel composite to enable efficient utilization in processes involving the use of cylindrical vessels. Alternatively, segmented non-woven sheet may be pre-wound with another non-permeable layer adjoining its major surface and a gel precursor may be infused into the fiber matrix along the axis of the winding, subsequently unwound after gel formation and further processed to produce a dry segmented gel composites. More importantly, most of the visible air gaps in the gel composite as produced in the cylindrical form, between adjoining segments, effectively disappear upon unwinding into flat stock, ensuring that thermal performance of a typical aerogel-fiber composite is maintained. The final material can be unwound into a near perfect flat panel, enabling the efficient production of rigid panels or aerogel-based boards suitable for building and construction applications. What was surprising and unexpected was that when wound (either as wet or dry gel), the gaps, i.e. gaps between two adjoining segments separated in a clean line without shattering the wet or dried gel. Aerogels and other dried gels made from the gel precursors described in the present invention are fragile material that when subjected to any stress are prone to crack and shatter. However,

what we have found here is a process where the dried gels can be broken in clean lines at the gaps such that when subsequently unwound, they produce a substantially planar surface. This allows for efficient manufacturing of flat panels. Furthermore, individual segments are still rigid, even if they are amenable to be wound and unwound. This segment rigidity allows for the manufacturing of rigid panels with two or more of such manufactured fiber reinforced gel composite sheets using adhesives of various kind, using a non-adhesive mechanical fasteners, needling of the produced composites or sewing them using extraneous fibers.

We have reduced this invention to practice by producing small scale rolls of aerogel composites measuring 36" length and 8" width. Specifically, we have used segmented rotary-glass based glass wool sheet and other mineral wool sheets available in the market, to produce gel composite materials in a rolled-goods process. The non-woven and the gel composites were wound around a mandrel of 6" diameter. Using standard silica aerogel precursors (Tetraethoxysilane and its derivatives), wet gel composites were produced using this glass wool sheet (scored or segmented at 1 or 2" intervals along its length) and were subsequently rolled around a 6" diameter after a 12 minute period of syneresis. Upon winding, the wet gel cleanly fractures at the scores (or segmentations) to enable flexibility and maintain the integrity of the fiber/aerogel segments (Figure 4). Alternatively, the segmented fibrous battings or segmented open-cell foam sheets may be rolled in a cylindrical form and placed in a cylindrical container and gel –precursors may be infused or impregnated into the fiber or open-cell foam matrix and subsequently gelled in such combination. Vacuum or application of pressure may be used to facilitate the infusion or impregnation of the fibrous batting or open-cell foam with the gel-precursors.

The wound wet gel/fiber composite is now amenable to processing in a cylindrical vessel for aging, rinsing and supercritical CO₂ extraction and is in an ideal shape to maximize the volume of a cylindrical vessel. After removal of solvent via supercritical CO₂ extraction, or other drying techniques discussed elsewhere in this application, the material maintains sufficient flexibility such that it can be unwound into flat stock. In contrast to aerogel composites produced with non-segmented glass wool sheet of the same type, the use of a segmented glass wool sheet has significantly reduced/eliminated any material defects associated with winding and unwinding steps. The segmented gel composite maintains flexibility such that it can be unwound and panelized to produce a board stock (Figures 4, 5 and 6).

We have also successfully demonstrated that the use of the segmented aerogel/fiber composite can be used to produce flat board stock using inorganic or organic adhesives.

Specifically, we have produced prototypes using potassium silicate adhesives and two plies of segmented aerogel/fiber composites. The original purpose of the face sheet in the raw fiber reinforcement was to provide improved tensile strength and a carrier for the segments of fiber, but we have also discovered that such face sheet can now be oriented outwards to provide some level of dust containment for the final aerogel board stock.

