Pipe with polar resin inner layer

The multilayer pipe includes an inner layer comprising a polar functional olefin resin. Preferably the inner layer is extruded onto a barrier layer. Preferably the inner layer comprises a blend of polymers, and contains a polar stabiliser and filler. Preferably the polar functional olefin resin is a copolymer of an olefin, and an unsaturated acid, anhydride, ester, alcohol or epoxy compound. Preferably the pipe has at least three layers. The pipe can carry hot water.
MULTILAYER PIPE

This invention relates to multilayer pipes, and more particularly to multilayer pipes formed from extruded polyolefin polymers.

Extruded polyolefin pipes are well known for a variety of industrial applications. Typically they are used in the building industry for domestic water pipes, radiator pipes, floor-heating pipes and for similar applications in ship building etc. Polyolefin pipes can also be used as district heating pipes and as process pipes in the food industry etc. Other applications include the conveyance of gaseous fluids and slurries.

Multilayer pipes wherein at least one of the layers comprises an extruded polyolefin are also well known and a great many have been described in the literature. Multilayer pipes are used, for example, when improved long term strength at elevated temperatures is needed or, when barrier properties against oxygen permeation are necessary. Multilayer pipes can comprise dissimilar materials for particular applications. For example, multilayer pipes having diffusion barrier layers have been proposed. The diffusion barrier can be a polymeric layer such as EVOH, or a metallic layer which provides both a diffusion barrier and a strengthening layer.

In recent years multilayer pipes having aluminium based barrier layers have become very popular. When installing domestic heating systems the metal barrier provides a specific and important benefit, which is that when the pipe is bent it retains its new configuration,
in contrast to plastics pipes without a metal barrier layer, which tend to recover their original shape.

However, multilayer plastics pipes comprising two or more layers of polyolefin homopolymers or copolymers having an intermediate metallic barrier or strengthening layer disposed between them tend to have poorer performance over the long-term than, for example, PEX pipes, comprising a single layer of cross-linked polyethylene. In addition, the difference between the coefficients of thermal expansion of a metallic barrier layer and the plastics layers can lead to delamination. Nevertheless, the presence of a metal barrier layer is often very desirable in certain applications of plastics pipes, for example, in domestic and district heating and in the oil, petroleum and gas industries. Multilayer plastics pipes with metal barrier layers also find use in cold water applications where potable water needs to be protected from aromatic substances found in the soil.

A further benefit of plastics pipes with metallic barrier layers is that the metal layer prevents UV light from reaching the inner plastics layer(s) beneath it, thereby protecting these layer(s) from UV degradation. This protection obviates the need for the addition of UV stabilisers to the inner layer(s) and enables the stabiliser packages of the inner and outer plastics layers to be optimised, with the inner layer(s) requiring only thermal and chemical stabilisation. Examples of plastics pipes having metal barrier and strengthening layers and methods for their manufacture are disclosed in the following patents:

CH 655986
The entire disclosures of which are incorporated herein by reference for all purposes.

Typical multilayer pipe constructions consist of five layers where the innermost layer comprises, for example, PE-RT (polyethylene for higher temperatures), which is overlaid with a first adhesive layer, an overlapped or butt welded aluminium strengthening and barrier layer, a second adhesive layer and an outer layer of PE-RT or silane cross-linked PEX (cross-linked polyethylene). The adhesive layers are necessary because many polymers, including polyolefins, have very poor adhesion to aluminium.

This construction has several drawbacks. Firstly the inner plastics layer and the first adhesive layer are together rather thin and in some manufacturing processes the thickness of the first adhesive layer is difficult to control.

Secondly the first adhesive layer is usually made of a thermoplastic polymer that is mechanically weaker than the inner plastics layer and hence does not improve the long-term hydrostatic strength of the pipe. This means in practice that omitting the first adhesive layer would provide advantages in the form of improved long term strength, easier quality control and easier extrusion tool design.
Thirdly, in manufacturing processes wherein the inner plastics layer is directly extruded into a freshly formed and welded aluminium tube comprising the barrier layer, the thermal shrinkage of the hot extruded inner plastics layer tends to cause delamination, requiring the use of a high strength adhesive as the first adhesive layer.

It has been proposed to limit the thermal shrinkage of a thermoplastic polymer by compounding relatively large particle size fillers into the polymeric matrix. However, the loading level needs to be rather high in order to reach the desired effect and this reduces the flexibility of the pipe. The use of high levels of filler also introduces further problems, including the difficulty of obtaining good wetting of the filler by the polymeric matrix, which is necessary in order to obtain good mechanical properties. Polyolefins, for example, are non-polar and incompatible with hydrophilic fillers. Thus, poor adhesion between the filler surface and the matrix is a frequent outcome.

Some improvement in the wetting of the filler surface by the polymeric matrix may be obtained by the use of coating agents, for example, fatty acids such as stearic acid, and salts of fatty acids, which react with hydroxyl groups on the filler surface, but further improvements would be highly desirable.

The long-term performance of plastics pipes is typically evaluated using the SEM method where the pipe is pressurised at elevated temperatures and the time to burst is measured at different stress levels. Considerable research effort has been focused on so-
called stage III ruptures, which take place when the stabiliser package has ceased to be effective. If the stabilisers can migrate and leach out of the matrix easily the long-term endurance of the pipe is jeopardised.

A method for studying stabiliser migration involves immersing the pipe in boiling water with subsequent measurement of the OIT level, which gives an indication as to how easily the stabiliser is leaching out of the pipe wall.

It is apparent that there are several problems associated with existing multilayer plastics pipe constructions. In particular, improvements in adhesion of the inner polymer layer to any barrier or strengthening layer present and in reducing stabiliser leaching and migration would be highly desirable.

According to the present invention, a multilayer plastics pipe of improved performance comprises an inner polyolefin layer, which is made more polar by the presence of functional end groups.

