(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
22 January 2015 (22.01.2015)

WIPO | PCT

(10) International Publication Number
WO 2015/010090 A2

(51) International Patent Classification: *B32B 5/30* (2006.01)

(21) International Application Number: PCT/US2014/047300

(22) International Filing Date: 18 July 2014 (18.07.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/847,823 18 July 2013 (18.07.2013) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

WO 2015/010090 A2

(54) **Title**: NANOCOMPOSITE VESSELS

(57) **Abstract**: This invention provides a seamless nanocomposite vessel, which includes a high density polymer adapted into the shape of a desired vessel, the vessel having an inner surface sputtered with a metal and an outer surface, the inner surface defining a space; and a plurality of layers disposed over the inner surface of the vessel, the outer surface of the vessel, or both, each layer being independently selected from the group consisting of a thermoplastic material and a thermoset nanocomposite material. Methods for making and using such vessels also are provided.

NANOCOMPOSITE VESSELS

RELATED APPLICATIONS

[0001] This application claims benefit of U.S. Patent Application Serial No. 61/847,823, filed on July 18, 2013, which application is incorporated by reference herein in its entirety.

FIELD OF THE INVENTION

[0002] The present invention relates to nanocomposite vessels for use, *e.g.* as storage containers for liquids and gasses under high pressure, particularly containers for the storage of compressed natural gas (CNG).

BACKGROUND OF THE INVENTION

[0003] Pressure vessels are widely used to store liquids and gases under high pressure. The storage capacity of a pressure vessel depends on its internal volume and the pressure the vessel is capable of safety containing. In addition to its storage capacity the size shape and weight of the pressure vessel are often important in a particular application. For example, pressure vessels may be used to contain CNG. CNG is increasingly viewed as preferable for fueling vehicles. There are four types of CNG fuel tanks available in the market today:

1. Metallic non-composite container;
2. Metallic liner over which an overwrap such as carbon fiber or fiberglass is applied in a hoop wrapped pattern over the liner's cylinder sidewall;
3. Metallic liner over which an overwrap such as carbon fiber or fiberglass is applied in a full wrapped pattern over the entire liner, including the domes; and
4. Non-metallic liner over which an overwrap such as carbon fiber or fiberglass is applied in a full wrapped pattern over the entire liner, including the domes.

One objective of the present invention is to provide polymer nanocomposite containers for storing CNG, and using such containers as a fuel tank on automobiles. The application of polymer nanocomposite fuel containers for CNG storage service is governed by both technical and regulatory requirements (Department Of

Transportation requirements. DOT Part 571.304 Standard No. 304 Compressed Nagurl, Gas Fuel Container Integrity), hence another objective of the present invention is to design a nanocomposite vessel such that it is compliant with current regulatory requirements. Current vessels for storing CNG are expensive, are prone to leakage, and may not withstand high pressures. The present invention is directed, inter alia, to meeting the above-identified objectives and to overcoming the above-identified drawbacks.

SUMMARY OF THE INVENTION

[0004] Thus, one embodiment of the invention is a seamless nanocomposite vessel comprising: a high density polymer adapted into the shape of a desired vessel, the vessel having an inner surface sputtered with a metal and an outer surface, the inner surface defining a space; and a plurality of layers disposed over the inner surface of the vessel, the outer surface of the vessel, or both, each layer being independently selected from the group consisting of a thermoplastic material and a thermoset nanocomposite material.

[0005] Another embodiment of the invention is seamless nanocomposite vessel comprising: a high density polymer adapted into the shape of a desired vessel, the vessel having an inner surface sputtered with a metal and an outer surface, the inner surface defining a space; and a plurality of layers disposed over the inner surface of the vessel, the outer surface of the vessel, or both, each layer being independently selected from the group consisting of: a functionalized thermosetting resin, electrospun epoxy nanocomposite fibers, and a flame resistant agent.

[0006] Yet another embodiment of the invention is seamless nanocomposite tank comprising: a high density polyethylene (HDPE) blow molded into the shape of a gas tank, the gas tank having an inner surface and an outer surface, the inner surface defining a space; the inner surface sputtered with a metal for providing structural integrity, followed by a coating of functionalized epoxy for providing a barrier to hydrocarbons from exiting the tank; and the outer surface embedded with a first outer surface coating of functionalized epoxy followed by a first outer surface layer of electrospun epoxy nanocomposite fibers to provide reinforcement to the tank, followed by a second outer surface coating of functionalized epoxy, followed by a second outer surface layer of electrospun epoxy nanocomposite, followed by a third outer surface coating of functionalized epoxy for providing a barrier to oxygen from entering the tank, followed by a layer of flame resistant foam for providing resistance to wear and damage to the tank and fire.

[0007] Yet another embodiment of the invention is a method for making a seamless nanocomposite vessel. This method comprises: a) forming a vessel from a high density polymer, the vessel having an inner surface and an outer surface, the inner surface defining a space; b) sputtering the inner surface of the vessel with a metal to provide structural integrity to the vessel; c) coating the metal-sputtered inner surface of the vessel with a first functionalized thermosetting resin to provide a barrier for substantially preventing hydrocarbons stored in the space from escaping from the vessel; d) coating the outer surface of the vessel with a second functionalized thermosetting resin; e) coating the outer surface of the vessel after step d with a first electrospun epoxy nanocomposite fiber material to provide further structural support to the vessel; f) coating the electrospun epoxy nanocomposite fiber-embedded outer surface of the vessel with a third functionalized thermosetting resin; g) coating the outer surface of the vessel after step f, with a second electrospun epoxy nanocomposite fiber material; h) coating the outer surface of the vessel after step g, with a fourth functionalized thermosetting resin to provide a barrier for substantially preventing oxygen from the outside environment from penetrating into the vessel; and i) applying a flame resistant agent to the outer surface of the vessel after step h, wherein the first, second, third and fourth functionalized thermosetting resin are independently selected and may be the same or different resin.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] The following drawings form part of the present specification and are included to further demonstrate certain aspects of the present invention. The invention may be better understood by reference to one or more of these drawings in combination with the detailed description of specific embodiments presented herein.

