FLEXIBLE POLYMERIC TUBING WITH ADMIXED GRAPHENE FOR REDUCED GAS PERMEABILITY

BACKGROUND OF THE INVENTION

1. Field of the Invention

Embodiments of the invention relate generally to flexible polymeric tubing. More particularly, embodiments of the invention relate to the use of graphene for providing reduced gas permeability in flexible polymeric tubing.

2. Description of Prior Art and Related Information

The following background information may present examples of specific aspects of the prior art (e.g., without limitation, approaches, facts, or common wisdom) that, while expected to be helpful to further educate the reader as to additional aspects of the prior art, is not to be construed as limiting the present invention, or any embodiments thereof, to anything stated or implied therein or inferred thereupon.

Extruded plastic pipe or tubing is used for a variety of applications. For example, such plastic pipes are utilized for the transportation of water, more specifically delivery systems for hot and/or cold potable water, radiant floor heating, waste water and fire sprinkler systems, among other uses. Such plastic pipes can also be used as district heating pipes and as process pipes in the food industry, and other applications include the conveyance of liquids other than water, such as gases and slurries. Examples of thermoplastic polymers used for the manufacturing of such plastic pipes include polyolefins such as polyethylene (PE) (e.g., PE-raised temperature, or PE-RT), polypropylene (PP), polybutylenes (PB), and any copolymers thereof; polyolefin copolymers such as poly(ethylene-co-maleic anhydride); poly(vinyl chloride) (PVC); and chlorinated PVC, i.e., CPVC; and the like.

Cross-linked polyethylene (PEX) is commonly used for plastic pipes. There are several varieties of PEX that utilize a number of different crosslinking chemistries and processing technologies. Various PEX grades further contain other additives such as antioxidants and/or stabilizer packages in different concentrations and combinations. Three known varieties of PEX for pipe applications are PEX-a, PEX-b, and PEX-c.

In the PEX-a process, the crosslinking is induced by peroxide under the influence of heat and high pressure. The resultant PEX-a composition is crosslinked through carbon-carbon bonds to form the crosslinked polymer network. The crosslinking, which is considered to be homogeneous and uniform for PEX-a, gives degrees of crosslinking in the range of 70-90% for practical applications. Requirement for CCL is to be above 70% for PEX-a as defined in ASTM International's Standard for Crosslinked Polyethylene (PEX) Tubing, F 867-04 (approved May 1, 2004).

In the PEX-b process, the crosslinking is induced by moisture and heat over extended pre-determined times. The crosslinking occurs in a secondary post-extrusion process that is accelerated by a combination of heat and moisture. The latter combination is the active “reagent”, which is involved in the primary hydrolysis and condensation reaction. In principle, the extruded pipe is exposed to hot water and a steam bath. A fundamental difference to PEX-a, is that for PEX-b, the resultant crosslinks are not between carbon-carbon bonds, but instead, oxygen-silicon covalent bonds (siloxane “bridges”) are formed. In comparison with PEX-a, the crosslink density (CCL) are somewhat lower for PEX-b (65-70%), and the crosslinking is also less uniform.

In the PEX-c process, no chemicals are needed in order to facilitate the crosslinking process, but instead high energy electron beam (EB) irradiation is utilized to create the free radicals necessary for the hydrogen abstraction and subsequent crosslinking to take place. The high energy electron beams are non-selective, i.e., chemical bonds are cleaved in an un-controlled fashion. The latter has the consequence of creating side reactions, together with the reaction aimed for, i.e., the crosslinking of HDPE. The crosslinking density for PEX-c is typically in the 70-75% range, and caution has to be taken with irradiation time since a too long exposure may give discolored products and/or brittleness. PEX-c has been successfully used for many years despite the somewhat challenging production conditions.

A variety of plastic pipes may be produced in the form of multi-layer plastic pipes, wherein at least one of the layers comprise the extruded thermoplastic plastic pipe as described above. Multi-layer plastic pipes are well known in the industry and have been used for all applications described herein. Additional layers are currently used to provide various desired properties, for example oxygen barrier properties, UV light protection, scratch resistance and enhanced mechanical performance, long-term stability (known as chlorine resistance in accordance with F876 and ASTM 2023), visual appearance in order to create esthetic values and/or for labeling purposes, and the like.

