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(54) Title: CROSSLINKED COMPOSITIONS CONTAINING SILANE-GRAFTED POLYOLEFINS AND POLYPROPYLENE

(57) **Abrégé/Abstract:**

A moisture-crosslinkable polypropylene material, comprising a silane-grafted polyolefin or olefin-silane copolymer and a non-silane modified polypropylene homopolymer or copolymer; and a heat-shrinkable coating prepared therefrom. The coating material is formed by a process comprising: (a) reacting a polyolefin with a silane in the presence of a free-radical initiator to form a silane-grafted resin, or copolymerising a polyolefin with silane; (b) preparing a mixture of the silane-modified resin with a polypropylene and a silanol condensation catalyst; (c) forming the coating material by melt extruding the mixture formed in step (b); and (d) crosslinking the coating material by exposing it to combined heat and moisture.



## ABSTRACT OF THE DISCLOSURE

A moisture-crosslinkable polypropylene material, comprising a silane-grafted polyolefin or olefin-silane copolymer and a non-silane modified polypropylene homopolymer or copolymer; and a heat-shrinkable coating prepared therefrom. The coating material is formed by a process comprising: (a) reacting a polyolefin with a silane in the presence of a free-radical initiator to form a silane-grafted resin, or copolymerising a polyolefin with silane; (b) preparing a mixture of the silane-modified resin with a polypropylene and a silanol condensation catalyst; (c) forming the coating material by melt extruding the mixture formed in step (b); and (d) crosslinking the coating material by exposing it to combined heat and moisture.

## **CROSSLINKED COMPOSITIONS CONTAINING SILANE-GRAFTED POLYOLEFINS AND POLYPROPYLENE**

### **FIELD OF THE INVENTION**

The present invention relates to polymeric compositions and their uses, and more particularly to crosslinked compositions of silane-modified polyolefins blended with polypropylene homopolymers and/or copolymers, and their uses as heat shrinkable coating and insulating materials, and as wire and cable insulation materials.

### **BACKGROUND OF THE INVENTION**

Polypropylenes are known to be difficult materials to crosslink. Unlike similar materials, such as polyethylenes and copolymers of polyethylene, they have a preferential tendency towards structural breakdown rather than crosslinking when subjected to standard methods of crosslinking such as by electron beam irradiation or peroxides. It is therefore necessary to resort to alternative methods to crosslink polypropylene-based materials to satisfactory levels, as required, for example, in the production of heat-shrinkable articles, such as tubing, sheet, and moulded shapes, and of wire and cable insulations, for use in high-temperature applications.

Polypropylene is ideally suited to the preparation of coatings and insulations designed for use at operating temperatures in excess of those that can be withstood by other polyolefins, for example, polyethylene, which exhibit lower softening and melting temperatures. Other attractive features are its high rigidity, low cost and relatively low density. Applications would include polymeric insulation for electrical wires, and heat-shrinkable protective sleeves for high-

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temperature transmission pipelines, or applications requiring greater toughness and rigidity than is afforded by polyethylene-based systems. For example, heat-shrinkable sleeves used for the corrosion protection of high temperature pipeline joints are required to maintain dimensional stability and integrity at the operating temperature of the pipeline. Hence it is necessary to use a material, such as polypropylene, with a softening temperature or melting point high enough to prevent creeping or sagging of the sleeve from the pipe at the continuous operating temperature of the pipeline. Also, in order to maximise heat-resistance and physical properties, it is necessary to impart some thermoset characteristic to the material. This is done by crosslinking the polymer to some required degree. Crosslinking is also necessary for the production of heat-shrinkable articles to impart controlled shrinkage characteristics. The aim of this invention is to provide a means of preparing crosslinked, predominantly polypropylene-based materials, which can be used in the applications described, but not necessarily restricted thereto.

#### SUMMARY OF THE INVENTION

The present invention overcomes the above-discussed problems of the prior art by providing moisture crosslinkable compositions of silane-modified polyolefins, typically of polyethylenes and copolymers of polyethylene, blended with non-silane modified polypropylene, with or without an additional material added as a compatibilising agent for the polyolefin and polypropylene.

In the method of the present invention, polypropylene homopolymer or copolymer is blended with a polyolefin, preferably a polyethylene or copolymer of polyethylene, which has

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previously been reacted with silane to create a silane-grafted polyolefin. Alternatively, the silane may be incorporated during polymerisation of the polyolefin, to produce a silane-olefin copolymer.

Such polyolefins would include those materials known in the industry as low density polyethylene, high density polyethylene, linear low density polyethylene, copolymers of polyethylene, including those based on ethylene-butene, ethylene-hexene, ethylene-octene, ethylene-vinyl-acetate, ethylene-ethyl-acrylate, ethylene-methyl-acrylate, and similar materials, and ethylene-propylene or ethylene-propylene diene elastomers; and, in particular those prepared using so-called metallocene catalysts. The blended composition is then cross-linked in the presence of a silanol condensation catalyst, under suitable conditions of heat and moisture. The crosslinking also helps to compatibilize the normally incompatible polypropylene with the other polyolefin contained in the silane-grafted polyolefin composition.