[0009] Figure 1A shows the structural unit of clay. Figure 1B shows several sheet-like structures stacked together.

[0010] Figure 2A shows an unmodified organoclay. Figure 2B shows an organoclay modified with a transition metal ion (TMI), Fe^{2+}.

[0011] Figure 3 shows a schematic of a nanocomposite vessel of the present invention. Shown are a vessel (1) defining an inner space (5), the wall of the vessel (10) having an inner surface (15) and an outer surface (20). A schematic of the cross section of the wall of the vessel (10), shows a first thermosetting resin layer (21), a metal layer (25), a high density polymer adapted into the shape of the vessel (30), a second thermosetting resin layer (35), a first thermoplastic material layer (40), a third thermosetting resin layer (45), a second thermoplastic material layer (50), a fourth thermosetting resin layer (55) and a flame resistant layer (60). Also shown is an opening (65) to allow filling of the vessel and discharge of the contents therefrom.

DETAILED DESCRIPTION OF THE INVENTION

[0012] While designing polymer-nanocomposite CNG storage containers/fuel tanks, achieving enhanced mechanical and barrier properties is of key importance. Traditionally these fuel tanks were made up of metal, and with the advent of polymer nanocomposite materials, one of the key challenges in developing these storage containers is its ability to withstand high hydrostatic pressure. These containers should be rated equivalent to their metallic counterparts, as the CNG is a pressurized gas stored at a high pressure of 3600 psi.

[0013] The weakest point in any composite container is its joint. Currently there are a number of joining systems available, which, include Butt-and-Wrap, O-Ring, Flush Thread, Flanged, Keyway Joint, Socket Joint (coupled), Threaded and Bonded, Bell and Spigot (matched tapered). The strongest joint is a butt-and-wrap joint, but unfortunately this type of joint is both labor and time intensive, requiring multiple applications of resin and reinforcing material with curing time between each application. Coupled joints require gluing or cementing the joints together using couplings made of the same material. This system works well with low-pressure distribution systems, but is generally not used in high pressure applications. A variation of this is the couple-and-wrap method similar to a butt-and-wrap with a coupling. Threaded FRP pipe with a box and pin configuration is also widely used in oilfield applications. Maintaining a complete seal in natural gas containers at higher pressures however is a challenge with this method of connection. Flanged connection is quick to install, but larger diameters are difficult to work with, and flanged pipe is not cost competitive.

[0014] Clay minerals are the basic component for the preparation of organoclays, the most common type of nanofillers. Essentially clay minerals may be defined as hydrous-layered silicates, which consist of two types of continuous sheet-like structural units. One is a tetrahedral sheet of silica, which is arranged as a hexagonal network in which the tips of all the tetrahedral units point in one direction. The other structural unit (octahedral sheet) consists of two layers of closely packed oxygen or hydroxyl groups in which aluminum, iron or magnesium atoms are embedded at equidistant from oxygen or hydroxyl as shown in Figure1A.

[0015] Stacking of the layers leads to a regular van-der Waals gap between the layers called the interlayer space or silicate gallery (Figure 1B). Isomorphic substitution within the layers (i.e. of Si by Al or of Si by Mg) generates negative charges at layer surfaces that for some clays may be counterbalanced by monovalent cations such as Na^+,K^+,Li^+ residing in the interlayer space. For certain classes of clays (i.e. smectites) such cations may be exchanged for other metal or organic cations. The ability to exchange cations is an important feature of clay minerals. This can be beneficial in introducing other characteristic via clay modification process.

[0016] In view of the foregoing, the present invention is directed to combining nanocomposite materials and various other layers into a vessel that provides an improved container for CNG, particularly a vessel that may function as a fuel tank for use in the automobile industry. Thus, one embodiment of the invention is a seamless nanocomposite vessel comprising: a high density polymer adapted into the shape of a desired vessel, the vessel having an inner surface sputtered with a metal and an outer surface, the inner surface defining a space; and a plurality of layers disposed over the inner surface of the vessel, the outer surface of the vessel, or both, each layer being independently selected from the group consisting of a thermoplastic material and a thermoset nanocomposite material.

[0017] As used herein a “high density polymer” is any polymer which provides the requisite characteristics of the vessel, *e.g.* strength and heat resistance. High density polymers include but are not limited to polyolefins such as polyethylene, polypropylene, polymethylpentene, polybutene-1 and copolymers thereof. Other high density polymers include polyamides and polyamide-imides. In some embodiments the high density polyamide is high-density polyethylene (HDPE).

[0018] The high density polymer may be adapted into a desired shape by one of many means known to the art. Such means include, but are not limited to blow molding, compression molding, extrusion molding, injection molding and vacuum formation. In some embodiments the high density polymer is adapted into a desired shape by blow molding.

[0019] Another embodiment of the invention is seamless nanocomposite vessel comprising: a high density polymer adapted into the shape of a desired vessel, the vessel having an inner surface sputtered with a metal and an outer surface, the inner surface defining a space; and a plurality of layers disposed over the inner surface of the vessel, the outer surface of the vessel, or both, each layer being independently selected from the group consisting of: a functionalized thermosetting resin, electrospun epoxy nanocomposite fibers, and a flame resistant agent.

