

Description**Field of the Invention**

6 The present invention relates to polyolefins. In another aspect the invention relates to polyolefins containing starch. In still yet another aspect the present invention relates to catalyst systems for the polymerization of olefins.

Background of the Invention

10 In view of the large number of products that are now being produced from polymers, there has developed an interest in producing some polymers that can be easily disintegrated or degraded to aid in the waste disposal of the products.

One approach that has been taken in the past has been the formation of polymer/starch composites. 15 The presence of starch in the composites makes the products biodegradable, i.e. the products disintegrate into less bulky materials more readily due to the action of living organisms such as bacteria and fungi upon the starch.

One method which has been used in the past to make such polymer/starch composites has been the blending of the starch with molten polymer, for example in an extruder or mixer. This technique in many 20 cases involves first pretreating the starch to make it more compatible with the polymer. In some cases a prodegradant such as an organometallic compound is also added to the polymer. As the starch is biodegraded the article prepared from such a polymer loses its physical integrity. The article simply falls apart leaving material that is less bulky. When a prodegradant is employed, oxidation of the remaining polymer can result in additional disintegration. The preparation of such polymer/starch composites by 25 blending is difficult and has often been found to be destructive to both the equipment employed and the polymer properties.

Another technique of preparing polymer/starch composites has involved gelling the starch in water and mixing the resulting product with molten polyolefin. This technique often results in a more homogeneous mixture but can result in composites having less than desirable physical properties.

30 Still another technique that has been proposed for preparing polymer/starch composites involves actually forming the polymer in the presence of starch using soluble transition metal catalysts. Such techniques are disclosed in U.S. Patent No. 3,704,271 and U.S. Patent No. 4,431,788. One of the drawbacks of such processes is that the starch has an adverse effect upon the activity of catalysts of the type disclosed in those patents. As a result, it will be noted that the polymer/starch composites disclosed in 35 those two patents do not contain large amounts of polymer. For example, those two patents do not indicate that such processes would be capable of producing polymer/starch composites which contain at least 80 wt. % or more of polymer.

Since the polymer/starch composites of those two aforementioned patents have relatively large amounts of starch there is obviously a limitation on the extent to which the desirable properties of the polyolefin can 40 be carried forward into the composite. An object of the present invention is to provide a method in which a polymer/starch composite can be prepared which contains a more substantial amount of polymer.

Another object of the present invention is to provide a method for promoting the activity of certain highly active particulate olefin polymerization catalysts.

Summary of the Invention

45 In accordance with the present invention, a process is provided for preparing a polymer/starch composite and polymer containing starch, respectively, comprising polymerizing at least one olefin under suitable polymerization conditions in the presence of (a) particles of starch, (b) an organometallic cocatalyst, 50 and (c) a particulate olefin polymerization catalyst comprising a transition metal.

Another aspect of the present invention involves the discovery that small amounts of starch can actually improve the activity of a highly active particulate olefin polymerization catalyst.

Detailed Description of the Invention

55 Starch is a naturally occurring polymer isolated from corn, lignin, potato, rice, etc. and is made of repeating amylose units. Each amylose unit contains 3-OH groups. Starch has been referred to as a high polymeric carbohydrate composed of α -glucopyranose units joined together by α -1,4-glycosidic linkages. A

further description of starch is provided in the publication entitled "Starch" by Whistler and Paschall, Vols. I and II (1965 and 1967). The term "starches" as used herein is intended to include all types of starches as well as chemically and/or physically modified starches and starch degradation products such as starch hydrolyzates including starch saccharification products. Granular cereal starches, especially cornstarch, or root or tuber starches, especially potato starch, or modified degraded starches are generally preferred. The terms "modified starch" and "starch degradation products" include for example pregelatinized starches (cold swelling starch), acid modified starches, oxidized starches, slightly crosslinked starches, starch ethers, starch esters, dialdehyde starches, and degradation products of starch hydrolyzed products and dextrans.

If a starch contains an excess amount of water it has been found that the water can totally poison the transition metal containing catalyst. Accordingly it is generally preferred that the starch be dried to a sufficient level of moisture content. Typically this would involve drying the starch so it has a water content of less than 7 wt. % and more preferably less than 1 wt. %. The size of the starch particles can vary widely. Large and small particles can be employed depending on the type of starch employed, the desired results, and the ultimate use. In general, it is desirable to employ small discrete particles of starch, for example particles of from 0.05 to 100 microns, more preferably 1 to 50 microns and still more preferably 1.5 to 25 microns.