Aerogel production processes involving the use of high pressures necessarily involve cylindrical pressure vessels. Even low pressure steps such as aging or rinsing are efficiently carried out using cylindrical vessels. Fluid handling is easier in cylindrical vessels than vessels of any other shape. In order to fully maximize the use a cylindrical vessel, one must process a flexible gel composite such that it adopts a cylindrical-like shape and thus fills any vessel to nearly 100% of the available volume. In order to accomplish this, the fiber reinforcement of the aerogel composite must be able to sustain winding and unwinding and must conform without failure to small radius on the order of 3 to 18 inches. The present invention enables non-woven fiber reinforcements that are sufficiently rigid, or non-woven fiber reinforcements typically containing appreciable amounts of binder to be used as reinforcements for manufacturing aerogel/fiber composites. Because these non-woven materials are typically lower in cost than the other types of non-wovens (i.e. needlepunched), the present invention has the capability of substantially lowering the cost of fiber-reinforced gel composite insulation.

In another embodiment, an integrated process is provided for making a rigid panel from segmented non-woven reinforcement materials (Figure 6). A segmented non-woven sheet (1) is unrolled onto a moving conveyor belt and gel precursor in a liquid form is applied on top of the unrolled non-woven and allowed to infuse into the non-woven to become a gel sheet during its travel through the conveyor belt. At the end of the conveyor belt, the gel-infused non-woven (a wet gel composite sheet) is rolled onto a mandrel (2). This rolling may visibly show the gaps between the segments. Thus rolled wet gel composite is transferred to a vessel to allow the aging to take place resulting in a gel composite with various desired strength and other properties. Optionally, the rolls may be rinsed with a solvent and in yet another embodiment treated with hydrophobic agents to impart surface hydrophobicity. The roll is subsequently dried using various methods including ambient pressure, subcritical, supercritical carbon dioxide drying. The dried gel may be optionally carried through an oven to further remove any residual solvent or water. Thus dried two gel

composite rolls are unrolled as illustrated in the Figure 5(bottom) with segmented side of the sheets simultaneously applied with an adhesive (5). The adhesive may be an organic or an inorganic adhesive. After the application of the adhesive, the rolls are joined together and passed between a pair of rotating nip rollers where the two gel-composite layers are compressed together. Additional nip rollers (4) may be added to this set up depending on the adhesive used and the compression needed to make the sheets into rigid panels (6). Thus formed rigid panels may be cut into desired sizes and packaged for shipment or for additional inspection and further processing or drying as appropriate.

In another embodiment, the segmented fiber reinforcement sheet may be prepared such that the size of the segments along the length are not uniform. Specifically, the segment sizes may be gradually increased. This helps in winding the gel-sheets prepared from such reinforcement sheets where winding creates a gradually increasing radius of curvature. A segmented fiber reinforcement sheet illustrating this embodiment is shown in Figure 7.

The segmented reinforcement in a sheet form useful in the present invention may be of several types. Non-wovens of several types made with continuous fibers, or chopped fibers may be used. When chopped fibers are used, in some embodiments, the non-woven may contain binders. In another embodiment, the non-woven sheets useful in the present invention may be needle-punched to form felt-like materials. The above described materials may be segmented by scoring them across their thickness using a knife, hot knife, saw blade or any other scoring technique known in the art. The fibers useful to prepare the fiber-reinforcements of the present invention includes, mineral wool, glass wool, fiber glass, polyester, polyolefin terephthalates, poly(ethylene) naphthalate, polycarbonates and Rayon, Nylon, cotton based lycra (manufactured by DuPont), Carbon based fibers like graphite, precursors for carbon fibers like polyacrylonitrile(PAN), oxidized PAN, uncarbonized heat treated PAN such as the one manufactured by SGL carbon, fiberglass based material like S-glass, 901 glass, 902 glass, 475 glass, E-glass, silica based fibers like quartz, quartzel (manufactured by Saint-Gobain), Q-felt (manufactured by Johns Manville), Saffil (manufactured by Saffil), Durablanket (manufactured by Unifrax) and other silica fibers, Polyaramid fibers like Kevlar, Nomex, Sontera (all manufactured by DuPont) Conex (manufactured by Taijin), polyolefins like Tyvek (manufactured by DuPont), Dyneema (manufactured by DSM), Spectra (manufactured by Honeywell), other polypropylene fibers like Tyvar, Xavan (both manufactured by DuPont), fluoropolymers like PTFE with trade names as Teflon(manufactured by DuPont), Goretex (manufactured by GORE), Silicon

carbide fibers like Nicalon (manufactured by COI Ceramics), ceramic fibers like Nextel (manufactured by 3M), Acrylic polymers, fibers of wool, silk, hemp, leather, suede, PBO – Zylon fibers (manufactured by Tyobo), Liquid crystal material like Vectan (manufactured by Hoechst), Cambrelle fiber (manufactured by DuPont), Polyurethanes, polyamides, Wood fibers, Boron, Aluminum, Iron, Stainless Steel fibers and other thermoplastics like PEEK, PES, PEI, PEK, PPS and combinations thereof.