In a first aspect, the present invention provides a multilayer plastics pipe having an outer layer and an inner layer, wherein the inner layer comprises an extruded polar functional polyolefin polymer.

In a second aspect the invention provides a method of producing a multilayer pipe comprising an outer layer and an inner layer, which comprises extruding a polymeric composition comprising a polar functional polyolefin polymer to form an inner polymeric layer.
In a first preferred embodiment, the multilayer pipe of the invention comprises an inner polymeric layer and an outer barrier layer surrounding the inner polymeric layer, the inner polymeric layer comprising a polar functional polyolefin polymer.

In a second preferred embodiment, the multilayer pipe of the invention comprises an inner polymeric layer comprising a polar functional polyolefin polymer and at least one polar stabiliser.

In a third preferred embodiment, the multilayer pipe of the invention comprises an inner polymeric layer comprising a polar functional polyolefin polymer and at least one filler.

In a fourth preferred embodiment, the multilayer pipe of the invention comprises an inner polymeric layer and an outer barrier layer surrounding the inner polymeric layer, the inner polymeric layer comprising a polar functional polyolefin polymer, at least one polar stabiliser and at least one filler.

By a multilayer pipe in this specification is meant a pipe having two or more layers, at least one of which layers can be a barrier or strengthening layer. A multilayer pipe has an inner layer, which is in direct contact with the fluidic material (gas, liquid or slurry) conveyed by the pipe, and an outer layer, which may be in contact with the environment, or which may be surrounded by additional outer layer(s). In certain preferred embodiments the multilayer pipe has a polymeric or
metallic barrier layer disposed between the plastic inner layer and one or more additional outer layers.

In this specification, a polar functional polyolefin is defined as a semi-crystalline polyolefin polymer comprising amorphous regions, wherein functional polar substituent groups are present within the amorphous regions. Polar functional substituent groups comprise at least one polar covalent bond in which the electrons are not shared equally because one atom attracts them more strongly than the other. The bond therefore has a permanent dipole moment. Typically polar functional substituent groups are asymmetric and comprise at least one hetero-atom, for example, O, N, S, or P. Functional groups in this specification are defined as substituent groups that, when present in a polymeric matrix, are capable of interacting with substituent groups on other molecules in order to bond thereto by intermolecular forces of attraction. Such forces include, for example, Van der Waals forces (including dispersion forces and dipole-dipole interactions), hydrogen bonding, ionic bonding, co-ordinate (dative covalent) bonding, and any combination thereof.

The polar functional polyolefin polymer can be produced by co-polymerisation of an olefin with an olefinically unsaturated comonomer having the desired polar functional substituent group. Suitable comonomers include, for example, unsaturated aliphatic or aromatic acids, anhydrides, esters, and alcohols.

Preferred polar functional polyolefin polymers include, for example, acrylic acid functionalised polyolefins, for example, polypropylene (PP-g-AA), and
maleic anhydride functionalised polyolefins, for example, polyethylene (PE-g-MAH), polypropylene (PP-g-MAH and PR-g-MAH) and ethylene-propylene rubber (EPR-g-MAH). Polyolefins can also be functionalised by the introduction of oxy, epoxy and -OH groups. For example, copolymers of ethylene and 10-undecenol yield (PE-co-OH1) type functional polyolefin polymers. Other comonomers that can be used to functionalise olefin polymers include butyl acrylate and glycidyl methacrylate.

The functionality of the polar functional polymer can be expressed as the weight percent of the comonomer (typically having a -COOH or -OH group) present. Preferably the olefinically unsaturated comonomer is present in at least 0.01 weight percent, more preferably at least 0.1 weight percent, especially from 1 to 20 weight percent, most preferably from 1 to 10 weight percent, based on the total weight of the polyolefin polymer. In other embodiments, the polar functional polyolefin polymer can be produced by grafting, in particular by radiation grafting or free radical grafting, of polar functional groups onto a polyolefin backbone. In such polymers the functionality can be expressed as the weight percent of notional comonomer present.

Preferably the polar functional polyolefin polymer is a polar functional polypropylene. Suitable polar functional polypropylenes include, for example, oxypolypropylene (containing peroxide groups in the polymer chains) manufactured by Basell, BB125E manufactured by Borealis (PP-g-MAH) (MAH=0.5 % per weight) and Polybond 1002 manufactured by Uniroyal (PP-g-AA) (AA~6.0 % per weight).
Preferably the inner layer of the multilayer pipe comprises a blend of a non-polar semi-crystalline polyolefin polymer and a polar functional polyolefin polymer. In one embodiment the non-polar semi-crystalline polyolefin polymer is present in a major amount of at least 50 weight percent, preferably from 80 to 99 weight percent. In another embodiment the non-polar semi-crystalline polyolefin polymer is present in a minor amount of less than 50 weight percent, preferably from 1 to 20 weight percent.

In a particularly preferred embodiment, the inner layer comprises a blend of a polypropylene (PP) and a polar functional polypropylene. Preferably the polar functional polypropylene is present in the blend in a minor amount, more preferably in an amount of from 3 to 20 weight percent, especially from 5 to 15 weight percent, most preferably around 10 weight percent, based on the total weight of the blend.

Preferably the polypropylene (PP) is a polypropylene homopolymer, preferably with a narrow molecular weight distribution (MWD), and preferably with a low crystallinity. Preferably the polypropylene homopolymer comprises at least 70 weight percent of fractions having a weight average molecular weight of at least $7 \times 10^5$.

The inner layer polymer blend can comprise, for example, a random polypropylene (PP). An example of a random polypropylene pipe composition is described in WO 03/037981, the entire disclosure of which is incorporated herein by reference for all purposes.
Preferably the polypropylene (PP) has a high molecular weight with a narrow molecular weight distribution and the polar functional polypropylene has a lower molecular weight and a narrow molecular weight distribution. With an appropriate selection of molecular weights such a combination can form a bimodal material with good strength properties which is nevertheless easy to extrude.