[0020] In some embodiments the thermoplastic material comprise electrospun nanocomposite fibers.

[0021] In some embodiments the electrospun nanocomposite fibers further comprise a filler.

[0022] Such fillers include, but are not limited to a silica, a nanoclay, carbon black, carbon nanotubes, graphite, graphene, fullerenes, carbon onions, aluminum silicate nanotubes, nanocrystalline aluminum alloys reinforced with a ceramic, nanocrystalline semiconductors, cerium oxide nanoparticles, gold nanoparticles, silver nanoparticles, titanium dioxide nanoparticles, palladium nanoparticles, zinc oxide nanoparticles, copper nanoparticles, phosphate nanoparticles, iron-aluminum nanoparticles, calcium phosphate nanoparticles, and combinations thereof.

[0023] Nanoclays include, but are not limited to clays of the montmorillonite, bentonite, kaolinite, hectorite, halloysite and smectite classes. Nanoclayc also include organically modified organoclays. Organoclays can be further modified, e.g. by the introduction of transition metal ions such as iron, nickel, manganese, cobalt, copper, or combinations thereof.

[0024] In some embodiments the filler is selected from the group consisting of nanoclay, carbon black, carbon nanotubes, graphite, graphene, fullerenes, carbon onions, and combinations thereof.

[0025] As used herein a “flame resistant agent” is any agent that provides thermal protection. Preferred flame resistant agents provide resistance to wear and damage to the vessel Examples of flame resistant agents include, but are not limited to flame resistant foams.

[0026] Functionalized thermosetting resin include, but are not limited to the group consisting of vinyl ester, epoxy, acrylic, urethane, and combinations thereof. In some embodiments the functionalized thermosetting resin is epoxy.

[0027] As used herein a “functionalized thermosetting resin” is a resin containing functional groups that improve a desired property, e.g. strength, resistance to heat, resistance to hydrocarbon permeation or resistance to oxygen permeation. Functionalized thermosetting resins and methods of their preparation are well known in the art. For example, US 20060173142 A1 (Nava and Small), U.S. Patent 8,119,702 B2 (Luan et al.) and U.S. patent 5,227,463 A (Arsenault), the contents of each of which are incorporated by reference herein in their entireties.

[0028] In some embodiments the functionalized thermosetting resin is functionalized to reduce hydrocarbon permeability.

[0029] In some embodiments the functionalized thermosetting resin is functionalized to reduce hydrocarbon permeability.

[0030] In some embodiments the vessel is selected from the group consisting of a fuel tank, a storage tank, a reaction vessel, a column, a surface condenser, a pressure vessel, and an industrial column. In some embodiments the fuel tank is a compressed gas fuel tank. In some embodiments the compressed gas fuel tank is a natural gas fuel tank.

[0031] In some embodiments the total number of layers, including the high density polymer is between about 6 to about 12.

[0032] In some embodiments the total number of layers, including the high density polymer, is at least 9.

[0033] In some embodiments the vessel has structural properties sufficient to be rated at least FMVSS 304 compliant or a substantial equivalent.

[0034] In some embodiments the vessel has sufficient structural integrity to store a gas at a pressure of at least 4,000 psi.

[0035] Yet another embodiment of the invention is seamless nanocomposite tank comprising: a high density polyethylene (HDPE) blow molded into the shape of a gas tank, the gas tank having an inner surface and an outer surface, the inner surface defining a space; the inner surface sputtered with a metal for providing structural integrity, followed by a coating of functionalized epoxy for providing a barrier to hydrocarbons from exiting the tank; and the outer surface embedded with a first outer surface coating of functionalized epoxy followed by a first outer surface layer of electrospun epoxy nanocomposite fibers to provide reinforcement to the tank, followed by a second outer surface coating of functionalized epoxy, followed by a second outer surface layer of electrospun epoxy nanocomposite, followed by a third outer surface coating of functionalized epoxy for providing a barrier to oxygen from entering the tank, followed by a layer of flame resistant foam for providing resistance to wear and damage to the tank and fire.

[0036] Yet another embodiment of the invention is a method for making a seamless nanocomposite vessel. This method comprises: a) forming a vessel from a high density polymer, the vessel having an inner surface and an outer surface, the inner surface defining a space; b) sputtering the inner surface of the vessel with a metal to provide structural integrity to the vessel; c) coating the metal-sputtered inner surface of the vessel with a first functionalized thermosetting resin to provide a barrier for substantially preventing hydrocarbons stored in the space from escaping from the vessel; d) coating the outer surface of the vessel with a second functionalized thermosetting resin; e) coating the outer surface of the vessel after step d with a first electrospun epoxy nanocomposite fiber material to provide further structural support to the vessel; f) coating the electrospun epoxy nanocomposite fiber-embedded outer surface of the vessel with a third functionalized thermosetting resin; g) coating the outer surface of the vessel after step f, with a second electrospun epoxy nanocomposite fiber material; h) coating the outer surface of the vessel after step g, with a fourth functionalized thermosetting resin to provide a barrier for substantially preventing oxygen from the outside environment from penetrating into the vessel; and i) applying a flame resistant agent to the outer surface of the vessel after step h, wherein the first, second, third and fourth functionalized thermosetting resin are independently selected and may be the same or different resin.

[0037] The following examples are provided to further illustrate the methods and compositions of the present invention. These examples are illustrative only and are not intended to limit the scope of the invention in any way.