The present invention is considered applicable to any particulate solid olefin polymerization catalysts comprising a transition metal. Typical such transition metal catalysts are solids containing Group IVB through VIII metals, e.g. titanium, zirconium, hafnium, thorium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, and iron. The currently most preferred catalysts for polymerizing the olefins in accordance with the present invention are those which contain titanium, vanadium, or mixtures thereof. A further preferred olefin polymerization catalyst comprises titanium and magnesium. Particularly, said catalyst is prepared by a process involving forming a solution from titanium tetraethoxide and magnesium dichloride, reacting said solution with an organoaluminum halide to obtain a precipitate, and contacting the resulting precipitate with titanium tetrachloride. Some of the more specific particulate high activity olefin polymerization catalysts which are useful in the present invention include those disclosed in U.S. Patent Nos. 4,363,746; 4,325,837; 4,326,988; 4,397,763; 4,394,291; 4,477,588; 4,555,496; 4,562,168; 4,107,414; 4,391,736; 4,384,982; and 4,514,514.

The organometallic cocatalysts suitable for use in accordance with the present invention are selected from organometallic compounds in which the metal is selected from the metals of Groups I to III of the Periodic Table. Some typical examples include lithium alkyls, Grignard reagents, dialkyl magnesium compounds, dialkyl zinc compounds, and organoaluminum compounds. Some typical organoaluminum compounds include hydrocarbylaluminum hydrides, trihydrocarbylaluminum, dihydrocarbylaluminum monohalides, monohydrocarbylaluminum dihalides, and hydrocarbylaluminum sesquihalides. Some preferred organoaluminum compounds can be represented by the formulas R_3Al , R_2AlX , $RAlX_2$, and $R_3Al_2X_3$, respectively, wherein each R is individually selected from hydrocarbyl radicals containing from 1 to 20 carbon atoms per radical and can be the same or different and each X is a halogen atom and can be the same or different. More preferred are compounds of the formula R_nAlX_{3-n} , wherein R is an alkyl or aryl group, n is a number in the range of 1 to 3, and X is a halogen. Particularly the organoaluminum cocatalyst is selected from trialkylaluminum compounds in which each alkyl group has from 1 to 4 carbon atoms. Some specific examples of such organoaluminum compounds include trimethylaluminum, triethylaluminum, triisopropylaluminum, tridecylaluminum, triicosylaluminum, tricyclohexylaluminum, tri-phenylaluminum, 2-methylpentyl-diethylaluminum, trisoprenylaluminum, methylaluminum dibromide, ethylaluminum dichloride, ethylaluminum diiodide, isobutylaluminum dichloride, ethylaluminum diiodide, isobutylaluminum dichloride, dodecylaluminum dibromide, dimethylaluminum bromide, methyl-n-propylaluminum bromide, diphenylaluminum chloride, dicyclohexylaluminum bromide, methylaluminum sesquibromide and ethylaluminum sesquichloride. The currently preferred cocatalysts for use with titanium-containing catalysts are the hydrocarbyl aluminum compounds such as triethylaluminum or trimethylaluminum.

A process for improving the activity of a particulate olefin polymerization catalyst which comprises a transition metal, comprises contacting said catalyst with an organometallic cocatalyst and starch wherein said cocatalyst is present when said catalyst is first contacted with said starch.

In order to obtain maximum catalyst activity it is preferred that the organoaluminum compound be present when the particulate catalyst is first brought into contact with the starch. Accordingly it is within the scope of the present invention to combine the starch and the cocatalyst and then combine that mixture with the catalyst. Alternatively it is within the scope of the present invention to combine the catalyst and cocatalyst and then combine that mixture with the starch. Generally the catalyst, cocatalyst, and starch are combined together in a suitable diluent. Diluents of the type generally used in the past with such particulate polymerization catalysts are considered to be suitable. Examples include substantially dry hydrocarbons,

such as isobutane, heptane, hexane, pentane, methylcyclohexane, toluene and xylene.

The polymerizable olefins which can be employed in this process include any of those which can be polymerized with the particulate catalyst of the type specified. Mono-1-olefins having 2 to 12 carbon atoms per molecule are generally most preferred. Such mono-1-olefins can be copolymerized with other olefins and/or with other smaller amounts of other ethylenically unsaturated monomers, such as 1,3-butadiene, isoprene, 1,3-pentadiene, styrene, α -methylstyrene, and similar ethylenically unsaturated monomers which do not impair the catalyst.

