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(54) **METHODE DE PREPARATION DE COMPOSITION A BASE D'ELASTOMERE POLYOLEFINIQUE THERMOPLASTIQUE**

(54) **PROCESS FOR PRODUCING POLYOLEFIN THERMOPLASTIC ELASTOMER COMPOSITION**

(57) A process for producing a polyolefin thermoplastic elastomer composition having superior rubbery elasticity, mechanical properties, etc. and also having improved processing fluidity, workability, etc. is provided, which process comprises blending (A) 40 to 80% by weight of an ethylene-propylene copolymer rubber and/or an ethylene-propylene-diene a terpolymer, as a soft segment component, (B) 60 to 20% by weight of a crystalline ethylene-propylene block copolymer having an ethylene content of at least 5% by weight and a melt flow index of 0.5 to 30 g/10 minutes or a crystalline ethylene-propylene random copolymer having an ethylene content of at least 1.5% by weight and a melt flow index of 0.5 to 30 g/ 10 minutes, each as a hard segment, and based upon 100 parts by weight of the total of (A) and (B), (C) 0.3 to 5 parts by weight of an organosilane, (D) 0.1 to 3 parts by weight of an organic radical-generator, (E) 0 to 5 parts by weight of white carbon, and (F) 0 to 100 parts by weight of an extender oil, followed by subjecting the resulting blend to dynamic partial crosslinking.

ABSTRACT OF THE DISCLOSURE

A process for producing a polyolefin thermoplastic elastomer composition having superior rubbery elasticity, mechanical properties, etc. and also having improved processing fluidity, workability, etc. is provided, which process comprises blending

(A) 40 to 80% by weight of an ethylene-propylene copolymer rubber and/or an ethylene-propylene-diene terpolymer, as a soft segment component,

(B) 60 to 20% by weight of a crystalline ethylene-propylene block copolymer having an ethylene content of at least 5% by weight and a melt flow index of 0.5 to 30 g/10 minutes or a crystalline ethylene-propylene random copolymer having an ethylene content of at least 1.5% by weight and a melt flow index of 0.5 to 30 g/10 minutes, each as a hard segment, and

based upon 100 parts by weight of the total of (A) and (B),

(C) 0.3 to 5 parts by weight of an organosilane,

(D) 0.1 to 3 parts by weight of an organic radical-generator,

(E) 0 to 5 parts by weight of white carbon, and

(F) 0 to 100 parts by weight of an extender oil,

followed by subjecting the resulting blend to dynamic partial crosslinking.

SPECIFICATION

TITLE OF THE INVENTION

Process for producing polyolefin thermoplastic elastomer composition

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a process for producing a polyolefin thermoplastic elastomer composition. More particularly it relates to a process for producing a partially crosslinked polyolefin thermoplastic elastomer composition suitable to extrusion molding or injection molding for thick products.

2. Description of the Related Art

In the case of subjecting conventional rubbers to injection molding, there have been problems that since the process requires steps of blending additives into a rubber, kneading the resulting blend, filling into a mold and vulcanizing, a particular molding machine is required, the cycle time becomes longer and the steps are troublesome. In the case of the extrusion molding, too, similar problems have been raised. Thus, as a stock, a composition substituted for rubbers, which is moldable even without vulcanization and yet provided with rubbery properties has been researched. Among stocks having such properties, soft plastics such as

soft vinyl chloride resin, ethylene-vinyl acetate resin, low density polyethylene, etc. are superior in the aspect of both moldability and softness, but on the other hand are inferior in the aspect of heat resistance, mechanical strengths, repellent elasticity, etc.; hence these plastics have been restricted in the use applications.

Thus, in recent years, as materials having intermediate properties between those of vulcanized rubbers and those of soft plastics, compositions comprising an olefin copolymer rubber and an olefin plastic have been noted among thermoplastic elastomers. Namely, research has been made around polypropylene and ethylene-propylene copolymer rubber, for example, a composition obtained by melt-kneading a polyolefin resin with an ethylene-propylene copolymer rubber, disclosed in Japanese patent application laid-open No. Sho 49-53938/1974, a composition having an improved impact strength, obtained by blending an olefin copolymer rubber with an olefin plastic at two stages, disclosed in Japanese patent application laid-open No. Sho 60-71652/1985, etc.

Among these compositions, olefin thermoplastic elastomers having the rubbery part therein partially crosslinked at the time of melt-kneading are so superior in the heat resistance and rubbery elasticity that development thereof has been advanced as a most promising

composition. Partially crosslinked olefin thermoplastic elastomers have generally been produced by mechanically melt-kneading an olefin rubber such as ethylene-propylene copolymer rubber or ethylene-propylene-non-conjugated diene terpolymer rubber with polypropylene usually by means of Bambury mixer, kneader, etc. and at the same time adding a crosslinking agent such as organic peroxide, etc. to effect partial crosslinking. As such a process for obtaining thermoplastic elastomers, for example, the following have been proposed: a process of partially crosslinking the rubbery part at melt-kneading (Japanese patent publication No. Sho 53-34210/1977); a process of crosslinking the same by using an organic peroxide, (Japanese patent application laid-open No. Sho 57-172944/1982); a process of partially crosslinking the same by using divinylbenzene as a crosslinking auxiliary (Japanese patent application laid-open No. Sho 57-135846/1982), a process of completely vulcanizing the same with sulfur (Japanese patent application laid-open No. Sho 52-13541/1977); a process of using an organosilane (Japanese patent application laid-open No. Sho 57-23651/1982); etc.

