

Description

This invention relates to compositions containing hydrolyzable silyl modified olefin polymers and a cure booster.

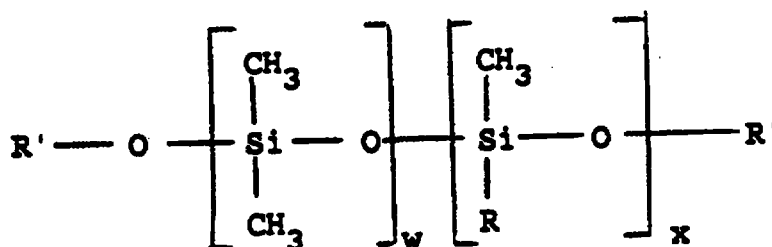
Hydrolyzable silyl modified olefin polymers are commercially attractive because they can be simply and effectively cured with water. They are, therefore, susceptible to a broad range of processing conditions, e.g., these polymers can be extruded at temperatures far in excess of the maximum processing temperatures used in extruding peroxide containing compositions. Being capable of extrusion at high temperatures, these compositions can be extruded at faster rates and at lower pressures, and are consequently more cost effective.

The curing or crosslinking of these silyl modified olefin polymers is effected by exposing these polymers to moisture. The moisture in the atmosphere is usually sufficient to permit curing to occur over a period of up to 48 hours, especially when a silanol condensation catalyst has been added to the polymers. Since the greater the amount of crosslinking, the better the mechanical properties, the art has sought to increase the crosslinking. To this end, more catalyst was added, but this resulted in scorching, i.e., premature crosslinking, in the extruder.

An object of this invention, therefore, is to provide a hydrolyzable silyl modified polymer composition having increased crosslinking capability without the scorching problem attendant with the use of additional catalyst.

According to the present invention, the above object is met by providing a water curable composition comprising:

- (a) at least one polymer selected from silane grafted homopolymers of ethylene, propylene, or 1-butene; silane grafted copolymers wherein a major proportion thereof is attributed to an ethylene, propylene, or 1-butene monomer; and a copolymer wherein a major proportion thereof is attributed to an ethylene, propylene, or 1-butene monomer and a minor proportion thereof is attributed to silane, each polymer having at least one silane moiety containing at least one hydrolyzable group; and
- (b) at least one polysiloxane having the following formula:



wherein:

R = $\text{C}_3\text{H}_5(\text{OC}_3\text{H}_5)_y(\text{OC}_2\text{H}_4)_z\text{OR}'$

R' = a radical selected from hydrogen, an alkyl radical having 1 to 4 carbon atoms, an alkyl acetyl radical wherein the alkyl group has 1 to 4 carbon atoms, and a trimethyl silyl radical, and each R' can be alike or different

w = 20 to 120

x = 0 to 24

y = 0 to 10

z = 4 to 25

y + z = 5 to 30.

The present invention furthermore relates to a process for increasing crosslinking in thermoforming type compositions comprising at least one of the above-mentioned polymers (a), which process comprises admixing with said polymer (a) at least one polysiloxane (b) as defined above and at least one silanol condensation catalyst; forming a product from the mixture at a temperature above the melting point of the polymer; and exposing the product to moisture for a sufficient time to cure the product.

It is understood that the term "copolymer" includes polymers having two or more different monomers incorporated into the same polymer chain. A major proportion, i.e., more than 50 percent by weight, of each copolymer is attributed to ethylene, propylene, or 1-butene. The balance of the copolymer is attributed to silane and/or various organic compounds having 2 to 20 carbon atoms such as vinyl esters, alkyl methacrylates, alkyl acrylates, alpha-olefins, and diolefins. Examples of these compounds are 1-hexene, 4-

methyl-1-pentene, 1-undecene, ethyl acrylate, vinyl acetate, methyl methacrylate, 1,4-hexadiene, ethylidene norbornene, dicyclopentadiene, butyl acrylate, and methyl acrylate. Terpolymers such as ethylene/propylene/ethylidene norbornene rubbers are of particular interest.

The silane grafted olefin homopolymer or copolymer can be prepared by the technique described in examples 1 and 2 below. In this polymer, the portion attributed to the silane is present in an amount of 0.5 percent to 10 percent by weight based on the weight of the polymer or copolymer and is preferably incorporated into the polymer or copolymer in an amount of 0.5 to 4 percent by weight. The silane used to modify the polymer or copolymer can be, among others, a vinyl trialkoxy silane such as vinyl trimethoxy silane, vinyl triethoxy silane, or vinyl isopropoxy silane. Generally speaking, any unsaturated monomeric silane can be used. If slower water cure or better shelf stability is desired, vinyl triisobutoxy silane or vinyl tris-(2-ethyl-hexoxy) silane can be used.

A free radical generator or catalyst is used in the preparation of the silane grafted polymer. Among the most useful free radical generators are dicumyl peroxide, lauroyl peroxide, azobisisobutyronitrile, benzoyl peroxide, tertiary butyl perbenzoate, di(tertiary-butyl) peroxide, cumene hydroperoxide, 2,5-dimethyl-2,5-di (t-butyl-peroxy) hexyne, 2,5-dimethyl-2,5-di (t-butylperoxy)hexane, tertiary butyl hydroperoxide, and isopropyl percarbonate. The organic peroxides are preferred. 0.001 to 5 percent by weight of free radical generator based on the weight of the polymer or copolymer is used, preferably 0.001 to 0.05 percent by weight.