The amount of starch, catalyst, and cocatalyst employed can vary over a wide range depending upon the particular results desired. In preparing polymers which can be viewed as being particularly biodegradable it is generally preferred to use starch in an amount sufficient to insure that the resulting polymer/starch composite will contain 1 to 40 wt. % starch. A currently more preferred range is 3 to 15 wt. % starch. For the amounts of catalyst and cocatalyst to be employed reference can be made to the amounts that have been used in the past when such catalysts were used for polymerizing olefins in the absence of starch. A preferred molar ratio of the cocatalyst to titanium in the catalyst is in the range of 10:1 to 350:1. Particularly good results have been obtained using triethylaluminum cocatalyst in combination with a catalyst of the type disclosed in U.S. 4,326,988 or 4,325,837, typically the molar ratio of the triethylaluminum cocatalyst to Ti is in the range of 10/1 to 350/1. The ratio of starch to titanium can vary widely. Preferably it is such that the catalyst is more active than if the starch were not employed. Typically the molar ratio of starch to titanium would be in the range of 111 to 4000/1 or higher, preferably in the range of 250:1 to 4000:1, particularly in the range of 250:1 to 2000:1.

One of the features of the present invention is that, at lower levels the starch molecule has been found to actually promote the activity of the particulate catalyst. Further, if the amount of starch employed is such that it has an adverse effect upon the productivity of the catalyst it has been found that one can counteract that affect by further increasing the amount of cocatalyst employed.

The polymer/starch composite produced in accordance with this invention can have a variety of uses depending upon the physical properties of the particular composite. Preferably the polymer produced contains up to 20 weight percent starch. The composite containing at least 80 weight percent polymer, especially when the polymer is a polyolefin such as polyethylene or polypropylene, will generally be useful in preparing articles such as trash bags, shopping bags, 6-pack rings, and various types of bottles, containers, and wrappers. In a preferred embodiment the polymer as obtained is used for making shaped articles, preferably films and containers.

A further understanding of the present invention, its objects, and advantages will be provided by the following examples. In the examples unless indicated otherwise the starch was dried in vacuum at 110°C until a moisture analysis of approximately 0.5 % by weight was obtained.

Example I

A series of runs were conducted to determine the effect of the starch on the polymerization of ethylene with a catalyst sold by Catalyst Resources, Inc. which was prepared by a process of the general type disclosed in U.S. Patent Nos. 4,363,746; 4,325,837; and 4,326,988 and contained about 12 wt. % titanium. The catalyst is one which is prepared by forming a solution of titanium tetraethoxide and magnesium chloride and then precipitating a solid from that solution by the addition of ethylaluminum sesquichloride under conditions such that prepolymer is deposited upon the solid. The resulting solid is then contacted with titanium tetrachloride. Such catalysts generally contain 1 to 30 weight percent prepolymer, more typically 4 to 10 weight percent prepolymer. The cocatalyst is trialkylaluminum, preferably triethylaluminum. In this example a 15 wt. % solution of triethylaluminum in heptane was used as the cocatalyst. The hydrocarbon solvents employed were degassed and dried over activated alumina or molecular sieves before use. The catalyst and the starch were each individually slurried in cyclohexane so that they could be transferred using a syringe or through a valve and needle assembly. Ultrasound was used to ensure that the slurries remained uniform. The polymerization reactions were conducted in a 1-gallon stirred autoclave. The catalyst, cocatalyst, and starch were charged to a dry reactor under counterflow of ethylene at ambient temperature. In this example the catalyst and cocatalyst were brought into contact with each other before the catalyst was brought into contact with the starch. The reactor was sealed and ethylene flow was stopped. Isobutane was then added as reaction solvent. The reactor temperature was then increased to 90°C at which time hydrogen was added to provide a partial pressure of 0.42 MPa (47 psig). Ethylene was added to provide a partial pressure of 1.48 MPa (200 psig). The reaction temperature and ethylene pressure were maintained for 1 hour. After that the solvent was removed and the polymer was collected as a dry fluff. The polymerization variables and the results obtained are shown in Table I.

Table I
The effect of starch on the polymerization of ethylene.^a

Run	Et ₂ Al Conc.	Starch	Activity g PE/g XPF/h	Starch/Ti ^b	% Starch ^c	HL	HLMI	Density	GPC Analysis ^d	
									M _w	M _n
1 (control)	$1.7 \times 10^{-3} M$	0 g	25,000	0	0	0.60	21.2	0.9607	150	29.7
2	$1.7 \times 10^{-3} M$	1 g	27,000	250	0.4	0.56	18.0	0.9617	146	28.6
3	$1.7 \times 10^{-3} M$	2 g	30,000	500	0.7	0.47	14.9	0.9625	165	24.2
4	$1.7 \times 10^{-3} M$	4 g	30,000	1,000	1.3	0.27	9.4	0.9638	186	36.0
5	$1.7 \times 10^{-3} M$	8 g	24,000	2,000	3.3	0.39	14.1	0.9732	181	33.5
6	$1.7 \times 10^{-3} M$	16 g	11,000	4,000	12.6	0.17	5.4	(e)	206	30.6
7	$2.8 \times 10^{-3} M$	16 g	20,000	4,000	7.5	0.36	10.8	(e)	--	--
8	$3.9 \times 10^{-3} M$	16 g	33,000	4,000	4.6	0.56	17.8	0.9771	147	23.2

a) Conditions: 1-gal Autoclave reactor; iso-butane solvent (2 L); 1 hr; XPF catalyst (10 mg); AP(H₂)=0.42 MPa(47 psig); AP(C₂H₄)=1.48 MPa(200 psig).

