

Description

This invention relates to a process for crosslinking hydrolyzable copolymers using a silanol condensation catalyst prepared in situ, and compositions therefor.

5 Scorch, i.e., premature crosslinking, in water curable resin systems is a widely recognized problem. It can result in numerous ways. The most difficult to control can be referred to as process scorch, which takes place in the presence of a silanol condensation catalyst. Process scorch is manifested just after the addition of the silanol condensation catalyst to the resin and, again, during the continuous processing of the water curable resin in, for example, an extruder. The former occurs with a rapid build up in viscosity and, in many cases, can be dramatic. The latter, generally, involves a more subtle build up of viscosity over time. In both cases, the extrusion is rendered difficult and ultimately results in an unacceptable extrudate and a shutdown of the operation.

The art is constantly searching for processes and compositions which lead to a diminution or elimination of process scorch.

15 EP-A-207 627 and EP-A-169 070 disclose corresponding processes wherein specific dihydrocarbyltin dicarboxylate silanol condensation catalysts are employed. In said tin compounds the carboxylate moieties are derived from a polymer having pendant carboxylate moieties and a dicarboxylic acid, respectively.

EP-A-71 237 is concerned with one component room temperature setting compositions which are reported to have an excellent storage stability due to the presence of, besides a vinyl polymer having a hydrolyzable silyl group and a hardener, certain stabilizer compounds. As hardener e.g. organic tin oxides and reaction products thereof with ester compounds are used.

EP-A-274 428 describes coating compositions comprising, among others, a vinyl polymer having a hydrolyzable silyl group and, as optional component, a hardening accelerator, e.g. dihydrocarbyltin dicarboxylates or reaction products of dihydrocarbyltin oxides and ester compounds. Said coating compositions are said to show excellent storage stability and to result in coating films having excellent properties.

An object of this invention is to provide a crosslinking process which solves the problem of process scorch and a composition useful in the process.

Other objects and advantages will become apparent hereinafter.

According to the present invention the above object is met by a process for crosslinking comprising the following steps:

(a) admixing, in a processing zone, a copolymer containing at least one hydrolyzable silane moiety; a dihydrocarbyltin oxide; and

(i) a carboxylic acid;

(ii) a compound bearing at least one carboxylate moiety, which is capable of forming a carboxylic acid when subjected to heat and/or moisture; or

(iii) mixtures thereof,

with the proviso that:

(A) in the event that component (ii) is present, the conditions in the processing zone are such that the carboxylate moiety forms a carboxylic acid;

(B) the residence time of the mixture in the processing zone is sufficient to at least partially complete the processing of the copolymer, but of sufficient brevity to substantially avoid a reaction of the carboxylic acid with the dihydrocarbyltin oxide; and

(b) passing the mixture from step (a) into a crosslinking zone under such reaction conditions that the carboxylic acid reacts with the dihydrocarbyltin oxide to form dihydrocarbyltin carboxylate, said crosslinking zone having a moisture content sufficient to crosslink the hydrolyzable copolymer in the presence of the dihydrocarbyltin carboxylate.

Detailed Description

50 The hydrolyzable resins useful in subject process derive their hydrolyzability from silane modification. They are commercially attractive because they can be simply and effectively cured with water. These copolymers are, therefore, susceptible to a broad range of processing conditions and are particularly useful in the preparation of extruded wire coatings, foams, pipe, and pond liners.

The curing or crosslinking of these silane modified copolymers is effected by exposing the copolymers to moisture. Without a silane condensation catalyst, however, moisture cure is exceedingly slow and, in the short time it takes to pass the resin through, e.g., an extruder, the amount of crosslinking achieved is negligible.

It is understood that the term "copolymer" as used in this specification may include silane grafted olefin homopolymers and copolymers, and copolymers of one or more olefin monomers and an olefin silane monomer. The monomers on which the homopolymers and copolymers are based can be alpha-olefins or diolefins having 2 to 20 carbon atoms, particularly the lower alpha-olefins having 2 to 12 carbon atoms. Preferably, a major proportion, i.e., more than 50 percent by weight, of each copolymer is attributed to ethylene, propylene, or 1-butene. The silane monomer, which is either grafted or copolymerized, is unsaturated and has at least one hydrolyzable group. Various useful alkenyl alkoxy silanes are mentioned below.

In addition to the alpha-olefin, diolefin, and silane monomers, the balance of the copolymer can be based on one or more various olefin monomers having 2 to 20 carbon atoms. Examples of useful monomers are the vinyl esters, alkyl methacrylates, and alkyl acrylates. Examples of these compounds are 1-hexene, 4-methyl-1-pentene, 1-undecene, ethyl acrylate, vinyl acetate, methyl methacrylate, 1,4-hexadiene, ethylenenorbornene, dicyclopentadiene, butyl acrylate, and methyl acrylate. Silane modified terpolymers such as ethylene/propylene/ethylidene norbornene rubbers are of particular interest.