Alternatively, an additional material may be incorporated to act as a compatibilising agent for the silane-modified polyolefin and the polypropylene. Such materials would include the polyolefin materials described above, polyolefins modified with reactive functional groups, such as acrylates, methacrylates and anhydrides, and block copolymers, such as styrene-butadiene.

Accordingly, in one aspect, the present invention provides a heat shrinkable coating material comprising a crosslinked composition comprising a silane-modified, preferably silane-grafted, polyolefin and non-silane modified polypropylene, said material being formed by a process comprising: (a) reacting a polyolefin with a silane to form a silane-grafted resin or silane-

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olefin copolymer; (b) blending the silane-modified polyolefin with the polypropylene homopolymer or copolymer and a silanol condensation catalyst; (c) forming the coating material by melt extruding the mixture formed in step (b); and (d) crosslinking the coating material by exposing it to combined heat and moisture.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The crosslinking of polymers, in particular polyolefins, by the combined process of chemical grafting of silane molecules onto the polymer to form a silane-grafted resin, followed by catalysed hydrolysis and condensation of the silane, is a well known and established process such as is described in US Patent No. 3,646,155.

The preferred polyolefins for use in the compositions of the present invention include polyethylene or co-polymers of ethylene prepared by polymerising ethylene with one or more of an unsaturated olefin monomer having from 3 to 20 carbon atoms, preferably propylene, butylene, hexene or octene, a substituted olefin such as vinyl acetate, ethyl acrylate, methyl acrylate or butyl acrylate, or a diene monomer, such as methylene norbornene. The polyolefin is preferentially present in the form of high-density polyethylene, linear low-density polyethylene or an ethylene-octene copolymer polymerised using a so-called metallocene catalyst. Preferably, the polyolefin resin comprises about 50 to 100% by weight ethylene, more preferably about 60 to

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90% by weight ethylene, and most preferably about 80 to 95% by weight ethylene.

Preferably, the density of the polyethylene or the ethylene co-polymer is in the range of about 0.85 to about 0.95 g/cm<sup>3</sup>, and more preferably from about 0.85 to about 0.94 g/cm<sup>3</sup>.

The polymer as described above is reacted in the molten state with an organic silane having the general formula RR'SiY<sub>2</sub>, wherein R represents a monovalent olefinically unsaturated hydrocarbon radical, Y represents a hydrolysable organic radical and R' represents an R radical or a Y radical. The monovalent olefinically unsaturated hydrocarbon radical preferably comprises vinyl, allyl, butenyl, cyclohexenyl, cyclopentadienyl, or cyclohexadienyl radicals.

The group Y may represent any hydrolysable organic radical, for example an alkoxy radical such as methoxy, ethoxy and butoxy radicals; an acyloxy radical, for example the formyloxy, acetoxy or propionoxy radicals; oximo radicals such as -ON=C(CH<sub>3</sub>)<sub>2</sub>, -ON=CCH<sub>3</sub>C<sub>2</sub>H<sub>5</sub> and ON=C(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>; or substituted amino radicals such as alkylamino and arylamino radicals, examples of which are -NHCH<sub>3</sub>, -NHC<sub>2</sub>H<sub>5</sub> and -NH(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>.

Preferably, the silane has general formula RSiY<sub>3</sub>, with the most preferred group R being the vinyl radical, and the most preferred Y group being the methoxy and ethoxy radical. Accordingly, the most preferred silanes for use in the present invention are vinyltriethoxysilane and vinyltrimethoxysilane.

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The amount of silane reacted with the polymer depends in part upon the reaction conditions and the degree of modification desired in the polyolefin. The proportion may vary from about 0.1 to about 50% by weight based on the total weight of the silane-grafted resin, more preferably from about 0.5 to 10% by weight, and most preferably from about 1.5 to 2.5% by weight.

A free-radical initiator is also incorporated into the resin to initiate the graft polymerization reaction. Most preferred free-radical initiators are organic peroxides such as benzoyl peroxide, dichlorobenzoyl peroxide, dicumyl peroxide, di-tertiarybutyl peroxide. The most preferred free-radical initiator for use in the compositions of the present invention is dicumyl peroxide. The criteria for choosing an appropriate free-radical initiator are known to persons skilled in the art and are described in the above-mentioned U.S. Patent No. 3,646,155 and will not be repeated here.

Preferably, the organic peroxide free-radical initiator is added in an amount of from about 0.1 to about 1.0% by weight of the silane-grafted resin, more preferably from about 0.05 to 0.2% by weight.