b) Mole ratio based on the formula weight of starch.

c) Weight percent starch in product.

d) M_w = weight ave. mol. wt./10³; M_n = number ave. mol. wt./10³; HL = heterogeneity index (M_w/M_n).

e) Between 0.99 and 1.13 g/mL.

The data in Table I illustrates that at lower levels the presence of the starch actually improves the activity of the Catalyst Resources, Inc. catalyst. When no starch was added to the reactor, the productivity of the catalyst was 25,000 grams of polyethylene per gram of catalyst per hour. The addition of 1 gram of dried starch, i.e. a starch/titanium molar ratio of 250, caused the productivity to increase to 27,000 grams of polyethylene per gram of catalyst per hour. The productivity further increased to 30,000 grams of

polyethylene per gram of catalyst per hour for starch to titanium molar ratios of 500 and 1,000. The data reveals that once the starch to titanium ratio has been raised to about 2,000 the catalyst is no more active than when no starch was employed in a combination with a catalyst. The fact that the starch actually increases the activity of the catalyst is particularly surprising since each amylose group of the starch contains 3-OH groups which would have been expected to poison the catalyst.

The loss in productivity observed at high starch to titanium mole ratios is shown by the table to be reversible. Thus, while run 6 gives a productivity of only 11,000 grams of polyethylene per gram of catalyst per hour at a starch to titanium molar ratio of 4,000, by increasing the triethylaluminum the productivity can be raised again. By increasing the triethylaluminum from 1.7 to 2.8 to 3.9×10^{-3} M, the productivity improved from 11,000 to 20,000 to 33,000 grams of polyethylene per gram of catalyst per hour, respectively. In Runs 1-6 the molar ratio of aluminum/titanium, i.e. the gram atom ratio, was about 132/1. In Runs 7 and 8 the molar ratio of aluminum to titanium was about 220/1 and 307/1, respectively. It is believed that the starch and the catalyst solids are heterogeneously dispersed in the liquid medium whereas the triethylaluminum is in solution and is free to interact with either solid.

Run 8 demonstrates that it is possible to obtain high yields of polymer while at the same time producing a composite containing more than enough starch to be considered biodegradable.

Example II

This example is set forth to demonstrate the effects of charge order, starch content, moisture content in the starch, and comonomer on the polymerization. The catalyst and cocatalyst were the same as set forth in Example I. Runs 1-3 are the same as in Example I. In this example the phrase [Al/XPF] is intended to denote that the cocatalyst and the catalyst were combined together prior to contact with the starch. The phrase [Al/St] is intended to indicate that the cocatalyst and the starch were combined together before being contacted with the catalyst. Finally the phrase [XPF/St] is intended to indicate that the catalyst was combined with the starch prior to being combined with the cocatalyst.

The polymerizations were carried out using the same general conditions that were used in Example I.

Table II

The effects of charge order, starch, moisture content in starch, and comonomer on the starch induced increase in catalyst productivity.

Run	Charge Order ^b	Starch	H ₂ O	Hexene	Activity g PE/g XPF/h	HI	HLM	Density	GPC Analysis ^c		
									M _w	M _n	HI
1 (control)	Al/XPF	0 g	--	--	25,000	0.60	21.2	0.9607	150	29.7	5.1
2	[Al/XPF]St	1 g (potato)	0.50	--	27,000	0.56	18.0	0.9617	146	28.6	5.1
3	[Al/XPF]St	2 g (potato)	0.50	--	30,000	0.47	14.9	0.9625	165	24.2	6.8
9	[Al/St]XPF	1 g (potato)	0.50	--	28,000	0.54	18.8	0.9615	154	29.7	5.2
10	[Al/St]XPF	2 g (potato)	0.50	--	30,000	0.48	14.7	0.9624	160	29.3	5.4
11	Al[XPF/St]	2 g (potato)	0.50	--	6,600	0.29	10.3	0.9732	178	30.7	5.8
12	[Al/XPF]St	2 g (potato)	9.48	--	0	--	--	--	--	--	--
13	[Al/XPF]St	2 g (corn)	0.50	--	30,000	0.38	12.7	0.9623	161	29.4	5.5
14 (control)	Al/XPF	0 g	--	90 g	25,000	1.32	35.1	0.9501	117	26.9	4.3
15	[Al/XPF]St	2 g (potato)	0.50	90 g	28,000	2.00	53.1	0.9542	105	20.7	5.1

a) Conditions: 1-gal Autoclave reactor; iso-butane solvent (2L); 90°C; 1 hr; XPF catalyst (10 mg); 1.7×10^{-3} H

[Et, Al]; $\Delta P(H_2) = 0.42$ MPa (47 psig); $\Delta P(C_2H_6) = 1.48$ MPa (200 psig).

b) Al = Et, Al; St = starch; [] = reaction prior to reactor charge.

c) M_w = weight ave. mol. wt./10³; M_n = number ave. mol. wt./10³; HI = heterogeneity index (M_w/M_n).

