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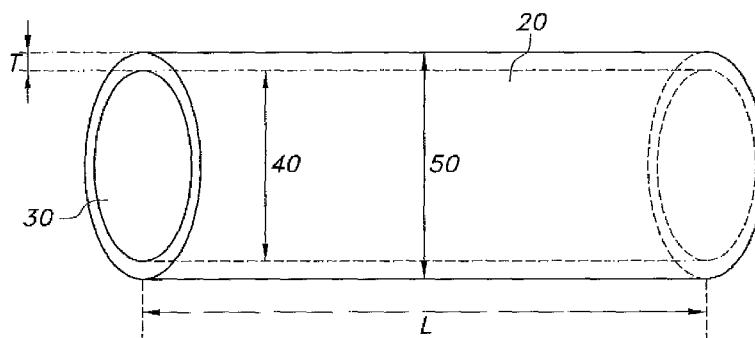


FIG. 1

(57) Abstract: The disclosures herein relate to hydrophobic thermoplastic nylon resins, their manufacture and to hollow conduits, pipes and articles produced from these resins. The conduits, pipes and articles from these resins exhibit increased water resistance and burst stress values.

HYDROPHOBIC THERMOPLASTIC NYLON COMPOSITIONS, ARTICLES AND METHODS FOR MAKING

FIELD OF THE INVENTION

This disclosure relates to hydrophobic thermoplastic nylon compositions and to pipes and hollow conduits and to methods for making the same.

BACKGROUND OF THE INVENTION

High pressure pipe systems are used to gather oil and gas from their source and transfer to refineries, for transport of hydrocarbon containing fluids, for water transportation in fracking applications, for water systems in residential and commercial facilities and for transport of compatible chemicals. Traditionally, such pipelines, especially when used to transfer oil and gas from their source to refineries, have been made from steel. While steel pipelines have acceptable pressure ratings for these uses and relatively low production costs, they are very expensive to transport and to install and are susceptible to corrosion, thus requiring corrosion protection. For this reason, there has been a transition to use of alternative materials for pipelines.

Polyethylene (HDPE) pipes and fittings have been in use for oil and gas distribution since the 1970s. Some advantages over steel pipelines include an ability to be coiled, lower susceptibility to corrosion and a reduced leakage means to transport fluids. However, polyethylene pipes have best performance at pressures below about 10 bars.

To improve higher pressure performance of PE, reinforcing materials can be used to increase their pressure limits. However, this may be costly to implement and may require multiple layers of pipe or pipes wrapped with reinforcing materials.

Additional materials used in production of pipes include polyamide 11 (e.g. coiled N11 high pressure gas pipes at diameters up to 2 inches have been disclosed by Arkema); polyamide 12 (e.g. Evonik Degussa provides a polyamide 12 pipe known as VESTAMID® NRG for use by the gas distribution energy; and UBESTA provides polyamide 12 for burial and rehabilitation of existing cast iron and steel gas mains) and polyamide 612 (e.g. DuPont provides PIPELON® to the

industry, a polyamide 612 pipe requiring a plasticizer and used in the oil and gas industry requiring a plasticizer and more frequently employed as a liner for high performance piping); and polyvinylidene difluoride (PVDF). However the relatively low tensile strength of the foregoing materials may still require reinforcement for use in the field.

It is desirable, however, to use alternative polyamides with a higher tensile strength than HDPE, N11, N12, N612 and PVDF in pipeline construction.

Nevertheless, prior attempts at making pipeline articles from, for example, polyhexamethylenedipamide (N66) have shown limited success, resulting in poor quality pipes. It is generally believed that manufacturing N66 pipes using extrusion or blow molding requires a base polymer polyamide to have a very high melt viscosity and higher molecular weight. As a further liability, it is known from Margolis J.M. "Engineering Thermoplastics Properties and Applications"; Marcel Dekker, Inc. 1985, New York and Basel, page 117) that N66 and N6 are more susceptible or sensitive to stress crack formation.

Surface super-hydrophobic properties are known to include high contact angles, rolling and bounding behavior of liquid droplets, and the "self-cleaning" of particle contaminants observed on the leaves and petals of lotus plants and often referred to as the "Lotus Effect." These properties of the lotus plant arise from a combination of low interfacial energy and rough surface topography of waxy deposits covering their leaves.

United States Patent Number 7,485,343 discloses a method for preparing a hydrophobic coating by preparing a precursor sol comprising a metal alkoxide, a solvent, a basic catalyst, a fluoroalkyl compound with water, depositing the precursor sol as a film onto a surface, such as a substrate or a pipe, heating the film and exposing the film to a hydrophobic silane compound to form a hydrophobic coating with a contact angle greater than approximately 150°.

Methods for extending the useable life of a polyamide pipe having an outer metal housing for use in a water-oil gas environment are known from United States Patent Application No. 2004/0045620. These methods include incorporating a chain extender or desiccant into a polyamide liner, incorporating hydrophobic moieties or hydrophobic polymers into the polyamide liner or

providing a sheath which is less permeable to water at the inner surface of the polyamide liner.

The PCT publication WO 2011/163190 discloses a steel conduit with a hydrophobic inner wall of hydrate anti-agglomerate molecules and methods for making the same to prevent hydrate blockage.

SUMMARY OF THE INVENTION

The disclosures herein provide a composition for articles and a method for making the composition useful for extruded hydrophobic polyamide pipes and conduits which are able to meet performance standards applicable for use in oil and gas transport.

The disclosures herein relate to articles and more particularly to conduit structures and structures described by the term "pipe." A pipe may embody either right-cylindrical geometry, *i.e.*, having circular cross sectional shape, and other cross sectional shapes which may be elongated in one axis perpendicular to the conduit long axis, for example, obround and oval shapes.

More specifically, in an embodiment, these disclosures provide a thermoplastic nylon resin, comprising a functional additive selected from the group consisting of: neo-alkoxy titanates and neo-alkoxy zirconates.

In an embodiment, these disclosures provide a thermoplastic nylon resin, comprising about 60 weight percent to about 99.9 percent by weight of a polyamide; and about 0.1 percent by weight to about 40 percent by weight of an impact modifier selected from the group consisting of: maleic anhydride and a functional equivalent of maleic anhydride; and wherein the composition has a moisture level less than about the equilibrium moisture content of the polyamide.

In an embodiment, these disclosures provide a thermoplastic nylon resin, wherein the nylon resin is a high tensile strength polyamide.

In an embodiment, these disclosures provide a thermoplastic nylon resin, wherein the high tensile strength nylon resin is a polyamide selected from the group consisting of polyamides: N66, N6, N46, N56, N7, N610, N612, N6T, N6I, N9T, NDT, NDI, ND6, N11, N12 and combinations thereof.

In an embodiment, these disclosures provide a thermoplastic nylon resin, wherein the nylon is N66 having an initial formic acid test method based relative viscosity (RV) of at least 35.

In an embodiment, these disclosures provide a thermoplastic nylon resin, wherein the moisture level of the resin is less than about 0.15 weight percent.

In an embodiment, these disclosures provide a thermoplastic nylon resin, wherein the nylon resin is N66 having an initial formic acid test method based relative viscosity (RV) of at least 48.

In an embodiment, these disclosures provide a thermoplastic nylon resin, wherein the moisture level of the resin is less than about 0.05 weight percent.

In an embodiment, these disclosures provide a thermoplastic nylon resin, wherein the nylon resin is N66 having an initial formic acid test method based relative viscosity (RV) of at least 80.

In an embodiment, these disclosures provide a thermoplastic nylon resin, wherein the moisture level of the resin is at most about 0.03 weight percent.

In an embodiment, these disclosures provide a thermoplastic nylon resin, wherein the nylon resin is N66 having an initial formic acid test method based relative viscosity (RV) of at least about 240.

In an embodiment, these disclosures provide a thermoplastic nylon resin, wherein the moisture level of the resin is at most about 0.005 weight percent.

In an embodiment, these disclosures provide a thermoplastic nylon resin, wherein the impact modifier has an effective maleic anhydride level of less than about 1 weight percent.

In an embodiment, these disclosures provide a thermoplastic nylon resin, wherein the impact modifier has an effective maleic anhydride level of about 0.044 to about 0.11 weight percent.

In an embodiment, these disclosures provide a thermoplastic nylon resin, wherein the impact modifier comprises a maleated ethylene propylene diene (EPDM) rubber.

In an embodiment, these disclosures provide a thermoplastic nylon resin, further comprising a heat stabilizer.

In an embodiment, these disclosures provide a thermoplastic nylon resin, further comprising a colorant.

In an embodiment, these disclosures provide a thermoplastic nylon resin, comprising a granulate physical form.

