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POLYPROPYLENE

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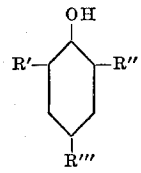
No Drawing. Original application July 20, 1970, Ser. No. 56,659, now Patent No. 3,723,402, dated Mar. 27, 1973. Divided and this application Apr. 26, 1972, Ser. No. 247,656

Int. Cl. C08f 29/02

U.S. Cl. 264—211 4 Claims

ABSTRACT OF THE DISCLOSURE

The production of shaped polypropylene articles by melt extrusion of thermally degraded isotactic polypropylene can be carried forward at lower temperatures than were heretofore required by incorporating in the polypropylene prior to thermal degradation thereof, from 0.01 to 5 percent by weight, based on the weight of the polypropylene, or (a) a silane or siloxane having at least one $\equiv SiCH_2NR_2$ group where R is hydrogen or a hydrocarbon radical, (b) an organosilicon compound of the general formula



wherein R', R'' and R''' are each a hydrogen atom, an alkyl radical of 1–18 carbon atoms, an aralkyl radical of less than 19 carbon atoms or Q_3SiCH_2— where Q is alkyl, alkenyl or aryl of less than 19 carbon atoms, at least one R', R'' or R''' being Q_3SiCH_2—, or (c) mixture of (a) and (b).

This is a division, of application Ser. No. 56,659, filed July 20, 1970.

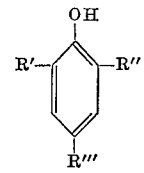
This invention relates to improvements in relating to the melt extrusion of polypropylene and relates in particular to the melt spinning of polypropylene having a stereoregular structure.

It is well-known to prepare shaped articles by the melt extrusion of polypropylene. In particular it is known to prepare filaments of polypropylene by the melt spinning of crystalline, that is isotactic, polypropylene. In order to improve the tensile characteristics of the filament it is usual to subject the filament after melt spinning and quenching to drawing at elevated temperatures to orient the filament. It is also known that filaments of polypropylene having high tenacities may be produced by degrading the polypropylene by drastic thermal treatment, that is by exposure to temperatures of about 260° C. or above, prior to extrusion through the filament-forming orifice. The use of such high temperatures however introduces considerable processing difficulties since they approximate closely to the temperature at which the polypropylene chars and is rendered unsuitable for use. We have now discovered that certain organosilicon compounds have the effect of lowering the temperature at which a given degree of degradation occurs in polypropylene, thereby permitting the melt spinning of polypropylene into high tenacity fibres and filaments under less severe thermal conditions.

It is an object of this invention to introduce an improved method for melt extruding polypropylene. Another object is a method for melt extrusion of polypropylene wherein the required polypropylene degradations can be carried forward at a lower temperature than heretofore

required. Other objects and advantages of the invention are detailed in, or will be apparent from the disclosure and claims following.

This invention provides a process for the production of a shaped article by the melt extrusion of thermally-degraded isotactic polypropylene wherein the thermal degradation of the polypropylene is carried out in the presence of from 0.01 to 5% by weight based on the weight of polypropylene, of (a) an organosilicon compound which is an organosilane or organosiloxane having at least one silicon-bonded group of the general formula $—CH_2NR_2$ wherein each R represents a hydrogen atom or a monovalent hydrocarbon radical, (b) an organosilicon compound of the general formula



wherein R', R'' and R''' each represents a hydrogen atom, an alkyl radical having up to 18 carbon atoms, an aralkyl radical having up to 18 carbon atoms or a Q_3SiCH^2- group, wherein Q represents an alkyl, alkenyl or aryl radical having up to 18 carbon atoms, at least one of R', R'' and R''' being the Q_3SiCH_2—group, or (c) mixtures of (a) and (b).

In a further aspect the invention also includes a thermally-degradable composition comprising isotactic polypropylene and from 0.01 to 5% by weight of one or more of the specified organosilicon compounds (a) and (b).

As the organosilicon compound there can be employed any organosilane or organosiloxane containing the grouping $-CH_2NR_2$ bonded to at least one silicon atom. In said group, each R represents a hydrogen a hydrogen atom or monovalent hydrocarbon radical, for example the methyl, ethyl, t-butyl, hexyl, octadecyl, vinyl, phenyl, tolyl or benzyl radical. Preferred as the organosilicon compounds (a) are the organosilanes and the substantially linear polydiorganosiloxanes of low molecular weight, for example the di-, tri- and tetrasiloxanes having therein the specified $-CH_2NR_2$ groups, any other substituents on the silicon atoms being monovalent hydrocarbon or halohydrocarbon radicals and oxygen atoms present as siloxane (Si O Si) linkages.