In one example, for an oxygen barrier, such additional layers may be produced from thermoplastic non-crosslinked poly(ethylvinylalcohol) (EvOH). For the same purpose, metallic layers can be used, for example aluminum or stainless steel. The metal layer in such cases will provide oxygen barrier properties. In some instances, metal coatings may be applied using vacuum deposition, from which the final metal coatings will have thicknesses in the nanometer range. The metallic layer may also act as a strengthening layer, and in such cases, the metal layer will be thicker, i.e., in the micrometer range. In addition, colored low density polyethylene resins are commonly used to create colored pipes, typically blue for cold potable water applications, and red for hot water. Furthermore, outer coating layers may be applied in the form of crosslinked polyethylene, for example PEX-b.

In any case, where thermoplastic polymers, such as EvOH, polyethylene, PEX-b pre-polymers, or the like, co-extrusion technology is commonly used for this purpose. Co-extrusion is a process whereby a coating layer is applied to a polymeric pipe (e.g., a PEX pipe) by extruding a polymer-based material through a ring shaped die as the polymeric pipe is passed through the die. Because of difficulties in obtaining thin coating layers with the co-extrusion process, the practical lower limit for the coating layer thickness is about 100 μm. Co-extrusion also presents other challenges, for example limited flexibility in operating conditions and in potential raw materials, high energy requirements, costly start-up times and purge requirements, and general difficulties with quality control such as obtaining a consistent coating layer thickness and an inability to effectively level the surface of the pipes. In the case where PEX-b technology is used for the outer layers, a secondary time-consuming and costly operation step is necessary.

As can be seen, there is a need for providing a reduced gas permeable polymeric pipe that can be prepared as a single layer extruded product.

SUMMARY OF THE INVENTION

Embodiments of the present invention provide a method and apparatus that reduces the gas permeability of polymeric pipe, such as PEX tubing.

Embodiments of the present invention also provide a method for reducing permeability of a gas through a polymeric material comprising admixing graphene with a polymeric mixture prior to formation of the polymeric material; and forming the polymeric material with the graphene dispersed therein.

In some embodiments, the graphene is evenly dispersed in the polymeric material.

In some embodiments, the polymeric material is a tubing. In some embodiments, the tubing is a polyethylene tubing. In some embodiments, the tubing is a cross-linked polyethylene (PEX) tubing.

In some embodiments, the method further includes incorporating the tubing in a closed loop circulation system. In some embodiments, the closed loop circulation system is a heating system. In some embodiments, the heating system is a radiant heating system.

In some embodiments, the method further includes mixing the graphene with a polymeric starting material. In some embodiments, the polymeric starting material is solid polyethylene.

In some embodiments, the method includes mixing the graphene with molten, cross-linked polymeric starting material. In some embodiments, the cross-linked polymeric starting material is cross-linked polyethylene.

Embodiments of the present invention also provide a polymeric tubing comprising a polymeric material extruded into the polymeric tubing; and graphene admixed with the polymeric material. In some embodiments the polymeric tubing is cross-linked polyethylene (PEX) tubing.

These and other features, aspects and advantages of the present invention will become better understood with reference to the following drawings, description and claims.

BRIEF DESCRIPTION OF THE DRAWINGS

Some embodiments of the present invention are illustrated as an example and are not limited by the figures of the accompanying drawings, in which like references may indicate similar elements.

The Figure illustrates the peroxide, the silane and irradiation crosslinking methods for making PEX tubing, where graphene can be added at various stages of the process.

Unless otherwise indicated illustrations in the figures are not necessarily drawn to scale.

The invention and its various embodiments can now be better understood by turning to the following detailed description wherein illustrated embodiments are described. It is to be expressly understood that the illustrated embodiments are set forth as examples and not by way of limitations on the invention as ultimately defined in the claims.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS AND BEST MODE OF INVENTION

The terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting of the invention. As used herein, the term "and/or" includes any and all combinations of one or more of the associated listed items. As used herein, the singular forms "a," "an," and "the" are intended to include the plural forms as well as the singular forms, unless the context clearly indicates otherwise. It will be further understood that the terms "comprises" and/or "comprising," when used in this specification, specify the presence of stated features, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, steps, operations, elements, components, and/or groups thereof.

Unless otherwise defined, all terms (including technical and scientific terms) used herein have the same meaning as commonly understood by one having ordinary skill in the art to which this invention belongs. It will be further understood that terms, such as those defined in commonly used dictionaries, should be interpreted as having a meaning that is consistent with their meaning in the context of the relevant art and the present disclosure and will not be interpreted in an idealized or overly formal sense unless expressly so defined herein.