In addition to the fiber materials described in the present invention, foam materials and in specific embodiments, rigid foam boards may be made into segmented sheets using a face sheet and processed using the techniques described in this application, thus produced gel-foam rigid composite sheets that may be further be made into rigid panels as described above. In another embodiment, the foam materials may be open pore foams.

In general, the gel precursors useful in the present invention comprise metal oxides that are compatible with the sol-gel process where upon polymerization form a gel network(s). The silica precursors used may be chosen from but are not limited to: alkoxysilanes, partially hydrolyzed alkoxysilanes, tetraethoxysilane (TEOS), partially hydrolyzed TEOS, condensed polymers of TEOS, tetramethoxysilane (TMOS), partially hydrolyzed TMOS, condensed polymers of TMOS, tetra-n-propoxysilane, partially hydrolyzed and/or condensed polymers of tetra-n-propoxysilane, or combinations thereof. TEOS, partially hydrolyzed polyethysilicates, and polyethysilicates are some of the more common commercially available silica precursors. The fillers may be dispensed in the gel precursor solution at any point before a gel is formed. Gel formation may be viewed as the point where a solution (or mixture) exhibits resistance to flow and/or forms a continuous polymeric network throughout its volume. Preferably the mixture comprising fillers and precursors is a homogenous solution, conducive to gel formation. In addition to the silica based precursors, precursors of zirconia, yttria, hafnia, alumina, titania, ceria are useful. In additional embodiments, organic precursors such as polyacrylates, polystyrenes, polyacrylonitriles, polyurethanes, polyimides, polyfurfural alcohol, phenol furfuryl alcohol, melamine formaldehydes, resorcinol formaldehydes, cresol formaldehyde, phenol formaldehyde, polyvinyl alcohol dialdehyde, polycyanurates, polyacrylamides, various epoxies, agar, and agarose and combinations of the above may be used as gel precursors in the present invention. Additionally, hybrid organic-inorganic gel precursors with various combinations of the species described above may be used.

Suitable solvents for use herein include: lower alcohols with 1 to 6 carbon atoms, preferably 2 to 4, although other solvents can be used as is known in the art. Ethanol, is

typically a favored solvent used. Examples of other useful solvents include but are not limited to: ethyl acetate, ethyl acetoacetate, acetone, dichloromethane, tetrahydrofuran, methanol, isopropyl alcohol and the like. Of course in order to achieve a desired level of dispersion or solution certain gel precursor/filler systems, or a multi-solvent approach may be required.

Generally, gels may be formed via maintaining the mixture in a quiescent state for a sufficient period of time, changing the pH of the solution, directing a form of energy onto the mixture, or a combination thereof. Exemplary forms of energy include: a controlled flux of electromagnetic (ultraviolet, visible, infrared, microwave), acoustic (ultrasound), or particle radiation. In the present invention the gel is formed after the gel precursor is combined with the segmented reinforcements of the present invention.

Gels may be additionally aged prior to drying to further strengthen the gel structure by increasing the number of cross-linkages. This procedure is useful for preventing potential volume loss during drying, or simply a stronger final gel. Aging can involve: maintaining the gel (prior to drying) at a quiescent state for an extended period, maintaining the gel at elevated temperatures, addition of cross-linkage promoting compounds or any combination thereof. Aging time period typically requires between about 1hr and several days. The preferred temperatures are usually between about 10°C and about 100°C. Additionally, surface hydrophobicity imparting agents such as hexamethyldisilazane, hexamethyldisiloxane, trimethylethoxysilane, methylethoxysilane, methylmethoxy silane, propyltriethoxysilane, propyltrimethoxysilane, trimethylchlorosilane, trimethylmethoxysilane, triethylethoxysilane, tri-ethylmethoxysilane, dimethyldichlorosilane, dimethyldiethoxysilane, methyltrichlorosilane, ethyltrichlorosilane, may be used to render the gel/fiber composites hydrophobic. Such agents may be mixed with a solvent such as the solvent used in the prior steps and flowed through the rolled gel sheets during the aging step as described above.