In an embodiment, these disclosures provide a thermoplastic nylon resin article extruded from the thermoplastic resin of any one of the foregoing embodiments.

In an embodiment, these disclosures provide a thermoplastic nylon resin extruded article comprising a resin fully saturated with water, the article having a burst stress value of about 7000 pounds per square inch to about 10000 pounds per square inch.

In an embodiment, these disclosures provide a thermoplastic nylon resin extruded hollow conduit having an interior first surface and an exterior second

surface, said conduit comprising, a thermoplastic resin comprising about 60 weight percent to about 99.9 weight percent of a polyamide; and further comprising about 0.1 weight percent to about 40 weight percent of an impact modifier selected from the group consisting of: maleic anhydride and a functional equivalent of maleic anhydride; and wherein, the composition has a moisture level less than or equivalent to the equilibrium moisture content of the polyamide prior to being formed into an article ; and further comprising, a functional coating to increase water resistance and a burst stress value of said conduit in a fully water saturated state; and wherein, the functional coating is applied to the first surface or the second surface or to both surfaces of the conduit.

In an embodiment, these disclosures provide a thermoplastic nylon resin extruded hollow conduit wherein the nylon resin is a high tensile strength polyamide.

In an embodiment, these disclosures provide a thermoplastic nylon resin extruded hollow conduit wherein the nylon resin is selected from the group consisting of polyamides: N66, N6, N46, N56, N7, N610, N612, N6T, N6I, N9T, NDT, NDI, ND6, N11, N12 and combinations thereof.

In an embodiment, these disclosures provide a thermoplastic nylon resin extruded hollow conduit the nylon resin is polyamide N66 having an initial formic acid test method based relative viscosity (RV) of at least about 35.

In an embodiment, these disclosures provide a thermoplastic nylon resin extruded hollow conduit comprising a polyamide having a moisture level of less than about 0.15 weight percent.

In an embodiment, these disclosures provide a thermoplastic nylon resin extruded hollow conduit comprising N66 having an initial formic acid test method based relative viscosity (RV) of at least about 48.

In an embodiment, these disclosures provide a thermoplastic nylon resin extruded hollow conduit wherein the moisture level of the resin is less than about 0.05 weight percent prior to being transformed into the article of interest.

In an embodiment, these disclosures provide a thermoplastic nylon resin extruded hollow conduit wherein the resin is polyamide N66 having an initial formic acid test method based relative viscosity (RV) of at least about 80.

In an embodiment, these disclosures provide a thermoplastic nylon resin extruded hollow conduit wherein the nylon resin moisture level is at most about 0.03 weight percent.

In an embodiment, these disclosures provide a thermoplastic nylon resin extruded hollow conduit wherein the resin is polyamide N66 having an initial formic acid test method based relative viscosity (RV) of at least about 240.

In an embodiment, these disclosures provide a thermoplastic nylon resin extruded hollow conduit wherein the resin moisture level is 0.005% by weight or less.

In an embodiment, these disclosures provide a thermoplastic nylon resin extruded hollow conduit comprising an impact modifier additive wherein the additive has an effective maleic anhydride level of at most about 1 weight percent.

In an embodiment, these disclosures provide a thermoplastic nylon resin extruded hollow conduit comprising an impact modifier additive wherein the additive has an effective maleic anhydride level of about 0.044 weight percent to about 0.11 weight percent.

In an embodiment, these disclosures provide a thermoplastic nylon resin extruded hollow conduit comprising an impact modifier additive wherein the additive comprises a maleated ethylene propylene diene (EPDM) rubber.

In an embodiment, these disclosures provide a thermoplastic nylon resin extruded hollow conduit comprising an impact modifier additive and further comprising a heat stabilizer.

In an embodiment, these disclosures provide a thermoplastic nylon resin extruded hollow conduit comprising an impact modifier additive and further comprising a colorant.

In an embodiment, these disclosures provide a thermoplastic nylon resin extruded hollow conduit comprising an impact modifier additive, wherein the conduit resin is fully saturated with water, and wherein the conduit has a burst stress value of about 7000 pounds per square inch to about 10000 pounds per square inch.

In an embodiment, these disclosures provide a method for increasing the burst stress value of a extruded conduit comprising a thermoplastic resin fully saturated with water, the method comprising;
providing a functional additive selected from the group consisting of:
neo-alkoxy titanates and neo-alkoxy zirconates to a thermoplastic resin prior to extruding the conduit.

In an embodiment, these disclosures provide a method for increasing the burst stress value of a extruded conduit comprising a thermoplastic resin wherein the resin comprises about 60 weight percent to about 99.9 weight percent of a polyamide; and
providing to the resin an impact modifier additive selected from the group consisting of: maleic anhydride and a functional equivalent of maleic anhydride, in an amount of about 0.1 weight percent to about 40 weight percent.

In an embodiment, these disclosures provide a method for increasing the burst stress value of an extruded hollow conduit having an interior first surface and an exterior second surface, said method comprising,

providing a thermoplastic resin comprising about 60 weight percent to about 99.9 weight percent of a polyamide; and
providing to the resin an impact modifier selected from the group consisting of: maleic anhydride and a functional equivalent of maleic anhydride in an amount of about 0.1 weight percent to about 40 weight percent, and
providing a functional coating to increase water resistance and a burst stress value of said conduit in a fully water saturated state;
and wherein the functional coating comprises a hydrophobic polymer selected from the group consisting of:
maleated ethylene tetrafluoroethylene copolymer; maleated fluorinated ethylene propylene copolymer; and maleated polyfluorinated ethylene;
and
applying the functional coating to the first surface or the second surface or to both surfaces of the conduit.

In an embodiment, these disclosures provide a method for increasing the burst stress value of an extruded hollow conduit according to any one of the foregoing method embodiments and wherein the burst stress value of the conduit is increased to about 7000 pounds per square inch to about 10000 pounds per square inch.

In an embodiment, these disclosures provide an extruded thermoplastic resin hollow conduit the conduit further comprising a substantially right cylindrical pipe.

BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 provides a representation of a thermoplastic pipe of the present invention.

FIG. 2 is a representation of log-log plot of stress (in psi) versus exposure time, measured according to the ASTM D2837 method, for an embodiment according to Example 1.

DETAILED DESCRIPTION OF THE INVENTION

Typical polyamides are hygroscopic (absorb water), and the water plasticizes the polymer and thereby decreases its mechanical properties (e.g. tensile strength, flexural modulus or rigidity). The disclosures herein and specific embodiments which follow provide a method to overcome such deficiencies of the polyamide polymer.

Accordingly, the addition of bulky groups such as neo-alkoxy-titanates to polyamide polymer resin or by coating articles made from the polyamide resin with a hydrophobic (water repelling) permanent layer, functions to improve properties affected by water exposure. The coatings repel water sufficient to achieve "dry as molded" or "dry as extruded" (DAM/DAE) properties with these polyamides (even at two times the saturated moisture values). Significantly, an improved chemical resistance to strong acids and bases is achieved. That feature along with substantially lowered friction enables the use of such modified polyamide polymers in high wear applications, while still utilizing traditional joining techniques such as thermal butt fusion, vibrational welding, and mechanical fittings.

This present invention provides hydrophobic thermoplastic polyamide resins and articles made of these resins in the form of hollow conduits and pipes having increased water resistance and/or burst stress values and methods for their production.

Thermoplastic resins of the present comprise 60 to 99.9% by weight of a polyamide. In an embodiment, the polyamide is a "high tensile strength"

polyamide. A "high tensile strength" polyamide resin, for the purposes of this disclosure, will have a maximum stress at failure from about 20 MPa to about 200 MPa at the typical temperature range for application. A more preferable high tensile strength polyamide exhibits a tensile strength at 100% saturation with water of greater than 20 MPa at 23°C.

Examples of high tensile strength polyamides for use in these compositions include, but are not limited to group consisting of polyamides: polyhexamethylene adipamide (N66), polycaproamide (N6), polytetramethylene adipamide (N46), polypentamethylene adipamide (N56), polyenanthamide (N7), polyhexamethylene decamide (N610), polyhexamethylene dodecamide (N612), polyhexamethylene terephthalamide (N6T), polyhexamethylene isophthalamide (N6I), polynonamethylene terephthalamide (N9T), poly-2-methylpentamethylene terephthalamide (NDT), poly-2-methyl-pentamethylene isophthalamide (NDI), poly-2-methyl-pentamethylene adipamide (ND6), polyundecamethyleneamide (N11), polydodecamethyleneamide (N12) and combinations thereof. By "combinations thereof" with respect to polyamides, it is meant to include, but is not limited to, block copolymers, random copolymers, terpolymers, as well as melt blends.