In another preferred embodiment according to the invention, the inner layer comprises a blend of a polyethylene polymer, for example, PE-RT, and a polar functional polyethylene polymer. Preferably the polar functional polyethylene is present in the blend in a minor amount, more preferably in an amount of from 2 to 20 weight percent, most preferably around 10 weight percent, based on the total weight of the blend.

In yet another preferred embodiment, the inner layer comprises a blend of a polar functional polypropylene admixed with from 2 to 20 weight percent, for example, about 10 weight percent, of linear low density polyethylene.

Preferably the inner layer polymer blend is cross-linked, for example, by the addition of a chemical cross-linking agent, or by radiation or silane cross-linking.

In the first preferred embodiment of the invention the multilayer pipe is provided with an outer barrier layer surrounding the inner polymeric layer. The outer barrier layer is preferably a metallic layer and is preferably also a strengthening layer. The outer barrier layer can comprise, for example, aluminium, stainless
steel, copper, or any other suitable metal. The metal can comprise a welded sheet, for example, a welded aluminium sheet. In other embodiments the metal layer can be sputtered, galvanically-coated or electro-deposited, or can comprise a wound and/or corrugated metal sheet. Preferably the outer barrier layer is directly bonded to the inner polymeric layer, although it is also possible for the barrier layer to be bonded to the inner polymeric layer through an adhesive layer, as will be more fully described hereinafter.

Preferably the inner polymeric layer comprises a polymeric matrix provided with functional groups that increase the wetting of the metal barrier layer by the polymeric matrix. Such groups can, for example, decrease the contact angle of the polymeric matrix with the metal barrier layer.

In a further and independent aspect of the invention, it is also possible to modify the surface of the metal barrier layer to improve its wetting behaviour. The metal barrier layer can be treated, for example, by physical surface modification, for example, plasma treatment, abrasion, ablation, or cleaning; or by chemical surface modification, for example, solvent or chemical cleaning, treatment with chemical modifying agents to introduce surface functional groups, deposition of surface layers by, for example, plasma deposition of a polymeric layer containing functional groups, deposition of a glassy layer, or other surface coating techniques. Such techniques are particularly preferred where they permit direct bonding of the inner polymeric layer to the metal barrier layer and enable the separate adhesive layer or layers to be omitted.
In the second preferred embodiment of the invention the multilayer pipe of the invention comprises an inner polymeric layer comprising a polar functional polyolefin polymer and at least one polar stabiliser. By a polar stabiliser in this specification is meant a stabiliser comprising at least one functional polar group comprising at least one polar covalent bond. Typically functional polar groups are asymmetric and comprise at least one hetero-atom, for example, O, N, S, or P.

Stabilisation of polyolefins is usually accomplished by melt blending with one or more stabilisers. In this way a heterophase polymer/stabiliser system is formed, which may be best described as a physical dispersion of a low molecular weight stabiliser in a polymer matrix. The vast majority of commercial stabiliser compounds have very different chemical structure from that of the non-polar host polyolefin. For this reason, the compatibility of various conventional stabilisers with polyolefins is poor, leading to migration of admixed stabilisers across the boundary of the polyolefin with neighbouring fluids, liquids, gases or solid materials. This loss of stabiliser substantially shortens the lifetime of the polyolefin. The migration of stabilisers into drinking water can also have unpredictable toxic effects on consumers.

Without been bound by any particular theory it is believed that in certain preferred embodiments of the invention the migration and leaching of the polar stabiliser from the polyolefin matrix is substantially reduced by interaction with the polar groups in the polar functional polyolefin polymer.
Stabilisers suitable for use in the present invention include polar compounds known to impart improved thermal stability to polyolefins, compounds with antioxidant properties, radical scavengers, anti-ageing compounds and compounds which act as light and UV stabilisers. Preferably the stabilisers also have low toxicity and good organoleptic properties. One or more stabilisers or co-stabilisers can be employed in any suitable combinations in order to achieve the desired properties. For example, the co-stabiliser could have lesser hydrophobicity than the thermal stabiliser.

Examples of preferred polar stabilisers include phenolic antioxidants, particularly high molecular weight sterically-hindered phenols, for example, pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, Ethanol®330 manufactured by Ethyl Corporation, Irganox®1076, Irganox®3114 and Irganox®1010 manufactured by Ciba-Geigy and Cyanox®1790 manufactured by American Cyanamid.

The sterically-hindered phenolic stabilisers can be used together with co-stabilisers acting as hydroperoxide decomposers, for example, Cyanox®1212 manufactured by American Cyanamid.

Other useful stabilisers include phosphites, for example, tris(2,4-di-tertiary-butylphenyl) phosphate, phosphonites and benzotriazoles. Useful light and UV stabilisers include sterically-hindered amines, for example, piperidine compounds such as those based on tetramethyl piperidine.
Preferably the stabiliser is present in the inner polymeric layer in an amount of from 0.01 to 5 weight percent, more preferably from 0.1 to 1 weight percent, based on the weight of the inner polymeric layer.

In a third preferred embodiment of the invention, the multilayer pipe comprises an inner polymeric layer comprising a polar functional polyolefin polymer and at least one filler. By filler in this specification is meant a particulate, inorganic-based or organic material which is dispersed in a polymeric matrix to improve mechanical properties, provide reinforcement, increase bulk, or reduce cost.

Preferably the filler has a high aspect ratio.

Without wishing to be bound by any particular theory, it is believed that the action of the filler is two-fold. On the one hand, the filler can reduce the tendency of the polyolefin polymer to shrink on cooling after extrusion. This reduces the possibility of shrink-back and delamination from the metallic barrier layer where present and may permit direct extrusion of the inner layer against the metallic barrier layer without the need for additional adhesive layers, which tend to weaken the construction.

Without being bound to any particular theory, it is believed that the filler particles and the polar stabiliser molecules tend to reside in the amorphous regions of the semi-crystalline polyolefin polymer matrix of the inner layer where they may interact with the functional groups on the polar functional polyolefin
forming physical entanglements and Intermolecular attractions.