The silane and peroxide are reacted with the polyolefin above the melting point of the polyolefin under conditions in which the polyolefin is subjected to mechanical working, using processes known to those skilled in the art.



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Alternatively, the silane-containing polyolefin may be prepared by copolymerising an unsaturated olefinic monomer, such as ethylene, with an unsaturated silane monomer containing one or more hydrolysable groups, such as vinyltrimethoxy silane, as is disclosed in US Patent 4413066, for example.

The silane-grafted resin, or silane-olefin copolymer, so produced is subsequently melt-extruded with an amount of polypropylene and a silanol condensation catalyst, and optionally with one or more of a number of other ingredients, such as pigmenting agents, mineral fillers, flame-retardant additives, antioxidants, stabilisers, lubricants, compatibilisers and the like, to form a composition according to the invention.

The polypropylene may be selected from any of the classes known as homopolymers or copolymers, being preferentially isotactic in nature, with a melt viscosity chosen to be similar and compatible in value to the silane grafted polyolefin, for maximum compatibility. The polypropylene is preferably added in an amount of from about 10 to about 90 percent by weight of the composition, more preferably from about 20 to about 80 percent by weight, and most preferably from about 40 to about 60 percent by weight.

The silanol condensation catalyst is typically selected from the group comprising organic bases, carboxylic acids and organometallic compounds including organic titanates and complexes or carboxylates of lead, cobalt, iron, nickel, zinc and tin. Preferably, the catalyst is selected from dibutyltin dilaurate, dibutyltin diacetate, dibutyltin octanoate, dioctyltin maleate, dibutyltin oxide

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and titanium compounds such as titanium-2-ethylhexoxide. The most preferred silanol condensation catalyst is dibutyltin dilaurate, though any material which will catalyse the silane condensation reaction is suitable for the invention. The condensation catalyst is preferably added in an amount of from about 0.01 to about 1 percent by weight of the coating material, more preferably about 0.05 to about 0.5 percent by weight, and most preferably about 0.1 to 0.2 percent by weight.

Subjecting the composition to combined heat and moisture will induce cross-linking of the silane groups via a combined hydrolysis and condensation reaction. Atmospheric moisture is usually sufficient to permit the cross-linking to occur, but the rate of cross-linking may be increased by the use of an artificially moistened atmosphere, or by immersion in liquid water. Most preferably, cross-linking is effected at a temperature above 50°C and most preferably by exposing the composition to a temperature of 85°C and a relative humidity of 90% for approximately 100 hours.

A particularly preferred process for forming a composition of the present invention will now be described below.

The polyolefin, silane, free-radical initiator and optional processing stabiliser are pre-blended and passed through an extruder at a temperature above the melting point of the polyolefin, in order to accomplish grafting of the silane to the polyolefin. The grafted material is then passed through a multi-strand die into a trough of cooled water and is subsequently chopped

into pellets with a strand pelletizer.

The graft polymer pellets are then blended, and melt extruded to the desired shape, with a quantity of polypropylene as described above, the silane condensation catalyst, an antioxidant stabiliser, as well as any number of optional ingredients, including colorants, fillers, flame retardants, compatibilisers, and processing aids.

The extruded or moulded material is then subjected to combined conditions of heat and moisture to effect crosslinking, as described above.

The composition of the invention thus produced exhibits the property of softening but not melting when re-heated above its softening point or crystalline melting point. This is desirable for the manufacture of heat-shrinkable articles since the polymer may be stretched beyond the original extruded or moulded dimensions without rupture using relatively low forces, and can then be frozen in the stretched state by cooling it rapidly to below the melting point. Stretching can be accomplished by mechanical or pneumatic or hydraulic means. At this point the stretched crosslinks are held in a stable state by the re-formed solid crystalline regions. Subsequent re-heating of the stretched article above the melting point will cause the crystalline regions to re-melt and the structure to revert to its original extruded or moulded dimensions.

The invention is further illustrated by the following Examples:

**EXAMPLE 1**

This example lists the preferred silane-grafted, moisture-cross-linkable resins according to the present invention.

The following resins were grafted with vinyl triethoxysilane according to the general procedure mentioned above and known to those skilled in the art.

TABLE 1

<b>Polymer Type</b>	<b>Copolymer Content (%)</b>	<b>Density (g/cm<sup>3</sup>)</b>	<b>Melt Index (g/10min)</b>
Linear Low Density Polyethylene	-	0.919	6.0
Ethylene Octene Copolymer	14	0.902	4.3
Ethylene Vinyl Acetate Copolymer	18	0.940	8.0
Ethylene Ethyl Acrylate Copolymer	18	0.931	6.0

**EXAMPLE 2**

This example describes the production of a crosslinked, extruded sheet according to the present invention.