In the thermoplastic resins of the present disclosures, the moisture level is decreased to less than the equilibrium moisture content of the polyamide to improve the melt strength and melt quality of the resin and articles produced from the resins. At higher moisture content levels, melt fracture, low melt stability, poor appearance and other undesirable surface defects are observed. For purposes of the present disclosure, by "equilibrium moisture content," it is meant the level of moisture in a selected polyamide in a molten phase which allows the molecular weight of the selected polyamide to remain stable and not degrade for a period of time required to process it.

According to a non-limiting embodiment, the resin herein is a polyamide (N66) having an initial solution relative viscosity (RV) measured by the formic acid test method according to ASTM D789, of at least 35. In this embodiment, the moisture level of the composition is reduced by drying to less than the equilibrium moisture content of N66, 0.15% by weight.

According to a non-limiting embodiment, the resin herein is a polyamide (N66) having an initial solution relative viscosity (RV) measured by the formic acid test method according to ASTM D789, of at least 48. In this embodiment, the moisture level of the composition is decreased to 0.05% by weight or less.

According to a non-limiting embodiment, the resin herein is a polyamide (N66) having an initial solution relative viscosity (RV) measured by the formic acid test method according to ASTM D789, of at least 80. In this embodiment, the moisture level is decreased to 0.03% by weight or less.

According to yet another non-limiting embodiment, the resin herein is a polyamide (N66) having an initial solution relative viscosity (RV) measured by the formic acid test method according to ASTM D789, of at least 240. In this embodiment, the moisture level is decreased to 0.005% by weight or less.

Various methods for reducing the moisture level of the polyamide to less than the equilibrium moisture content of the polyamide are used generally within the knowledge of the skilled person. According to one non-limiting embodiment, a thermoplastic resin is first dried to a moisture level less than the equilibrium moisture content for the polyamide. Drying of the resin can be achieved by any means including, but not limited to, use of a desiccant bed dryer with appropriate heat, IR heating, forced diffusion using dry air, use of a vented twin screw extruder, microwave heating followed by forced air diffusion, or use of twin screw extruder preferably with atmospheric and vacuum vents, use of a vented single screw extruder, or a combination of the above.

In another embodiment, moisture content is reduced during the extrusion of the thermoplastic polyamide resin in the melt phase. Non-limiting examples of apparatus which can be used for extrusion and reducing the moisture content of a molten resin include, but are not limited to, vented single and twin extruders.

As will be understood by the skilled person upon reading this disclosure, alternative methods and apparatus to those exemplified herein which result in a decrease in the moisture level of the resin to less than the equilibrium moisture content for the polyamide are available and use thereof is encompassed by the present invention.

Thermoplastic resins of the disclosed herein further comprise 0.1 to 40% by weight of an impact modifier; an additive to the polyamide resin. Suitable impact

modifiers for use herein include those known in the art that impart improved impact strength when combined with polyamide resins. United States Patent Numbers 4,346,194; 6,579,581; and 7,671,127; herein incorporated by reference in their entirety, disclose and/or teach either solely or in combination, nylon resins provided with impact modifying additives.

In an embodiment, the thermoplastic polyamide resins herein are provided with an impact modifying additive containing maleic anhydride or a functional equivalent thereof. For impact modifiers containing maleic anhydride, it is preferred that the impact modifier has an effective maleic anhydride level of less than 1% by weight. More preferred is that the impact modifier has an "effective maleic anhydride level" of 0.044 to 0.11% by weight.

The "effective maleic anhydride level", for the purposes herein is based upon the amount of maleic anhydride containing impact modifier added to the composition and the maleation level of the selected impact modifier. According to a non-limiting example, a 100 gram portion of a composition of the present invention comprising 78 grams of polyamide and 22 grams of impact modifier having a maleation level ranging from 0.2% to 0.5% will have an effective maleic anhydride level of 0.044% to 0.11%. As will be understood by the skilled person upon reading this disclosure, the amount of impact modifier added to the composition is adjustable and based upon its maleation level so that the effective maleic anhydride level is preferably provided at less than 1% by weight.

Examples of commercially available impact modifiers containing maleic anhydride useful in the present invention include, but are not limited to: Amplify™ GR216, a maleic anhydride polyolefin elastomer sold by Dow®; Lotader® 4700, a random terpolymer of ethylene, ethyl acrylate and maleic anhydride, and Oervac® IM300, a maleic anhydride modified low-density polyethylene, each sold by Arkema®; and Exxelor™ VA 1840, a semi-crystalline ethylene copolymer functionalized with maleic anhydride sold by ExxonMobil®.

According to an embodiment of the resin composition herein, the impact modifier comprises a maleated ethylene propylene diene (EPDM) rubber.

By "functional equivalents" with respect to the impact modifier, it is meant to include impact modifiers, which upon reading this disclosure, would be understood

by those skilled in the art, to provide impact modifying characteristics to polyamides similar to the above impact modifiers containing maleic anhydride.

Suitable elastomers for the impact modifier include, but are not limited to, polymers or copolymers of ethylene, propylene, octene with alkyl acrylate or alkyl methacrylate. Other suitable elastomers for the impact modifier include, but are not limited to, styrene-butadiene two-block copolymers (SB), styrene-butadiene-styrene three-block copolymers (SBS), and hydrogenated styrene-ethene/butene-styrene three-block copolymers (SEBS). Other elastomers that may be used in the impact modifiers include terpolymers of ethylene, of propylene, and of a diene (EPDM rubber).

The impact modifier further comprises a functional group such as, but not limited to, a carboxylic acid group, a carboxylic anhydride group, a carboxamide group, a carboximide group, an amino group, a hydroxyl group, an epoxy group, a urethane groups or an oxazoline groups.

According to an embodiment, the impact modifier comprises an elastomeric polyolefinic polymer functionalized with an unsaturated carboxylic anhydride. In this embodiment, it is preferred to use an impact modifier having an unsaturated carboxylic anhydride content in the range from about 0.2 to about 0.6 by weight percent.

As will be understood by the skilled person upon reading this disclosure, that different polyamides and copolyamides used herein each have their own associated equilibrium moisture content. As a result, in order to obtain the desired melt strength and viscoelastic behaviors herein, effective maleation levels and moisture content may need to be balanced in a range which may vary from the specific ranges disclosed. These variations in effective maleation level and/or moisture content for the different polyamides and copolyamides disclosed are encompassed by the present invention and serve to enable achievement of the desired melt strength and viscoelastic behaviors described herein.

Preferably, the thermoplastic resins disclosed exhibit a melt strength of at least 0.08N, more preferably at least 0.12N. Melt strength refers to how strong the polyamide and/or resin is in a molten state and is essential to shaping of the polyamide and/or resin, based upon both hang strength and melt integrity, into the desired shape. For purposes herein, the melt strength is determined as the load

at break. In addition or alternatively, the thermoplastic resins herein will preferably have a shear viscosity from about 500 to about 3000 Pa-sec when tested at a shear rate of about 50 sec^{-1} and a melt temperature of 270-280°C, and a moisture level from about 0.03 to about 0.15%. The shear viscosity of the resin at various shear rates is an indicator of the melt viscosity of the thermoplastic resin, an important characteristic to determine if the thermoplastic pipe can be extruded and formed to its desired shape.

The thermoplastic resins of this disclosure may further comprise a heat stabilizer and/or colorant. Suitable heat stabilizers include, but are not limited to hindered phenols, amine antioxidants, hindered amine light stabilizers (HALS), aryl amines, phosphorus based antioxidants, copper heat stabilizers, polyhydric alcohols, tripentaerythritol, dipentaerythritol, pentaerythritol and combinations thereof. According to an embodiment, the amount of heat stabilizer added to the resin ranges from about 0.004 to about 5% by weight. In a non-limiting embodiment, the heat stabilizer is Cu-Hs and is added in an amount up to about 200 ppm. In another non-limiting embodiment, an antioxidant such as Irganox[®] BASF Schweiz AG or Irgafos[®] BASF Schweiz AG is added to provide processing stability. In another non-limiting embodiment, the heat stabilizer is a polyhydric alcohol like dipentaerythritol, and is added in an amount up to 5% by weight to provide processing and longer term heat stabilization.

Colorant can be added to increase resistance to ultraviolet light and subsequent degradation of conduits, pipes and other articles formed from the polyamide resin. Suitable colorants include, but are not limited to, carbon black and nigrosine. In one embodiment, colorant concentrate in a range of about 0.01 to about 9% by weight percent is added to increase the UV resistance and prevent wear of the thermoplastic pipe or other component. In an embodiment, colorant level of the pipe or article typically ranges from about 0.01 to about 2.5%.