Silane grafted copolymers can be prepared by the technique described below. In this copolymer, the portion attributed to the silane is present in an amount of about 0.1 percent to about 10 percent by weight based on the weight of the copolymer and is preferably incorporated into the copolymer in an amount of about 0.5 to about 4 percent by weight. The silane used to modify the copolymer can be, among others, a vinyl trialkoxy silane such as vinyl trimethoxy silane, vinyl triethoxy silane, or vinyl triisopropoxy silane. Generally speaking, any unsaturated monomeric organosilane having one or more hydrolyzable groups can be used. If slower water cure or better shelf stability is desired, vinyl triisobutoxy silane, vinyl tributoxysilane, 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 copolymer. Among the most useful free radical generators are dicumyl peroxide, lauryl peroxide, azobisisobutyronitrile, benzoyl peroxide, tertiary butyl perbenzoate, di(tertiary-butyl) peroxide, cumene hydroperoxide, 2,5-dimethyl-2,5-di(t-butylperoxy) hexene, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, tertiary butyl hydroperoxide, and isopropyl percarbonate. The organic peroxides are preferred. About 0.001 to about 5 percent by weight of free radical generator based on the weight of the polymer or copolymer is used, preferably about 0.001 to about 0.5 percent by weight.

A typical technique for preparing a silane grafted polyethylene is as follows: the polyethylene used can be, for example, a low density polyethylene having a density of 0.90 and a melt index of 1.0. It can be made by the processes described in European Patent Applications 0 120 501 and 0 120 503, both published on October 3, 1984, 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 ethylene copolymer, 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 tris-(2-ethyl-hexoxy) silane are mixed in a laboratory Brabender mixer at a temperature in the range of about 80°C to about 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 about 150°C to about 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. This technique can be repeated, for example by using 3 parts of vinyltriisobutoxysilane; 0.1 part dicumyl peroxide; and 0.1 part of the antioxidant, tetrakis [methylene(2-5-di-tert-butyl-4-hydroxyhydrocinnamate) methane; initial mixing is in the range of 110°C to 120°C; grafting is for 5 minutes at 185°C.

A copolymer of ethylene and silane can be prepared by the process described in United States Patent 3,225,018 issued on December 21, 1965 or United States Patent 4,574,133 issued on March 4, 1986. The portion of the copolymer attributed to the silane is in the range of about 0.5 to about 10 percent by weight based on the weight of the copolymer and is preferably in the range of about 0.5 to about 4 percent by weight.

Various other processes for preparing silane grafted 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 United States patents 3,075,948; 4,412,042; 4,413,066; and 4,593,071.

The dihydrocarbyltin oxide can have the formula:



wherein R is an alkyl or aryl radical and R can be alike or different. The R radical can have 1 to 20 carbon atoms and preferably has 1 to 8 carbon atoms. Examples of the R radical are methyl, ethyl, propyl, n-butyl, isobutyl, pentyl, hexyl, phenyl, and octyl. Examples of dihydrocarbyltin oxides useful in subject invention are dimethyltin oxide, dibutyltin oxide, dioctyltin oxide, diphenyltin oxide, methylphenyltin oxide, and dibenzyltin oxide. These organotin oxides are, generally, high melting, dispersible powdered solids, which show little or no activity in the crosslinking of hydrolyzable silane resins.

The carboxylic acids can be aliphatic or aromatic carboxylic acids having 1 to 30 carbon atoms, preferably 1 to 12 carbon atoms, and can be unsubstituted or substituted provided that the substituent is inert to the materials and conditions in the processing and crosslinking zones. Examples of suitable carboxylic acids are acetic, formic, propionic, butyric, octanoic, benzoic, salicylic, citric, maleic, oleic, isostearic, succinic, phthalic, stearic, and lauric. The carboxylate moieties of these, and other carboxylic acids, are examples of the carboxylate moieties which can be included in the compounds referred to below. The carboxylic acids react with the dihydrocarbyltin oxide at temperatures in the range of about 20 °C to about 350 °C and preferably about 50 °C to about 150 °C.

Compounds bearing carboxylate moieties which form carboxylic acid when subjected to heat and/or moisture can be exemplified by silane carboxylates, compounds or complexes formed by the combination of fillers and carboxylate moieties, organic acid anhydrides, and resins.