In these regions the filler particles possibly act as permeation modifiers, creating long and tortuous migration path lengths for the stabiliser molecules and maintaining a physical barrier preventing the stabiliser molecules from reaching the surface of the polymer matrix. In preferred embodiments of the invention migration and leaching of the polar stabiliser can therefore be substantially reduced by the combination of the physical barrier of the filler particles and the physical barrier of the outer metallic layer. This is particularly advantageous when the multilayer pipe of the invention is employed in, for example, conventional hot water systems.

Furthermore, by retaining the stabiliser molecules within the polymer matrix the attack of catalytic metal ions and the oxidising attack by oxygen, acids, and bases as well as of free chlorine and other halogens can be successfully counteracted even at elevated temperatures, and the resistance of the inner layer of the multilayer pipe against these media can be accordingly increased.

Any suitable inorganic-based filler can be used in the inner layer of the multilayer pipe of the invention. Examples include talc, mica, calcium carbonate, kaolin, clay, magnesium hydroxide, calcium silicate, carbon black, graphite, iron powder, silica, diatomite, titanium oxide, iron oxide, pumice, antimony oxide, dolomite, dawsonite, zeolitic filler, vermiculite, montmorillonite and the like. These fillers may be subjected to various surface treatments with organic wetting or coating agents.
as appropriate. Mixtures of different fillers can also be used.

The inorganic-based filler preferably has a mean particle diameter of up to 10 μm, more preferably up to 4 μm. If the mean particle diameter of the inorganic-based filler exceeds 10 μm, the inorganic-based filler tends to show poor dispersability resulting in a failure to provide a reinforcing effect. The mean particle diameter of the filler may be determined by a laser diffraction scattering method.

The inorganic-based filler(s) content of the inner polymeric layer is preferably from 0.1 to 25 weight percent, preferably from 0.5 to 25 weight percent, based on the weight of the polymeric matrix. If the filler content is less than 0.5 weight percent, the resulting product may be insufficiently reinforced for some applications. If it exceeds 25 % by weight, polymer-free regions between inorganic-based filler particles may be enlarged to an extent that impairs the reinforcing effect. Most preferably the filler content is from 1 to 20 weight percent, based on the weight of the polymeric matrix.

Preferred fillers are those having functional groups, for example, hydroxyl groups, on their surface, or which have been treated to produce such surface functional groups. Surface functional groups are those capable of interaction, either chemical or physical, with the polymeric matrix and/or the polar functional groups on the polar functional polyolefin polymer or the stabiliser. Among the above-listed fillers, talc and mica are particularly preferred.
Especially preferred are fine grades of talc or other platelet (flake) formed fillers having a particle size in the range of 0.01 to 200 μm, preferably 0.1 to 10 μm, a maximum equivalent diameter of about 25 μm, and an average thickness of less than 0.5 μm. The talc is preferably present in an amount of from 1 to 5 weight percent, based on the weight of the inner polymeric layer. When mica filler is used, preferably it is present in an amount of less than 5 weight percent, based on the weight of the inner polymeric layer, the mica preferably having a particle size of less than 74 μm and an aspect ratio of from 10 to 150 μm.

Calcium carbonate, optionally treated at its surface with a fatty acid coating agent, is also preferred for its ability to improve the impact resistance of the polymeric matrix. Suitable fatty acids having good processability include those having a carboxyl group attached to a terminal of a straight-chain alkyl or alkenyl residue containing from 5 to 30 carbon atoms. Specific examples include oleic acid, elaidic acid, stearic acid, eicosanoic acid, undecanoic acid, erucic acid, behenic acid, linoleic acid and the like. This surface treatment is, however, not always necessary because the polar functional polyolefin polymer can also improve the wetting of the filler particles by the polyolefin polymer matrix.

Where calcium carbonate is used as the inorganic-based filler, its content in the polyolefin polymer matrix is preferably within the range of 0.5 to 20 weight
percent, based on the weight of the inner polymeric layer.

In preferred inorganic-based filler, calcium carbonate is used as a co-filler together with talc.

Particularly preferred fillers for use in the present invention are nano-sized fillers. In this specification, nanofillers are defined as materials having one dimension below 200 nm. The use of nanofillers is especially preferred because in general the required loading levels are much lower than for conventional fillers. It is believed that the improved results obtained using nanofillers are due to their extremely high aspect ratio compared to conventional fillers. The use of nanosized fillers in the inner layer of the plastic multilayer pipe can give better adhesion to the outer metallic barrier layer and at the same time the thermal shrinkage of the polymeric matrix can be reduced.

Especially suitable nanofillers can be derived from inorganic materials, for example, intercalated and exfoliated (delaminated) clays (layered silicates), calcium carbonate, calcium phosphate, silicon carbide SiC (nanowhiskers) and silica SiO2. Nanotube fillers can also be used, for example, carbon nanotubes and nanotubes formed from synthetic polymers.

The nanofiller is preferably used in an amount of from about 1% to about 5% by volume, based on the volume of the inner polymeric layer. The nanofiller particles are preferably substantially uniformly dispersed in the inner polymeric layer. Preferably at least 50% of the nanofiller particles are less than about 20 layers thick,
the layers of the nanofiller particles having a unit thickness of from about 0.7nm to 1.2nm.

Preferably the nanofiller is a layered silicate comprising particles having one average dimension of 0.002 to 1 μm and a thickness of 0.6 to 2.0 nm. Preferably the nanofiller particles are uniformly dispersed in the polyolefin polymer and have an average interlayer distance of 2.0 nm or more. In this context, the interlayer distance refers to the distance between the gravity centers of flat plates of the layered silicate, and uniform dispersion refers to the dispersed state in which each one sheet of the layered silicate or a multilayer of 5 layers or less on an average exists in parallel or randomly, or where parallel and random states exist in mixture, with 50% or more, preferably 70% or more, thereof forming no local mass.