Examples of other additives to be included as non-limiting embodiments of the thermoplastic resins disclosed herein are: lubricants, mineral fillers, pigments, dyes, antioxidants, hydrolysis stabilizers, nucleating agents, flame retardants, blowing agents and combinations thereof. Suitable mineral fillers include, but are

not limited to, kaolin, clay, talc, and wollastonite, diatomite, titanium dioxide, mica, amorphous silica, glass beads, glass fibers and combinations thereof.

Further according to embodiments of the present disclosure, it may be desirable to increase the melt viscosity of the thermoplastic resin by addition of 0.1 to 5%, more preferably 1% or less, of an olefin (ethylene, styrene, vinyl acetate)-maleic anhydride copolymer. In a preferred embodiment, the olefin and maleic anhydride copolymer have a molecular weight in the range of about 500 to about 400,000 g/mol. Suitable melt viscosity enhancers for use herein present include any known to the person skilled in the art. Accordingly, in a non-limiting embodiment, a preferred olefin is ethylene. A commercially available 1:1 copolymer of ethylene-maleic anhydride is sold under the name ZeMac[®] by Vertellus[®]. A commercially available styrene-maleic anhydride copolymer is sold by Cray Valley (a TOTAL brand).

Suitable thermoplastic resins according to the present disclosures further comprise a silicon-based additive; e.g. the resin may comprise 0.5 to 25% by weight of a silicon-based additive. In an embodiment, the silicon-based additive comprises an ultrahigh molecular weight siloxane polymer and a binding agent. A preferred siloxane polymer is an ultrahigh molecular weight siloxane polymer unfunctionalized and non-reactive with the polyamide resin. Furthermore, it is more preferred that the unfunctionalized siloxane polymer not be a gel or oil. Suitable binding agents for the silicone based additive include, but are not limited to fumed silica. In an embodiment, the silicone based additive is provided in a pelletized silicone gum formulation. According to a non-limiting example, a commercially available formulation is sold under the name Genioplast[®] Pellet S by Wacker Chemie AG.

In an optional embodiment of the present invention, the thermoplastic resin may further comprise a plasticizer.

In an embodiment, the above-described thermoplastic resins are extruded to form a hollow conduit or pipe which is then functionally coated on its interior and/or exterior surface to increase its water resistance and/or burst stress values under fully saturated conditions with water.

In another embodiment of the disclosures herein, neo-alkoxy titanate or neo-alkoxy zirconate may be added to the thermoplastic polyamide resin prior to

extrusion of a hollow conduit or pipe to increase its water resistance and/or burst stress values under fully saturated conditions with water.

In an embodiment, the thermoplastic polyamide resin is granulated or pelletized to a form for facilitating extrusion of pipes and other articles from the compositions.

The thermoplastic resins disclosed herein can be used in articles of manufacture comprising at least one component formed from a resin of the present disclosure. Examples of components which can be formed from the thermoplastic resins herein include, but are not limited to: hollow conduits, pipes, sheets, films, tapes, fibers, laminates, caps and closures, geo-membranes and molded articles formed by processes including, but not limited to extrusion, co-extrusion, blow molding, calendering, compression molding, injection molding, injection compression, thermoforming hot stamping and coating.

The present disclosures further provide hydrophobic thermoplastic pipes extruded from the thermoplastic resins disclosed herein. The hydrophobic thermoplastic pipes extruded from a resin herein exhibit increased water resistance and/or burst stress values and are useful for oil and gas pipeline, for transporting hydrocarbon containing fluids, water transportation in hydrofracking, water systems for residential and commercial facilities and/or transport of compatible chemicals. It is preferred that the hydrophobic thermoplastic pipes of this disclosure have a quick burst stress of at least 4000 pounds per square inch (psi) when fully water saturated, more preferably 7000 psi to 10000 psi, a quick burst stress of at least 6000 psi, more preferably 7000-10,000 psi without saturation, a LTHS of at least 1000 psi at 82°C, a LTHS of at least 2000 psi at 23°C, preferably an LTHS ranging from 2000-5000 psi, and/or a pressure design basis for a 89 mm O.D and 8 mm wall thickness pipe ("3-inch SDR 11" pipe according to the nominal Iron Pipe Size or IPS Standard) of at least 400 pounds per square inch gage (psig). SDR is standard dimension ratio of the pipe or conduit.

FIG. 1 provides a diagram of a thermoplastic pipe 10 of the present disclosure having a length, l , and a wall of thickness, t , wherein the pipe has an outer surface 20 and an inner surface 30, and wherein the outer surface defines

an outer diameter 50 of the thermoplastic pipe and the inner surface defines an inner diameter 40 of the thermoplastic pipe.

In an embodiment, a pipe according to the present disclosures is extruded from a thermoplastic resin comprising neo-alkoxy titanate or neo-alkoxy zirconate or -titanate. In this embodiment, the thermoplastic resin may further comprise 60 to 99.9% by weight of a polyamide, wherein the moisture level of the composition is less than the equilibrium moisture content of the polyamide, and 0.1 to 40% by weight of an impact modifier containing maleic anhydride or a functional equivalent thereof. Alternatively, in this embodiment, the thermoplastic resin may have a melt strength of at least 0.08N, more preferably at least 0.12N.

Alternatively in this embodiment, the thermoplastic resin may have a shear viscosity from 500 to 3000 Pa-sec when tested at a shear rate of 50 sec^{-1} and a melt temperature of 270-280°C, and a moisture level from 0.03 to 0.15%.

In another embodiment, a pipe of the present invention is extruded from a thermoplastic resin comprising 60 to 99.9% by weight of a polyamide, wherein the moisture level of the composition is less than the equilibrium moisture content of the polyamide, and 0.1 to 40% by weight of an impact modifier containing maleic anhydride or a functional equivalent thereof; a thermoplastic resin having a melt strength of at least 0.08N, more preferably at least 0.12N; or a thermoplastic resin having a shear viscosity from about 500 to about 3000 Pa-sec when tested at a shear rate of 50 sec^{-1} and a melt temperature of 270-310°C, and a moisture level from about 0.03 to about 0.15%, and then coated on its inner and/or outer surface with a functional coating.

Hydrophobic thermoplastic pipes of the present invention have been demonstrated to exhibit a long term hydrostatic burst stress (50 year life) of at least 2500-10000 psi in a 100% water environment at 23°C.

In an embodiment, the hydrophobic pipe of the present invention has an SDR from about 3 to about 30, more preferably from about 7 to about 25, more preferably from about 10 to about 12. The standard dimension ratio or SDR of the thermoplastic pipe is measured by dividing the outer diameter 50 by the wall thickness t . In an embodiment of the present invention, the outer diameter of the pipe ranges from about 1 inch to about 10 inches while the wall thickness ranges

from about 0.03 inch to about 4 inches. In these embodiments, it is preferred that the pipe have a diameter to wall thickness ratio ranging from 5 to 32.

It is also preferred in these embodiments, that the polyamide be a high tensile strength polyamide. Examples of high tensile strength polyamides for use in these compositions include, but are not limited to group consisting of polyamides: polyhexamethylene adipamide (N66), polycaproamide (N6), polytetramethylene adipamide (N46), polypentamethylene adipamide (N56), polyenanthamide (N7), polyhexamethylene decamide (N610), polyhexamethylene dodecamide (N612), polyhexamethylene terephthalamide (N6T), polyhexamethylene isophthalamide (N6I), polynonamethylene terephthalamide (N9T), poly-2-methylpentamethylene terephthalamide (NDT), poly-2-methyl-pentamethylene isophthalamide (NDI), poly-2-methyl-pentamethylene adipamide (ND6), N11, N12 and combinations thereof. By "combinations thereof" with respect to polyamides, it is meant to include, but is not limited to, block copolymers, random copolymers, terpolymers, as well as melt blends.

In some embodiments, at least a portion of an outer surface of a hydrophobic thermoplastic pipe of the present disclosure is covered by a reinforcing material. Examples of reinforcing materials include, but are not limited to, glass fiber, carbon fiber, nylon fiber, polyester fibers and steel wire and combinations thereof.

Reinforcing materials as described herein can also be sandwiched between two or more layers of the extruded polyamide resin to form a pipe of the present invention.

In some embodiments, the pipe is coated with a colorant such as paint to increase resistance to ultraviolet light. Coating a pipe of the present invention with an acrylic white paint was found to minimize moisture absorption and to significantly reduce pipe surface temperature increase when exposed to sunlight by 15 to 30°C as compared to an uncoated pipe.

In an embodiment, to further improve moisture resistance and minimize abrasion, the outer and inner surface of the hydrophobic thermoplastic pipe may be covered by a second thermoplastic material. The second thermoplastic material may be bonded or unbonded to the thermoplastic pipe. Examples of

bonded or unbonded pipes are disclosed in PCT publication WO 02/061317 and United States Patent Application Number 2012/0261017 A1. The outer covering is often referred to as an outer sheath while the inner covering is often referred to as an inner sheath.