Silane carboxylates includes those compounds having the formula:



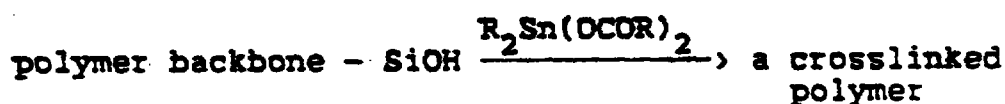
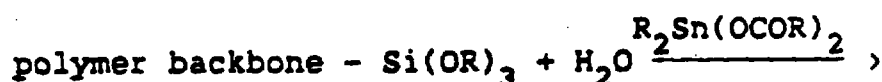
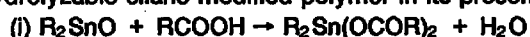
wherein R' is hydrogen or an aliphatic or aromatic radical and R'' is an aliphatic or aromatic radical. The aliphatic or aromatic radical can have 1 to 30 carbon atoms and preferably has 1 to 12 carbon atoms. The radical can be alkyl, alkaryl, aryl, cycloaliphatic, or heterocyclic. Examples of suitable radicals are methyl, ethyl, propyl, n-butyl, isobutyl, pentyl, hexyl, octyl, lauryl, phenyl, and benzyl. The silicone carboxylates can be exemplified by methyl triacetoxysilane, butyl triacetoxysilane, vinyl triacetoxysilane, methyl tribenzoxysilane, butyl tribenzoxysilane, and vinyl tribenzoxysilane.

The carboxylate moiety can also be attached to the surface of a conventional filler, by reaction to form a compound, e.g., $Mg(OH_2 \cdot OCOR'')$, or a complex, e.g., $Al(OH)_3 \cdot HOCOR''$. In both cases, R'' is as described above. Another example of a useful filler is $Ca(OH)_2$.

The organic acid anhydrides can have 4 to 20 carbon atoms and preferably 4 to 10 carbon atoms. Examples of suitable anhydrides are maleic anhydride, itaconic anhydride, crotonic anhydride, benzoic anhydride, and phthalic anhydride.

Resins having carboxylate moieties are exemplified by ethylene/vinyl acetate copolymer, ethylene/ethyl acrylate copolymer, ethylene/methylacrylate/acrylic acid terpolymer, and ethylene/acrylic acid copolymer.

The reaction of the dihydrocarbyltin oxide with the carboxylate moiety to place the tin oxide in an activated state, i.e., to provide a silanol condensation catalyst, and the subsequent crosslinking of a hydrolyzable silane modified polymer in its presence, can be illustrated as follows:



The processing zone can be a conventional extruder, e.g., a single screw type. A typical extruder has a hopper at its upstream end and a die at its downstream end. The hopper feeds into a barrel, which contains a screw. At the downstream end, between the end of the screw and the die, is a screen pack and a breaker plate. The screw portion of the extruder is considered to be divided up into three sections, the feed section, the compression section, and the metering section, and two zones, the back heat zone and the front heat zone, the sections and zones running from upstream to downstream. If it has more than one barrel, the barrels are connected in series. The length to diameter ratio of each barrel is in the range of about 16:1 to about 30:1.

The processing zone can also be a conventional injection molding apparatus, or a rotomolding apparatus.

In the event that the compound bearing the carboxylate moiety is present, the conditions in the processing zone are such that the carboxylate moiety forms a free carboxylic acid. As noted, this is accomplished through the application of heat and/or moisture. The temperature in the processing zone will generally be in the range of about 20°C to about 350°C and is preferably in the range of about 50°C to about 150°C. These are conventional extrusion and injection molding temperatures. In the case of ethylene/vinyl acetate copolymers, the heat will be sufficient to form the carboxylic acid. With respect to those compounds which need moisture to form the carboxylic acid, the formation is generally facilitated by the presence of heat in the ranges mentioned above.

The residence time of the mixture in the processing zone is, for example, of sufficient length to complete all or part of the extrusion or injection molding. This time is in the range of about 20 to about 2000 seconds and is preferably about 60 to about 1000 seconds. In view of this brief residence time, the reaction of the carboxylic acid with the dihydrocarbyltin oxide is substantially avoided, i.e., kept to a minimum.

The crosslinking zone is usually a water bath through which the extruded or injection molded resin, i.e., the processed resin, is passed. The crosslinking zone can be operated at a temperature in the range of about 20°C to about 200°C and is preferably operated at a temperature in the range of about 50°C to about 90°C. The residence time in this zone can be in the range of about 0.01 to about 72 hours and is preferably about 1 to about 24 hours. As an alternative to the water bath, the zone can be humidified, the relative humidity being at least about 50 percent.

In the crosslinking zone, the carboxylic acid reacts with the dihydrocarbyltin oxide to provide the silanol condensation catalyst, which accelerates the moisture cure of the hydrolyzable resin.