The grafted pellets produced according to Example 1 were blended with the ingredients indicated in Table 2, namely polypropylene, antioxidant and dibutyltin dilaurate as the condensation catalyst. The combined ingredients were fed at a melt temperature of approximately

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180°C through a 24:1 L/D single screw extruder equipped with a single layer sheet die. The extruded sheet was fixed to the required dimensions of width and thickness by passing it through a cooled roll-stack or calendering stack, then wound onto reels.

The sheet was crosslinked by conditioning the reeled sheet at a temperature of 85°C and a relative humidity of 90% for approximately 120 hours. This crosslinked sheet was then tested to determine the degree of crosslinking and viscoelastic properties using a dynamic mechanical analyzer.

TABLE 2

(Moisture-Crosslinkable, Polypropylene Material)

Ingredient	Percent by Weight
Silane-Grafted Resin	39.2
Polypropylene Homopolymer*	56.8
Antioxidant**	2
Dibutyltin Dilaurate***	2

\*Density 0.89 g/cm<sup>3</sup> and MI 2.0

\*\*Blend of hindered phenol and phosphite stabiliser

\*\*\*Added as a 2% masterbatch in polyethylene

### EXAMPLE 3

This example describes the production of a heat-shrinkable, extruded sheet product

according to the present invention.

The crosslinked sheet prepared in Example 2 was re-heated to above the softening point and mechanically stretched in the longitudinal direction on an apparatus designed specifically for this purpose. The stretched sheet was mechanically tested for suitability as a heat-shrink coating for high-temperature pipeline joints to specifications common to the industry.

Although the invention has been described in relation to certain preferred embodiments, it will be appreciated that it is not intended to be limited thereto. Rather, the invention is intended to encompass all embodiments which fall within the scope of the following claims.

What is claimed is:

1. A coating or insulating material comprising a crosslinked composition containing a silane-modified polyolefin and a non-silane modified polypropylene homopolymer or copolymer, said material being formed by a process comprising:
  - (a) creating a mixture of the silane-modified polyolefin with the polypropylene and a silanol condensation catalyst, wherein the silane-modified polyolefin comprises a silane-grafted polyolefin or a silane-olefin copolymer;
  - (b) forming the coating or insulating material by melt extruding the mixture prepared in step (a); and
  - (c) crosslinking the coating or insulating material by exposing it to moisture at elevated temperature.
2. A coating or insulating material according to claim 1, where the material is heat-shrinkable, and wherein said process further comprises the following step after said step (c):
  - (d) stretching said material above its softening or melting point, and then freezing said material in its stretched form to form a heat-shrinkable article.
3. The coating or insulating material according to claim 1 or 2, wherein the polyolefin is selected from the group comprising polyethylene and copolymers of ethylene with an olefin having from 3 to 20 carbon atoms.
4. The coating or insulating material according to claim 1 or 2, wherein the polyolefin comprises a copolymer of ethylene with one or more of propylene, butylene, hexene, octene, methylene norbornene, vinyl acetate, methyl acrylate, ethyl acrylate and butyl acrylate.
5. The coating or insulating material according to any one of claims 1 to 4, wherein the density of the polyolefin is from about 0.85 to about 0.95 g/cm<sup>3</sup>.

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6. The coating or insulating material according to any one of claims 1 to 5, wherein the polypropylene is selected from the group comprising polypropylene homopolymers and copolymers of propylene with an olefin other than propylene, of density from about 0.86 to 0.90.
  7. The coating or insulating material according to any one of claims 1 to 6, wherein the silane-modified polyolefin comprises an ethylene-based polyolefin which has been reacted with a silane of the general formula  $RR'SiY_2$  wherein R represents a monovalent olefinically unsaturated hydrocarbon or hydrocarbonoxy radical, Y represents a hydrolysable organic radical and R' represents a monovalent olefinically unsaturated hydrocarbon or hydrocarbonoxy radical, or a hydrolysable organic radical.
  8. The coating or insulating material according to claim 7, wherein the monovalent olefinically unsaturated hydrocarbon or hydrocarbonoxy radical is selected from the group comprising vinyl, allyl, butenyl, cyclohexenyl, cyclopentadienyl, and cyclohexadienyl.
  9. The coating or insulating material according to claim 7 or 8, wherein Y represents a hydrolysable organic radical selected from the group comprising methoxy, ethoxy, butoxy, formyloxy, acetoxy, propionoxy; an oximo radical selected from the group comprising  $-ON=C(CH_3)_2$ ,  $-ON=C(CH_3)(C_2H_5)$  and  $-ON=C(C_6H_5)_2$ ; and substituted amino radicals selected from the group comprising alkylamino and arylamino radicals.
  10. The coating or insulating material according to claim 9, wherein said alkylamino radicals and arylamino radicals are selected from the group comprising  $-NHCH_3$ ,  $-NHC_2H_5$  and  $-NH(C_6H_5)$ .
  11. The coating or insulating material according to any one of claims 7 to 10, wherein the silane has general formula  $RSiY_3$ , wherein R is vinyl and Y is methoxy or ethoxy.
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12. The coating or insulating material according to any one of claims 7 to 11, wherein the amount of the silane reacted with the polyolefin is from about 0.5 to about 2.5 percent by weight of the silane-grafted resin.
13. The coating or insulating material according to any one of claims 1 to 12, wherein the polypropylene is added to the mixture of step (a) in an amount of from about 10 to about 90 percent by weight of the coating or insulating material.
14. The coating or insulating material according to any one of claims 1 to 13, wherein the polypropylene is added to the mixture of step (a) in an amount of from about 20 to about 80 percent by weight of the coating or insulating material.
15. The coating or insulating material according to any one of claims 1 to 14, wherein the silanol condensation catalyst is selected from the group comprising dibutyltin dilaurate and dibutyltin oxide.
16. The coating or insulating material according to any one of claims 1 to 15, wherein the silanol condensation catalyst is added to the mixture of step (a) in an amount of about 0.05 to 0.2 percent by weight of the coating or insulating material.
17. The coating or insulating material according to any one of claims 1 to 16, further comprising one or more ingredients selected from the group comprising antioxidants, fillers, colorants, UV stabilizers, compatibilisers and lubricants.
18. The coating or insulating material according to claim 17, wherein the compatibiliser is selected from the group comprising polyolefins, polyolefins modified with reactive functional groups and block copolymers.