Accordingly, in some embodiments of the present invention, at least a portion of the outer surface of the pipe and/or the inner surface of the pipe is bonded with a second thermoplastic material. Examples of second thermoplastic materials which can be bonded to at least a portion of the outer and/or inner surface of the pipe include, but are not limited to, high density polyethylene (HDPE), polyamide, polypropylene, polyphenylene sulfide, polyetheretherketone and rubber, and combinations thereof.

In some embodiments, at least a portion of the outer and/or inner surface of the pipe is covered or lined by an unbonded second thermoplastic material. Examples of unbonded second thermoplastic materials which can cover at least a portion of the outer surface of the pipe or line at least a portion of the inner surface of the pipe include, but are not limited to, high density polyethylene (HDPE), polyamide, polypropylene, polyphenylene sulfide, polyetheretherketone and rubber, and combinations thereof.

In some embodiments, the pipes according to the present disclosure may further comprise a silicone based additive. In one embodiment, the pipe comprises 0.5 to 25% by weight of a silicon based additive. In one embodiment, the silicon based additive comprises an ultrahigh molecular weight siloxane polymer and a binding agent. Preferred is that the ultrahigh molecular weight siloxane polymer be unfunctionalized and non-reactive with the polyamide in the pipe. Further preferred is that the unfunctionalized siloxane polymer not be considered as either a gel or an oil. Suitable binding agents for the silicone based additive include, but are not limited to fumed silica. A nonlimiting example of a commercially available formulation is sold under the name Genioplast® Pellet S by Wacker.

An advantage of the conduits and pipes according to the disclosures herein is that they are capable of being thermally butt fused with another thermoplastic pipe of the same composition and/or coupled with another pipe of the same or different composition through electrofusion, mechanical, compression fitting

and/or transition fitting. In a non-limiting embodiment, a pipe of the present invention is electrofused, mechanically joined, compression fitted or transition fitted to a steel pipe or fitting. In another non-limiting embodiment, a pipe of the present invention is electrofused, compression fitted, or transition fitted to another thermoplastic pipe of the same composition. In yet another non-limiting embodiment, a pipe according to the disclosures herein is electrofused, compression fitted or transition fitted to another thermoplastic pipe of a different composition.

In an embodiment, a pipe according to the disclosures herein further comprises a second polymer, copolymer, or terpolymer made by combining two or more polymers. Examples include, but are not limited to polyamides: polyhexamethylene adipamide (N66), polycaproamide (N6), polytetramethylene adipamide (N46), polypentamethylene adipamide (N56), polyenanthamide (N7), polyhexamethylene decamide (N610), polyhexamethylene dodecamide (N612), polyhexamethylene terephthalamide (N6T), polyhexamethylene isophthalamide (N6I), polynonamethylene terephthalamide (N9T), poly-2-methylpentamethylene terephthalamide (NDT), poly-2-methyl-pentamethylene isophthalamide (NDI), poly-2-methyl-pentamethylene adipamide (ND6), N11, N12, polyolefins, polyesters and copolyesters and combinations thereof. By "combinations thereof" with respect to polyamides, it is meant to include, but is not limited to, block copolymers, random copolymers, terpolymers, as well as melt blends. In this embodiment, the second polymer, copolymer or terpolymer can be added prior to extrusion as a melt blend or co-extruded with the resin of the present disclosure, or added as a separate layer before or after the extrusion of resin of the present invention by, for example, a cross-head, spraying on as a coating, or via a dip coating process.

Provided according to the embodiments disclosed herein, are processes for extruding hydrophobic thermoplastic pipes. Manufacture of hollow conduits, including pipe and similar articles via extrusion requires the base polymer to have high melt strength. High melt strength is desirable in obtaining good hang strength and enabling production of a uniform shape or form to be extruded and maintained as the polymer crystallizes. Other desired parameters for pipe extrusion include, but are not limited to, consistent ovality and thickness, smooth

inside surface without deformities, ability to coil without crushing upon itself; and no tears or holes on the outer surface. To make pipes with good melt strength, the extrusion process may be started with a high melt strength polymer of the same or another family, and then gradually transitioned to another desired polymer. It is desirable for the process of transition to pure low melt strength polymer to take place over a period of about 10 minutes from start-up to minimize waste formation. When using a low melt strength polymer, the gap between the die head/pipehead and the calibrator must within a range of between about 0.5 mm to about 75mm, more preferably between about 1mm to about 3 mm.

In these processes, a melted thermoplastic resin as described herein is extruded and passed through a pipe forming zone of an extrusion apparatus to form the thermoplastic pipe.

Various methods and apparatuses for extruding thermoplastic resins into pipes are known and can be used for production of the hydrophobic thermoplastic pipes of the instant invention. For example, in one embodiment, melting may be done in a single screw greater than or equal to 1" or a 25 mm or greater vented or unvented twin screw extruder to produce a homogeneous melt. The extruders may be with or without a vent. Pipe head temperature is maintained within 30 °C of the melt temperature of polymer. A calibrator with a coolant, preferably water in the temperature range of 16 °C to 23 °C, is also used. The flow rate of water in the cooling tank is maintained such that outside skin freezes instantaneously upon contact, and the outside pipe temperature is within 50 °C to about 75 °C of the glass transition temperature of polymer.

In one embodiment, the extrusion apparatus comprises a static mixer and a rotating screw design configured to melt the polyamide containing thermoplastic resin. In alternative embodiments, a single screw extruder, a twin screw extruder, a vented single screw extruder or a vented twin screw extruder is used.

In one embodiment, the thermoplastic resin is melted at temperature ranging between about 260 °C and about 310 °C.

The melted polyamide containing thermoplastic resin is then extruded and passed through a pipe forming zone of the extrusion apparatus to form the thermoplastic pipe. Positive pressure may be applied to the internal cavity of the formed pipe through mandrel or pin. In one aspect of this embodiment, the

process further comprises the step of passing the portion of a thermoplastic pipe through a dryer.

In one embodiment of this process herein, the residence time from extrusion to pipe forming is less than 20 minutes, more preferably less than 10 minutes, more preferably less than 6 minutes. Examples of pipe forming zones include, but are not limited to, spiral or basket shaped die head, transition zone, a heated mandrel with or without a heated pin which forms at least a portion of a thermoplastic pipe. When using a heated mandrel or pin, positive pressure may be applied to the internal cavity of the formed pipe through mandrel or pin.

In one embodiment, the process of the present disclosure further comprises passing the melted polyamide containing thermoplastic resin through a screen to remove any contaminants or unmelted portions prior to extrusion. In this embodiment, the screen may be reinforced by a breaker plate to create pressure in the extruding apparatus.

In embodiments of the present disclosure wherein the thermoplastic resin does not comprise neoalkoxy titanate or neoalkoxy zirconate, the inner and/or outer surface of the pipe is coated with a functional coating.

The present disclosure further provides extruded hydrophobic thermoplastic pipes which maintain their ovality. This allows the pipe to be coiled in a spool for storage and transport and to be readily installed from the spools. By maintaining their ovality, the pipes can be used for fluid transfer along long distances. This is useful for application in, for example, oil and gas pipeline, for transporting hydrocarbon containing fluids, water transportation in fracking, water systems for residential and commercial facilities and/or transport of compatible chemicals. The present disclosures further provide articles of manufacture comprising a coiled pipe of the present invention as well as methods for coiling the pipe.

In one embodiment of the present disclosure, the hydrophobic thermoplastic pipe herein is coiled onto a coiling apparatus without exceeding the elastic limit such that there is no loss in LTHS or tensile strength. The hydrophobic thermoplastic pipe is capable of being clamped by a squeeze-off tool to control the flow of fluid through the pipe and then, upon release of the pipe from the squeeze-off tool, substantially return to its original shape. It is further expected

that the hydrophobic thermoplastic pipe herein disclosed can be subjected to hot oil treatment at up to 150°C without dimensional distortion.