Conventional additives can be added to the mixture introduced into the processing zone. The amount of additive is usually in the range of about 0.01 to about 50 percent based on the weight of the resin. Useful additives are antioxidants, ultraviolet absorbers, antistatic agents, pigments, dyes, fillers, slip agents, fire retardants, plasticizers, processing aids, lubricants, stabilizers, and smoke inhibitors. Blends of the hydrolyzable polymer and other polymers can be prepared in the processing zone provided that the resins to be blended with the hydrolyzable copolymer will not crosslink. Examples of these resins are low density polyethylene, high density polyethylene, polypropylene, linear low density polyethylene, and very low density polyethylene (equal to or less than 0.915 grams per cubic centimeter).

The patents and applications mentioned in this specification are incorporated by reference herein.

The invention is illustrated by the following examples:

Examples 1 to 4

The addition copolymer of ethylene and vinyltrimethoxysilane is fluxed in a Brabender mixer at 130°C and, in examples 2, 3 and 4, different masterbatches are added and dispersed during 30 seconds. After discharge, rheometer plaques are pressed, placed in a water bath at 70°C, and rheometer readings are taken at various intervals.

The masterbatch added in Example 2 is made up of 90 percent by weight ethylene/ethyl acrylate copolymer and 10 percent by weight dibutyltin dilaurate.

The masterbatch added in Example 3 is made up of 92 percent by weight ethylene/ethyl acrylate copolymer and 8 percent by weight dibutyltin oxide.

The masterbatch added in example 4 is made up of 88.9 percent by weight ethylene/ethyl acrylate copolymer; 8 percent by weight dibutyltin oxide; and 3.1 percent by weight maleic anhydride.

The rheometer test procedure is described in United States Patent 4,108,852 issued on April 19, 1977. The rheometer reading is in pound-inches (lb.-in.).

The rheometer readings for the various time intervals are as follows:

Example	1	2	3	4
Time Interval (hours in 70 °C H ₂ O)				
0	5	9	5	9
1	-	15	6	18
4	-	26	6	30
24	-	40	10	50
48	7	51	16	55
96	13	-	23	-
336	25	-	39	-

Examples 5 to 9

The addition copolymer of ethylene and vinyltrimethoxysilane is fluxed in a Brabender mixer at 130 °C, additives are added and mixed and dispersed during one minute. After discharge, rheometer plaques are pressed, placed in a water bath at 70 °C, and rheometer readings are taken at zero and 16 hours. Components, proportions, and results are as follows:

Example	5	6	7	8	9
Components	(parts by weight)				
copolymer	100	100	100	100	100
dibutyltin oxide	0.05	-	-	0.05	0.05
stearic acid	-	0.12	-	0.12	-
ethyltriacetoxysilane	-	-	0.03	-	0.03
rheometer reading					
0 hours	5	7	7	8	8
16 hours	7	12	8	16	14

Claims

1. A process for crosslinking comprising the following steps:

(a) admixing, in a processing zone, a copolymer containing at least one hydrolyzable silane moiety; a dihydrocarbyltin oxide; and

(i) a carboxylic acid;

(ii) a compound bearing at least one carboxylate moiety, which is capable of forming a carboxylic acid when subjected to heat and/or moisture; or

(iii) mixtures thereof,

with the proviso that:

(A) in the event that component (ii) is present, the conditions in the processing zone are such that the carboxylate moiety forms a carboxylic acid;

(B) the residence time of the mixture in the processing zone is sufficient to at least partially complete the processing of the copolymer, but of sufficient brevity to substantially avoid a reaction of the carboxylic acid with the dihydrocarbyltin oxide; and

(b) passing the mixture from step (a) into a crosslinking zone under such reaction conditions that the carboxylic acid reacts with the dihydrocarbyltin oxide to form dihydrocarbyltin carboxylate, said crosslinking zone having a moisture content sufficient to crosslink the hydrolyzable copolymer in the presence of the dihydrocarbyltin carboxylate.

2. The process defined in claim 1 wherein the copolymer is based on one or more alpha-olefin comonomers and on one or more alkenyl alkoxy silane comonomers and is an ethylene/vinyl trimethoxy silane copolymer.