EXAMPLES

EXAMPLE 1

Issues in Storage of Fuel

[0038] There are three main issues in storage of fuel:

1. Mechanical (including pressure rating) and permeability properties of the fuel container;
2. Weight of the fuel containers; and
3. Cost effectiveness.

[0039] Fuel containers for CNG storage are developed that address each of these issue independently to present a comprehensive solution. Polymer nanocomposite fuel tanks primarily are developed using HDPE (high density polyethylene). Physical properties are of key importance in storage tanks developed using polymers. Mechanical properties can be tailored in many ways using various categories of fillers, but barrier properties remain a big challenge. To be an effective barrier, it is necessary not only to maintain its physical integrity when exposed to chemicals, but to also perform as a barrier against these chemicals. Whilst chemical resistance tests provide a measure of resilience, the measure of barrier performance is the permeation rate. This is where HDPE fails as a hydrocarbon resistant barrier because polyethylene and other common homogeneous geo-synthetic membrane materials are readily permeable to hydrocarbons, because they are hydrocarbons themselves. Hydrocarbons are non-polar in nature hence there is a need of a polar layer to create an effective barrier for hydrocarbons. Also, thermoplastic material is susceptible to a reduction in mechanical properties at elevated temperature, which limits usage of HDPE containers. It is imperative to design multi-component, multi-layer polymer nanocomposite materials, which account for enhanced mechanical, reduced barrier and high pressure withholding, properties.

[0040] A combination of thermoplastic and thermoset nanocomposite layers is introduced to reinforce the container thus addressing all such issues. In addition, introduction of fillers in thermoplastic layers enhances the mechanical properties at elevated temperature and provide improved barrier properties. Thermosetting resins, such as vinyl ester or epoxy can be used to develop layers, which are a part of the container, provide enhanced mechanical properties and have much better resistance to heat. Introduction of fillers such as nanoclay, further enhances these properties. Another layer could be a hybrid layer made up of carbon or glass fibers in the matrix of epoxy resin. This allow for the use of different materials in different layers to design vessels with high barrier and thermal properties and enhanced mechanical strength with high-pressure rating according to the desired end-use.

EXAMPLE 2

Nanocomposite Technology

[0041] Supercritical CO_2-processed polymer/clay nanocomposites are developed and characterized for use in natural gas fuel containers. A superior quality polymer nanocomposite material, which leads to platform technologies for manufacturing economical and high-performance (higher strength and low permeability) natural gas fuel containers with requisite pressure rating is developed. Property enhancements in such polymer–nanocomposites are governed by the extent of dispersion of clay particles in the polymer matrix, and the degree of interaction between clay particles and polymer. Supercritical CO_2 technology for exfoliation and dispersion of clay is utilized to accomplish this objective.

[0042] This technology creates a strong barrier and strengthens the polymer nanocomposites. The fillers processed via supercritical fluid processing technology can be then introduced in a spectrum of polymers (thermoplastic and thermosetting) resins. These fillers have proved to enhance properties without diminishing or altering core polymeric properties. Materials thus produced could be used on existing processing procedures or production lines, and no new setup is required. This technology enables controlled placement and dispersion of nanoparticles, which can then be dispersed in a controlled manner within polymer resins. The resulting material has shown drastic improvements in mechanical and permeability properties.

EXAMPLE 3

Polymer Layer Modification Using Scavengers and Repellants

[0043] Scavenging agent and repellants are introduced in clay to enhance the barrier properties of the resulting polymer nanocomposite film. For containers containing CNG gas it is imperative that a dual barrier is created, which creates a barrier for oxygen to permeate into the containers and stored CNG to escape from the containers. Introduction of oxygen scavenging agents on the inside ensure that any oxygen inside is absorbed in the layer and removed from the mix. Creating a barrier on the outer surface ensures a barrier against oxygen. The inside surface of the container is coated in such a manner that hydrocarbons are repelled and it does not allow hydrocarbons to escape from the container.

[0044] Oxygen scavenging materials are useful in packaging materials, storage containers especially for applications where contamination can result in disaster, providing a longer shelf life to contents. In industry using metallic scavengers (transition metal ions such as Fe, Cu etc.) is common practice and they are used in the form of powder packed in a sachet, which is inserted in the product. The most commonly used oxygen scavengers are based on the principle of iron oxidation. Not wishing to be bound to a particular theory, the inventors beleive that all the transition metal ions (TMI), which are susceptible to oxidation in the presence of air, can be used as oxygen scavengers. TMI especially iron (Fe) and copper (Cu) which show multiple oxidation states, are of great interest due to their catalytic activity for specific reactions such as hydrosilylation, oxidation, C–C coupling, and selective hydrogenation. Such transition metal ions not only act as oxygen scavengers, but also improve thermal characteristics. The compatibility of TMI and polymer matrices is important to consider when using TMI as oxygen scavengers for polymers matrices. Organoclays can be made compatible with both transition metal compounds and polymers, and thus can serve as media for the introduction of TMI into polymer matrices. Introducing transition metal ion and reduction of their oxidation state enhances the oxygen scavenging properties of these ions when present in the clay. Figures 2A and 2B schematically compare the appearance of an unmodified organoclay to one containing a transition metal compound.

[0045] Hydrocarbons are non-polar in nature hence it is imperative that they do not interact with any non-polar components in the fuel container else permeation will occur. To be able to create a high-barrier for hydrocarbons, the layer interacting with the hydrocarbons can be highly polar in nature coupled with a barrier created by fillers that are introduced in this layer. An inner-polar layer, which will protect hydrocarbons from escaping and a non-polar outside layer acting as a barrier against oxygen is therefore desirable.