Most preferably the organosilicon compounds (a) have the general formula

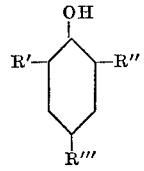
$$A_nSi[CH_2NR_2]_{4-n}$$

wherein each A represents a radical having from 1 to 18 carbon atoms and is a monovalent hydrocarbon radical, an alkoxy radical, an alkoxyalkyl radical, an alkoxyaryl radical or an alkoxyalkoxy radical, *n* is 0, 1, 2 or 3 but is preferbly 3 and R is as hereinabove defined. As the A radicals in the general formula there may be present one or more of alkyl radicals, for example methyl, ethyl, propyl, butyl, decyl, and octadecyl, alkenyl radicals such as vinyl and allyl and aryl radicals such as phenyl, naphthyl, tolyl and benzyl. The A radicals can so comprise alkoxy radicals, for example methoxy, ethoxy and propoxy radicals for example radicals and alkoxyalkyl, alkoxyaryl and alkoxyalkoxy radicals for example methoxyethyl, ethoxypropyl, methoxyphenyl and methoxyethoxy radicals. Preferably however A is an alkyl radical having less than 9 carbon atoms or a phenyl radical.

For optimum results it is believed that the organosilicon compounds should be compatible, at least to some extent, with the isotactic polypropylene and some adjustment of the compatibility of the particular type of compound chosen can be achieved by variation of the A radicals.

Some of the organosilicon compounds (a) employed in the process of this invention are well-known materials and others can be prepared according to the method described in U.S. Pat. No. 3,504,007.

The organosilicon compounds (b) which can be employed to assist in the degradation of polypropylene according to this invention may be broadly termed as silyl-substituted phenols. They are more particularly described by the general formula



wherein R', R'' and R''' each represents a hydrogen atom or an alkyl or aralkyl radical having up to 18 carbon atoms, for example the methyl, ethyl, propyl, t-butyl, heyl, dodecyl, benzyl or 2-phenylethyl radical, or a Q_3SiCH_2— group wherein each Q represents an alkyl, alkenyl or aryl radical having having up to 18 carbon atoms. At least one of R', R'' and R''' should be the Q_3SiCH_2— radical, examples of which are the trimethylsilylmethyl diphenylmethylsilylmethyl, vinyldimethylsilylmethyl and dimethylbenzylsilylmethyl radicals. The preferred compounds (b) are those wherein the radicals represented by R', R'', R''' and Q are selected from alkyl radicals having less than 9 carbon atoms and phenyl radicals.

Organosilicon compounds (b) can be prepared, for example, by the reaction in the presence of magnesium of a phenolic compound having substituted therein a halomethyl group with an organosilicon compound Q_3SiHal wherein Q is as hereinabove defined and Hal represents a halogen atom, preferably the chlorine or bromine atom. Such a method is more completely described in our copending U.S. application Ser. No. 752,790, filed Aug. 15th 1968.

When carrying out the process of this invention the organosilicon compound can be introduced into the polymer by an suitable procedure. For example, a solvent solution or dispersion of the organosilicon compound can be employed to coat granules of the polypropylene prior to melting, or the organosilicon compound can be added directly to the polypropylene melt. We have found that degradation of the polypropylene to an extent suitable for performing the melt extrusion process can be achieved at temperatures of 230° C. or lower in the presence of the organosilicon compound.

Although applicable in the production of any shaped article such as sheets, by melt extrusion, the process of this invention finds particular application in the formation of fibres and filaments of polypropylene by melt spinning. In common with known techniques the fibres or filaments can be quenched following spinning and are then subjected to drawing at elevated temperatures to bring about orientation of the fibre or filament to provide the desired high tensile properties.

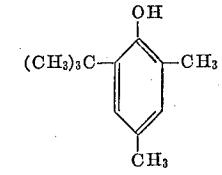
In addition to assisting the thermal degradation of polypropylene at temperatures above about 180° C. the organosilicon compounds (a) and (b) employed herein also function to stabilise the polypropylene against oxidation at temperatures up to about 120–150° C. The use of the organosilicon compounds according to this invention therefore performs the dual function of assisting in the formation of high tenacity fibres and films during the melt spinning operation and subsequently serves to protect the spun fibre against oxidation at lower temperatures.

The following examples illustrate the invention.

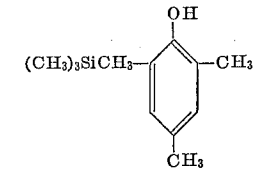
EXAMPLE 1

To a series of 2½ g. samples of isotactic polypropylene granules were added 25 ml. solutions in pentane of the following compounds, the concentration of the solutions being such as to deposit on the granules by evaporation of the pentane 1.0 percent of their weight of compound.