In describing the invention, it will be understood that a number of techniques and steps are disclosed. Each of these has individual benefit and each can also be used in conjunction with one or more, or in some cases all, of the other disclosed techniques. Accordingly, for the sake of clarity, this description will refrain from repeating every possible combination of the individual steps in an unnecessary fashion. Nevertheless, the specification and claims should be read with the understanding that such combinations are entirely within the scope of the invention and the claims.

In the following description, for purposes of explanation, numerous specific details are set forth in order to provide a thorough understanding of the present invention. It will be evident, however, to one skilled in the art that the present invention may be practiced without these specific details.

The present disclosure is to be considered as an exemplification of the invention and is not intended to limit the invention to the specific embodiments illustrated by the figures or description below.

As is well known to those skilled in the art, many careful considerations and compromises typically must be made when designing for the optimal configuration of a commercial implementation of any system, and in particular, the embodiments of the present invention. A commercial implementation in accordance with the spirit and teachings of the present invention may be configured according to the needs of the particular application, whereby any aspect(s), feature(s), function(s), result(s), component(s), approach(es), or step(s) of the teachings related to any described embodiment of the present invention may be suitably omitted, included, adapted, mixed and matched, or improved and/or optimized by those skilled in the art, using their average skills and known techniques, to achieve the desired implementation that addresses the needs of the particular application.

Broadly, embodiments of the present invention provide apparatus and methods for producing oxygen barrier PEX pipes that can be used in, for example, closed loop heating systems. This oxygen barrier poly pipe must be used in closed loop heating systems to protect against oxygen entering the system and corroding the insides of heating boiler or other sensitive components. There are standards that must be met for this type of polymeric pipe listed as Oxygen Barrier DIN 4726, approved for radiant heating systems. Unlike conventional systems that use a complicated layering process for these pipes, which is typically not 100% efficient at keeping oxygen out of the system, the oxygen barrier pipe using graphene provides an improved and cost efficient product for oxygen barrier pipes.

The Figure illustrates the peroxide, the silane and irradiation crosslinking methods for making conventional PEX tubing. In each method, a hydrogen atom is removed from the polyethylene chain (top center), either by radiation (hν) or by peroxides (R-O-O-R), forming a radical. Then, two radical chains can crosslink, either directly (bottom left) or indirectly via silane compounds (bottom right).

Graphene may be intermixed with molten plastic prior to extrusion and then the pipe is extruded using conventional tubing extrusion methods. In some embodiments, the graphene may be added to the polyethylene powder at the start of the cross-linking process. In other embodiments, the graphene may be added after the cross-linking process is complete.

In some embodiments, Graphene may be coated on an interior or an exterior of conventional polymeric tubing. For example, a polymer material may be carbonized via heating to form a graphene layer. Other methods for forming a graphene layer, as may be known in the art, may be used within the scope of the present invention.

Such a polymeric tubing containing graphene may reduce or eliminate the oxygen permeability of the tubing, thus making the tubing particularly applicable in closed systems where dissolved oxygen in the fluid flow may be detrimental. The graphene containing polymeric tubing may also be useful for reducing or eliminating other gases from permeating into or out through the tubing.

Building on the idea that graphene can be used to reduce or eliminate gas permeability through a membrane or a material, other embodiments of the present invention include the use of graphene to reduce or eliminate the escape of gas from an enclosed space. Examples of such items include air-inflated boats, balloons, laminated sails that have composite material coatings, methane biogas holding bladders, methane digest balloons filled with animal or human waste liquid and allowed, for example, in the sun, for warming to produce usable biogas for cooking and the like. Larger balloons, using graphene to reduce or eliminate escape of gases therefrom, can be used for multi-family use or in third-world countries to produce and safely store methane gas. Similarly, blimps, hot air balloons, or even simply rubber or mylar balloons, all may benefit through the use of graphene to help reduce or eliminate the escape of gases therefrom.

In another embodiment, graphene may be used in various products to not only reduce gas permeability, but also to reduce or eliminate liquid permeability through a membrane. Some exemplary items that could benefit by incorporating graphene therein can include surgical latex gloves, diaper plastics, boat bottom anti-fouling paints, colostomy bags and the like.

Accordingly, aspects of the present invention can include graphene infused polymers, not only for plumbing applications, such as with PEX tubing, but for other applications where liquid and/or gas flow through the polymeric material is not desired.