However, compositions obtained by merely melt-kneading an olefin copolymer rubber and an olefin plastic are inferior in the heat resistance and mechanical strength and also inferior in the practical utility. Further, the process accompanied with crosslinking is superior in

obtaining a product having a heat resistance, a rubbery elasticity and a mechanical strength, but inferior in the processing fluidity, resulting in an inferior appearance of the resulting molded product. Further, in the case of using an organosilane as a crosslinking auxiliary, a process of post-crosslinking by immersing in hot water in the presence of a catalyst such as dibutyltin dilaurate is required; hence there occurs a new problem of inferior processability.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a process for producing a polyolefin thermoplastic elastomer composition having overcome the drawbacks of conventional melt-kneaded compositions of an olefin copolymer rubber and an olefin plastic, and having superior rubbery elasticity, mechanical properties, etc., and also having improved processing fluidity, process-ability, etc.

The present inventors have made extensive research in order to achieve the above object, and as a result, have found that when the components (A) to (F) described below are fed directly to a twin-screw extruder and dynamically partially crosslinked, a polyolefin thermo-plastic elastomer having improved heat-resistance, mechanical strength, rubbery elasticity and processing

fluidity is obtained, and have attained the present invention.

The present invention resides in:

a process for producing a polyolefin thermoplastic elastomer composition, which comprises blending

(A) 40 to 80% by weight of an ethylene-propylene copolymer rubber and/or an ethylene-propylene-diene terpolymer, as a soft segment component,

(B) 60 to 20% by weight of a crystalline ethylene-propylene block copolymer having an ethylene content of at least 5% by weight and a melt flow index of 0.5 to 30 g/10 minutes or a crystalline ethylene-propylene random copolymer having an ethylene content of at least 1.5% by weight and a melt flow index of 0.5 to 30 g/10 minutes, each as a hard segment, and

based upon 100 parts by weight of the total of (A) and (B),

(C) 0.3 to 5 parts by weight of an organosilane,

(D) 0.1 to 3.0 parts by weight of an organic radical-generator exhibiting a half-life period of one minute at a temperature of 170°C or higher,

(E) 0 to 5 parts by weight of white carbon, and

(F) 0 to 100 parts by weight of an extender oil,

followed by subjecting the resulting blend to dynamic partial crosslinking.

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In another aspect, the present invention provides a process for producing a polyolefin thermoplastic elastomer composition, comprising the steps of: forming a blend of

(a) 50 to 80% by weight of a soft segment component selected from the group comprising an ethylene-propylene copolymer rubber and an ethylene-propylene-diene terpolymer;

(b) 50 to 20% by weight of a hard segment selected from the group comprising a crystalline ethylene-propylene block copolymer having an ethylene content of at least 5% by weight and a melt flow index of 0.5 to 30 g/10 minutes, and a crystalline ethylene-propylene random copolymer having an ethylene content of at least 1.5% by weight and a melt flow index of 0.5 to 30 g/10 minutes, based upon 100 parts by weight of the total of (a) and (b);

(c) 0.3 to 5 parts by weight of an organosilane;

(d) 0.1 to 3 parts by weight of an organic radical generator exhibiting a half-life period for one minute at a temperature of 170^{o}C or higher;

(e) 0 to 100 parts by weight of an extender oil; and

(f) 0 to 5 parts by weight of white carbon;

followed by subjecting the resulting blend to dynamic partial crosslinking carried out by using a twin-screw extruder under the conditions of a temperature of 190^{o}C to 270^{o}C and a retention time of 20 to 180 seconds in said extruder so that the residue in xylene after reflux for

6 hours is in the range of 20 to 70% by weight in the resultant partially crosslinked composition, a specific energy W of 0.08 to 0.8, expressed by the formula:

$$W = \sqrt{3} \cdot (I-I_o) \cdot E \cdot \Phi/1000 \cdot Q$$

wherein

W = specific energy (Kwhr/Kg),

I = loaded current (A),

I_o = loaded current at the time of empty-driven screw (A),

E = voltage (v),

Φ = power factor, and

Q = extruded quantity (Kg/hr).

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The main portion of the composition of the present invention is composed of a hard segment and a soft

segment, and among these segments, the component constituting the soft segment is preferable to be an ethylene-propylene copolymer rubber (hereinafter referred to as EPM) having a Mooney viscosity ML_{1+4} (100°C) of 10 to 100 and a propylene content of 20 to 50% by weight, or an ethylene-propylene-diene terpolymer (hereinafter referred to as EPDM) having a Mooney viscosity ML_{1+4} (100°C) of 10 to 110, using as the third component diene to be copolymerized, any one of ethylidene, norbornene and 1,4-hexadiene, and having a iodine value (degree of unsaturation) of preferably 16 or less.