The copolymer of ethylene and silane can be prepared by the process described in US-A- 3 225 018 and 4 574 133. The portion of the copolymer attributed to the silane is in the range of 0.5 to 10 percent by weight based on the weight of the copolymer and is preferably in the range of 0.5 to 4 percent by weight.

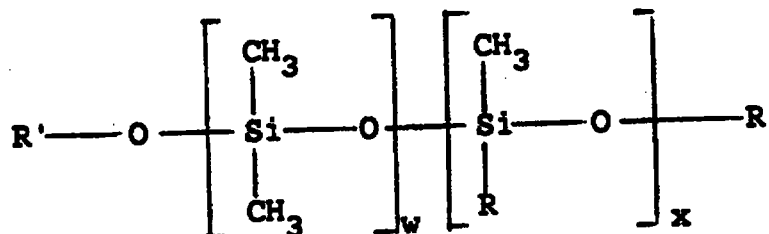
Various other processes for preparing silane grafted polyethylene and ethylene/silane copolymers and numerous unsaturated silanes suitable for use in preparing these polymers and bearing hydrolyzable groups such as alkoxy, oxy aryl, oxyaliphatic, and halogen are mentioned in US-A- 3 075 948; 4 412 042; 4 413 066; and 4 593,071.

The compositions of this invention are thermoforming and find utility in thermoforming operations, especially in molding and extrusion applications. They are particularly useful in the insulation and jacketing of wires and cables.

It will be understood that, for industrial purposes, the polysiloxane is packaged in a variety of different ways, e.g., (i) silane grafted polymer or copolymer + polysiloxane; (ii) silane grafted polymer or copolymer + polysiloxane + silanol condensation catalyst; (iii) polysiloxane + monomeric unsaturated silane; (iv) polysiloxane + monomeric unsaturated silane + organic peroxide; (v) polysiloxane + monomeric unsaturated silane + organic peroxide + silanol condensation catalyst.

As pointed out above, the hydrolyzable silyl modified olefin polymers can be cured or crosslinked by exposing the polymer to moisture. The crosslinking is accelerated in the presence of a conventional silanol condensation catalyst such as dibutyl tin dilaurate, dioctyl tin maleate, stannous acetate, stannous octoate, lead naphenate, zinc octoate, iron 2-ethyl hexoate, and other metal carboxylates. Further acceleration of crosslinking can be accomplished by adding a cocatalyst such as tetramethoxy titanate, tetraisopropyl titanate, tetramethyl titanate, or other organo titanates mentioned in US-A- 4 446 279. The catalysts can be introduced into the composition in conventional amounts, typically 0.005 to 1 part by weight of primary catalyst per 100 parts by weight of polymer and 0.25 to 10 parts by weight of cocatalyst per 100 parts by weight of polymer.

The components which is responsible for the increase in crosslinking (also referred to as a cure booster), is an organomodified polydimethyl siloxane (or polysiloxane) having the following formula:



wherein

R = $\text{C}_3\text{H}_6(\text{OC}_3\text{H}_6)_y(\text{OC}_2\text{H}_4)_z\text{OR}'$

R' = a radical selected from the group consisting of hydrogen, an alkyl radical having 1 to 4

carbon atoms, an alkyl acetyl radical wherein the alkyl group has 1 to 4 carbon atoms, and a trimethyl silyl radical, and each R' can be alike or different

w = 20 to 120

x = 0 to 24

y = 0 to 10

z = 4 to 25

y+z = 5 to 30.

A preferred polysiloxane has a molecular weight of less than about 20,000; $w + x = 60$ to 120; $w/x > 10$; $y = 0$; and $z = 4$ to 10.

In a specific embodiment, $w = 72$; $x = 5$; $y = 0$; and $z = 6.6$.

The polysiloxane component and a process for preparing it are described in US-A- 4 046 930 and 4 535 113.

The polysiloxane component can be present in the water curable composition in an amount of 0.01 to 3 parts by weight of polysiloxane per 100 parts by weight of polymer and is preferably used in an amount of 0.05 to 1 part by weight per 100 parts by weight of polymer. It is understood that when the polymer is referred to, the total polymer content of the composition is contemplated.

In addition to the components mentioned above, various conventional additives can be added in conventional amounts to the compositions. Typical additives are antioxidants, ultraviolet absorbers, antistatic agents, pigments, dyes, fillers including carbon black and aluminum silicate, slip agents, fire retardants, stabilizers, crosslinking agents, halogen scavengers, smoke inhibitors, processing aids, flow aids, lubricants, plasticizers, and viscosity control agents.

The invention is illustrated by the following examples. Parts and percentages are by weight.

Example 1

The formulation and procedure for preparing a silane grafted polyethylene is described.