Example	1	2	3	4
Time Interval (hours in 70 °C H ₂ O)				
0	5	9	5	9
1	-	15	6	18
4	-	26	6	30
24	-	40	10	50
48	7	51	16	55
96	13	-	23	-
336	25	-	39	-

Examples 5 to 9

The addition copolymer of ethylene and vinyltrimethoxysilane is fluxed in a Brabender mixer at 130 °C, additives are added and mixed and dispersed during one minute. After discharge, rheometer plaques are pressed, placed in a water bath at 70 °C, and rheometer readings are taken at zero and 16 hours. Components, proportions, and results are as follows:

Example	5	6	7	8	9
Components	(parts by weight)				
copolymer	100	100	100	100	100
dibutyltin oxide	0.05	-	-	0.05	0.05
stearic acid	-	0.12	-	0.12	-
ethyltriacetoxysilane	-	-	0.03	-	0.03
rheometer reading					
0 hours	5	7	7	8	8
16 hours	7	12	8	16	14

Claims

1. A process for crosslinking comprising the following steps:

(a) admixing, in a processing zone, a copolymer containing at least one hydrolyzable silane moiety; a dihydrocarbyltin oxide; and

(i) a carboxylic acid;

(ii) a compound bearing at least one carboxylate moiety, which is capable of forming a carboxylic acid when subjected to heat and/or moisture; or

(iii) mixtures thereof,

with the proviso that:

(A) in the event that component (ii) is present, the conditions in the processing zone are such that the carboxylate moiety forms a carboxylic acid;

(B) the residence time of the mixture in the processing zone is sufficient to at least partially complete the processing of the copolymer, but of sufficient brevity to substantially avoid a reaction of the carboxylic acid with the dihydrocarbyltin oxide; and

(b) passing the mixture from step (a) into a crosslinking zone under such reaction conditions that the carboxylic acid reacts with the dihydrocarbyltin oxide to form dihydrocarbyltin carboxylate, said crosslinking zone having a moisture content sufficient to crosslink the hydrolyzable copolymer in the presence of the dihydrocarbyltin carboxylate.

2. The process defined in claim 1 wherein the copolymer is based on one or more alpha-olefin comonomers and on one or more alkenyl alkoxy silane comonomers and is an ethylene/vinyl trimethoxy silane copolymer.



3. The process defined in claim 1 wherein the copolymer is a silane grafted homopolymer or copolymer or a copolymer of an olefin and a silane.
- 5 4. The process defined in at least one of the claims 1-3 wherein the dihydrocarbyl tin oxide has the formula R_2SnO wherein R is an alkyl or aryl radical and each R can be alike or different.
- 10 5. The process defined in at least one of the claims 1-4 wherein a carboxylic acid or an organic acid anhydride is present.
- 15 6. The process defined in at least one of the claims 1-4 wherein a compound having 1 to 30 carbon atoms and at least one carboxylate moiety, which is capable of forming a carboxylic acid when subjected to heat and/or moisture, is present.
- 15 7. The process defined in at least one of the claims 1-6 wherein the residence time in the processing zone is in the range of 20 to 2000 seconds.
- 15 8. The process defined in at least one of the claims 1-7 wherein the temperature in the processing zone is in the range of 20 °C to 350 °C.
- 20 9. The process defined in at least one of the claims 1-8 wherein the processing zone is an extrusion zone.
- 20 10. The process defined in at least one of the claims 1-9 wherein the temperature in the crosslinking zone is in the range of 20 °C to 200 °C.
- 25 11. The process defined in at least one of the claims 1-4 and 7-10 wherein a homopolymer or copolymer bearing at least one carboxylate moiety is present.
- 25 12. A composition adapted to provide a silanol condensation catalyst comprising:
 - 30 (i) a dihydrocarbyltin oxide; and
 - (ii) a carboxylic acid; a compound having at least one carboxylate moiety, which is capable of forming a carboxylic acid when subjected to heat and/or moisture; or mixtures thereof.
- 35 13. The composition defined in claim 12 wherein the dihydrocarbyl tin oxide has the formula R_2SnO wherein R is an alkyl or aryl radical and each R can be alike or different.
- 35 14. The composition defined in at least one of the claims 12-13 wherein a carboxylic acid or an organic acid anhydride is present.
- 40 15. The composition defined in at least one of the claims 12-13 wherein a compound having 1 to 30 carbon atoms and at least one carboxylate moiety, which is capable of forming a carboxylic acid when subjected to heat and/or moisture, is present.
- 45 16. The composition defined in at least one of the claims 12-13 wherein a homopolymer or copolymer bearing at least one carboxylate moiety is present.
- 45 17. A composition comprising a copolymer containing at least one hydrolyzable silane moiety; a dihydrocarbyltin oxide; and (i) a carboxylic acid, (ii) a compound bearing at least one carboxylate moiety, which is capable of forming a carboxylic acid when subjected to heat and/or moisture, or (iii) mixtures thereof.
- 50 18. The composition defined in claim 17 wherein the copolymer is based on one or more alpha-olefin comonomers and on one or more alkenyl alkoxy silane comonomers and is an ethylene/vinyl trimethoxy silane copolymer.
- 55 19. The composition defined in claim 17 wherein the copolymer is a silane grafted homopolymer or copolymer or a copolymer of olefin and a silane.