Examples of suitable nanofillers include montmorillonites, such as Cloisite 6A and Cloisite15A manufactured by Southern Clay Products Inc.

In the fourth, and particularly preferred embodiment of the invention, the multilayer comprises an inner polymeric layer and a barrier layer surrounding the inner polymeric layer, the inner polymeric layer comprising a polar functional polyolefin polymer, at least one stabiliser and at least one filler. In this embodiment, the interaction between the polar functional polyolefin polymer and the stabiliser, and the barrier effect of the filler, combine to retain the stabiliser within the matrix of the inner polymeric layer and tend to prevent, or at least reduce, leaching. The filler content can also reduce thermal shrinkage of the inner polymeric
layer and thereby contributes to reducing the risk of delamination. In addition, the polar groups on the polar functional polyolefin polymer act to improve the adhesion of the inner polymeric layer to the barrier layer and may obviate the necessity to provide a separate adhesive layer. Finally, the barrier layer (i) substantially reduces oxidative attack on the inner polymeric layer from the environment, and (ii) reduces the diffusion of gases and liquids from the environment into the inner wall of the pipe and thence into the medium flowing through the pipe. As a result, the chemical and thermal resistance of the inner layer is increased and the medium flowing through the pipe is protected.

In the method of the invention an inner polymeric layer of a multilayer pipe is produced by extruding a polymeric composition comprising a polar functional polyolefin polymer. Any suitable extruder can be used, including, for example, a conical disc type extruder or a single-screw or twin-screw extruder.

In a preferred method of the invention, the inner polymeric layer is extruded directly against an outer barrier layer, thereby avoiding the need to provide an adhesive layer between the inner polymeric layer and the outer polymeric layer.

In a first preferred embodiment of the method of the invention the matrix polyolefin, the functional olefin, the stabilizers and the fillers are all mixed together in a conical extruder having good compounding properties and directly extruded into the metallic barrier pipe to form an inner polymeric layer comprising the inner passageway of the pipe.
In a second preferred embodiment of the method of the invention, comprises extruding a polymeric composition comprising a polar functional polyolefin polymer into strands, the strands are pelletised and the pellets extruded to form the inner polymeric layer. Preferably the polymeric composition is extruded through a screen having a mesh size of at least 70.

In a particularly preferred embodiment of the method of the invention a bimodal compound is formed by mixing two narrow molecular weight polyolefins having different molecular weights, at least one of which is provided with polar functional groups, and optionally adding one or more polar stabilisers or fillers to the compound, which is then extruded to form the inner layer of the multilayer pipe.

In certain embodiments, notwithstanding any improvement in adhesion obtained by using the polar functional polyolefin polymer, it may still be necessary or desirable to include one or more adhesive layers in the multilayer pipe to ensure the desired level of bonding of the inner polymeric layer(s) to the barrier layer.

An adhesive layer can comprise, for example, a polymer comprising one or more functional groups that can react or interact with the inner surface of the barrier layer. Examples of suitable functional groups include carboxyl, carboxylic (for example maleic, phthalic, itaconic, citraconic, or glutaconic) anhydride, epoxy, hydroxyl, isocyanate, aldehyde, ester, acid amide, amino, hydrolysable silyl and cyano groups. Where the metal
layer is treated to be compatible with a polyamide polymer, carboxyl, carboxylic anhydride, epoxy and hydroxyl groups are, among others, preferred because of their high reactivity with amino groups.

Various methods can be employed for preparing polymers containing a reactive functional group for use in the adhesive layer. According to a preferred method, an unsaturated monomer containing a reactive functional group is polymerised or copolymerised with another unsaturated monomer. Examples of the monomers containing reactive functional groups are unsaturated monocarboxylic acids such as acrylic, methacrylic, vinylacetic, pentenoic, hexenoic, octanoic, decenoic, dodecenoic and oleic acids, and derivatives thereof, for example, salts, esters, amides and anhydrides; unsaturated dicarboxylic acids such as fumaric, itaconic, citraconic and glutaric acids, unsaturated alcohols such as allyl alcohol, butenol, pentenol, hexenol and dodecenol, and derivatives thereof; and unsaturated compounds containing epoxy groups, such as glycidyl methacrylate, glycidyl acrylate and acrylglycidyl ether. Monomers wherein one or more hydrogen atoms bonded to carbon are substituted by fluorine atoms are also included.

Preferred copolymers include copolymers of ethylene with at least one monomer chosen from (i) unsaturated carboxylic acids, their salts and their esters, (ii) vinyl esters of saturated carboxylic acids, (iii) unsaturated dicarboxylic acids, their salts, their esters, their half-esters and their anhydrides and (iv) unsaturated epoxides, these copolymers optionally being grafted with unsaturated dicarboxylic acid anhydrides.
such as maleic anhydride or unsaturated epoxides such as glycidyl methacrylate.

According to another preferred method for preparing a polymer containing a reactive group, a compound containing a reactive functional group is grafted to a polymer after its polymerization. The compound can, for example, contain a graft bonding group (e.g. an unsaturated bond) together with a functional group. The compound can be grafted to the polymer by a free radical reaction using peroxides or other initiators.

Suitable grafted polymers include, for example, grafts of polyethylene, polypropylene, copolymers of ethylene with at least one alpha-olefin, and blends of these polymers. The polymers may be grafted with, for example, unsaturated carboxylic acid anhydrides such as maleic anhydride.

The adhesive layer can also comprise a high temperature tolerant section covered with adhesive layers that give controlled bonding to the inner polymeric layer and the optionally corrugated barrier layer. The adhesive layers are advantageously chosen from co-polyamides and functionalised polyolefins.

Various other additives may be added to the polyolefin polymer matrix, including co-stabilisers, weather resistance additives, lubricants, nucleating agents, processing aids, pigments, coloring agents and the like.