The polyethylene used in this example is a low density polyethylene having a density of 0.90 and a melt index of 1.0. The low density polyethylene can be made by the processes described in EP-A- 120 501 and 120 503, wherein ethylene is polymerized together with an alpha olefin comonomer having 3 to 8 carbon atoms or by other conventional techniques. In the present application, low density polyethylenes are considered to include copolymers of ethylene and a minor proportion of alpha olefin.

100 parts of polyethylene, 0.2 part of polymerized 1,3-dihydro-2,2,4-trimethylquinoline (an antioxidant), 0.1 part of dicumyl peroxide, and 4 parts of vinyl tri-2-ethyl-hexoxy silane are mixed in a laboratory Brabender mixer at a temperature in the range of 80 °C to 115 °C, a temperature low enough to keep the dicumyl peroxide below its decomposition temperature.

After mixing for five minutes, the temperature is raised to a temperature in the range of 150 °C to 220 °C. The batch is then mixed for 5 to 10 minutes during which grafting of the silane to the polyethylene occurs.

The antioxidant is used as a radical trap to control the amount of crosslinking.

The silane grafted polyethylene is tested for reactivity as follows: 104.3 parts of silane grafted polyethylene is mixed with 0.5 part of dibutyl tin dilaurate or dioctyl tin maleate for five minutes at about 160 °C.

A test slab, three inches by 17.78 cm (seven inches) by 0.19 cm (0.075 inch) thick, is compression molded at about 150 °C from the mixture and then cooled in the mold.

The slab is tested immediately in a rheometer at 182 °C. The torque reading is 8 to 10 units. The slab is then placed in water at 70 °C for 48 hours and tested, once more, in a rheometer at 182 °C. The torque reading is 40 to 50 units. This indicates that water crosslinking has occurred. The increase in torque units indicates the degree of crosslinking.

Example 2

Example 1 is repeated except that 3 parts of vinyltriisobutoxysilane and 0.1 part of the antioxidant, tetrakis [methylene(3-5-di-tert-butyl-4-hydroxyhydro-cinnamate)] methane, are used; initial mixing is in the range of 110 °C to 120 °C; grafting is for 5 minutes at 185 °C; first rheometer test is at 182 °C with same result; slab is immersed in water for 16 hours; and second torque reading is 40 units.

Example 3

In this example and examples 4 to 18, the polysiloxane has the formula set forth above wherein $w = 72$; $x = 5$; $y = 0$; and $z = 6.6$.

The following composition is used in the example:

	Weight Percent
1. high density polyethylene (density >0.941)	80.01
2. linear low density polyethylene (density <0.925)	15.04
3. carbon black	2.28
4. antioxidant	0.37
5. ground silica	0.80
6. polysiloxane	0.80
7. dicumyl peroxide	0.09
8. dibutyltin dilaurate	0.03
9. vinyl trimethoxy silane	0.98

Grafting of vinyl trimethoxy silane to the polyethylenes occurs by decomposition of the dicumyl peroxide when the composition is heated.

A. The composition is exposed to water for 18 hours after silane grafting. The degree of crosslinking is determined by Monsanto rheometer torque increase, i.e., torque after crosslinking minus torque before silane grafting and exposure to water. The torque increase is 3.28 Nm (29 inch-pounds).

B. The example is repeated except that components 5 and 6 are excluded. The torque increase is only 1.58 Nm (14 inch-pounds),

Example 4

Two compositions are prepared as follows:

	Weight Percent	
	A	B
1. ethylene/silane copolymer (density = 0.923; melt index = 2; silane portion 1.5% by weight)	95	95
2. dioctyltin maleate	0.08	0.08
3. tetrakis [methylene (3,5-di-tert-butyl-4-hydroxy hydro-cinnamate)] methane	0.13	0.13
4. polysiloxane	0.06	0.06
5. carbon black	0	0.45
6. polyethylene (density = 0.918)	balance	balance

Both compositions exhibit crosslinking similar to Example 1A.

Examples 5 to 8

The following components are used in the examples:

1. ethylene/silane copolymer (melt index = 1.5; density = 0.923)
2. catalyst masterbatch:

	Weight Percent
linear low density polyethylene (melt index = 2.0; density = 0.918)	92.5
antioxidant (see example 4, component 3)	5.0
dioctyltin maleate	1.25
fluorocarbon flow aid	1.25

3. polysiloxane

4. linear low density polyethylene (melt index = 2.0; density = 0.918)

The materials are dry mixed and extruded through a Brabender extruder (20/60/20 screen pack) at a melt temperature of 185°. The 0.51 mm (20 mil) tapes produced are cured in 90°C water for 2 hours or 18 hours. A measure of the crosslinking that results is obtained by carrying out the ICEA (Insulated Cable Engineers Association) Hot Creep Test (publication T-28-562). Lower values indicate a greater degree of crosslinking. The test measures percent elongation of a tensile bar when subjected to 20 N/cm² at 150°C for 15 minutes.

The variables and results are shown in Table I.