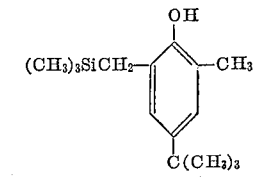
Compound A



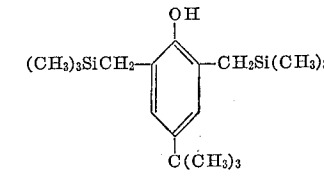
Compound B



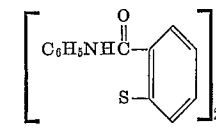
Compound C



Compound D



Compound E



The melt index of each of the treated samples was then measured according to British Standard 2782, Part 1, 1965, Method 105C using a 2.16 kg. load, a reservoir temperature of 230° C. and a 0.0825 in. orifice, the measurements being carried out at periods of 3 minutes and 13 minutes after introduction of the sample into the heated reservoir. Each measurement of the quantity extruded through the orifice was taken over 0.5 minutes and the value obtained converted to give a figure for the prescribed 10 minute extrusion period. The melt index, that is the amount of polypropylene in grams extruded over a 10 minute period, for each of the samples is given in the following table, together with a control measurement carried out on an untreated polypropylene sample.

Compound	Melt index	
	3 min.	13 min.
Control	2.1	2.5
A	1.9	2.0
B	2.7	7.4
C	2.9	4.2
D	4.0	11.0
E	2.6	3.9

Compounds A and E were included for comparative purposes and the melt index value for Compound A indicated that it was ineffective in assisting degradation of the polypropylene at 230° C. On the other hand Compounds B, C and D all increased the melt index value significantly and were at least as effective as Compound E which is a commercially available peptiser.

EXAMPLE 2

The compound $(CH_3)_3SiCH_3NH.C_6H_5$ was employed to treat two samples isotactic polypropylene granules in the manner described in Example 1, the amount of compound deposited being 0.1 percent in one case and 1.0

percent in the other, each based on the weight of polypropylene.

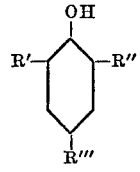
Measurements of the melt index of the sample containing 0.1 percent of compound was performed after 3 minutes and 13 minutes. In the manner described in Example 1. Values of 2.8 and 5.0 were obtained. When similar measurements were performed after 3 minutes and 4 minutes on the 1.0 percent sample values of melt index of 2.7 and 20.0 were obtained. When the compound

$$(CH_3)_3CCH_2NH.Ph$$

was similarly tested at the 0.1% level for comparative purposes melt index values of 2.3 and 2.6 were obtained after 3 minutes and 13 minutes respectively.

That which is claimed is:

1. A process for the production of a shaped article by the melt extrusion of thermally degraded isotactic polypropylene wherein the thermal degradation of the polypropylene is carried out in the presence of from 0.01 to 5 percent by weight, based on the weight of polypropylene of (a) an organosilicon compound which is an organosilane or organosiloxane having therein at least one silicon-bonded group of the general formula $—CH_2NR_2$, wherein each R represents a hydrogen atom or a monovalent hydrocarbon radical, (b) an organosilicon compound of the general formula



wherein R', R'' and R''' each represent a hydrogen atom, an alkyl radical having up to 18 carbon atoms, an aralkyl radical having up to 18 carbon atoms or a $Q_3SiCH_2—$ group, wherein Q represents an alkyl, alkenyl or aryl radical having up to 18 carbon atoms at least one of R', R'' and R''' being the $Q_3SiCH_2—$ group, or (c) mixtures of (a) and (b).

2. A process as claimed in Claim 1 wherein the organosilicon compound (a) has the general formula

$$A_nSi[CH_2NR_2]_{4-n}$$

wherein each A represents a radical having from 1 to 18 carbon atoms inclusive and is a monovalent hydrocarbon radical, an alkoxy radical, an alkoxyalkyl radical, an alkoxyaryl radical or an alkoxyalkoxy radical, *n* is 0, 1, 2 or 3 and R is a hydrogen atom amonovalent hydrocarbon.

3. A process as claimed in Claim 2 wherein each A represents an alkyl radical having less than 9 carbon atoms or an aryl radical and *n* is 3.

4. A process as claimed in Claim 1 wherein each Q is an alkyl radical having less than 9 carbon atoms or a phenyl radical.

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U.S. Cl. X.R.

260—93.7, 94.9 GD, 43 Digest, 96 D, 94.7 D; 264—130, 170