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19. A crosslinked, predominantly polypropylene-based article comprising:
- (a) a silane-modified ethylene-based polyolefin comprising either a silane grafted polyolefin or a silane-olefin copolymer;
  - (b) at least 50 percent by weight of a non silane-modified polypropylene; and
  - (c) a silanol condensation catalyst;

wherein the article is moisture crosslinked to a sufficient degree that it possesses thermoset properties such that, when the article is heated to a temperature above the crystalline melting point of the non silane-modified polypropylene, it is softened but does not become liquid.

20. The crosslinked, predominantly polypropylene-based article according to claim 19, wherein at least 50 percent of monomer units in the article are propylene monomer units.

21. The crosslinked, predominantly polypropylene-based article according to claim 19, wherein at least 50 percent of monomer units in the non silane-modified polypropylene are propylene monomer units.

22. The crosslinked, predominantly polypropylene-based article according to any one of claims 19 to 21, said article being heat shrinkable.

23. The crosslinked, predominantly polypropylene-based article according to any one of claims 19 to 22, wherein the ethylene-based polyolefin subjected to silane modification is selected from the group comprising polyethylene and copolymers of ethylene with an olefin other than ethylene having from 3 to 20 carbon atoms.

24. The crosslinked, predominantly polypropylene-based article according to claim 23, wherein said olefin other than ethylene comprises one or more members of the group comprising propylene, butylene, hexene, octene, methylene norbornene, vinyl acetate, methyl acrylate, ethyl acrylate and butyl acrylate.

25. The crosslinked, predominantly polypropylene-based article according to any one of claims 19 to 24, wherein the non silane-modified polypropylene is selected from the group comprised of polypropylene homopolymers and of copolymers of propylene with an olefin other than propylene.

26. The crosslinked, predominantly polypropylene-based article according to any one of claims 19 to 25, wherein the silane modified ethylene-based polyolefin comprises an ethylene-based polyolefin which has been reacted with a silane of the general formula  $RR'SiY_2$  wherein R represents a monovalent olefinically unsaturated hydrocarbon or hydrocarbonoxy radical, Y represents a hydrolysable organic radical and R' represents a monovalent olefinically unsaturated hydrocarbon or hydrocarbonoxy radical, or a hydrolysable organic radical.

27. The crosslinked, predominantly polypropylene-based article according to claim 26, wherein the monovalent olefinically unsaturated hydrocarbon or hydrocarbonoxy radical is selected from the group comprising vinyl, allyl, butenyl, cyclohexenyl, cyclopentadienyl, and cyclohexadienyl.

28. The crosslinked, predominantly polypropylene-based article according to claim 26 or 27, wherein Y represents a hydrolysable organic radical selected from the group comprising methoxy, ethoxy, butoxy, formyloxy, acetoxy, propionoxy; oximo radicals selected from the group comprising  $-ON=C(CH_3)_2$ ,  $-ON=C(CH_3)(C_2H_5)$  and  $-ON=C(C_6H_5)_2$ ; and substituted amino radicals selected from the group comprising alkylamino and arylamino radicals.

29. The crosslinked, predominantly polypropylene-based article according to claim 28, wherein said alkylamino radicals and arylamino radicals are selected from the group comprising  $-NHCH_3$ ,  $-NHC_2H_5$  and  $-NH(C_6H_5)$ .

30. The crosslinked, predominantly polypropylene-based article according to any one of claims 26 to 29, wherein the silane has general formula  $RSiY_3$ , with R being vinyl and Y being methoxy or ethoxy.