EXAMPLE 4

Nanocomposite Fuel Tanks

[0046] A multilayer, multi-polymer, multi–filler polymer nanocomposite fuel container compliant with Department Of Transportation requirement for storing CNG is developed.

1. A multi layer composite material enhances mechanical and barrier properties along with thermal stability.
2. Selection of material is strictly based on pressure rating, as for storing CNG a container must be able to withhold 3600 or more psi.
3. Weight is kept at its minimum hence the architecture of multi-component polymer composite is such that weight doesn't increase the current weight of a vehicle.

EXAMPLE 5

Prototype Fuel Tank

[0047] A design of a nanocomposite fuel tank according to the present invention, which provides mechanical and barrier properties as desired and is able to withhold hydrostatic pressure of 3600 psi or more is developed. Design of tank has multiple layers and multiple components and each individual layer has unique characteristics and contributes towards multiple properties. The design can be broken down into individual layers with various characteristics.

[0048] Material of construction is a mix of thermoplastic and thermosetting layers. Each layer is modified using fillers that enhance different properties of the polymer. Clay is a sheet like material and it provides tortous path for the any permeating molecule, hence increasing the physical barrier for the permeating molecule. Thermal stability of material increases with the inclusion of clay. Hence inclusion of clay in each individual layer increases thermal stability of that layer and enhances the barrier properties of these layers. Overall, use of clay creates a thermally stable and high barrier multi-layer material for application in fuel tanks. Carbon black is a small sheet-like hexagonal nano plate material which forms network points in the polymer matrix and increases the strength of material. Inclusion of carbon black increases the strength of each individual layer, and the over all mechanics of the multilayer material increases. These are low cost additives and are used to enhance the mechanical, thermal and barrier properties of material for storing CNG. Surface modification of epoxy with, *e.g.*, florination or sulfonation, provides a chemical barrier by repelling action and hence improves specific barrier properties of these layers. The inside layers may be coated with modified epoxy such that hydrocarbons cannot escape. Also, the metallic layer provides a strong barrier for permeating hydrocarbon molecules, if any. This eliminates the possibility of leaks in the fuel tank.

[0049] In a composite fuel tank there are usually two stresses that can develop one along the circumference and other along the tangential axis. Wrapping of epoxy nanocomposite fibers takes care of such stresses and provide requisite strength to the core shell. Conventionally carbon fibers have been used to provide this strength; here a similar strength is achieved using epoxy nanocomposite fibers. An outermost layer of foam provides impact resistance to the gas tank and will protect from regular wear tare. This protective foam can be flame retardant hence protecting the contents of tank in an event of fire.

[0050] In this design the approximate dimensions of the CNG fuel tank are:

Length 55 to 56 inches

Diameter 16 inches

Weight 45 to 50 kgs

Thickness of walls 2”

Volume of water 130L

[0051] This is illustrated in Figure 3, which shows construction of a nanocomposite vessel of the present invention wherein multiple layers of various resins which contain multiple components are used to achieve desired properties.

[0052] In particular, Figure 3 shows a fuel tank (1) having the following layers:

a) A functionalized epoxy coating (21);
b) A sputtered metallic coating (25);
c) A HDPE nanocomposite layer (30);
d) A functionalized epoxy nanocomposite coating (35);
e) Electrospun epoxy nanocomposite fibers (40);
f) A functionalized epoxy nanocomposite coating (45);
g) Electrospun epoxy nanocomposite fibers (50);
h) A functionalized nanocomposite coating as a barrier against O_2 (45); and
i) A protective foam layer.

[0053] The HDPE nanocomposite layer (30) is a core shell blown molded out of HDPE nanocomposite material. HDPE nanocomposite material is developed using

HDPE modified with clay and carbon black to provide strength and reduced permeability to the HDPE layer. The sputtered metallic coating (25) is present on the inside of the core shell followed by the functionalized epoxy coating (21) (innermost layer) which is epoxy modified coating to provide a barrier against hydrocarbon. The functionalized epoxy nanocomposite coating (35) is modified epoxy to act as an adhesive layer between HDPE and electrospun fibers. The electrospun epoxy nanocomposite fibers (40) are woven to provide strength. Epoxy is modified with fillers like clay, and carbon black to provide enhanced barrier and mechanical properties. This epoxy is drawn as an elctrospun fiber and wrapped around the core shell in weaved pattern and then allowed to cure on this surface. Adhesive present in the functionalized epoxy nanocomposite coating (35) cure along with this layer such that there is no phase separation. The functionalized epoxy nanocomposite coating layer (45) is a modified epoxy to act as an adhesive layer between the two layers of electrospun fibers. The electrospun epoxy nanocomposite fibers (50) are woven to provide strength. Epoxy is modified with fillers like clay, and carbon black to provide enhanced barrier and mechanical properties. This epoxy is drawn as an elctrospun fiber and wrapped in a weaved pattern. The functionalized nanocomposite coating as a barrier against O_2 (55) is the outermost layer of coating which is formulated using modified epoxy such that there is no permeation into the gas tank. The protective foam layer (60) is an external sleeve of foam which provides resistance towards damage and fire. It is an impact resistant layer in the tank to minimize damage due to wear and tear.

[0054] Although illustrative embodiments of the present invention have been described herein, it should be understood that the invention is not limited to those described, and that various other changes or modifications may be made by one skilled in the art without departing from the scope or spirit of the invention.