20. The composition defined in at least one of the claims 17-19 wherein the dihydrocarbyltin oxide has the formula R_2RnO wherein R is an alkyl or aryl radical and each R can be alike or different.
21. The composition defined in at least one of the claims 17-20 wherein a carboxylic acid or an organic acid anhydride is present.
22. The composition defined in at least one of the claims 17-20 wherein a compound having 1 to 30 carbon atoms and bearing at least one carboxylate moiety, which is capable of forming a carboxylic acid when subjected to heat and/or moisture, is present.
23. The composition defined in at least one of the claims 17-20 wherein a homopolymer or copolymer bearing at least one carboxylate moiety is present.

Patentansprüche

1. Verfahren zur Vernetzung, das die folgenden Schritte umfaßt:
- (a) Vermischen in einer Verarbeitungszone eines Copolymers, das wenigstens eine hydrolysierbare Silankomponente enthält, eines Dihydrocarbylzinnoxids und
- (i) einer Carbonsäure,
- (ii) einer Verbindung, die wenigstens eine Carboxylat-Komponente aufweist, die eine Carbonsäure bilden kann, wenn sie Hitze- und/oder Feuchtigkeit ausgesetzt wird oder
- (iii) Mischungen von diesen,
- unter der Voraussetzung, daß
- (A) im Falle, daß Komponenten (ii) anwesend ist, die Bedingungen in der Verarbeitungszone derart sind, daß die Carboxylat-Komponente eine Carbonsäure bildet;
- (B) die Verweilzeit der Mischung in der Verarbeitungszone ausreichend ist, um wenigstens teilweise die Verarbeitung des Copolymers zu vollenden, jedoch von ausreichender Kürze, um im wesentlichen eine Umsetzung der Carbonsäure mit dem Dihydrocarbylzinnoxid zu vermeiden; und
- (b) Überleiten der Mischung aus Schritt (a) in eine Vernetzungszone unter solchen Reaktionsbedingungen, daß sich die Carbonsäure mit dem Dihydrocarbylzinnoxid umsetzt, um Dihydrocarbylzinn-carboxylat zu bilden, wobei die genannte Vernetzungszone einen ausreichenden Feuchtigkeitsgehalt hat, um das hydrolysierbare Copolymer in Anwesenheit des Dihydrocarbylzinn-carboxylats zu vernetzen.
2. Verfahren nach Anspruch 1, worin das Copolymer auf einem oder mehreren α -olefin-Comonomer(en) und einem oder mehreren Alkenylalkoxysilan-Comonomer(en) basiert und ein Ethylen/Vinyltrimethoxysilan-Copolymer ist.
3. Verfahren nach Anspruch 1, worin das Copolymer ein Homopolymer mit aufgepfropftem Silan oder ein Copolymer eines Olefins und eines Silans ist.
4. Verfahren nach wenigstens einem der Ansprüche 1-3, worin das Dihydrocarbylzinnoxid die Formel R_2SnO aufweist, worin R eine Alkyl- oder Arylgruppe ist und R jeweils gleich oder verschieden sein kann.
5. Verfahren nach wenigstens einem der Ansprüche 1-4, worin eine Carbonsäure oder ein organisches Säureanhydrid anwesend ist.
6. Verfahren nach wenigstens einem der Ansprüche 1-4, worin eine Verbindung mit 1 bis 30 Kohlenstoffatomen und wenigstens eine Carboxylat-Komponente, die - wenn sie Hitze und/oder Feuchtigkeit ausgesetzt wird - eine Carbonsäure bilden kann, anwesend ist.
7. Verfahren nach wenigstens einem der Ansprüche 1-6, worin die Verweilzeit in der Verarbeitungszone im Bereich von 20 bis 2000 Sekunden liegt.
8. Verfahren nach einem der Ansprüche 1-7, worin die Temperatur in der Verarbeitungszone im Bereich von 20° C bis 350° C liegt.