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31. The crosslinked, predominantly polypropylene-based article according to any one of claims 26 to 30, wherein the amount of the silane reacted with the ethylene-based polyolefin is from about 0.5 to about 2.5 percent by weight of the silane-modified polyolefin.
32. The crosslinked, predominantly polypropylene-based article according to any one of claims 19 to 31, comprising the non silane-modified polypropylene in an amount of from 50 to 90 percent by weight.
33. The crosslinked, predominantly polypropylene-based article according to any one of claims 19 to 32, comprising the non silane-modified polypropylene in an amount of from 60 to 90 percent by weight.
34. The crosslinked, predominantly polypropylene-based article according to any one of claims 19 to 33, wherein the silanol condensation catalyst is selected from the group comprising dibutyltin dilaurate and dibutyltin oxide.
35. The crosslinked, predominantly polypropylene-based article according to any one of claims 19 to 34, comprising the silanol condensation catalyst in an amount of from 0.05 to 0.2 percent by weight.
36. The crosslinked, predominantly polypropylene-based article according to any one of claims 19 to 35, further comprising additional ingredients selected from the group comprising antioxidants, fillers, colorants, UV stabilizers, compatibilisers and lubricants.
37. The coating or insulating material according to claim 36, wherein the compatibiliser is selected from the group comprising polyolefins, polyolefins modified with reactive functional groups and block copolymers.
38. The crosslinked, predominantly polypropylene-based article according to any one of claims 19 to 37, wherein the article is selected from the group comprising coating materials,
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insulating materials, and sheet materials.

39. The crosslinked, predominantly polypropylene-based article according to any one of claims 19 to 38, wherein the article is a heat-shrinkable sleeve for a high-temperature transmission pipeline.

40. A method for producing a crosslinked, predominantly polypropylene-based article comprising a crosslinked composition containing a silane-modified polyolefin and a non silane-modified polypropylene, said method comprising:

(a) preparing said silane-modified polyolefin by reacting an ethylene-based polyolefin with a silane, said silane-modified polyolefin comprising either a silane-grafted polyolefin or a silane-olefin copolymer;

(b) preparing a mixture comprising said silane-modified polyolefin, said non silane-modified polypropylene and a silanol condensation catalyst, said non silane-modified polypropylene being added in a sufficient amount that the article comprises at least 50 percent by weight of the non silane-modified polypropylene;

(c) forming the article by melt processing the mixture prepared in step (b); and

(d) crosslinking the article by exposing it to moisture at elevated temperature, wherein said crosslinking provides said article with thermoset properties such that, when the article is heated to a temperature above the crystalline melting point of the non silane-modified polypropylene, it is softened but does not become liquid.

41. The method according to claim 40, wherein at least 50 percent of monomer units in the article are propylene monomer units.

42. The method according to claim 40, wherein at least 50 percent of monomer units in the non silane-modified polypropylene are propylene monomer units.

43. The method according to any one of claims 40 to 42, wherein said article is heat-shrinkable and wherein said method further comprises:

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(e) softening the article crosslinked in step (d) by application of heat thereto, stretching said heated article and then freezing said material in its stretched form.

44. The method according to any one of claims 40 to 43, wherein the ethylene-based polyolefin is selected from the group comprising polyethylene and copolymers of ethylene with an olefin other than ethylene having from 3 to 20 carbon atoms.

45. The method according to claim 44, wherein said olefin other than ethylene comprises one or more members of the group comprising propylene, butylene, hexene, octene, methylene norbornene, vinyl acetate, methyl acrylate, ethyl acrylate and butyl acrylate.

46. The method according to any one of claims 40 to 45, wherein the non silane-modified polypropylene is selected from the group comprising polypropylene homopolymers and copolymers of propylene with an olefin other than propylene.

47. The method according to any one of claims 40 to 46, wherein the silane has the general formula  $RR'SiY_2$  wherein R represents a monovalent olefinically unsaturated hydrocarbon or hydrocarbonoxy radical, Y represents a hydrolysable organic radical and R' represents a monovalent olefinically unsaturated hydrocarbon or hydrocarbonoxy radical, or a hydrolysable organic radical.

48. The method according to any one of claims 40 to 47, wherein the silane has general formula  $RSiY_3$ , with R being vinyl and Y being methoxy or ethoxy.

49. The method according to any one of claims 40 to 48, wherein the amount of the silane reacted with the ethylene-based polyolefin is from about 0.5 to about 2.5 percent by weight of the silane-modified polyolefin.

50. The method according to any one of claims 40 to 49, wherein the non silane-modified

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polypropylene is added to the mixture of step (b) in an amount of from 50 to 90 percent by weight of the mixture.

51. The method according to any one of claims 40 to 50, wherein the non silane-modified polypropylene is added to the mixture of step (b) in an amount of from 60 to 90 percent by weight of the mixture.