In addition to the inner polymeric layer, the multilayer pipes of the invention can comprise one or
more additional outer polymeric layers. For example, one or more outer polymeric layers can be extruded around the outer barrier layer to provide corrosion protection, environmental protection, or mechanical protection, or to provide additional strength, identification or decorative properties. The additional outer polymeric layer(s) can comprise any suitable polymer or blend of polymers including polyolefins, for example, polyethylene and polypropylene; polyamides, for example, Nylon; polyesters; and polyvinylhalides, for example, PVC. A particularly preferred additional outer polymeric layer comprises cross-linked polyethylene (PEX-a).

The multilayer pipes of the invention can be used in a broad range of applications, but certain preferred embodiments find particular application in water transport, especially in pipes intended for the conveyance of hot (up to 110 deg) water, or warm water.

The invention is illustrated by the following non-limiting Examples:

Example 1

Nucleated polypropylene, having -OH polar functional groups and a functionality of 0.2 weight percent is blended with from 1 to 50 weight percent, preferably from 5 to 40 weight percent, more preferably from 10 to 40 weight percent (calculated from the total weight of the composition) of talc and 5 weight percent of phenolic stabiliser to form a masterbatch. The talc used has a particle size in the range of from 0.01 to 100 \( \mu \text{m} \), preferably from 0.1 to 10 \( \mu \text{m} \). This masterbatch is then blended with a semi-crystalline polypropylene polymer,
for example, of random block copolymer type, in a ratio of about 1:10.

The resultant compound is extruded using a conical disc extruder, a screen with a mesh size of at least 70, and an extrusion temperature of 220°C, directly onto the inner wall of an aluminium barrier layer tube to form an inner layer of thickness 1 mm. The inner layer is found to adhere strongly to the aluminium barrier layer with no noticeable delamination, such that a separate adhesive layer is not required.

The long-term performance of the resultant pipe is evaluated using the SEM method and is found to give excellent results. Testing by immersing the pipe in boiling water and measuring the OIT level indicates a very low level of leaching of the stabiliser from the pipe.

Example 2

77 weight % of a propylene homopolymer, 10 weight % of hydroxyl end group modified polypropylene, 8 weight % of talc with a mean particle diameter of 4 μm, and 5 weight % of calcium carbonate filler are blended to provide a polyolefin resin composition. This resin composition is then supplied to a twin-screw kneading and extruding machine and extruded into strands. The strands are then cut by a pelletizer into pellets. The pellets are fed into a single-screw extruder and extruded into tubular form. The tube is used to form the inner layer of a multilayer pipe.
The reader's attention is directed to all papers and
documents which are filed concurrently with or previous
to this specification in connection with this application
and which are open to public inspection with this
specification, and the contents of all such papers and
documents are incorporated herein by reference.

All of the features disclosed in this specification
(including any accompanying claims, abstract and
drawings), and/or all of the steps of any method or
process so disclosed, may be combined in any combination,
except combinations where at least some of such features
and/or steps are mutually exclusive.

Each feature disclosed in this specification
(including any accompanying claims, abstract and
drawings), may be replaced by alternative features
serving the same, equivalent or similar purpose, unless
expressly stated otherwise. Thus, unless expressly
stated otherwise, each feature disclosed is one example
only of a generic series of equivalent or similar
features.

The invention is not restricted to the details of
any foregoing embodiments. The invention extends to any
novel one, or any novel combination, of the features
disclosed in this specification (including any
accompanying claims, abstract and drawings), or to any
novel one, or any novel combination, of the steps of any
method or process so disclosed.
CLAIMS

1. A multilayer pipe having an outer layer and an inner layer, wherein the inner layer comprises an extruded polar functional polyolefin polymer.

2. A multilayer pipe according to claim 1, which comprises an inner polymeric layer and an outer barrier layer surrounding the inner polymeric layer, the inner polymeric layer comprising a polar functional polyolefin polymer.

3. A multilayer pipe according to claim 1 or 2, wherein the inner polymeric layer comprises a polar functional polyolefin polymer and at least one polar stabiliser.

4. A multilayer pipe according to any one of the preceding claims, wherein the inner polymeric layer comprises a polar functional polyolefin polymer and at least one filler.

5. A multilayer pipe according to any one of the preceding claims, which comprises an inner polymeric layer and an outer barrier layer surrounding the inner polymeric layer, the inner polymeric layer comprising a polar functional polyolefin polymer, at least one stabiliser and at least one filler.

6. A multilayer pipe according to any one of the preceding claims, which has an outer barrier layer disposed between the inner layer and one or more additional outer layers.
7. A multilayer pipe according to any one of the preceding claims, wherein the polar functional polyolefin polymer comprises a co-polymer of an olefin with an olefinically unsaturated comonomer having a polar functional substituent group.

8. A multilayer pipe according to claim 7, wherein the comonomer is an unsaturated aliphatic or aromatic acid, an unsaturated anhydride, an unsaturated ester, or an unsaturated alcohol.

9. A multilayer pipe according to claim 7 or 8, wherein the comonomer is acrylic acid, maleic anhydride, 10-undecenol, butyl acrylate, or glycidyl methacrylate.

10. A multilayer pipe according to any one of the preceding claims, wherein the polar functional polyolefin polymer comprises oxy, epoxy, or -OH groups.

11. A multilayer pipe according to any one of the preceding claims, wherein the polar functional polyolefin polymer comprises an acrylic acid functionalised polypropylene, a maleic anhydride functionalised polyethylene, a maleic anhydride functionalised polypropylene, or a maleic anhydride functionalised ethylene-propylene rubber.

12. A multilayer pipe according to any one of claims 7 to 11, wherein the olefinically unsaturated comonomer is present in an amount of from 1 to 20 weight percent.
13. A multilayer pipe according to any one of the preceding claims, wherein the polar functional polyolefin polymer is a polar functional polypropylene.

14. A multilayer pipe according to claim 13, wherein the polar functional polypropylene is oxypolypropylene.

15. A multilayer pipe according to any one of the preceding claims, wherein the inner layer comprises a blend of a non-polar polyolefin polymer and a polar functional polyolefin polymer wherein the non-polar polyolefin polymer is present in an amount of at least 50 weight percent.