9. Verfahren nach einem der Ansprüche 1-8, worin die Verarbeitungszone eine Strangpreßzone ist.
10. Verfahren nach einem der Ansprüche 1-9, worin die Temperatur in der Vernetzungszone im Bereich von 20° C bis 200° C liegt.
- 5 11. Verfahren nach einem der Ansprüche 1-4 und 7-10, worin ein Homopolymer oder Copolymer, das wenigstens eine Carboxylat-Komponente aufweist, anwesend ist.
12. Zusammensetzung, geeignet zur Schaffung eines Silanol-Kondensations-Katalysators, die umfaßt:
 - 10 (i) ein Dihydrocarbylzinnoxid und
 - (ii) eine Carbonsäure, eine Verbindung mit wenigstens einer Carboxylat-Komponente, die - wenn sie Hitze und/oder Feuchtigkeit ausgesetzt wird - eine Carbonsäure bilden kann, oder Mischungen von diesen.
13. Zusammensetzung nach Anspruch 12, worin das Dihydrocarbylzinnoxid die Formel R_2SnO hat, worin R eine Alkyl- oder Arylgruppe ist und R jeweils gleich oder verschieden sein kann.
14. Zusammensetzung nach wenigstens einem der Ansprüche 12-13, worin eine Carbonsäure oder ein organisches Säureanhydrid anwesend ist.
- 20 15. Zusammensetzung nach wenigstens einem der Ansprüche 12-13, worin eine Verbindung mit 1 bis 30 Kohlenstoffatomen und wenigstens eine Carboxylat-Komponente, die - wenn sie Hitze und/oder Feuchtigkeit ausgesetzt wird - eine Carbonsäure bilden kann, anwesend ist.
- 25 16. Zusammensetzung nach wenigstens einem der Ansprüche 12-13, worin ein Homopolymer oder Copolymer, das wenigstens eine Carboxylat-Komponente aufweist, anwesend ist.
17. Zusammensetzung, die ein Copolymer, das wenigstens eine hydrolysierbare Silan-Komponente enthält, ein Dihydrocarbylzinnoxid und (i) eine Carbonsäure, (ii) eine Verbindung mit wenigstens einer Carboxylat-Komponente, die - wenn sie Hitze und/oder Feuchtigkeit ausgesetzt wird - eine Carbonsäure bilden kann oder (iii) Mischungen von diesen, umfaßt.
- 30 18. Zusammensetzung nach Anspruch 17, worin das Copolymer auf einem oder mehreren α -olefin-Comonomer(en) und einem oder mehreren Alkenylalkoxysilan-Comonomer(en) basiert und ein Ethylen/Vinyltrimethoxysilan-Copolymer ist.
- 35 19. Zusammensetzung nach Anspruch 17, worin das Copolymer ein Homopolymer mit aufgepfropftem Silan oder ein Copolymer eines Olefins und eines Silans ist.
- 40 20. Zusammensetzung nach wenigstens einem der Ansprüche 17-19, worin das Dihydrocarbylzinnoxid die Formel R_2SnO aufweist, worin R eine Alkyl- oder Arylgruppe ist und R jeweils gleich oder verschieden sein kann.
21. Zusammensetzung nach wenigstens einem der Ansprüche 17-20, worin eine Carbonsäure oder ein organisches Säureanhydrid anwesend ist.
- 45 22. Zusammensetzung nach wenigstens einem der Ansprüche 17-20, worin eine Verbindung mit 1 bis 30 Kohlenstoffatomen und wenigstens eine Carboxylat-Komponente, die eine Carbonsäure bilden kann, wenn sie Hitze und/oder Feuchtigkeit ausgesetzt wird, anwesend ist.
- 50 23. Zusammensetzung nach wenigstens einem der Ansprüche 17-20, worin ein Homopolymer oder Copolymer mit wenigstens einer Carboxylat-Komponente anwesend ist.

Revendications

- 55 1. Procédé de réticulation, comprenant les étapes suivantes :
 - (a) le mélange, dans une zone de traitement, d'un copolymère contenant au moins un groupement silane hydrolysable ; d'un oxyde de dihydrocarbylétain ; et



- (i) d'un acide carboxylique,
- (ii) d'un composé portant au moins un groupement carboxylate, qui est capable de former un acide carboxylique lorsqu'il est soumis à de la chaleur et/ou de l'humidité, ou
- (iii) d'un de leurs mélanges,

sous réserve que :

(A) dans le cas où le constituant (ii) est présent, les conditions dans la zone de traitement soient telles que le groupement carboxylate forme un acide carboxylique ;

(B) le temps de séjour du mélange dans la zone de traitement soit suffisant pour achever au moins partiellement le traitement du copolymère, mais soit suffisamment bref pour éviter pratiquement une réaction de l'acide carboxylique avec l'oxyde de dihydrocarbylétain ; et

(b) le passage du mélange de l'étape (a) dans une zone de réticulation dans des conditions de réaction telles que l'acide carboxylique réagisse avec l'oxyde de dihydrocarbylétain en formant un carboxylate de dihydrocarbylétain, ladite zone de réticulation ayant une teneur en humidité suffisante pour provoquer la réticulation du copolymère hydrolysable en présence du carboxylate de dihydrocarbylétain.