X 0.42 MPa

The data in Table II shows that the order in which the three components, i.e. starch, catalyst, and cocatalyst, are added is important. When they are charged in the order of cocatalyst then starch then catalyst or in the order of cocatalyst then catalyst then starch good productivity was observed. If the catalyst and the starch were mixed prior to the addition of the cocatalyst, a drastic reduction in activity was

observed. It is believed that this may possibly be due to the water associated with the starch even though the amount of water is very low. It is considered that the cocatalyst in some way possibly acts as a scavenger for the water in the system. Run 12 shows that if the starch is not predried it completely poisons the catalyst. A comparison of Runs 10 and 13 shows that there is no detectable difference in productivity or polymer properties resulting from substituting dried cornstarch for dried potato starch. A comparison of Runs 14 and 15 shows that the addition of a comonomer into the polymerization also had no effect on the observed increase in activity which is provided by the starch.

Example III

Polymer/starch composites were prepared by using dry soluble starch and virgin polyethylene fluff by mixing in a Brabender Plasti-corder mixer (control run). The mixtures were made under nitrogen at 150 °C using a residence time of 30 minutes. The polymer/starch resins produced by blending were hot pressed into films. Similar films were prepared by hot pressing the polymer/starch composites which were produced by polymerizing ethylene in the presence of the starch in accordance with the present invention.

Both types of films were dipped into aqueous iodine solution so that the surface active starch particles could be readily observed and micrographs were taken. The film prepared from the polymer/starch composites prepared by polymerization compare quite well visually with films prepared from the polymer/starch prepared by physically blending (control run). The starch granules in both are homogeneously dispersed throughout the film matrix. The availability of the starch at the surface of the composites prepared by polymerization indicates that the process does not deny access to the starch by encapsulation.

Since the density of starch is approximately 1.3 grams/milliliter, the density of the polymer/starch blends should generally increase with increasing starch content. The data in Tables I and II indicate that such is observed. The densities of the polymer/starch composites prepared by polymerization and by physically blending are quite comparable. For instance the densities of resins containing 3.3% starch prepared by the two techniques were 0.9732 and 0.9729 grams/milliliters respectively.

Example IV (Comparative Example)

A few additional runs were made attempting to prepare polymer/starch composites but with liquid transition metal compounds rather than the particulate transition metal catalyst required by the present invention.

In these runs the transition metal compound catalyst was combined with a toluene solution of starch and trialkylaluminum cocatalyst. In one case the starch/cocatalyst solution was prepared using triethylaluminum (TEA) as the cocatalyst. That solution was about 1.1 molar aluminum. The other starch/cocatalyst solution was prepared using trimethylaluminum (TMA) as the cocatalyst and the solution was about 1.2 M aluminum.

In one of the polymerizations 5 milliliters of the starch/TMA solution, i.e. about 5.5 millimoles aluminum was combined with about 0.5 milliliters of a 0.01 M toluene solution of cyclopentadienylzirconium dichloride, i.e. about 0.05 millimole zirconium. The polymerization was conducted at 50 °C and 3.9 MPa (550 psig) ethylene for about 1 hour. About 2.86 grams of white polymer was recovered. This translated into a productivity of about 7,800 grams of polymer/gram Zr/hour.

In another polymerization about 5 milliliters of the starch/TEA solution, i.e. about 6 millimole of aluminum, was combined with about 1 milliliter of a 0.01 M cyclohexane solution of titanium tetrachloride, i.e. about 0.01 millimole titanium. Again the polymerization was conducted at about 50 °C and 3.9 MPa (550 psig) ethylene for about 1 hour. About 5.81 grams of white polymer was recovered. This translated into a productivity of about 13,000 grams of polymer/gram titanium/hour.

In still another polymerization 5 milliliters of the starch/TEA solution, i.e. about 6 millimoles of aluminum, was combined with 9 milliliters of the 0.01 M cyclohexane/titanium tetrachloride solution, i.e. about 0.09 millimoles titanium. The polymerization was again conducted at about 50 °C and 3.9 MPa (550 psig) ethylene. About 19.9 grams of white polymer was recovered. This translates into a productivity of about 4,700 grams of polymer per gram titanium per hour.