Drying plays an important role in engineering the properties of aerogels, such as porosity and density which influence the material thermal conductivity. To date, numerous drying methods have been explored. U.S. patent 6,670,402 teaches drying via rapid solvent exchange of solvent(s) inside wet gels using supercritical CO₂ by injecting supercritical, rather than liquid, CO₂ into an extractor that has been pre-heated and pre-pressurized to substantially supercritical conditions or above to produce aerogels. U.S. patent 5,962,539 describes a process for obtaining an aerogel from a polymeric material that is in the form a sol-gel in an organic solvent, by exchanging the organic solvent for a fluid having a critical

temperature below a temperature of polymer decomposition, and supercritically drying the fluid/sol-gel. U.S. patent 6,315,971 discloses processes for producing gel compositions comprising: drying a wet gel comprising gel solids and a drying agent to remove the drying agent under drying conditions sufficient to minimize shrinkage of the gel during drying. Also, U.S. patent 5,420,168 describes a process whereby Resorcinol/Formaldehyde aerogels can be manufactured using a simple air drying procedure. Finally, US patent 5,565,142 herein incorporated by reference describes subcritical drying techniques. The embodiments of the present invention can be practiced with drying using any of the above techniques. In some embodiments, it is preferred that the drying is performed at vacuum to below supercritical pressures (pressures below the critical pressure of the fluid present in the gel at some point) and optionally using surface modifying agents. In another embodiment, the drying is accomplished using supercritical CO₂. Thus dried gel-fiber composites may be further dried by passing through an oven at elevated temperatures.

Various performance enhancing additives may be added to the gel-precursor before the gel is formed in the various embodiments of the present invention. They include of titanium dioxide, iron oxides, carbon black, graphite, aluminum hydroxide, phosphates, borates, metal silicates, metallocenes, molybdates, stannates, hydroxides, carbonates, zinc oxides, aluminum oxides, antimony oxides, magnesium-zinc blends, magnesium-zinc-antimony blends, silicon carbide, molybdenum silicide, manganese oxides, iron titanium oxide, zirconium silicate, zirconium oxide, iron (II) oxide, iron (III) oxide, manganese dioxide, iron titanium oxide (ilmenite), chromium oxide and a combination thereof.

It is noted that even though various embodiments of the present invention describe the methods and techniques for making reinforced aerogel based composites, same methods may be used to make reinforced composites based on other materials that are made from a liquid or a semi-liquid starting material. For example, reinforced plastic or polymeric materials may be made starting with either molten polymers or monomer or oligomers and combined with the reinforcements of the present invention to make a reinforced composite. Fillers and other materials disclosed in the present invention may be similarly added to such composites. Such non-aerogel composites may be even easier to make or handle as they may not be inherently as fragile as the aerogels by themselves. Another example is particulate silica materials or fumed silica materials may be incorporated into a fibrous batting or open-cell foam matrix through a liquid medium such as polymers or other sol-gel materials and the resulting composites will have the advantages of the aerogel composites described here and more.

It is noted that an open-cell foam sheet may replace a fiber-reinforced batting sheet in all of the various embodiments of the present invention, whether such open-cell foam based embodiment is expressed therein or otherwise and all such embodiments shall be understood such that open-cell foam sheet may replace or work in conjunction with fiber battings or mats. Furthermore, the reference to batting may include any of the fiber forms in a substantially sheet or flat form, including without limitation, battings, webs, mats, boards and the like.