What is claimed is:

1. A seamless nanocomposite vessel comprising:

 (a) a high density polymer adapted into the shape of a desired vessel, the vessel having an inner surface sputtered with a metal and an outer surface, the inner surface defining a space; and

 (b) a plurality of layers disposed over the inner surface of the vessel, the outer surface of the vessel, or both, each layer being independently selected from the group consisting of a thermoplastic material and a thermoset nanocomposite material.

2. A seamless nanocomposite vessel comprising:

 (a) a high density polymer adapted into the shape of a desired vessel, the vessel having an inner surface sputtered with a metal and an outer surface, the inner surface defining a space;

 (b) a plurality of layers disposed over the inner surface of the vessel, the outer surface of the vessel, or both, each layer being independently selected from the group consisting of: a functionalized thermosetting resin, electrospun epoxy nanocomposite fibers, and a flame resistant agent.

3. The seamless nanocomposite vessel according to claim 2 in which the electrospun nanocomposite fibers further comprise a filler.

4. The seamless nanocomposite vessel according to claim 3, wherein the filler is selected from the group consisting of nanoclay, carbon black, carbon nanotubes, graphite, graphene, fullerenes, carbon onions, and combinations thereof.

5. The seamless nanocomposite vessel according to claim 2, wherein the flame resistant agent is a flame resistant foam.

6. The seamless nanocomposite vessel according to claim 2, wherein the functionalized thermosetting resin is selected from the group consisting of vinyl ester, epoxy, acrylic and urethane.

7. The seamless nanocomposite vessel according to claim 6, wherein the functionalized thermosetting resin is epoxy.

8. The seamless nanocomposite vessel according to claim 2, wherein the functionalized thermosetting resin is functionalized to reduce hydrocarbon permeability.

9. The seamless nanocomposite vessel according to claim 2, wherein the functionalized thermosetting resin is functionalized to reduce oxygen permeability.

10. The seamless nanocomposite vessel according to claim 2, wherein the high density polymer is selected from the group consisting of high density polyethylene (HDPE), polypropylene, polymethylpentene, polybutene-1 polyamides polyamide-imides and combinationa thereof.

11. The seamless nanocomposite vessel according to claim 2, wherein the high density polymer is HDPE.

12. The seamless nanocomposite vessel according to claim 2, wherein the vessel is selected from the group consisting of a fuel tank, a storage tank, a reaction vessel, a column, a surface condenser, a pressure vessel, and an industrial column.

13. The seamless nanocomposite vessel according to claim 12, wherein the fuel tank is a compressed gas fuel tank.

14. The seamless nanocomposite vessel according to claim 13, wherein the compressed gas fuel tank is a compressed natural gas fuel tank.

15. The seamless nanocomposite vessel according to claim 2, wherein the total number of layers, including the high density polymer is between about 6 to about 12.

16. The seamless nanocomposite vessel according to claim 14, wherein the total number of layers, including the high density polymer, is at least 9.

17. The seamless nanocomposite vessel according to claim 2, which has structural properties sufficient to be rated at least FMVSS 304 compliant.

18. The seamless nanocomposite vessel according to claim 2, which has sufficient structural integrity to store a gas at a pressure of at least 4,000 psi.

19. A seamless nanocomposite tank comprising:

(a) a high density polyethylene (HDPE) blow molded into the shape of a gas tank, the gas tank having an inner surface and an outer surface, the inner surface defining a space;

i. the inner surface sputtered with a metal for providing structural integrity, followed by a coating of functionalized epoxy for providing a barrier to hydrocarbons from exiting the tank; and

ii. the outer surface embedded with a first outer surface coating of functionalized epoxy followed by a first outer surface layer of electrospun epoxy nanocomposite fibers to provide reinforcement to the tank, followed by a second outer surface coating of functionalized epoxy, followed by a second outer surface layer of electrospun epoxy nanocomposite, followed by a third outer surface coating of functionalized epoxy for providing a barrier to oxygen from entering the tank, followed by a layer of flame resistant foam for providing resistance to wear and damage to the tank and fire.

20. A method for making a seamless nanocomposite vessel comprising:

a. forming a vessel from a high density polymer, the vessel having an inner surface and an outer surface, the inner surface defining a space;
b. sputtering the inner surface of the vessel with a metal to provide structural integrity to the vessel;
c. coating the metal-sputtered inner surface of the vessel with a first functionalized thermosetting resin to provide a barrier for substantially preventing hydrocarbons stored in the space from escaping from the vessel;
d. coating the outer surface of the vessel with a second functionalized thermosetting resin;
e. coating the outer surface of the vessel after step d with a first electrospun epoxy nanocomposite fiber material to provide further structural support to the vessel;
f. coating the electrospun epoxy nanocomposite fiber-embedded outer surface of the vessel with a third functionalized thermosetting resin;
g. coating the outer surface of the vessel after step f, with a second electrospun epoxy nanocomposite fiber material;
h. coating the outer surface of the vessel after step g, with a fourth functionalized thermosetting resin to provide a barrier for substantially preventing oxygen from the outside environment from penetrating into the vessel; and

i. applying a flame resistant agent to the outer surface of the vessel after step h,

wherein the first, second, third and fourth functionalized thermosetting resin are independently selected and may be the same or different resin.