In contrast to these productivities of 5,000 to 13,000 grams of polymer/gram transition metal/hour, the inventive Runs 2-8 of Example I show productivities in the range of 93,000 to 300,000 grams polymer/gram transition metal/hour. This demonstrates that the present invention is capable of giving polymer/starch composites having much lower transition metal content than the polymer/starch composites prepared using the liquid transition metal compounds.

While the present invention has now been described in general terms and some specific examples have been given to illustrate the invention, it should be recognized that there are many variations and modifications can be made without departing from the spirit and scope of this invention.

5 Claims

1. A process for preparing a polymer containing starch including all types of starch as well as chemically and/or physically modified starches and starch degradation products such as starch hydrolyzates including starch saccharification products, characterized by polymerizing at least one olefin in the presence of particles of starch, an organometallic cocatalyst, and a particulate olefin polymerization catalyst comprising a transition metal.
2. The process of claim 1 wherein said organometallic cocatalyst is selected from compounds of the formula R_nAlX_{3-n} wherein R is an alkyl or aryl group, n is a number in the range of 1 to 3, and X is a halogen.
3. The process of claim 2 wherein said organoaluminum cocatalyst is selected from trialkylaluminum compounds in which each alkyl group has from 1 to 4 carbon atoms.
4. The process of claim 3 wherein said particulate olefin polymerization catalyst comprises titanium and magnesium.
5. The process of claim 4 wherein said particulate olefin polymerization catalyst is prepared by a process involving forming a solution from titanium tetraethoxide and magnesium dichloride, reacting said solution with an organoaluminum halide to obtain a precipitate, and contacting the resulting precipitate with titanium tetrachloride.
6. The process of claim 5 wherein said solution is reacted with ethylaluminum sesquichloride to obtain said precipitate.
7. The process of claim 6 wherein said particulate olefin polymerization catalyst contains from 1 to 30 weight percent polyethylene prepolymer.
8. The process of claim 7 wherein said cocatalyst is trialkylaluminum, preferably triethylaluminum.
9. The process of any of claims 4-8 wherein the molar ratio of starch to titanium is in the range of 250:1 to 4000:1.
10. The process of claim 9 wherein the molar ratio of starch to titanium is in the range of 250:1 to 2000:1.
11. The process of claim 9 or 10 wherein the molar ratio of the cocatalyst to titanium in the catalyst is in the range of 10:1 to 350:1.
12. The process of any of the preceding claims producing a polymer containing up to 20 weight percent starch.
13. The process of any of the preceding claims wherein said olefin is ethylene.
14. Process for making shaped articles, preferably films and containers, wherein a polymer is prepared according to any of the claims 1-13 and thereafter the polymer is formed into said shaped articles.
15. A process for improving the activity of a particulate olefin polymerization catalyst which comprises a transition metal, characterized by contacting said catalyst with an organometallic cocatalyst and starch including all types of starch as well as chemically and/or physically modified starches and starch degradation products such as starch hydrolyzates including starch saccharification products, wherein said cocatalyst is present when said catalyst is first contacted with said starch.
16. The process of claim 15 wherein said catalyst comprises titanium and magnesium.

While the present invention has now been described in general terms and some specific examples have been given to illustrate the invention, it should be recognized that there are many variations and modifications can be made without departing from the spirit and scope of this invention.