EXAMPLES

Example 1: The following example illustrates the preparation and performance of a segmented gel-fiber composites and an aerogel-based rigid panel in accordance with the above invention. Precise longitudinal segmentation of a commercially available glass wool non-woven sheet with an integrated face sheet, was accomplished via the use of utility knife or automated rotary tool in combination with a custom produced cutting jig aimed at accomplishing a cut depth of no less than 90% of the original thickness. Using this method, segmented glass wool sheets measuring 36" x 8" were produced with both 1" and 2" segments. A requisite amount of a soluble silica source (i.e. sol comprising hydrolyzed tetraethoxysilane and its derivatives) and condensation catalyst, aqueous ammonium hydroxide, were combined and allowed to penetrate the glass-wool non-woven sheet in a horizontal/flat configuration. After a syneresis period of 15 minutes the gel/fiber composite was wound around a mandrel possessing a 6" diameter. The rolling of such a composite was accomplished by ensuring that the segment gaps were facing away from the mandrel during winding. In such a way, the stresses of winding were relieved as gaps are formed along each segmentation. The gel/fiber composite in the cylindrical form was then subject to a period of aging in which the rolled composite was exposed to a hot ethanol solution of ammonium hydroxide and a hydrophobic agent containing alkyl and silyl groups (hexamethyldisilazane). After aging, the rolled composite was transferred to a cylindrical pressure vessel and was then dried using supercritical CO₂ extraction to remove the solvent.

The composite was then treated with heat to remove any residual moisture and/or volatiles. The material was then unwound horizontally to adopt a flat configuration. The heat treatment may also be applied after the composite was unrolled. After unwinding the composite, an organic based adhesive (Spray 78 or FastBond) was spray applied (to the aerogel side) at a nominal coat weight of 20-40 g/m². A second piece of segmented gel/fiber composite, processed in the same manner was then attached to the first piece such that the segmentations

are staggered and that the face sheets are orientated away from the bonding face. The material was then subject to a short period of compressive stress (<0.25 PSI) to ensure complete mating and curing of the adhesive. The compressive stress was then relieved and the resulting rigid panel was characterized for thermal conductivity. The following table provides the measured thermal conductivity of the rigid panels thus formed at two different temperatures while under a slight pressure of 2 psi.

Segment Size	Thermal Conductivity (mW/mK)	
	10 °C	37.5 °C
1"	14.7	16.1
2"	14.7	15.8

Example 2: One can also fabricate the segmented fiber reinforcements described above using any combination of binder containing fiber reinforcement and lightweight face sheets. For instance, a series of segmented fiber reinforcements suitable for aerogel production were produced using Knauf Batt Insulation (0.5", 2 lb/ft³) and a glass veil face sheet with a density of 10 g/m². These fiber reinforcements were fabricated using a two-step process involving the initial lamination of the face sheet to one side of the fiberglass batt using an acrylic based adhesive (Fastbond) along the entire length of the insulation batt, followed by a precise longitudinal segmentation to no less than 90% of the original thickness using a utility knife and/or automated rotary tool. The longitudinal segmentation was carried out in such a fashion to leave the laminated face sheet intact. Segmentation length was varied between 1 inch and 6 inches.

Using such pre-fabricated segmented materials, a series of aerogel composites measuring 12 inch x 24 inch were prepared in a horizontal configuration. Infiltration of a requisite amount of soluble silica source (i.e. sol comprising hydrolyzed tetraethoxysilane and its derivatives) and a suitable condensation catalyst were allowed to penetrate the fiber reinforcement pre-fabricated at a segmentation interval of 2 inches. After a syneresis period of 15 minutes the gel/fiber composite was wound around a mandrel possessing a 6" diameter. The rolling of such a composite was accomplished by ensuring that the segment gaps were facing away from the mandrel during winding. In such a way, the stresses of winding were relieved as gaps are formed along each segmentation. The gel/fiber composite in the cylindrical form was then subject to a period of aging in which the rolled composite was exposed to a hot