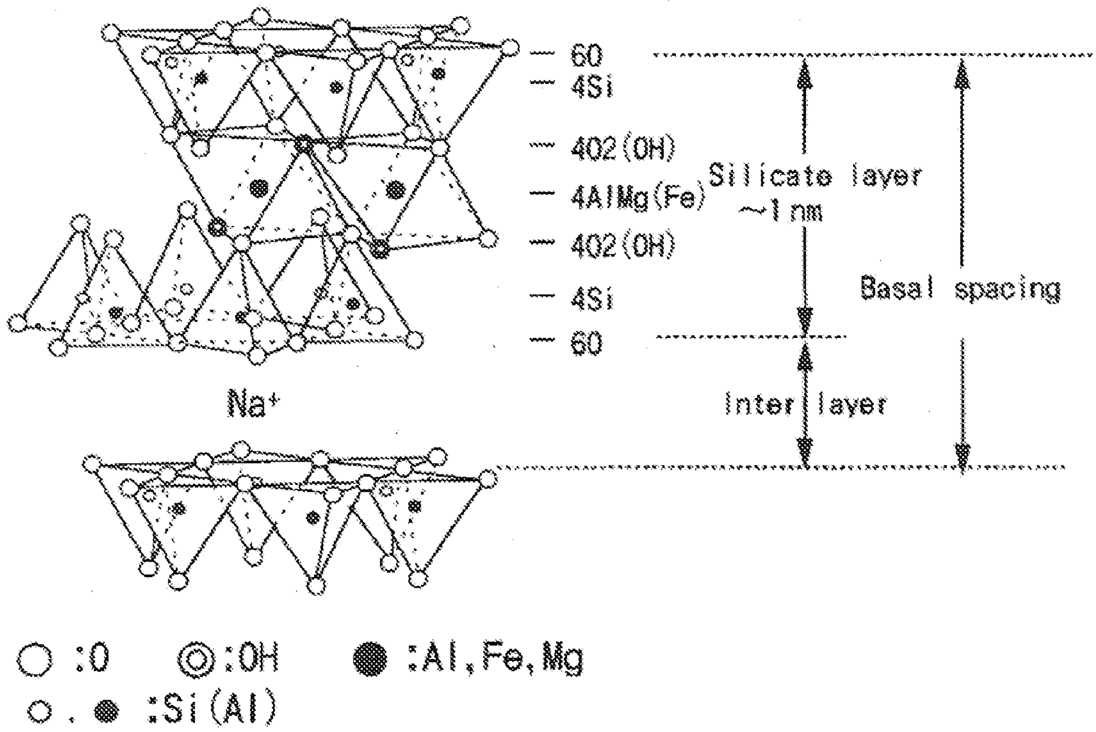

Figure 1A

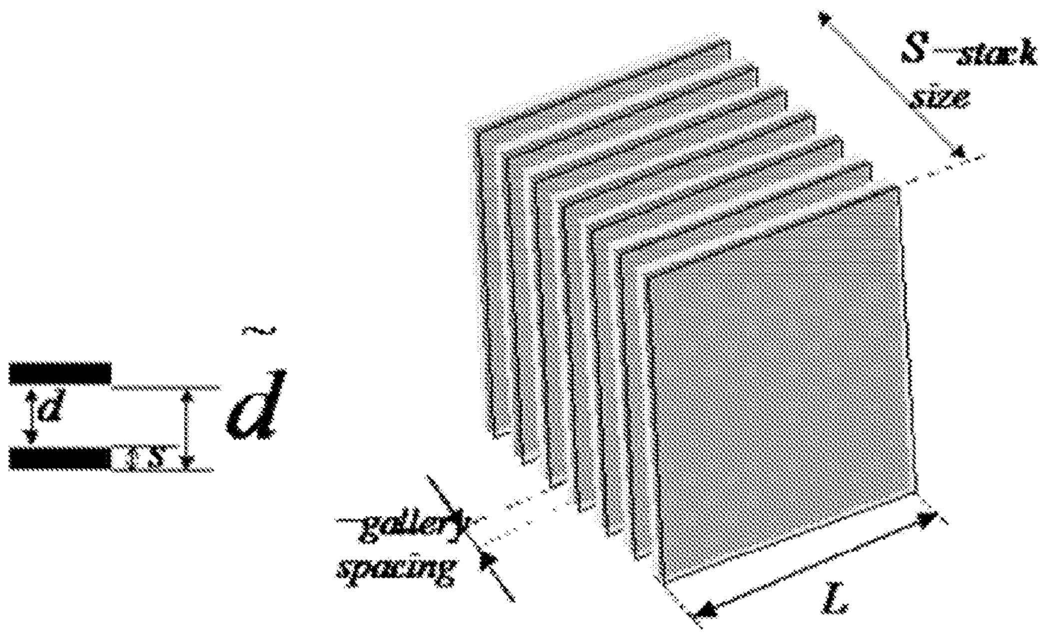

Figure 1B

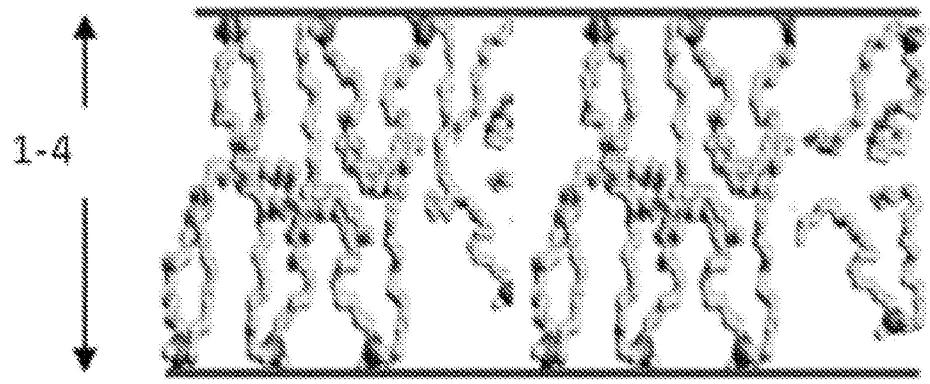