5 Claims

1. A process for preparing a polymer containing starch including all types of starch as well as chemically and/or physically modified starches and starch degradation products such as starch hydrolyzates including starch saccharification products, characterized by polymerizing at least one olefin in the presence of particles of starch, an organometallic cocatalyst, and a particulate olefin polymerization catalyst comprising a transition metal.
2. The process of claim 1 wherein said organometallic cocatalyst is selected from compounds of the formula R_nAlX_{3-n} wherein R is an alkyl or aryl group, n is a number in the range of 1 to 3, and X is a halogen.
3. The process of claim 2 wherein said organoaluminum cocatalyst is selected from trialkylaluminum compounds in which each alkyl group has from 1 to 4 carbon atoms.
4. The process of claim 3 wherein said particulate olefin polymerization catalyst comprises titanium and magnesium.
5. The process of claim 4 wherein said particulate olefin polymerization catalyst is prepared by a process involving forming a solution from titanium tetraethoxide and magnesium dichloride, reacting said solution with an organoaluminum halide to obtain a precipitate, and contacting the resulting precipitate with titanium tetrachloride.
6. The process of claim 5 wherein said solution is reacted with ethylaluminum sesquichloride to obtain said precipitate.
7. The process of claim 6 wherein said particulate olefin polymerization catalyst contains from 1 to 30 weight percent polyethylene prepolymer.
8. The process of claim 7 wherein said cocatalyst is trialkylaluminum, preferably triethylaluminum.
9. The process of any of claims 4-8 wherein the molar ratio of starch to titanium is in the range of 250:1 to 4000:1.
10. The process of claim 9 wherein the molar ratio of starch to titanium is in the range of 250:1 to 2000:1.
11. The process of claim 9 or 10 wherein the molar ratio of the cocatalyst to titanium in the catalyst is in the range of 10:1 to 350:1.
12. The process of any of the preceding claims producing a polymer containing up to 20 weight percent starch.
13. The process of any of the preceding claims wherein said olefin is ethylene.
14. Process for making shaped articles, preferably films and containers, wherein a polymer is prepared according to any of the claims 1-13 and thereafter the polymer is formed into said shaped articles.
15. A process for improving the activity of a particulate olefin polymerization catalyst which comprises a transition metal, characterized by contacting said catalyst with an organometallic cocatalyst and starch including all types of starch as well as chemically and/or physically modified starches and starch degradation products such as starch hydrolyzates including starch saccharification products, wherein said cocatalyst is present when said catalyst is first contacted with said starch.
16. The process of claim 15 wherein said catalyst comprises titanium and magnesium.



17. The process of claim 16 wherein said catalyst is prepared by a process as defined in claim 5 or 8.

Patentansprüche

- 5 1. Verfahren zur Herstellung eines Polymeren mit einem Gehalt an Stärke unter Einschluß von sämtlichen Stärketypen sowie von chemisch und/oder physikalisch modifizierten Stärken und Stärkeabbauprodukten, wie Stärkehydrolysaten, einschließlich Stärkeverzuckerungsprodukten, dadurch gekennzeichnet, daß man mindestens ein Olefin in Gegenwart von Stärketeilchen, eines Organometall-Cokatalysators und eines teilchenförmigen Olefin-Polymerisationskatalysators mit einem Gehalt an einem Übergangsmetall polymerisiert.
- 10 2. Verfahren nach Anspruch 1, wobei der Organometall-Cokatalysator unter Verbindungen der Formel R_nAlX_{3-n} ausgewählt wird, wobei R einen Alkyl- oder Arylrest bedeutet, n eine Zahl im Bereich von 1 bis 3 ist und X ein Halogenatom bedeutet.
- 15 3. Verfahren nach Anspruch 2, wobei der Organoaluminium-Cokatalysator unter Trialkylaluminium-Verbindungen ausgewählt wird, wobei die einzelnen Alkylreste 1 bis 4 Kohlenstoffatome aufweisen.
- 20 4. Verfahren nach Anspruch 3, wobei der teilchenförmige Olefin-Polymerisationskatalysator Titan und Magnesium enthält.
- 25 5. Verfahren nach Anspruch 4, wobei der teilchenförmige Olefin-Polymerisationskatalysator nach einem Verfahren hergestellt wird, daß die Bildung einer Lösung aus Titanetraethoxid und Magnesiumdichlorid, die Umsetzung der Lösung mit einem Organoaluminiumhalogenid unter Bildung eines Niederschlags und das Kontaktieren des gebildeten Niederschlags mit Titanetrachlorid umfaßt.
- 30 6. Verfahren nach Anspruch 5, wobei die Lösung mit Ethylaluminiumsesquichlorid unter Bildung des Niederschlags umgesetzt wird.
- 35 7. Verfahren nach Anspruch 6, wobei der teilchenförmige Olefin-Polymerisationskatalysator 1-30 Gew.-% Polyethylen-Prepolymeres enthält.
8. Verfahren nach Anspruch 7, wobei es sich beim Cokatalysator um Trialkylaluminium, vorzugsweise Triethylaluminium, handelt.
- 40 9. Verfahren nach einem der Ansprüche 4-8, wobei das Molverhältnis von Stärke zu Titan im Bereich von 250:1 bis 4000:1 liegt.
10. Verfahren nach Anspruch 9, wobei das Molverhältnis von Stärke zu Titan im Bereich von 250:1 bis 2000:1 liegt.
- 45 11. Verfahren nach Anspruch 9 oder 10, wobei das Molverhältnis des Cokatalysators zu Titan im Katalysator im Bereich von 10:1 bis 350:1 liegt.
- 50 12. Verfahren nach einem der vorstehenden Ansprüche zur Herstellung eines Polymeren mit einem Gehalt an bis zu 20 Gew.-% Stärke.
13. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß es sich beim Olefin um Ethylen handelt.
- 55 14. Verfahren zur Herstellung von Formkörpern, vorzugsweise von Filmen und Behältern, wobei ein Polymeres nach einem der Ansprüche 1 bis 13 hergestellt wird und anschließend zu den Formkörpern verformt wird.
15. Verfahren zur Verbesserung der Aktivität eines ein Übergangsmetall enthaltenden, teilchenförmigen Olefin-Polymerisationskatalysators, dadurch gekennzeichnet, daß man den Katalysator mit einem Organometall-Cokatalysator und mit Stärke unter Einschluß von sämtlichen Stärketypen sowie chemisch und/oder physikalisch modifizierten Stärken und Stärkeabbauprodukten, wie Stärkehydrolysaten, ein-