Table I

Examples:	5	6	7	8
Components	Weight Percent			
1	94	88	82	83.2
2	6	6	6	6
3	0	-	-	0
4	0	-	-	10.8
mixture of 3 & 4	0	6	12	0
The surface appearance of the Example 5 tape is better than the tapes of Examples 6, 7, and 8.				
Hot Creep After Cure				
2 hours	79	113	55	152
18 hours	59	42	42	46

Examples 9 to 18

The following components are used in the examples:

1. polysiloxane
2. ground silica
3. dicumyl peroxide
4. vinyl trimethoxy silane
5. dibutyltin dilaurate
6. linear low density polyethylene (density = 0.918; melt index = 2.0 decigrams/minute)
7. low density polyethylene (density = 0.92; melt index = 2.0 decigrams/minute)
8. high density polyethylene (density = 0.953; melt index = 7.5 decigrams/minute)
9. high density polyethylene (density = 0.948; melt index = 0.2 decigrams/minute)
10. linear low density polyethylene (density = 0.920; melt index = 0.8 decigrams/minute)
11. carbon black
12. antioxidant

High density polyethylene can be made by the process described in Introduction to Polymer Chemistry, Stille, publ. Wiley and Sons, 1962, section 9.1, particularly page 151, and linear low density polyethylene can be made by the process described in US-A- 4 076 698.

The procedure for these examples is to first prepare a mixture of the desired polyethylene(s) and components 1 to 6. This is the original or composition I. It is tested with a Monsanto oscillating disk rheometer (ODR) for torque at 360°F using rotor oscillation of a ± 5 degree arc. Results are given in pound-inches (lb.in.). Grafting is then undertaken in a press at 180°C for 15 minutes. A small amount of

5

10

15

Results

Composition I

Composition II

Composition III

Example 19

A solution of 89 parts of vinyltrimethoxy silane, 8.3 parts dicumyl peroxide, and 2.7 parts dibutyltin dilaurate is made up under nitrogen. This is solution 1. Two 135 gram aliquots of solution 1 are pipetted into flasks. To one flask is added 25 grams of the polysiloxane of examples 3 to 18 to form solution 2 and, to another flask, 25 grams of the polysiloxane having the above formula wherein R' = hydrogen; w is about 20 to 120, but averages 50; and x = 0 to form solution 3. Clear, homogeneous solutions are formed in each case.

To a glass jar containing 100 grams of granular ethylene/butene copolymer having a density of 897 kilograms per cubic meter and a melt flow index of 7.1 grams per 10 minutes (190°C; 2.16 kilogram) are added 1.35 grams of solution 1. Similarly, 1.6 grams of solutions 2 and 3 are added to 100 gram portions of the same copolymer. The jars are held at 50°C, with occasional shaking, for 2 hours to homogenize the mixtures.

Grafting of the resin is accomplished by charging a melt indexer with 7 grams of each mixture. The melt-indexer is held at 190°C and a preheat of 6 minutes is given. The melt index of the resin is measured using a weight of 2.16 kilograms. The extrudates are cut off and weighed over one minute intervals and the melt indices are calculated as a function of time. After 5 minutes, the weight is changed to 5 kilograms and the resulting extrudates are cut off over 30 second intervals and weighed to afford the 5 kilogram melt flow indices. The results are set forth in Table III.

The 5 kilogram extrudates are pressed into a flat film of about 1.5 millimeter thickness and immersed in water at 70°C for 18 hours. The degree of crosslinking is determined according to ASTM D2765 (16 hours in boiling decalin). The results are set forth in Table IV.

TABLE III

SOLUTIONS TIME (minutes)	1	2	3
	MELT INDEX (2.16 kilograms)		
7.5	1.35	0.9	1.1
8.5	1.3	0.95	0.85
9.5	0.9	0.85	0.75
10.5	0.8	0.8	0.75
11.5	0.75	0.8	0.75
	MELT INDEX (5 kilograms)		
13	2.9	3.4	3.1
13.5	2.9	3.35	2.9
14	2.4	3.2	3.1

TABLE IV

GEL CONTENT (percent)	47.1	61.5	57.0
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Claims

1. A water curable composition comprising:

- (a) at least one polymer selected from silane grafted homopolymers of ethylene, propylene, or 1-butene; silane grafted copolymers wherein a major proportion thereof is attributed to an ethylene, propylene, or 1-butene monomer; and a copolymer wherein a major proportion thereof is attributed to an ethylene, propylene, or 1-butene monomer and a minor proportion thereof is attributed to silane, each polymer having at least one silane moiety containing at least one hydrolyzable group; and

Example 19

A solution of 89 parts of vinyltrimethoxy silane, 8.3 parts dicumyl peroxide, and 2.7 parts dibutyltin dilaurate is made up under nitrogen. This is solution 1. Two 135 gram aliquots of solution 1 are pipetted into flasks. To one flask is added 25 grams of the polysiloxane of examples 3 to 18 to form solution 2 and, to another flask, 25 grams of the polysiloxane having the above formula wherein $R' = \text{hydrogen}$; w is about 20 to 120, but averages 50; and $x = 0$ to form solution 3. Clear, homogeneous solutions are formed in each case.