In an embodiment of the disclosures herein, the hydrophobic thermoplastic pipe is designed to ensure that the coiling strain is less than the yield strain of the polyamide to minimize memory effects and to eliminate or minimize the need for pipe straighteners to tamers. For purposes of the disclosures herein, coiling strain is determined by dividing the outer diameter of the pipe by the inner coil diameter and multiplying by 100. In an embodiment of the disclosures herein, the coiling strain from about 1% to about 30%, more preferably from about 3% to about 6%. The diameter and/or length of coiled pipe are selected based upon efficient transportation mode on trucks to meet Department of Transportation regulations and minimize costs. Hydrophobic thermoplastic pipes herein are coiled in lengths typically ranging from about 500 to about 3000 feet based upon the pipe diameter. For example, a 2 inch outer diameter pipe is typically coiled in a length of about 2000 feet to about 3000 feet; a 3 and 4 inch outer diameter pipe is typically coiled in a length of about 1000 feet to about 1500 feet; and a 6 inch outer diameter pipe is typically coiled in a length of about 300 feet to about 700 feet. It is preferred that the coiled pipes of present disclosure comprise 60% to 99.9% by weight of a polyamide, wherein the moisture level of the polyamide is less than the equilibrium moisture content of the polyamide, and 0.1% to 40% by weight of an impact modifier containing maleic anhydride or a functional equivalent thereof. A desired feature is that the polyamide be a high tensile strength polyamide. Examples of high tensile strength polyamides for use in these compositions include, but are not limited to group consisting of polyamides: polyhexamethylene adipamide (N66), polycaproamide (N6), polytetramethylene adipamide (N46), polypentamethylene adipamide (N56), polyenanthamide (N7), polyhexamethylene decamide (N610), polyhexamethylene dodecamide (N612), polyhexamethylene terephthalamide (N6T), polyhexamethylene isophthalamide (N6I), polynonamethylene terephthalamide (N9T), poly-2-methylpentamethylene terephthalamide (NDT), poly-2-methyl-pentamethylene isophthalamide (NDI), poly-2-methyl-pentamethylene adipamide (ND6), N11, N12 and combinations thereof. By "combinations thereof" with respect to polyamides, it is meant to

include, but is not limited to, block copolymers, random copolymers, terpolymers, as well as melt blends.

In a nonlimiting embodiment, the polyamide is N66 having an initial formic acid solution relative viscosity of 35 to 240 (measured according to ASTM D789) and the moisture level of less than 0.15% to 0.005% by weight. A further preference of this embodiment is that the impact modifier has an effective maleic anhydride level of less than 1% by weight, more preferably 0.044% to 0.11% by weight. In a nonlimiting embodiment, the impact modifier comprises a maleated ethylene propylene diene (EPDM) rubber. The thermoplastic resin may further comprise a heat stabilizer and/or colorant as well as additional additives such as, but not limited to, lubricants, mineral fillers, pigments, dyes, antioxidants, hydrolysis stabilizers, nucleating agents, flame retardants, blowing agents and combinations thereof. Suitable mineral fillers include, but are not limited to, kaolin, clay, talc, and wollastonite, diatomite, titanium dioxide, mica, amorphous silica, glass beads, glass fibers and combinations thereof.

Hydrophobic thermoplastic pipes of the present disclosure can be effectively coiled and uncoiled in sizes up to 6 inches. As non-limiting examples, an inside coiling diameter of about 52 inches can be used for a 2-inch outer diameter pipe, an inside coiling diameter of about 75 inches can be used for a 3-inch outer diameter pipe, and about 90 inches inside coiling diameter can be used for a 4-inch outer diameter pipe. The outer diameter of a 1000 feet coil made with 3-inch pipe is about 104 inches, while that for 4-inch pipe is about 126 inches.

In some embodiments of the present disclosure, it may be further desirable to increase the melt viscosity of the resin by addition of 0.1% to 5%, more preferably 1% or less, of an olefin (ethylene, styrene, vinyl acetate)-maleic anhydride copolymer. It is preferred that the olefin and maleic anhydride copolymer have a molecular weight in the range of about 500 g/mole to about 400,000 g/mole. Suitable melt viscosity enhancers for use herein include any known to the skilled person. In a nonlimiting embodiment, the olefin is ethylene. A commercially available 1:1 copolymer of ethylene-maleic anhydride is sold under the name ZeMac® by Vertellus®. A commercially available styrene-maleic anhydride copolymer is sold by Cray Valley (a TOTAL brand).

In one embodiment of the present disclosure the resin composition optionally comprises a plasticizer.

In a coiling process herein disclosed, an extruded hydrophobic thermoplastic polyamide pipe is coiled at a ratio of outer pipe diameter to coiling diameter of less than 30% and/or a coiling strain of about 1% to about 30%, more preferably about 3% to about 6%, more preferably less than 5%. Preferred in this process is that the coiling diameter be greater than or equal to 3 to 30 times the outer diameter of the pipe, preferably 15 to 25 times the outer diameter of the pipe. The length of pipe to be coiled, and therefore the coil diameter, is selected based upon efficient transportation mode on trucks to meet Department of Transportation regulations and minimize costs. Pipes of the present invention are coiled in lengths typically ranging from about 500 feet to about 2000 feet based upon the pipe diameter. For example, a 2 inch outer diameter pipe is typically coiled in a length of about 2000 feet, a 3 inch and 4 inch outer diameter pipe is typically coiled in a length of about 1000 feet, and a 6 inch outer diameter pipe is typically coiled in a length of about 500 feet.

In one embodiment, the coiling force to coil a 3" SDR11 pipe of the present invention in coils of diameter from 70 inches to about 90 inches has a power requirement from about 0.30 horsepower (hp) to about 1.6 hp, more preferred from about 0.08 hp to about 0.3 hp, and a torque of about 687 ft-lb, more preferably from 687 ft-lb to about 2632 ft-lb torque.

The coiled pipes of the present embodiment can be uncoiled and installed as straight pipe without any pipe straighteners or pipe tamers and can be bent at angles required for service. In one embodiment, the uncoiling force varies from about 440 lb to about 4543 lb, more preferably from about 440 lb to about 900 lb for safer installation.

All patents, patent applications, test procedures, priority documents, articles, publications, manuals, and other documents cited herein are fully incorporated by reference to the extent such disclosure is not inconsistent with the disclosures herein and for all jurisdictions in which such incorporation is permitted.

The following section provides further illustration of the resins, hollow conduits, pipes, articles and processes of the present invention. The resins and pipes exemplified herein comprise nonlimiting examples drawn to N66. However,

other polyamides known to those skilled in the art may be employed according to the disclosures herein. Such polyamides are high tensile strength polyamides, including, but are not limited to: polyhexamethylene adipamide (N66), polycaproamide (N6), polytetramethylene adipamide (N46), polypentamethylene adipamide (N56), polyenanthamide (N7), polyhexamethylene decamide (N610), polyhexamethylene dodecamide (N612), polyhexamethylene terephthalamide (N6T), polyhexamethylene isophthalamide (N6I), polynonamethylene terephthalamide (N9T), poly-2-methylpentamethylene terephthalamide (NDT), poly-2-methyl-pentamethylene isophthalamide (NDI), poly-2-methyl-pentamethylene adipamide (ND6), N11, N12 and combinations thereof. By "combinations thereof" with respect to polyamides, it is meant to include, but is not limited to, block copolymers, random copolymers, terpolymers, as well as melt blends, which are expected to exhibit similar desired melt strength and viscoelastic behaviors to those described herein for nylon 6,6 when effective maleation levels and moisture content are balanced and when hydrophobicity is increased in accordance with the disclosures herein. The following working examples are illustrative only and are not intended to limit the scope of the embodiments herein disclosed in any way.

EXAMPLES

As used herein, the "Exxelor™ VA 1840" is a semi-crystalline ethylene copolymer functionalized with maleic anhydride by reactive extrusion. Exxelor™ is a trademark of ExxonMobil and is described at the internet weblink:

[http://exxonmobilchemical.ides.com/en-](http://exxonmobilchemical.ides.com/en-US/ds135220/Exxelor%E2%84%A2%20VA%201840.aspx?l=74710&U=0)

[US/ds135220/Exxelor%E2%84%A2%20VA%201840.aspx?l=74710&U=0](http://exxonmobilchemical.ides.com/en-US/ds135220/Exxelor%E2%84%A2%20VA%201840.aspx?l=74710&U=0)

As used herein, the "Zytel® FE-7108 Cu" is a commercial product of DuPont. The DuPont™ Zytel® FE-7108 Cu is used as a heat stabilizer in the examples.

Example 1: Pipe Preparation

In this example and all subsequent examples the RV (solution relative viscosity) is determined according to ASTM Method D789.