schließlich Stärkeverzuckerungsprodukten, in Kontakt bringt, wobei der Cokatalysator vorhanden ist, wenn der Katalysator erstmals mit der Stärke in Kontakt kommt.

16. Verfahren nach Anspruch 15, wobei der Katalysator Titan und Magnesium enthält.

17. Verfahren nach Anspruch 16, wobei der Katalysator nach einem in Anspruch 5 oder 8 definierten Verfahren hergestellt worden ist.

Revendications

1. Un procédé pour préparer un polymère contenant de l'amidon, y compris tous les types d'amidon ainsi que les amidons chimiquement et/ou physiquement modifiés et les produits de dégradation de l'amidon tels que les hydrolysats d'amidon y compris les produits de saccharification de l'amidon, caractérisé en ce que l'on polymérise au moins une oléfine en présence de particules d'amidon, d'un cocatalyseur organométallique et d'un catalyseur particulaire de polymérisation des oléfines comportant un métal de transition.

2. Le processus de la revendication 1, dans lequel le cocatalyseur organométallique est choisi parmi les composés de formule R_nAlX_{3-n} , où R est un groupe alkyle ou aryle, n est un nombre allant de 1 à 3 et X est un halogène.

3. Le processus de la revendication 2, dans lequel le cocatalyseur organoaluminé est choisi parmi les composés de trialkylaluminium où chaque groupe alkyle comporte de 1 à 4 atomes de carbone.

4. Le processus de la revendication 3, dans lequel le catalyseur particulaire de polymérisation des oléfines comprend du titane et du magnésium.

5. Le processus de la revendication 4, dans lequel le catalyseur particulaire de polymérisation des oléfines est préparé par un procédé impliquant la formation d'une solution à partir de tétraéthoxyde de titane et de dichlorure de magnésium, la mise en réaction de cette solution avec un halogénure organoaluminé pour obtenir un précipité et la mise en contact du précipité résultant avec du tétrachlorure de titane.

6. Le processus de la revendication 5, dans lequel la solution est mise en réaction avec du sesquichlorure d'éthylaluminium pour obtenir le précipité.

7. Le processus de la revendication 6, dans lequel le catalyseur particulaire de polymérisation des oléfines contient de 1 à 30 % en poids de prépolymère de polyéthylène.

8. Le processus de la revendication 7, dans lequel le cocatalyseur est un trialkylaluminium, de préférence le triéthylaluminium.

9. Le processus de l'une des revendications 4 à 8, dans lequel le rapport molaire de l'amidon au titane est compris dans la plage allant de 250:1 à 4 000:1.

10. Le processus de la revendication 9, dans lequel le rapport molaire de l'amidon au titane est compris dans la plage allant de 250:1 à 2 000:1.

11. Le processus de la revendication 9 ou 10, dans lequel le rapport molaire du cocatalyseur au titane dans le catalyseur est compris dans la plage allant de 10:1 à 350:1.

12. Le processus de l'une des revendications précédentes, qui produit un polymère contenant jusqu'à 20 % en poids d'amidon.

13. Le processus de l'une des revendications précédentes, dans lequel ladite oléfine est l'éthylène.

14. Processus de fabrication d'articles conformés, de préférence de films et de récipients, dans lequel on prépare un polymère selon l'une des revendications 1 à 13 puis on forme le polymère pour donner



ledit article conformé.

15. Un processus pour améliorer l'activité d'un catalyseur particulaire de polymérisation des oléfines qui comprend un métal de transition, caractérisé par la mise en contact de ce catalyseur avec un cocatalyseur organométallique et de l'amidon, y compris tous les types d'amidon ainsi que les amidons chimiquement et/ou physiquement modifiés et les produits de dégradation de l'amidon tels que les hydrolysats de l'amidon y compris les produits de saccharification de l'amidon, le cocatalyseur étant présent lorsque le catalyseur est mis en premier en contact avec l'amidon.

16. Le processus de la revendication 15, dans lequel le catalyseur comprend du titane et du magnésium.

17. Le processus de la revendication 16, dans lequel le catalyseur est préparé par un processus tel que défini dans les revendications 5 ou 8.