While the addition of graphene to the tubing reduces or eliminates permeation of air, such as oxygen, as discussed above, such a composition can also add strength to the tubing. Such a tubing may remain flexible while possessing added strength in terms of break strength, puncture strength, or the like.

Many alterations and modifications may be made by those having ordinary skill in the art without departing from the spirit and scope of the invention. Therefore, it must be understood that the illustrated embodiments have been set forth only for the purposes of examples and that they should not be taken as limiting the invention as defined by the claims. For example, notwithstanding the fact that the elements of a claim are set forth in a certain combination, it must be expressly understood that the invention includes other combinations of fewer, more or different ones of the disclosed elements.

The words used in this specification to describe the invention and its various embodiments are to be understood not only in the sense of their commonly defined meanings, but to include by special definition in this specification the generic structure, material or acts of which they represent a single species.

The definitions of the words or elements of the following claims are, therefore, defined in this specification to not only include the combination of elements which are literally set forth. In this sense it is therefore contemplated that an equivalent substitution of two or more elements may be made for any one of the elements in the claims below or that a single element may be substituted for two or more elements in a claim. Although elements may be described above as acting in certain combinations and even initially claimed as such, it is to be expressly understood that one or more elements from a claimed combination can in some cases be excised from the combination and that the claimed combination may be directed to a subcombination or variation of a subcombination.

Insubstantial changes from the claimed subject matter as viewed by a person with ordinary skill in the art, now known or later devised, are expressly contemplated as being equivalently within the scope of the claims. Therefore, obvious substitutions now or later known to one with ordinary skill in the art are defined to be within the scope of the defined elements.

What is claimed is:

1. A method for reducing permeability of a gas through a polymeric material comprising:

admixing graphene with a polymeric mixture prior to formation of the polymeric material;

forming the polymeric material with the graphene dispersed therein.

2. The method of claim 1, wherein the graphene is evenly dispersed in the polymeric material.

3. The method of claim 1, wherein the polymeric material is a tubing.

4. The method of claim 3, wherein the tubing is a polyethylene tubing.

5. The method of claim 4, wherein the tubing is a cross-linked polyethylene (PEX) tubing.

6. The method of claim 3, further comprising incorporating the tubing in a closed loop circulation system.

7. The method of claim 6, wherein the closed loop circulation system is a heating system.

8. The method of claim 7, wherein the heating system is a radiant heating system.

9. The method of claim 1, further comprising mixing the graphene with a polymeric starting material.

10. The method of claim 9, wherein the polymeric starting material is solid polyethylene.

11. The method of claim 1, further comprising mixing the graphene with molten, cross-linked polymeric starting material.

12. The method of claim 11, wherein the cross-linked polymeric starting material is cross-linked polyethylene.

13. A polymeric tubing comprising:

a polymeric material extruded into the polymeric tubing; and

graphene admixed with the polymeric material.

14. The polymeric tubing of claim 13, wherein the polymeric tubing is cross-linked polyethylene (PEX) tubing.

15. The polymeric tubing of claim 13, wherein the graphene is mixed with a polymeric starting material.

16. The polymeric tubing of claim 15, wherein the polymeric starting material is solid polyethylene.

17. The polymeric tubing of claim 13, wherein the graphene is mixed with molten, cross-linked polymeric starting material.

18. The polymeric tubing of claim 17, wherein the cross-linked polymeric starting material is cross-linked polyethylene.

19. A method for reducing permeability of oxygen into a closed loop plumbing system formed from cross-linked polyethylene (PEX) tubing, the method comprising:

admixing graphene with a polymeric mixture prior to formation of the PEX tubing;

forming the PEX tubing with the graphene dispersed therein; and

using the PEX tubing in the closed loop plumbing system.

20. The method of claim 19, the closed loop plumbing system is a closed loop heating system.

ABSTRACT

Oxygen barrier PEX pipe can be used in, for example, closed loop heating systems. This oxygen barrier poly pipe must be used in closed loop heating systems to protect against oxygen entering the system and corroding the insides of heating boiler or other sensitive components. There are standards that must be met for this type of polymeric pipe listed as Oxygen Barrier DIN 4726, approved for radiant heating systems. Unlike conventional systems that use a complicated layering process for these pipes, which is typically not 100% efficient at keeping oxygen out of the system, the oxygen barrier pipe using graphene provides an improved and cost efficient product for oxygen barrier pipes.