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9.5	0.9	0.85	0.75
10.5	0.8	0.8	0.75
11.5	0.75	0.8	0.75
	MELT INDEX (5 kilograms)		
	13	2.9	3.4
	13.5	2.9	3.35
	14	2.4	3.2
			3.1

TABLE IV

GEL CONTENT (percent)	47.1	61.5	57.0
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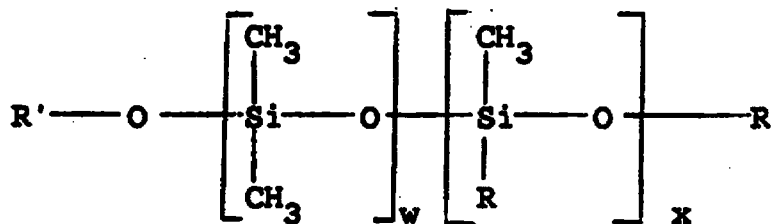
Claims

1. A water curable composition comprising:

- (a) at least one polymer selected from silane grafted homopolymers of ethylene, propylene, or 1-butene; silane grafted copolymers wherein a major proportion thereof is attributed to an ethylene, propylene, or 1-butene monomer; and a copolymer wherein a major proportion thereof is attributed to an ethylene, propylene, or 1-butene monomer and a minor proportion thereof is attributed to silane, each polymer having at least one silane moiety containing at least one hydrolyzable group; and



(b) at least one polysiloxane having the following formula:



wherein

R = $\text{C}_3\text{H}_5(\text{OC}_3\text{H}_5)_y(\text{OC}_2\text{H}_4)_z\text{OR}'$

R' = a radical selected from hydrogen, an alkyl radical having 1 to 4 carbon atoms, an alkyl acetyl radical wherein the alkyl group has 1 to 4 carbon atoms, and a trimethyl silyl radical, and each R' can be alike or different

w = 20 to 120

x = 0 to 24

y = 0 to 10

z = 4 to 25

y + z = 5 to 30.

2. The composition defined in claim 1 wherein the polysiloxane has a molecular weight of less than about 20,000; w + x = 60 to 120; w/x > 10; y = 0; and z = 4 to 10.

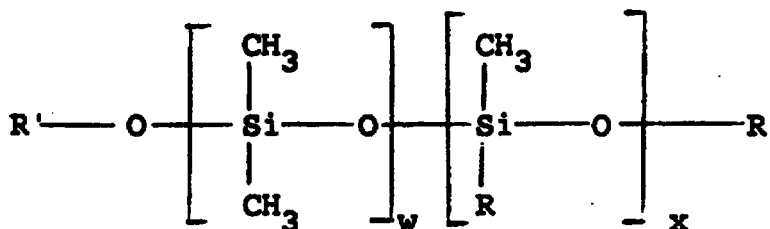
3. The composition defined in claim 1 or 2 wherein for each 100 parts by weight of polymer there are present 0.01 to 3 parts by weight, preferably 0.05 to 1 part by weight of polysiloxane.

4. The composition defined in any one of claims 1 to 3 wherein the monomer in major proportion is ethylene.

5. The composition defined in any one of claims 1 to 4 additionally containing a silanol condensation catalyst.

6. The composition defined in claim 5 wherein there is present 0.005 to 1 part by weight of catalyst per 100 parts by weight of polymer.

7. A composition comprising at least one polysiloxane having the following formula:



wherein

R = $\text{C}_3\text{H}_5(\text{OC}_3\text{H}_5)_y(\text{OC}_2\text{H}_4)_z\text{OR}'$

R' = a radical selected from hydrogen, an alkyl radical having 1 to 4 carbon atoms, an alkyl acetyl radical wherein the alkyl group has 1 to 4 carbon atoms, and a trimethyl silyl radical, and each R' can be alike or different

w = 20 to 120

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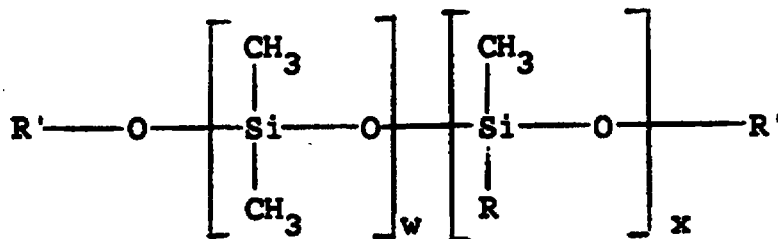


$z =$ 4 to 25

$y+z =$ 5 to 30

and a monomeric unsaturated silane having at least one hydrolyzable group.

- 5 8. The composition defined in claim 7 additionally containing an organic peroxide.
9. The composition defined in claim 7 or 8 additionally containing a silanol condensation catalyst.
10. The composition defined in any one of claims 7 to 9 wherein the silane is a vinyl trialkoxy silane, such as vinyl trimethoxy silane.
11. A process for increasing crosslinking in thermoforming type compositions comprising at least one polymer selected from silane grafted homopolymers of ethylene, propylene, or 1-butene; silane grafted copolymers wherein a major proportion thereof is attributed to an ethylene, propylene, or 1-butene monomer; and a copolymer wherein a major proportion thereof is attributed to an ethylene, propylene, or 1-butene monomer and a minor proportion thereof is attributed to silane, each polymer having at least one silane moiety containing at least one hydrolyzable group, the process comprising (a) admixing with the polymer, at least one polysiloxane having the following formula:



wherein

$\text{R} = \text{C}_3\text{H}_5(\text{OC}_3\text{H}_7)_y(\text{OC}_2\text{H}_5)_z\text{OR}'$

$\text{R}' =$ a radical selected from hydrogen, an alkyl radical having 1 to 4 carbon atoms, an alkyl acetyl radical wherein the alkyl group has 1 to 4 carbon atoms, and a trimethyl silyl radical, and each R' can be alike or different

$w =$ 20 to 120

$x =$ 0 to 24

$y =$ 0 to 10

$z =$ 4 to 25

$y+z =$ 5 to 30;

and at least one silanol condensation catalyst; (b) forming a product from the mixture at a temperature above the melting point of the polymer; and (c) exposing the product to moisture for a sufficient time to cure the product.