Figure 2A

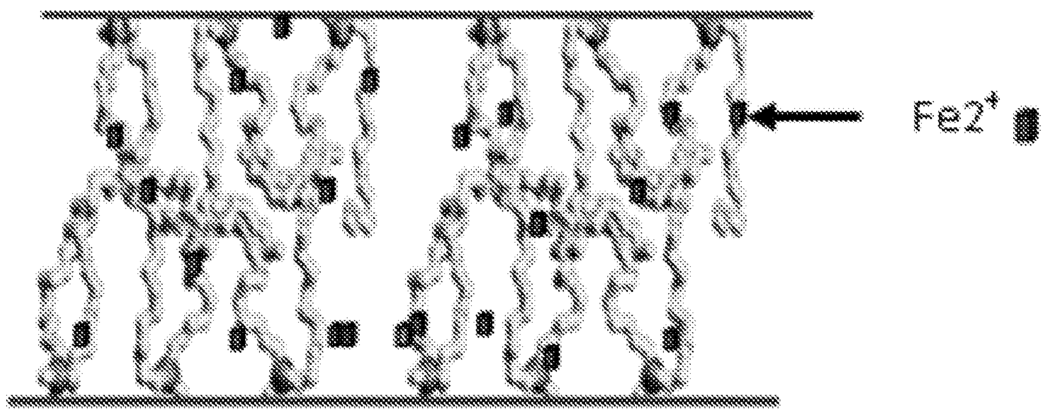

Figure 2B

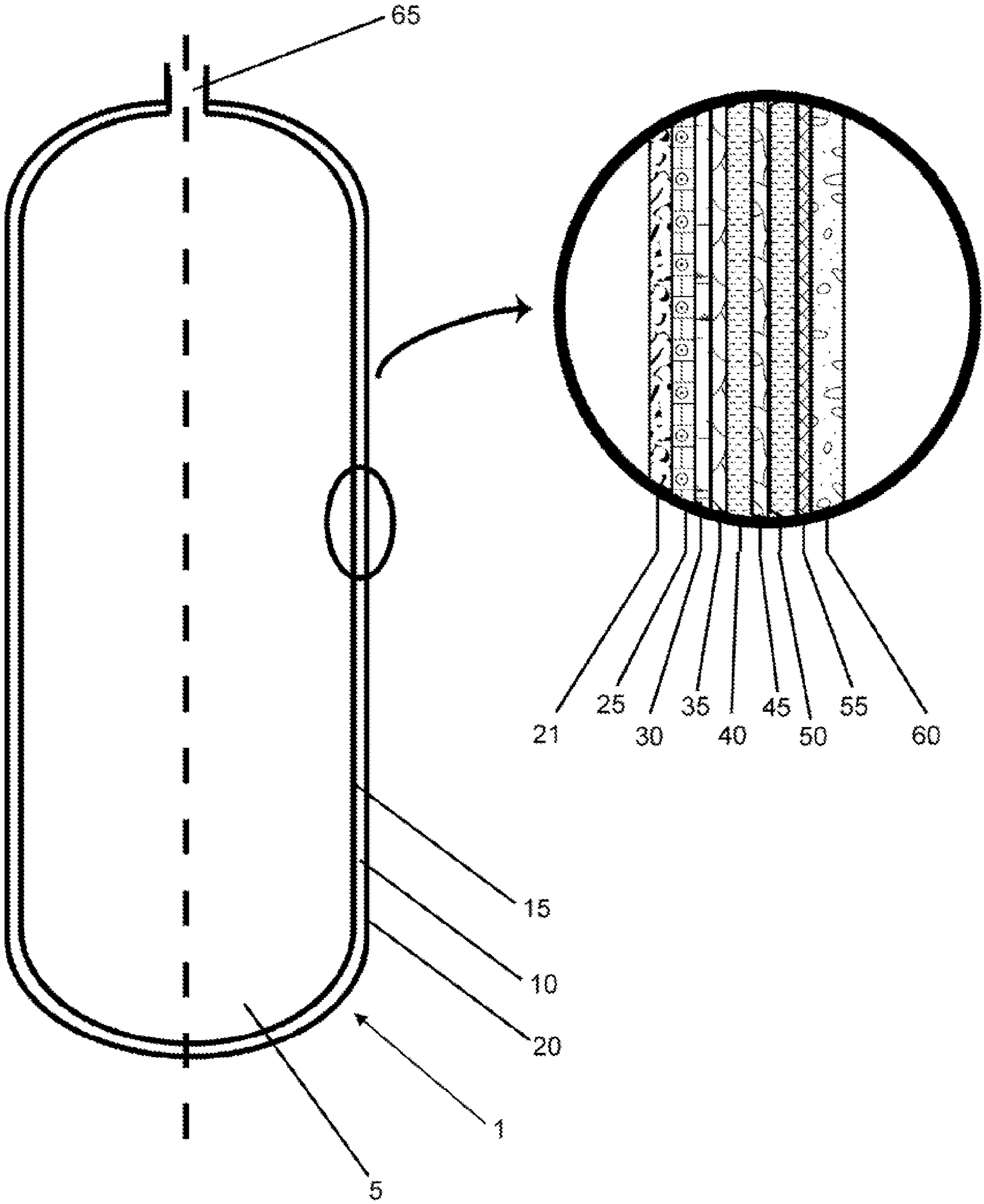

Figure 3