16. A multilayer pipe according to claim 15, wherein the non-polar polyolefin polymer is present in an amount of from 80 to 99 weight percent.

17. A multilayer pipe according to claim 15 or 16, wherein the inner layer comprises a blend of a polypropylene and a polar functional polypropylene.

18. A multilayer pipe according to claim 17, wherein the polar functional polypropylene is present in the blend in an amount of from 3 to 20 weight percent.

19. A multilayer pipe according to any one of claims 1 to 14, wherein the non-polar semi-crystalline polyolefin polymer is present in a minor amount of less than 50 weight percent.
20. A multilayer pipe according to claim 19, wherein the non-polar semi-crystalline polyolefin polymer is present in an amount of from 1 to 20 weight percent.

21. A multilayer pipe according to any one of claims 15 to 20, wherein the polypropylene is a polypropylene homopolymer with a narrow molecular weight distribution and a low crystallinity.

22. A multilayer pipe according to claim 21, wherein the polypropylene homopolymer comprises at least 70 weight per cent of fractions having a weight average molecular weight of at least 7 times $10^5$.

23. A multilayer pipe according to claim 17, wherein the polypropylene has a high molecular weight with a narrow molecular weight distribution and the polar functional polypropylene has a lower molecular weight and a narrow molecular weight distribution whereby the combination forms a bimodal material.

24. A multilayer pipe according to claim 15 or 16, wherein the inner layer comprises a blend of a polyethylene polymer and a polar functional polyethylene polymer.

25. A multilayer pipe according to claim 24, wherein the polar functional polyethylene is present in the blend in an amount of from 2 to 20 weight per cent.

26. A multilayer pipe according to claim 19 or 20, wherein the inner layer comprises a blend of a polar functional polypropylene and a linear low density polyethylene.
27. A multilayer pipe according to any one of claims 15 to 26, wherein the inner layer comprises a cross-linked polymer blend.

28. A multilayer pipe according to any one of claims 2 to 27, wherein the outer barrier layer is a metallic layer.

29. A multilayer pipe according to claim 28, wherein the outer barrier layer comprises aluminium, stainless steel, or copper.

30. A multilayer pipe according to claim 28 or 29, wherein the outer barrier layer comprises a welded metal sheet, or a sputtered, galvanically-coated, or electro-deposited metal layer, or a wound and/or corrugated metal sheet.

31. A multilayer pipe according to any one of claims 28 to 30, wherein the outer barrier layer is directly bonded to the inner polymeric layer.

32. A multilayer pipe according to claim 31, wherein the inner polymeric layer comprises a polymeric matrix provided with functional groups that increase the wetting of the metallic barrier layer by the polymeric matrix.

33. A multilayer pipe according to claim 32, wherein the functional groups decrease the contact angle of the polymeric matrix with the metallic barrier layer.
34. A multilayer pipe according to any one of claims 28 to 33, wherein the surface of the metallic barrier layer has been modified in order to improve its wetting behaviour.

35. A multilayer pipe according to claim 34, wherein the metallic barrier layer has been treated by physical surface modification.

36. A multilayer pipe according to claim 35, wherein the physical surface modification comprises plasma treatment, abrasion, ablation, or cleaning.

37. A multilayer pipe according to claim 33, wherein the metallic barrier layer has been treated by chemical surface modification.

38. A multilayer pipe according to claim 37, wherein the chemical surface modification comprises solvent or chemical cleaning, treatment with chemical modifying agents to introduce surface functional groups, deposition of surface layers by, for example, plasma deposition of a polymeric layer containing functional groups, deposition of a glassy layer, or other surface coating techniques.

39. A multilayer pipe according to any one of claims 3 to 38, wherein the polar stabiliser is a thermal stabiliser, and antioxidant, a radical scavenger, an anti-ageing compound, a light stabiliser, or a UV stabiliser.

40. A multilayer pipe according to claim 39, wherein the polar stabiliser comprises a sterically-hindered
phenol, a phosphite, a phosphonite, a benzotriazole, or a sterically-hindered amine.

41. A multilayer pipe according to claim 38 or 39, wherein the polar stabiliser is present in the inner polymeric layer in an amount of from 0.01 to 5 weight per cent, based upon the weight of the inner polymeric layer.

42. A multilayer pipe according to any one of claims 4 to 41, wherein the filler is a particulate filler having a high aspect ratio.

43. A multilayer pipe according to claim 42, wherein the filler is an inorganic-based particulate filler provided with functional groups disposed on its surface.

44. A multilayer pipe according to claim 42 or 43, wherein the filler comprises talc, mica, calcium carbonate, kaolin, clay, magnesium hydroxide, calcium silicate, carbon black, graphite, iron powder, silica, diatomite, titanium oxide, iron oxide, pumice, antimony, dolomite, dawsonite, zeolitic filler, vermiculite, or montmorillonite.

45. A multilayer pipe according to any one of claims 42 to 44, wherein the filler has a mean particle diameter of up to 10μm.

46. A multilayer pipe according to any one of claims 42 to 45, wherein the filler is present in an amount of from 0.5 to 25 weight per cent.
47. A multilayer pipe according to any one of claims 42 to 46, wherein the filler comprises talc or mica.

48. A multilayer pipe according to claim 47, wherein the talc has a particle size in the range of from 0.01 to 200µm, a maximum equivalent diameter of about 25µm, and an average thickness of less than 0.5µm, and is present in an amount of from 1 to 5 weight per cent, or wherein the mica has a particle size of less than 74µm and an aspect ratio of from 10 to 150µm, and is present in an amount of less than 5 weight per cent.

49. A multilayer pipe according to any one of claims 42 to 46, wherein the filler comprises calcium carbonate.

50. A multilayer pipe according to claim 49, wherein the calcium carbonate filler is present in an amount of from 0.5 to 20 weight per cent, based on the weight of the inner polymeric layer.