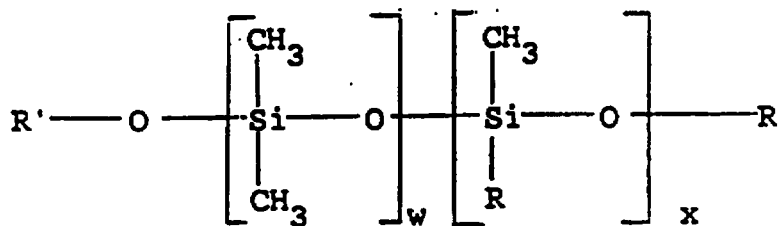
45 Patentansprüche

1. Wasserhärtende Zusammensetzung, umfassend:

(a) mindestens ein Polymer, das ausgewählt ist aus Silan-gepfropften Homopolymeren von Ethylen, Propylen oder 1-Buten; Silan-gepfropften Copolymeren, in denen ein größerer Teil davon auf ein Ethylen-, Propylen- oder 1-Buten-Monomer zurückzuführen ist; und einem Copolymer, in dem ein größerer Teil davon auf ein Ethylen-, Propylen- oder 1-Buten-Monomer zurückzuführen ist und ein kleinerer Teil davon auf Silan zurückzuführen ist, wobei jedes Polymer mindestens eine Silan-Einheit aufweist, die mindestens eine hydrolysierbare Gruppe enthält; und



(b) mindestens ein Polysiloxan mit der folgenden Formel:



worin

R = $\text{C}_3\text{H}_6(\text{OC}_3\text{H}_6)_y(\text{OC}_2\text{H}_4)_z\text{OR}'$

R' = ein aus Wasserstoff, einem Alkylrest mit 1 bis 4 Kohlenstoffatomen, einem Alkylacetylrest, in dem die Alkylgruppe 1 bis 4 Kohlenstoffatome aufweist, und einem Trimethylsilylrest ausgewählter Rest, und jedes R' gleich oder verschieden sein kann

w = 20 bis 120

x = 0 bis 24

y = 0 bis 10

z = 4 bis 25

y + z = 5 bis 30.

2. Zusammensetzung nach Anspruch 1, in der das Polysiloxan ein Molekulargewicht von weniger als etwa 20000 aufweist; $w + x = 60$ bis 120; $w/x > 10$; $y = 0$; und $z = 4$ bis 10.

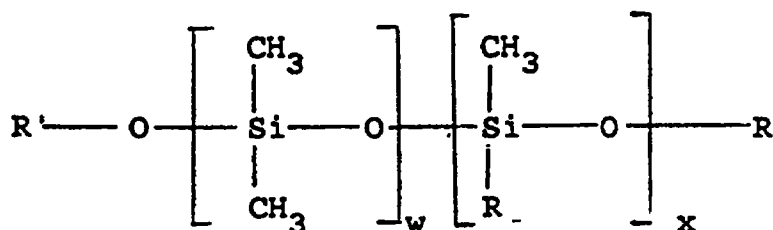
3. Zusammensetzung nach Anspruch 1 oder 2, in der pro 100 Gewichtsteile Polymer 0,01 bis 3 Gewichtsteile, vorzugsweise 0,05 bis 1 Gewichtsteil, Polysiloxan vorhanden sind.

4. Zusammensetzung nach irgendeinem der Ansprüche 1 bis 3, in der das Monomer im größeren Teil Ethylen ist.

5. Zusammensetzung nach irgendeinem der Ansprüche 1 bis 4, die zusätzlich einen Silanol-Kondensationskatalysator enthält.

6. Zusammensetzung nach Anspruch 5, in der 0,005 bis 1 Gewichtsteil Katalysator pro 100 Gewichtsteile Polymer vorhanden sind.