In this example, the main/thickest component of the pipe which accounts for at least 80% of the wall thickness. A composition comprised of 69.1% of a TORZEN™ PA66 U4800 NC01 nylon 6,6 pellet from INVISTA with the RV of 48, 22% of the impact modifier Exxelor™ VA1840, 0.9% of the heat stabilizer Zytel® FE-7108 Cu, and 2% nigrosine, a mixture of synthetic black dyes (referred to as Nylon 6,6 48RV) is fed through the feed throat of a 75mm vented twin screw extruder at an appropriate rate and RPM to ensure a homogeneous melt stream. This melt stream is then taken through a screen pack supported by an appropriately sized breaker plate, and then fed into a gear pump, which is used to maintain a constant volumetric flow of melt into a special pipe head. This pipe head also has the ability to accept additional melt stream(s) from one or more vented or unvented single screw or twin screw extruders feeding a functionalized hydrophobic polymer in the melt form in such a way that these polymers streams are brought together inside the die head to form a coating on the outside and inside layers of the main PA66 component. Thickness of these inside and outside layers can vary from 0.07mm to 1.5mm based on end application and pipe size. Examples of functionalized hydrophobic polymer used include maleated ETFE (ethylene tetrafluoroethylene copolymer), or maleated FEP (fluorinated ethylene propylene), or a maleated PFE (polyfluorinated ethylene). Die gaps are adjusted

such that proper draw down ratio is attained to defect free inside and outside surfaces.

Typical extrusion conditions are as follows:

Twin screw extruder:

Throughput – 227-816 kg/hr [500-1800 lb/hr]

Screw RPM – 70-300 RPM

Barrel temperatures – 265-304°C [510-580°F]

Pipe head temperature – 260-293°C [500-560°F]

Melt temperature – 265-304°C [510-580°F]

Single Screw extruder settings:

Screw RPM 40-200 RPM

Grooved bush temp = 4-93 °C [40-200 °F]

Barrel Temps. (5 barrels) = 263-304 °C [505-580 °F]

Die Temp. (5 die heads) = 260-293 °C [500-550 °F]

Melt temperature ranging from 265-304 °C [510–580 °F].

Once the composition passes through the die-gap, it is then passed through a calibrator ring, which is used to size the pipe to the correct outer diameter. Water may or may not be used in the calibrator ring as a lubricant to minimize sticking. The calibrator ring also has the ability to pull a vacuum for correctly sizing the outer diameter of the pipe. The pipe is then moved through two or more cooling tanks with either water spray of atomized droplets or a water bath to cool the pipe to less than 300°F. The extruded pipe used in most experiments herein has standard dimension ratio (SDR) ranging from 7 to 11 with an OD ranging from 3.5 to 4.5 inch diameter, and produced in a continuous fashion to either make continuous coils or cut into straight section of desired length using a saw. However, the same or similar conditions can be utilized to manufacture bigger or smaller pipe sizes with standard dimension ratios (SDR) varying from about 4 to about 32, preferably between about 7 to about 25.

Example 2: Burst Pressure Testing of Pipe:

In Hansen C.M., Progress in Organic Coatings, Vol 42, p167-178 (2001), the water uptake of about 0.5 mg/gm is measured for poly(ethylene-co-trifluoroethylene) or "ETFE" when exposed to water at 90°C. Hence, when ETFE is used as an inside and outside liner for PA66, it can be expected that maximum saturation level of PA66 can be reduced to about 0.5 mg/gm or 0.05%. This would result in burst stress of ETFE lined PA66 pipes to be in the range of 6500-7300 psi, and a long term hydrostatic strength ranging from 4000-5000 psi. In proxy testing of PA66 pipe, prepared according to the method described in Example 1, exposed to an environment of 50% RH (relative humidity) air at 23°C (73°F), we observe that the long term burst strength is about 4000 psi (see FIG. 3). FIG. 2 plots a log of stress (in psi) on the Y-axis, measured according to the ASTM D2837 method, versus the log of exposure time (in hours) on the X-axis for the PA66 pipe.

Example 3:

Using the extrusion equipment, conditions and settings described in Example 1, a thermoplastic pipe is co-extruded using NPD-078 (natural) as the skin layer and NPD-078 (black) as the core material. Performance properties of the co-extruded pipe for (i) adhesion of the skin layer to the core, (ii) moisture absorption from outside when subjected to 80°C water exposure for 30 days, (iii) quick burst pressure test, and (iv) butt fusion test are measured using the appropriate standard test methods.

In the below non-limiting examples, a functionalized hydrophobic polymer, such as maleated ethylene propylene diene (EPDM) rubber, and maleated ETFE (ethylene tetrafluoroethylene copolymer) are used for illustrative purposes.

Example 4:

The Example 3 preparation is repeated for a co-extruded thermoplastic pipe from maleated ethylene propylene diene (EPDM) rubber as the skin layer and NPD-078 (black) as the core material. Testing of the co-extruded pipe indicates improved

skin adhesion to the core, reduced moisture absorption from outside, acceptable quick burst pressure and improved butt fusion over those measured for the co-extruded pipe specimen of Example 3.

Example 5:

The Example 3 preparation is repeated for a co-extruded thermoplastic pipe from maleated ethylene tetrafluoroethylene copolymer (ETFE) as the skin layer and NPD-078 (black) as the core material. Testing of the co-extruded pipe indicates overall performance improvements over those measured for the co-extruded pipe specimen of Example 3.

Example 6:

A three-layer, co-extruded thermoplastic pipe specimen is prepared using the equipment, extrusion conditions and settings described in Example 1. Testing of the three-layer co-extruded pipe indicates overall performance improvements over those measured for the co-extruded pipe specimen of Example 3.

It should be noted that ratios, concentrations, amounts, and other numerical data may be expressed herein in a range format. It is to be understood that such a range format is used for convenience and brevity, and thus, should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. To illustrate, a concentration range of "about 0.1% to about 5%" should be interpreted to include not only the explicitly recited concentration of about 0.1 wt% to about 5 wt%, but also the individual concentrations (e.g., 1%, 2%, 3%, and 4%) and the sub-ranges (e.g., 0.5%, 1.1%, 2.2%, 3.3%, and 4.4%) within the indicated range. The term "about" can include $\pm 1\%$, $\pm 2\%$, $\pm 3\%$, $\pm 4\%$, $\pm 5\%$, $\pm 8\%$, or $\pm 10\%$, of the numerical value(s) being modified. In addition, the phrase "about 'x' to 'y'" includes "about 'x' to about 'y'".

What is Claimed is:

1. A thermoplastic nylon resin, comprising a functional additive selected from the group consisting of: neo-alkoxy titanates and neo-alkoxy zirconates.
2. The thermoplastic resin of Claim 1 comprising about 60 weight percent to about 99.9 percent by weight a polyamide; and about 0.1 percent by weight to about 40 percent by weight of an impact modifying additive selected from the group consisting of: maleic anhydride and a functional equivalent of maleic anhydride; and wherein the resin has a moisture level less than about the equilibrium moisture content of the polyamide.
3. The thermoplastic resin of claim 2 wherein the polyamide is a high tensile strength polyamide.
4. The thermoplastic resin of claim 3 wherein the high tensile strength polyamide is selected from the group consisting of polyamides: N66, N6, N46, N56, N7, N610, N612, N6T, N6I, N9T, NDT, NDI, ND6, N11, N12 and combinations thereof.
5. The thermoplastic resin of claim 3 wherein the polyamide is N66 having an initial formic acid test method based relative viscosity (RV) of at least 35.
6. The thermoplastic resin of claim 5 wherein the resin moisture level is less than about 0.15 weight percent.
7. The thermoplastic resin of claim 3 wherein the polyamide is N66 having an initial formic acid test method based relative viscosity (RV) of at least 48.

8. The thermoplastic resin of claim 7 wherein the resin moisture level is less than about 0.05 weight percent.

9. The thermoplastic resin of claim 3 wherein the polyamide is N66 having an initial formic acid test method based relative viscosity (RV) of at least 80.

10. The thermoplastic resin of claim 9 wherein the resin moisture level is at most about 0.03 weight percent.

11. The thermoplastic resin of claim 3 wherein the polyamide is N66 having an initial formic acid test method based relative viscosity (RV) of at least about 240.

12. The thermoplastic resin of claim 11 wherein the resin moisture level is at most about 0.005 weight percent.

13. The thermoplastic resin of claim 1 wherein the impact modifying additive has an effective maleic anhydride level of less than about 1 weight percent.

14. The thermoplastic resin of claim 13 wherein the impact modifying additive has an effective maleic anhydride level of about 0.044 to about 0.11 weight percent.

15. The thermoplastic resin of claim 1 wherein the impact modifying additive comprises a maleated ethylene propylene diene rubber.

16. The thermoplastic resin of claim 2 further comprising a heat stabilizer.

17. The thermoplastic resin of claim 2 further comprising a colorant.

18. The thermoplastic resin of any one of claim 1 through claim 17 comprising a granulated physical form.

19. An article extruded from the thermoplastic resin of any one of claim 1 through claim 17.

20. The article of claim 19 having a burst stress value of about 7000 to about 10000 pounds per square inch and comprising a thermoplastic resin fully saturated with water.