ethanol solution of ammonium hydroxide and a hydrophobic agent containing alkyl and silyl groups (hexamethyldisilazane). After aging, the rolled composite was transferred to a cylindrical pressure vessel and was then dried using supercritical CO₂ extraction to remove the solvent. The composite was then treated with heat to remove any residual moisture and/or volatiles. The dried aerogel material was then unwound horizontally to adopt a flat configuration. After unwinding the composite, an organic based adhesive (Spray 78 or FastBond that may be obtained from 3M, Minneapolis, MN) was spray applied (to the aerogel side) at a nominal coat weight of 20-40 g/m². A second piece of segmented gel/fiber composite, processed in the same manner was then attached to the first piece such that the segmentations are staggered and that the face sheets are orientated away from the bonding face. The material was then subject to a short period of compressive stress (<0.25 PSI) to ensure complete mating and curing of the adhesive. The compressive stress was then relieved and the resulting rigid panel was characterized for thermal conductivity. The following table provides the measured thermal conductivity of the rigid panels produced in quadruplicate at two different mean test temperatures. The thermal conductivity measurements were made subjecting the material to a slight pressure of 2 psi.

ID	Thickness (mm)	Thermal Conductivity at 10°C (mW/mK)	Thermal Conductivity at 37.5°C (mW/mK)
Segmented Knauf Panel 1	23.9	14.1	15.3
Segmented Knauf Panel 2	23.9	14.7	16.6
Segmented Knauf Panel 3	24.2	14.6	17.1
Segmented Knauf Panel 4	24.9	14.4	16.3

Example 3: Prefabricated segmented reinforcements is produced via the lamination of discontinuous pieces of fiber reinforcement to a suitable lightweight face sheet. A wide range of materials such as mineral wool slab, fiberglass batts, or rigid open celled-foams are cut longitudinally into discontinuous pieces at the preferred segmentation intervals of 1” to 6” and then laminated to a suitable face sheet to produce a segmented product suitable for aerogel production as described above in Example 1. Aerogel products and panels are produced with such reinforcements using the techniques outlined in Examples 1-2.

Example 4: The lightweight fibrous face sheets used in examples 1-3 is alternatively replaced with any chemically compatible polymeric films/laminates. Laminates with thermoplastic tie layers are heat set to a single side of continuous batts of fibrous insulation followed a precise longitudinal segmentation to a depth of no less than 90% of the original thickness. Polymeric films are applied via the application of a non-aqueous or aqueous coating, followed by appropriate cure methods to form a substantially continuous polymeric film with a suitable thickness. Longitudinal segmentation is conducted after film formation to produce segmented fiber reinforcement suitable for aerogel production using the experimental techniques outlined in Examples 1-2.

Example 5: A commercially available semi-rigid polyurethane foam sheet of about a little less than 10mm thickness and about the size of 48 inches x 144 inches is selected as the reinforcing material. The sheet is partially scored along its thickness in the direction of the width with scoring pitch of 1 inch using a utility knife. This reinforcing material is used in the same manner as the example 2 above. The resulting composite is unrolled and further attached to another composite made in a similar manner using Fast Bond. This results in a rigid board or panel of reinforced aerogel composite.

CLAIMS

1. A process of manufacturing a segmented reinforced gel composite sheet comprising the steps of:

providing a segmented reinforcement sheet comprising a segmented fiber reinforcement sheet or a segmented open cell foam reinforcement sheet;

combining the reinforcement sheet with a gel precursor;

gelling the precursor in the combination to make a composite sheet;

rolling the composite sheet; and

drying the composite sheet to make a segmented, reinforced gel composite sheet.

2. The process of claim 1 further comprising the steps of unrolling the dried composite sheet, applying an adhesive to at least one face of the composite sheet and attaching it to another planar material.

3. The process of claim 1, further comprising the steps of:

providing the dried composite sheet of claim 1 with at least two major surfaces and multiple segmented cross-sectional surfaces

applying an adhesive to at least one surface of said composite; and

attaching said composite to another dried gel composite sheet.

4. The process of any one of the preceding claims wherein the segmented reinforcement sheet has a facing layer or sheet attached to it.

5. The process of claim 4 wherein facing layer or sheet comprises fibers.

6. The process of any one of the preceding claims wherein the segmented reinforcement sheet comprises a fiber reinforcement sheet comprising non-continuous fibers.