7. Zusammensetzung, umfassend mindestens ein Polysiloxan mit der folgenden Formel:



worin

R = $\text{C}_3\text{H}_6(\text{OC}_3\text{H}_6)_y(\text{OC}_2\text{H}_4)_z\text{OR}'$

R' = ein aus Wasserstoff, einem Alkylrest mit 1 bis 4 Kohlenstoffatomen, einem Alkylacetylrest, in dem die Alkylgruppe 1 bis 4 Kohlenstoffatome aufweist, und einem Trimethylsilylrest ausgewählter Rest, und jedes R' gleich oder verschieden sein kann

w = 20 bis 120

x = 0 bis 24

y = 0 bis 10

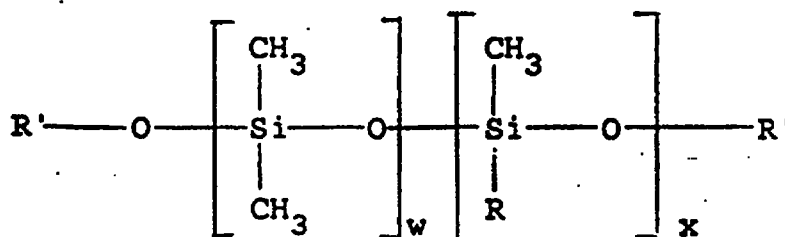


$z =$ 4 bis 25

$y+z =$ 5 bis 30

und ein monomeres ungesättigtes Silan mit mindestens einer hydrolysierbaren Gruppe.

- 5 8. Zusammensetzung nach Anspruch 7, die zusätzlich ein organisches Peroxid enthält.
9. Zusammensetzung nach Anspruch 7 oder 8, die zusätzlich einen Silanol-Kondensationskatalysator enthält.
- 10 10. Zusammensetzung nach irgendeinem der Ansprüche 7 bis 9, in der das Silan ein Vinyltrialkoxysilan, zum Beispiel Vinyltrimethoxysilan, ist.
11. Verfahren zur Erhöhung der Vernetzung in Zusammensetzungen vom Warmformungs-Typ, die umfas-
sen mindestens ein Polymer, das ausgewählt ist aus Silan-gepfropften Homopolymeren von Ethylen,
15 Propylen oder 1-Buten; Silan-gepfropften Copolymeren, in denen ein größerer Teil davon auf ein
Ethylen-, Propylen- oder 1-Buten-Monomer zurückzuführen ist; und einem Copolymer, in dem ein
größerer Teil davon auf ein Ethylen-, Propylen- oder 1-Buten-Monomer zurückzuführen ist und ein
kleinerer Teil davon auf Silan zurückzuführen ist, wobei jedes Polymer mindestens eine Silan-Einheit
aufweist, die mindestens eine hydrolysierbare Gruppe enthält, wobei das Verfahren umfaßt (a) das
20 Mischen mit dem Polymeren von mindestens einem Polysiloxan der folgenden Formel:



worin

$\text{R} =$ $\text{C}_3\text{H}_5(\text{OC}_3\text{H}_5)_y(\text{OC}_2\text{H}_4)_z\text{OR}'$

$\text{R}' =$ ein aus Wasserstoff, einem Alkylrest mit 1 bis 4 Kohlenstoffatomen, einem Alkylacetyl-
rest, in dem die Alkylgruppe 1 bis 4 Kohlenstoffatome aufweist, und einem Trimethylsilyl-
rest ausgewählter Rest, und jedes R' gleich oder verschieden sein kann

$w =$ 20 bis 120

$x =$ 0 bis 24

$y =$ 0 bis 10

$z =$ 4 bis 25

$y+z =$ 5 bis 30;

und mindestens einem Silanol-Kondensationskatalysator; (b) das Bilden eines Produktes aus der
Mischung bei einer Temperatur oberhalb des Schmelzpunktes des Polymeren; und (c) das Kontaktieren
des Produktes mit Feuchtigkeit für eine zur Härtung des Produktes ausreichende Zeit.

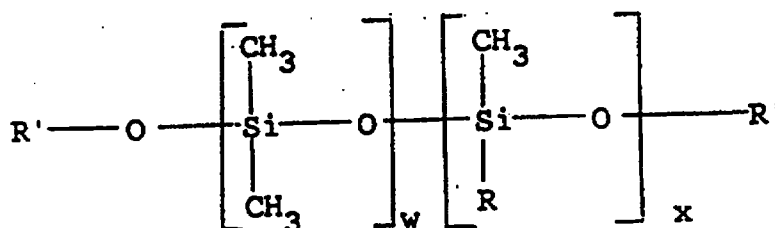
Revendications

1. Composition durcissable par l'eau, comprenant :

(a) au moins un polymère choisi entre des homopolymères d'éthylène, de propylène ou de 1-butène
greffés avec un silane ; des copolymères greffés avec un silane, dont une proportion dominante est
attribuée à un éthylène, propylène ou 1-butène monomère ; et un copolymère dont une proportion
dominante est attribuée à un éthylène, propylène ou 1-butène monomère et une proportion
secondaire est attribuée à un silane, chaque polymère portant au moins un motif silane contenant au
moins un groupe hydrolysable ; et



(b) au moins un polysiloxane répondant à la formule suivante :



dans laquelle

R

représente $\text{C}_3\text{H}_5(\text{OC}_3\text{H}_5)_y(\text{OC}_2\text{H}_4)_z\text{OR}'$