21. A extruded hollow conduit having an interior first surface and an exterior second surface, said conduit comprising,
a thermoplastic resin composition comprising about 60 weight percent to about 99.9 weight percent of a polyamide; and further comprising about 0.1 weight percent to about 40 weight percent of an impact modifying additive selected from the group consisting of: maleic anhydride and a functional equivalent of maleic anhydride; and wherein,
the composition has a moisture level less than the equilibrium moisture content of the polyamide;
and further comprising,
a functional coating to increase water resistance and a burst stress value of said conduit in a fully water saturated state; and wherein,
the functional coating is applied to the first surface or the second surface or to both surfaces of the conduit.

22. The extruded hollow conduit of claim 21 wherein the polyamide is a high tensile strength polyamide.

23. The conduit of claim 22 wherein the polyamide is selected from the group consisting of polyamides: N66, N6, N46, N56, N7, N610, N612, N6T, N6I, N9T, NDT, NDI, ND6, N11, N12 and combinations thereof.

24. The conduit of claim 22 wherein the polyamide is N66 having an initial formic acid test method based relative viscosity (RV) of at least about 35.

25. The conduit of claim 24 comprising a polyamide having a moisture level of less than about 0.15 weight percent.

26. The conduit of claim 22 wherein the polyamide is N66 having an initial formic acid test method based relative viscosity (RV) of at least about 48.

27. The conduit of claim 26 wherein the moisture level of the polyamide is less than about 0.05 weight percent.

28. The conduit of claim 22 wherein the polyamide is N66 having an initial formic acid test method based relative viscosity (RV) of at least about 80.

29. The conduit of claim 28 wherein the moisture level of the polyamide is at most about 0.03 weight percent.

30. The conduit of claim 22 wherein the polyamide is N66 having an initial formic acid test method based relative viscosity (RV) of at least about 240.

31. The conduit of claim 30 wherein the moisture level is 0.005% by weight or less.

32. The conduit of claim 21 wherein the impact modifying additive has an effective maleic anhydride level of at most about 1 weight percent.

33. The conduit of claim 21 wherein the impact modifying additive has an effective maleic anhydride level of about 0.044 weight percent to about 0.11 weight percent.

34. The conduit of claim 21 wherein the impact modifying additive comprises a maleated ethylene propylene diene rubber.

35. The conduit of claim 21 further comprising a heat stabilizer.

36. The conduit of claim 21 further comprising a colorant.

37. The conduit of claim 21 comprising a thermoplastic resin composition fully saturated with water and having a burst stress value of about 7000 pounds per square inch to about 10000 pounds per square inch.

38. A method for increasing the burst stress value of a extruded conduit comprising a thermoplastic resin composition fully saturated with water, the method comprising;
providing a functional additive selected from the group consisting of:
neo-alkoxy titanates and neo-alkoxy zirconates to the thermoplastic resin composition prior to extruding the conduit.

39. The method of claim 38 wherein the thermoplastic resin composition comprises a resin composition having about 60 weight percent to about 99.9 weight percent of a polyamide; and
providing to the composition an impact modifying additive selected from the group consisting of: maleic anhydride and a functional equivalent of maleic anhydride in an amount of about 0.1 weight percent to about 40 weight percent.

40. A method for increasing the burst stress value of an extruded hollow conduit having an interior first surface and an exterior second surface, said method comprising,
providing a thermoplastic resin composition comprising about 60 weight percent to about 99.9 weight percent of a polyamide; and
providing to the resin composition an impact modifying additive selected from the group consisting of: maleic anhydride and a functional equivalent of maleic anhydride in an amount of about 0.1 weight percent to about 40 weight percent,
and

providing a functional coating to increase water resistance and a burst stress value of said conduit in a fully water saturated state;
and wherein the functional coating comprises a hydrophobic polymer selected from the group consisting of:
maleated ethylene tetrafluoroethylene copolymer; maleated fluorinated ethylene propylene copolymer; and maleated polyfluorinated ethylene;
and
applying the functional coating to the first surface or the second surface or to both surfaces of the conduit.

41. The method of any of one of claim 38 through claim 40 wherein the burst stress value of the conduit is increased to about 7000 pounds per square inch to about 10000 pounds per square inch.

42. The extruded hollow conduit of any one of claim 21 through claim 38 in which the conduit comprises a substantially right cylindrical pipe.

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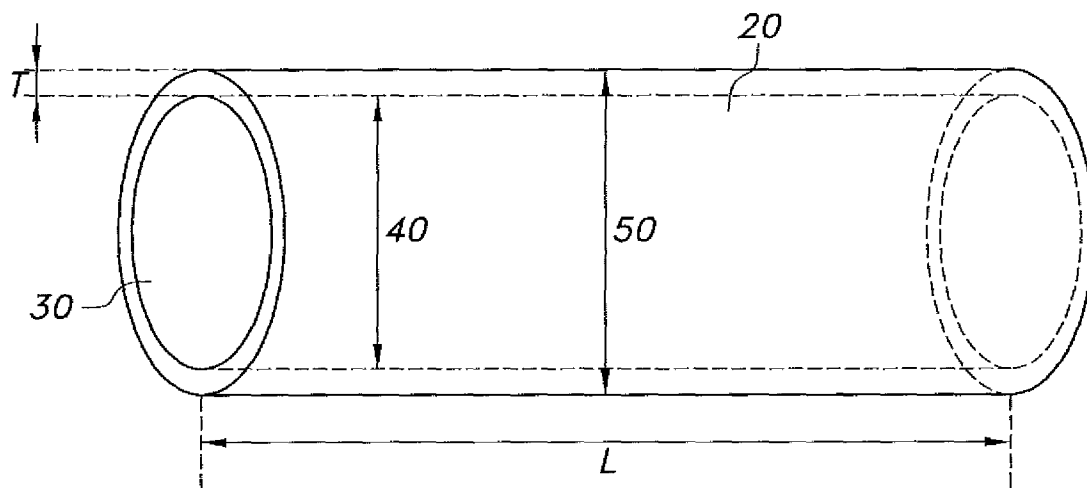


FIG. 1

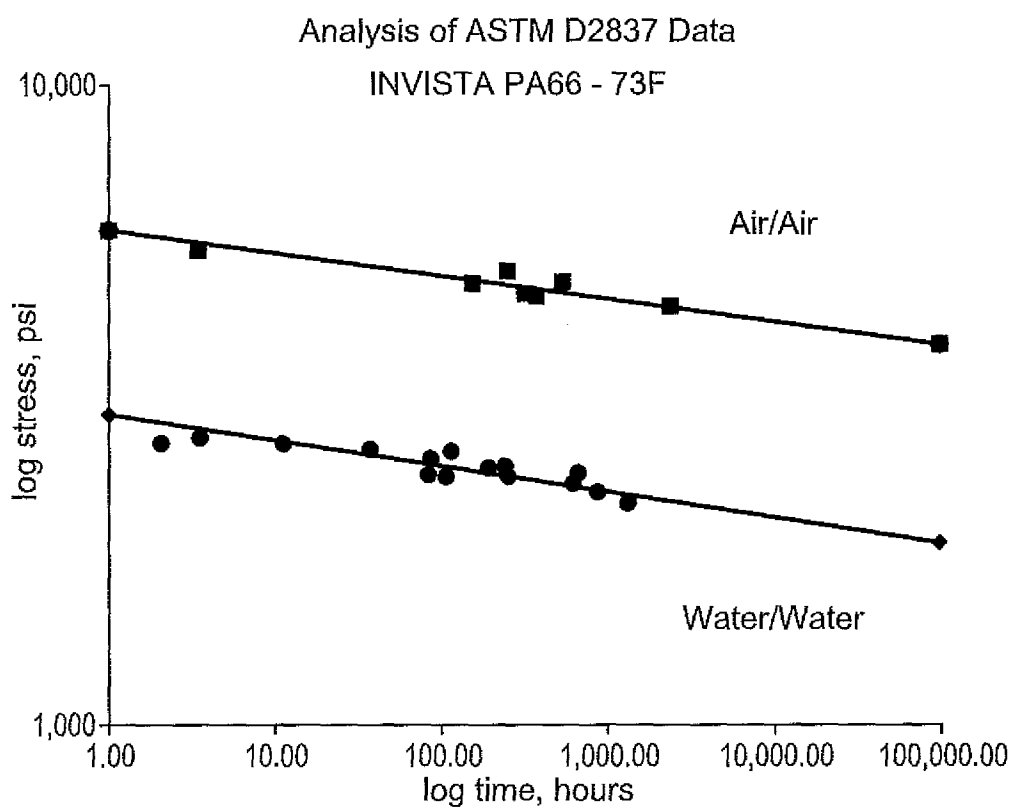


FIG. 2