7. The process of any one of the preceding claims further comprising the step of incorporating additives selected from the group consisting of titanium dioxide, iron oxides, carbon black, graphite, aluminum hydroxide, phosphates, borates, metal silicates, metallocenes, molybdates, stannates, hydroxides, carbonates, zinc oxides, aluminum oxides, antimony oxides, magnesium-zinc blends, magnesium-zinc-antimony blends, silicon carbide, molybdenum silicide, manganese oxides, iron titanium oxide, zirconium silicate, zirconium oxide, iron (II) oxide, iron (III) oxide, manganese dioxide, iron titanium oxide (ilmenite), chromium oxide and a combination thereof.

8. The process of any one of the preceding claims wherein the segmented reinforcement sheet comprises a fiber reinforcement sheet, and further comprising the step of adding at least a binder to the fibers in the fiber reinforcement sheet or using a fiber reinforcement sheet comprising at least one binder.

9. The process of any one of claims 1, 2 or 3, wherein at least a segment of the segmented reinforcement sheet is rigid.

10. The process of any one of the preceding claims, wherein the gel precursor or fiber reinforced gel composite comprises a material selected from the group consisting of zirconia, yttria, hafnia, alumina, titania, ceria, silica, polyacrylates, polystyrenes, polyacrylonitriles, polyurethanes, polyimides, polyfurfural alcohol, phenol furfuryl alcohol, melamine formaldehydes, resorcinol formaldehydes, cresol formaldehyde, phenol formaldehyde, polyvinyl alcohol dialdehyde, polycyanurates, polyacrylamides, various epoxies, agar, and agarose and combinations thereof.

11. The process of any one of the preceding claims wherein the segmented reinforcement sheet comprises a fiber reinforcement sheet comprising materials selected from the group consisting of mineral wool, glass wool, fiber glass, polyester, polyolefin terephthalates, poly(ethylene) naphthalate, polycarbonates and wood pulp, aliphatic polyimides, cotton based polyester-polyurethanes,

Carbon based fibers like graphite, precursors for carbon fibers like polyacrylonitrile(PAN), oxidized PAN, uncarbonized heat treated PAN, fiberglass based material, silica based fibers like quartz, silica fibers, Polyaramid fibers, polyolefins, polypropylene fibers, fluoropolymers like PTFE, Silicon carbide fibers, ceramic fibers, Acrylic polymers, fibers of wool, silk, hemp, leather, suede, , Liquid crystal materials, Polyurethanes, polyamides, Wood fibers, Boron, Aluminum, Iron, Stainless Steel fibers and other thermoplastics like PEEK, PES, PEI, PEK, PPS and combinations thereof.

12. The process of any one of claims 2-11 wherein the adhesive is selected from the group consisting of potassium water glass, sodium water glass, cement and alkali-activated aluminosilicates, polyethylene, poly-oxydiphenylene-pyromellitimide, polyurethane, polyester, natural rubber, synthetic rubber, chlorosulfonated polyethylene synthetic rubber, plastic alloys, PTFE, polyvinyl halides, polyester, polychloroprene, acrylics, nitriles, EPDM, polytrimethylene terephthalate, viton, vinyls, vinyl-acetate, ethylene-vinyl acetate, styrene, styrene-acrylates styrene-butadienes, polyvinyl alcohol, polyvinylchloride, acrylamids, phenolics and combinations thereof.

13. The process of any one of the claims 1-12 wherein the rolling of the composite sheet forms a roll having an interior axis through the interior of the roll, and wherein the rolling of the composite is such that the gaps formed between the segments face away from the interior axis of the roll.

14. A segmented gel composite sheet comprising a segmented reinforcement sheet comprising a segmented fiber reinforcement sheet or a segmented open cell foam reinforcement sheet, wherein the gel is continuous through the fiber or foam in at least one segment of the segmented reinforcement sheet, and at least one gap exists between at least two adjoining segments with discontinuity in both the gel and the fiber or open-cell foam.

15. A panel comprising at least two layers of reinforced gel composites wherein at least one layer comprises the segmented reinforced gel composite sheet of claim 14.