R'

est un radical choisi entre l'hydrogène, un radical alkyle ayant 1 à 4 atomes de carbone, un radical alkyl-acétyle dont le groupe alkyle a 1 à 4 atomes de carbone, et un radical triméthylsilyle, les radicaux R' pouvant être identiques ou différents,

w

a une valeur de 20 à 120

x

a une valeur de 0 à 24

y

a une valeur de 0 à 10

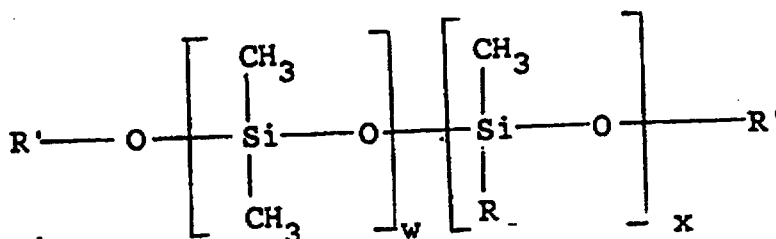
z

a une valeur de 4 à 25

la somme y + z

a une valeur de 5 à 30.

2. Composition suivant la revendication 1, dans laquelle le polysiloxane a un poids moléculaire inférieur à environ 20 000 ; la somme w + x a une valeur de 60 à 120 ; le rapport w/x est supérieur à 10 ; y est égal à 0 ; et z a une valeur 4 à 10.
3. Composition suivant la revendication 1 ou 2, dans laquelle 0,01 à 3 parties en poids, de préférence 0,05 à 1 partie en poids de polysiloxane, sont présentes pour 100 parties en poids de polymère.
4. Composition suivant l'une quelconque des revendications 1 à 3, dans laquelle le monomère est, en proportion dominante, de l'éthylène.
5. Composition suivant l'une quelconque des revendications 1 à 4, contenant en outre un catalyseur de condensation de silanol.
6. Composition suivant la revendication 5, dans laquelle est présente une proportion de 0,005 à 1 partie en poids de catalyseur pour 100 parties en poids de polymère.
7. Composition comprenant au moins un polysiloxane répondant à la formule suivante :



dans laquelle

R

représente $\text{C}_3\text{H}_5(\text{OC}_3\text{H}_5)_y(\text{OC}_2\text{H}_4)_z\text{OR}'$

R'

est un radical choisi entre l'hydrogène, un radical alkyle ayant 1 à 4 atomes de carbone, un radical alkyl-acétyle dont le groupe alkyle contient 1 à 4 atomes de carbone, et un radical triméthylsilyle, les radicaux R' pouvant être identiques ou



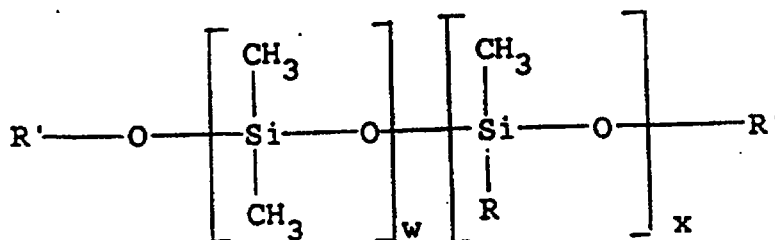
différents,
 w a une valeur de 20 à 120
 x a une valeur de 0 à 24
 y a une valeur de 0 à 10 z a une valeur de 4 à 25
 la somme y + z a une valeur de 5 à 30
 et un silane monomérique non saturé portant au moins un groupe hydrolysable.

8. Composition suivant la revendication 7, contenant en outre un peroxyde organique.

9. Composition suivant la revendication 7 ou 8, contenant en outre un catalyseur de condensation de silanol.

10. Composition suivant l'une quelconque des revendications 7 à 9, dans laquelle le silane est un vinyltrialkoxysilane tel que le vinyltriméthoxysilane.

11. Procédé pour accroître la réticulation dans des compositions du type mis en oeuvre par thermoformage, comprenant au moins un polymère choisi entre des homopolymères d'éthylène, de propylène et de 1-butène greffés avec un silane ; des copolymères greffés avec un silane, dont une proportion dominante est attribuée à un éthylène, propylène ou 1-butène monomère ; et un copolymère dont une proportion dominante est attribuée à un éthylène, propylène ou 1-butène monomère et une proportion secondaire est attribuée à un silane, chaque polymère ayant au moins un motif silane contenant au moins un groupe hydrolysable, le procédé comprenant (a) le mélange, avec le polymère, d'au moins un polysiloxane répondant à la formule suivante :



dans laquelle

R représente $\text{C}_3\text{H}_6(\text{OC}_3\text{H}_7)_y(\text{OC}_2\text{H}_5)_z\text{OR}'$
 est un radical choisi entre l'hydrogène, un radical alkyle ayant 1 à 4 atomes de carbone, un radical alkyl-acétyle dont le groupe alkyle contient 1 à 4 atomes de carbone, et un radical triméthylsilyle, les radicaux R' pouvant être identiques ou différents,

w a une valeur de 20 à 120

x a une valeur de 0 à 24

y a une valeur de 0 à 10

z a une valeur de 4 à 25

la somme y + z a une valeur de 5 à 30 ;

et au moins un catalyseur de condensation de silanol ; (b) le formage d'un produit à partir du mélange à une température au-dessus du point de fusion du polymère ; et (c) l'exposition du produit à l'humidité pendant une durée suffisante pour que le produit durcisse.