2. Procédé suivant la revendication 1, dans lequel le copolymère est basé sur un ou plusieurs comonomères alpha-oléfiniques et sur un ou plusieurs comonomères alcénylalkoxysilane et est un copolymère éthylène/vinyltriméthoxysilane.

3. Procédé suivant la revendication 1, dans lequel le copolymère est un homopolymère ou copolymère greffé avec un silane ou bien un copolymère d'une oléfine et d'un silane.

4. Procédé suivant au moins une des revendications 1 à 3, dans lequel l'oxyde de dihydrocarbylétain répond à la formule R_2SnO dans laquelle R représente un radical alkyle ou aryle, les groupes R pouvant être identiques ou différents.

5. Procédé suivant au moins une des revendications 1 à 4, dans lequel un acide carboxylique ou un anhydride d'acide organique est présent.

6. Procédé suivant au moins une des revendications 1 à 4, dans lequel un composé ayant 1 à 30 atomes de carbone et au moins un groupement carboxylate, qui est capable de former un acide carboxylique lorsqu'il est soumis à de la chaleur et/ou de l'humidité, est présent.

7. Procédé suivant au moins une des revendications 1 à 6, dans lequel le temps de séjour dans la zone de traitement est compris dans l'intervalle de 20 à 2000 secondes.

8. Procédé suivant au moins une des revendications 1 à 7, dans lequel la température dans la zone de traitement est comprise dans l'intervalle de 20 °C à 350 °C.

9. Procédé suivant au moins une des revendications 1 à 8, dans lequel la zone de traitement est une zone d'extrusion.

10. Procédé suivant au moins une des revendications 1 à 9, dans lequel la température de la zone de réticulation est comprise dans l'intervalle de 20 °C à 200 °C.

11. Procédé suivant au moins une des revendications 1 à 4 et 7 à 10, dans lequel un homopolymère ou copolymère portant au moins un groupe carboxylate est présent.

12. Composition apte à fournir un catalyseur de condensation de silanol, comprenant :

(i) un oxyde de dihydrocarbylétain ; et

(ii) un acide carboxylique ; un composé possédant au moins un groupement carboxylate, qui est capable de former un acide carboxylique lorsqu'il est soumis à de la chaleur et/ou de l'humidité ; ou un de leurs mélanges.

13. Composition suivant la revendication 12, dans lequel l'oxyde de dihydrocarbylétain répond à la formule R_2SnO dans laquelle R représente un radical alkyle ou aryle, les groupes R pouvant être identiques ou différents.



14. Composition suivant au moins une des revendications 12 et 13, dans lequel un acide carboxylique ou un anhydride d'acide organique est présent.
- 5 15. Composition suivant au moins une des revendications 12 et 13, dans lequel un composé ayant 1 à 30 atomes de carbone et au moins un groupement carboxylate, qui est capable de former un acide carboxylique lorsqu'il est soumis à de la chaleur et/ou de l'humidité, est présent.
16. Composition suivant au moins une des revendications 12 et 13, dans lequel un homopolymère ou copolymère portant au moins un groupement carboxylate est présent.
- 10 17. Composition comprenant un copolymère contenant au moins un groupement silane hydrolysable ; un oxyde de dihydrocarbylétain ; et (i) un acide carboxylique, (ii) un composé portant au moins un groupement carboxylate, qui est capable de former un acide carboxylique lorsqu'il est soumis à de la chaleur et/ou de l'humidité, ou (iii) un de leurs mélanges.
- 15 18. Composition suivant la revendication 17, dans laquelle le copolymère est à base d'un ou plusieurs comonomères alpha-oléfiniques et d'un ou plusieurs comonomères alcénylalkoxysilane et est un copolymère éthylène/vinyltriméthoxysilane.
- 20 19. Composition suivant la revendication 17, dans laquelle le copolymère est un homopolymère ou copolymère greffé avec un silane ou bien un copolymère d'une oléfine et d'un silane.
- 25 20. Composition suivant au moins une des revendications 17 à 19, dans laquelle l'oxyde de dihydrocarbylétain répond à la formule R_2R_nO dans laquelle R représente un radical alkyle ou aryle, les groupes R pouvant être identiques ou différents.
21. Composition suivant au moins une des revendications 17 à 20, dans laquelle un acide carboxylique ou un anhydride d'acide organique est présent.
- 30 22. Composition suivant au moins une des revendications 17 à 20, dans laquelle un composé ayant 1 à 30 atomes de carbone et portant au moins un groupement carboxylate, qui est capable de former un acide carboxylique lorsqu'il est soumis à de la chaleur et/ou de l'humidité, est présent.
- 35 23. Composition suivant au moins une des revendications 17 à 20, dans laquelle un homopolymère ou copolymère portant au moins un groupe carboxylate est présent.
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