51. A multilayer pipe according to any one of claims 42 to 50, wherein the filler comprises a mixture of calcium carbonate and talc.

52. A multilayer pipe according to any one of claims 4 to 51, wherein the filler is a nanofiller.

53. A multilayer pipe according to claim 52, wherein the nanofiller is derived from an intercalated and exfoliated clay, a layered silicate, calcium carbonate, calcium phosphate, silicon carbide, or silica.
54. A multilayer pipe according to claim 52, wherein the nanofiller comprises carbon nanotubes, or nanotubes formed from a synthetic polymer.

55. A multilayer pipe according to any one of claims 52 to 54, wherein the nanofiller is present in an amount of from 1% to 5% by volume, based on the volume of the inner polymeric layer.

56. A multilayer pipe according to any one of claims 52 to 55, wherein the particles of the nanofiller are substantially uniformly dispersed in the inner polymeric layer.

57. A multilayer pipe according to any one of claims 52 to 56, wherein at least 50% of the nanofiller particles are less than about 20 layers thick, the layers of the nanofiller particles having a unit thickness of from 0.7nm to 1.2nm.

58. A multilayer pipe according to any one of claims 52 to 57, wherein the nanofiller is a layered silicate comprising particles having one average dimension of 0.002 to 1μm and a thickness of 0.6 to 2.0nm, and wherein the particles are uniformly dispersed in the polyolefin polymer and have an average inter layer distance of 2.0nm or more.

59. A multilayer pipe according to any one of claims 2 to 30 and 34 to 58, wherein an adhesive layer is disposed between the inner polymeric layer and the barrier layer.
60. A multilayer pipe according to claim 59, wherein the adhesive layer comprises a polymer comprising one or more functional groups selected from carboxyl, carboxylic, anhydride, epoxy, hydroxyl, isocyanate, aldehyde ester, acid amide, amino, hydrolysable silyl, or cyano.

61. A multilayer pipe according to claim 59 or 60, wherein the adhesive layer comprises a polymer or co-polymer of an unsaturated monocarboxylic acid, an unsaturated dicarboxylic acid, an unsaturated alcohol, or an unsaturated epoxy compound.

62. A multilayer pipe according to any one of claims 59 to 61, wherein the adhesive layer comprises a co-polymer of ethylene with at least one monomer selected from unsaturated carboxylic acids, their salts and their esters, vinyl esters of saturated carboxylic acids, unsaturated dicarboxylic acids, their salts their esters, their half-esters and their anhydrides, or unsaturated epoxides.

63. A multilayer pipe according to any one of claims 59 to 62, wherein the adhesive layer comprises a grafted polymer of ethylene, or propylene, or a grafted co-polymer of ethylene with at least one alpha-olefin.

64. A multilayer pipe according to any one of the preceding claims, which is provided with an additional outer polymeric layer.
65. A multilayer pipe according to claim 64, wherein the additional outer polymeric layer comprises cross-linked polyethylene.

66. A multilayer pipe according to any one of the preceding claims substantially as hereinbefore described.

67. A method of producing a multilayer pipe comprising an outer later and an inner layer, which comprises extruding a polymeric composition comprising a polar functional polyolefin polymer to form an inner polymeric layer.

68. A method according to claim 67, wherein the polymeric composition comprises a polar functional polyolefin polymer according to any one of claims 7 to 14.

69. A method according to claim 67 or 68, wherein the polymeric composition comprises a polymer blend according to any one of claims 15 to 27.

70. A method according to claim 67, wherein a bimodal compound is formed by mixing two narrow molecular weight polyolefins having different molecular weights, at least one of which is provided with polar functional groups, and optionally adding one or more polar stabilisers or fillers to the compound, and extruding the compound to form the inner layer of the multilayer pipe.
71. A method according to any one of claims 67 to 70, wherein the polymeric composition comprises a polar stabiliser according to claim 39 or 40.

72. A method according to any one of claims 67 to 71, wherein the polymeric composition comprises filler according to any one of claims 42 to 58.

73. A method according to any one of claims 67 to 72, wherein the polymeric composition is extruded directly onto an outer barrier layer.

74. A method according to claim 73, wherein the outer barrier layer is a barrier layer as claimed in any one of claims 28 to 30.

75. A method according to any one of claims 67 to 74, wherein the polymeric composition is extruded using a conical disc type extruder.

76. A method according to claim 75, wherein a non-polar polyolefin polymer, a polar functional polyolefin polymer, a polar stabiliser and a filler are mixed together in the extruder and directly extruded into a metallic barrier tube to form an inner polymeric layer comprising the inner passageway of the pipe.

77. A method according to any one of claims 67 to 74, wherein the polymeric composition is extruded using a single screw extruder or a twin screw extruder.

78. A method according to claim 77, wherein the polymeric composition is extruded into strands,
pelletised, and the pellets are extruded to form the inner polymeric layer.

79. A method according to any one of claims 67 to 78, wherein the polymeric composition is extruded through a screen having a mesh size of at least 70.

80. A method according to any one of claims 67 to 79, substantially as described in the Examples.

81. A method according to any one of claims 67 to 80 substantially as hereinbefore described.

82. Use of a polymeric composition comprising a polar functional polyolefin polymer as an inner polymeric layer of a multilayer pipe.

83. Use according to claim 82, wherein the multilayer pipe is a pipe as claimed in any one of claims 1 to 66.

84. Use of a polymeric composition comprising a polar functional polyolefin polymer as an inner layer of a multilayer pipe for the conveyance of hot water.

85. Use according to claim 84, wherein the multilayer pipe is as claimed in any one of claims 1 to 66.
Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

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<tr>
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**Field of Search:**

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC:

- B5A; F2P

Worldwide search of patent documents classified in the following areas of the IPC:

- F16L

The following online and other databases have been used in the preparation of this search report:

- EPDOC; WPI; PAJ