52. The method according to any one of claims 40 to 51, wherein the silanol condensation catalyst is selected from the group comprising dibutyltin dilaurate and dibutyltin oxide.

53. The method according to any one of claims 40 to 52, wherein the silanol condensation catalyst is added to the mixture of step (b) in an amount of 0.05 to 0.2 percent by weight of the mixture.

54. The method according to any one of claims 40 to 53, wherein said mixture prepared in step (b) further comprises optional additional ingredients selected from the group comprising antioxidants, fillers, colorants, UV stabilizers, compatibilisers and lubricants.

55. The method according to claim 54, wherein the compatibiliser is selected from the group comprising polyolefins, polyolefins modified with reactive functional groups and block copolymers.

56. A coating or insulating material prepared by creating a mixture of:

- (a) a silane-modified ethylene-based polyolefin comprising either a silane-grafted polyolefin or a silane-olefin copolymer;
- (b) a non silane-modified polypropylene in an amount of 60-90% by weight; and
- (c) a silanol condensation catalyst;

followed by cross linking said mixture at elevated temperature with use of moisture; characterized in that

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the material formed exhibits the property of softening but not melting when reheated above its softening point or crystalline melting point, and having been stretched above its softening point followed by freezing said material in stretched form to form a heat shrinkable material.

57. The coating or insulating material according to claim 56, wherein the ethylene-based polyolefin subjected to silane modification is selected from the group comprising polyethylene and copolymers of ethylene with an olefin other than ethylene having from 3 to 20 carbon atoms.

58. The coating or insulating material according to claim 56 or 57, wherein said olefin other than ethylene comprises one or more members of the group comprising propylene, butylenes, hexene, octene, methylene norbornene, vinyl acetate, methyl acrylate, ethyl acrylate and butyl acrylate.

59. The coating or insulating material according to any one of claims 56 to 58, wherein the polypropylene is selected from the group comprising polypropylene homopolymers and copolymers of propylene with an olefin other than propylene.

60. The coating or insulating material according to any one of claims 56 to 59, wherein the silane modified ethylene-based polyolefin comprises an ethylene-based polyolefin which has been reacted with a silane of the general formula  $RR'SiY_2$  wherein R represents a monovalent olefinically unsaturated hydrocarbon or hydrocarbonoxy radical, Y represents a hydrolysable organic radical and R' represents a monovalent olefinically unsaturated hydrocarbon or hydrocarbonoxy radical or a hydrolysable organic radical.

61. The coating or insulating material according to claim 60, wherein the monovalent olefinically unsaturated hydrocarbon or hydrocarbonoxy radical is selected from the group comprising vinyl, allyl, butenyl, cyclohexenyl, cyclopentadienyl, and cyclohexadienyl.

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62. The coating or insulating material according to claim 60 or 61, wherein Y represents a hydrolysable organic radical selected from the group comprising methoxy, ethoxy, butoxy, formyloxy, acetoxyl, propionoxy; oximo radicals selected from the group comprising  $-\text{ON}=\text{C}(\text{CH}_3)_2$ ,  $-\text{ON}=\text{C}(\text{CH}_3)(\text{C}_2\text{H}_5)$  and  $-\text{ON}=\text{C}(\text{C}_6\text{H}_5)_2$ ; and substituted amino radicals selected from the group comprising alkylamino and arylamino radicals.
63. The coating or insulating material according to claim 62, wherein said alkylamino radicals and arylamino radicals are selected from the group comprising  $-\text{NHCH}_3$ ,  $-\text{NHC}_2\text{H}_5$  and  $-\text{NH}(\text{C}_6\text{H}_5)$ .
64. The coating or insulating material according to any one of claims 60 to 63, wherein the silane has general formula  $\text{RSiY}_3$ , and R being vinyl and Y being methoxy or ethoxy.
65. The coating or insulating material according to any one of claims 56 to 64, wherein the amount of the silane reacted with the ethylene-based polyolefin is from 0.5 to 2.5 percent by weight of the silane-modified polyolefin.
66. The coating or insulating material according to any one of claims 56 to 65, wherein the silanol condensation catalyst is selected from the group comprising dibutyltin dilaurate and dibutyltin oxide.
67. The coating or insulating material according to any one of claims 56 to 66, comprising the silanol condensation catalyst in an amount of from 0.05 to 0.2 percent by weight.
68. The coating or insulating material according to any one of claims 56 to 67, further comprising additional ingredients selected from the group comprising antioxidants, fillers, colorants, UV stabilizers, compatibilizers and lubricants.
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69. The coating or insulating material according to claim 68, wherein the compatibiliser is selected from the group comprising polyolefins, polyolefins modified with reactive functional groups and block copolymers.
70. The coating or insulating material according to claim 57, wherein the ethylene-based polyolefin is selected from the group comprising high density polyethylene, linear low density polyethylene and copolymers of ethylene and octene.
71. The coating or insulating material according to claim 70, wherein the ethylene-based polyolefin comprises from about 50 to 100% by weight ethylene.
72. The coating or insulating material according to claim 70, wherein said copolymers of ethylene and octene are polymerized using a metallocene catalyst.
73. The coating or insulating material according to claim 59, wherein the polypropylene is isotactic.
74. The coating or insulating material according to claim 59, wherein the polypropylene comprises polypropylene homopolymer.
75. A method for producing a heat-shrinkable, crosslinked, coating or insulating material as claimed in any one of claims 56 to 74, comprising a crosslinked composition containing a silane-modified polyolefin and a non silane-modified polypropylene, said method comprising:
- (a) preparing said silane-modified polyolefin by reacting an ethylene-based polyolefin with a silane, said silane-modified polyolefin comprising either a silane-grafted polyolefin or silane-olefin copolymer;
  - (b) preparing a mixture comprising said silane-modified polyolefin, said polypropylene and a silanol condensation catalyst;
  - (c) forming the coating material by melt processing the mixture prepared in step (b);
  - (d) crosslinking the coating material by exposing it to moisture;