16. The segmented gel composite of claim 14 or claim 15 further comprising fillers selected from the group consisting of titanium dioxide, iron oxides, carbon black, graphite, aluminum hydroxide, phosphates, borates, metal silicates, metallocenes, molybdates, stannates, hydroxides, carbonates, zinc oxides, aluminum oxides, antimony oxides, magnesium-zinc blends, magnesium-zinc-antimony blends, silicon carbide, molybdenum silicide, manganese oxides, iron titanium oxide, zirconium silicate, zirconium oxide, iron (II) oxide, iron (III) oxide, manganese dioxide, iron titanium oxide (ilmenite), chromium oxide and a combination thereof.

17. The segmented gel composite of claims 14-16 further comprising a segmented reinforcement sheet comprising at least a binder in the fiber.

18. The segmented gel composite of claims 14-17 wherein the segmented reinforcement sheet has a facing layer or sheet attached to it.

19. The segmented gel composite of claim 18 wherein the facing layer comprises fibers.

20. The segmented gel composite of claims 14-19 wherein the segmented reinforcement sheet comprises a fiber reinforcement sheet comprising non-continuous fibers.

21. The segmented gel composite of claims 14-20 further comprising additives selected from the group consisting of titanium dioxide, iron oxides, carbon black, graphite, aluminum hydroxide, phosphates, borates, metal silicates, metallocenes, molybdates, stannates, hydroxides, carbonates, zinc oxides, aluminum oxides, antimony oxides, magnesium-zinc blends, magnesium-zinc-antimony blends, silicon carbide, molybdenum silicide, manganese oxides, iron titanium oxide,

zirconium silicate, zirconium oxide, iron (II) oxide, iron (III) oxide, manganese dioxide, iron titanium oxide (ilmenite), chromium oxide and a combination thereof.

22. The segmented gel composite of claims 14-21 wherein the segmented reinforcement sheet comprises a fiber reinforcement sheet, and further comprising at least a binder in the fibers or using a fiber comprising at least one binder.

23. The segmented gel composite of claims 14-22 wherein at least a segment of the segmented reinforcement sheet is rigid.

24. The segmented gel composite of claims 14-23, wherein the gel precursor comprises a material selected from the group consisting of zirconia, yttria, hafnia, alumina, titania, ceria, silica, polyacrylates, polystyrenes, polyacrylonitriles, polyurethanes, polyimides, polyfurfural alcohol, phenol furfuryl alcohol, melamine formaldehydes, resorcinol formaldehydes, cresol formaldehyde, phenol formaldehyde, polyvinyl alcohol dialdehyde, polycyanurates, polyacrylamides, various epoxies, agar, and agarose and combinations thereof.

25. The segmented gel composite of claims 14-24 wherein the segmented reinforcement sheet comprises a fiber reinforcement sheet comprising fiber materials selected from the group consisting of mineral wool, glass wool, fiber glass, polyester, polyolefin terephthalates, poly(ethylene) naphthalate, polycarbonates and wood pulp, aliphatic polyimides, cotton based polyester-polyurethanes, Carbon based fibers like graphite, precursors for carbon fibers like polyacrylonitrile(PAN), oxidized PAN, uncarbonized heat treated PAN, fiberglass based material, silica based fibers like quartz, silica fibers, Polyaramid fibers, polyolefins, polypropylene fibers, fluoropolymers like PTFE, Silicon carbide fibers, ceramic fibers, Acrylic polymers, fibers of wool, silk, hemp, leather, suede, , Liquid crystal materials, Polyurethanes, polyamides, Wood fibers, Boron, Aluminum, Iron, Stainless Steel fibers and other thermoplastics like PEEK, PES, PEI, PEK, PPS and combinations thereof.

26. The panel of claim 15 further comprising an adhesive selected from the group consisting of potassium water glass, sodium water glass, cement and alkali-activated aluminosilicates, polyethylene, poly-oxydiphenylene-pyromellitimide, polyurethane, polyester, natural rubber, synthetic rubber, chlorosulfonated polyethylene synthetic rubber, plastic alloys, PTFE, polyvinyl halides, polyester, polychloroprene, acrylics, nitriles, EPDM, polytrimethylene terephthalate, viton, vinyls, vinyl-acetate, ethylene-vinyl acetate, styrene, styrene-acrylates styrene-butadienes, polyvinyl alcohol, polyvinylchloride, acrylamids, phenolics and combinations thereof.