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(e) softening the coating material crosslinked in step (d) by application of heat thereto, stretching said heated coating material and then freezing said material in its stretched form.

76. The method according to claim 75, wherein the ethylene-based polyolefin is selected from the group comprising polyethylene and copolymers of ethylene with an olefin other than ethylene having from 3 to 20 carbon atoms.

77. The method according to claim 76, wherein said olefin other than ethylene comprises one or more members of the group comprising propylene, butylenes, hexane, octene, methylene norbornene, vinyl acetate, methyl acrylate, ethyl acrylate and butyl acrylate.

78. The method according to any one of claims 75 to 77, wherein the polypropylene is selected from the group comprising polypropylene homopolymers and copolymers of propylene with an olefin other than propylene.

79. The method according to any one of claims 75 to 78, wherein the silane has the general formula  $RR'SiY_2$  wherein R represents a monovalent olefinically unsaturated hydrocarbon or hydrocarbonoxy radical, Y represents a hydrolysable organic radical and R' represents a monovalent olefinically unsaturated hydrocarbon or hydrocarbonoxy radical, or a hydrolysable organic radical.

80. The method according to claim 79, wherein the monovalent olefinically unsaturated hydrocarbon or hydrocarbonoxy radical is selected from the group comprising vinyl, allyl, butenyl, cyclohexenyl, cyclopentadienyl, and cyclohexadienyl.

81. The method according to claim 79 or 80, wherein Y represents a hydrolysable organic radical selected from the group comprising methoxy, ethoxy, butoxy, formyloxy, acetoxy, propionoxy; oximo radicals selected from the group comprising  $-ON=C(CH_3)_2$ ,  $-ON=C(CH_3)(C_2H_5)$  and  $-ON=C(C_6H_5)_2$ ; and substituted amino radicals selected from the group comprising alkylamino and arylamino radicals.

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82. The method according to any one of claims 79 to 81, wherein said alkylamino radicals and arylamino radicals are selected from the group comprising  $\text{-NHCH}_3$ ,  $\text{-NHC}_2\text{H}_5$  and  $\text{-NH(C}_6\text{H}_5)$ .
83. The method according to any one of claims 79 to 82, wherein the silane has general formula  $\text{RSiY}_3$ , with R being vinyl and Y being methoxy or ethoxy.
84. The method according to any one of claims 75 to 83, wherein the amount of the silane reacted with the ethylene-based polyolefin is from 0.5 to 2.5 percent by weight of the silane-modified polyolefin.
85. The method according to any one of claims 75 to 84, wherein the polypropylene is added to the mixture of step (b) in an amount of from 60 to 90 percent by weight of the mixture.
86. The method according to any one of claims 75 to 85, wherein the silanol condensation catalyst is selected from the group comprising dibutyltin dilaurate and dibutyltin oxide.
87. The method according to any one of claims 75 to 86, wherein the silanol condensation catalyst is added to the mixture of step (b) in an amount of 0.05 to 0.2 percent by weight of the mixture.
88. The method according to any one of claims 75 to 87, wherein said mixture prepared in step (b) further comprises optional additional ingredients selected from the group comprising antioxidants, fillers, colorants, UV stabilizers, compatibilizers and lubricants.
89. The method according to claim 88, wherein the compatibiliser is selected from the group comprising polyolefins, polyolefins modified with reactive functional groups and block copolymers.

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90. Use of the heat-shrinkable coating or insulating material as claimed in any one of claims 56 to 74 as a heat-shrinkable sleeve for corrosion protection of pipeline joints.

91. Use of the heat-shrinkable coating or insulating material as claimed in any one of claims 56 to 74 as a protective sleeve for a transmission pipeline.