The component constituting the hard segment in the composition of the present invention is preferred to be a crystalline ethylene-propylene block copolymer having an ethylene content of at least 5% by weight and a melt flow index of 0.5 to 30 g/10 minutes. This copolymer is a crystalline ethylene-propylene block copolymer obtained by copolymerizing ethylene with propylene at two stages. In the first stage copolymerization, an ethylene-propylene copolymer (hereinafter referred to as polymer 1) having an ethylene content of 0 to 5% by weight is formed so as to occupy 20 to 95% by weight, preferably 50 to 95% by weight of the total quantity polymerized, and in the second stage copolymerization, an ethylene-propylene copolymer (hereinafter referred to as polymer 2) having an ethylene content of 50 to 85% by weight is formed

so as to occupy 80 to 5% by weight, preferably 50 to 5% by weight of the total quantity polymerized. As a result, a crystalline ethylene-propylene block copolymer (hereinafter referred to as polymer 3) is obtained. In the case where the polymer 3 as the ultimate composition is used as the hard segment, the higher the proportion ratio of polymer 2 is, the more the quantity of the soft segment used as the component (A) can be reduced.

Further, as another hard segment, a crystalline ethylene-propylene random copolymer having an ethylene content of at least 1.5% by weight and a melt flow index of 0.5 to 30 g/10 minutes can be preferably used, too. This polymer is a crystalline ethylene-propylene random copolymer obtained by copolymerizing ethylene with propylene at one stage. In addition, propylene homopolymer is inferior in the compatibility with EPM or EPDM to reduce rubbery elasticity.

The organosilane compound (C) in the present invention refers to a silane expressed by the formula $RR'SiX_2$ wherein R represents an organic group including vinyl group, chloro group, amino group, mercapto group, glycidoxy group, methacryloxy group, etc., X represents a hydrolyzable organic group such as methoxy group, ethoxy group, etc., R' represents R or X and the respective Rs (in the case of two Rs) and the respective Xs may be different from each other. Examples of

the silane are vinyltrimethoxysilane, vinyltriethoxysilane, 3-aminopropyltriethoxysilane, n-(2-aminoethyl)-3-amino-propyltrimethoxysilane, 3-glycydoxypropyltrimethoxysilane, 3-chloropropyltrimethoxysilane, 3-methacryloxypropyl-trimethoxysilane, 3-mercaptopropyltrimethoxysilane, etc. Among these, 3-methacryloxypropyltrimethoxysilane is preferably used. The quantity of the organosilane compound blended is 0.3 to 5 parts by weight, preferably 1 to 3 parts by weight based upon 100 parts by weight of (A)+(B). If it is less than 0.3 part by weight, the improving effect is small, while if it exceeds 5 parts by weight, the processing fluidity lowers.

As the organic radical-generator used in the present invention, those having a half-life period of one minute at a temperature of 170°C or higher are preferred. For example, di-t-butylperoxydiisopropylbenzene, 2,5-dimethyl-2,5-di-(t-butylperoxy)hexane, dicumyl peroxide, etc. are mentioned. The quantity of the organic radical-generator blended is 0.1 to 3 parts by weight, preferably 0.5 to 2 parts by weight based upon 100 parts by weight of (A)+(B). If it is less than 0.1 part by weight, the improving effect is small, while if it exceeds 3 parts by weight, the effect is saturated, and disadvantageous economically.

In the present invention, the crystalline ethylene-propylene block copolymer or the crystalline ethylene-

propylene radom copolymer, each used as the hard segment may be in a pellet form, but preferably in a powder form in the aspect of dispersibility.

It is desirable to blend white carbon into the composition of the present invention. Since X of the organosilane compound $RR'SiX_2$ used in the present invention is a hydrolyzable organic radical, a cross-linking reaction is liable to proceed with lapse of time due to moisture in air, etc., but when white carbon is added, it is possible to inhibit the crosslinking reaction with lapse of time, and it is also possible to stabilize the quality of the composition. Further, since the organosilane compound is a liquid, when it is mixed with the powder of the crystalline ethylene-propylene copolymers as the hard segment component, the mixture becomes so viscous that the quantity of the mixture fed to the extruder at the time of granulation varies to make the quality of the composition unstable, whereas, addition of white carbon overcomes such a defect. The quantity of white carbon blended is 0 to 5 parts by weight, preferably 0.3 to 2 parts by weight based upon the total 100 parts by weight of (A)+(B). Even if it exceeds 5 parts by weight, the effect is saturated, and the case is economically undesirable.

Further, an extender oil may be included in the composition of the present invention. This extender

oil may be any of paraffin, naphthene and aromatic ones, and a paraffinic processing oil is most preferable in the aspects of hue, odor, etc. The quantity of the extender oil blended is 0 to 100 parts by weight, preferably 0 to 50 parts by weight based upon the total 100 parts by weight of (A)+(B). It may be added over 100 parts by weight, but the strength tends to lower.

In the present invention, the above components (A) to (F) are preliminarily mixed by means of Henschel mixer, tumbler mixer, etc., followed by dynamic partial crosslinking. This dynamic partial crosslinking refers to a process of extruding the mixture of the above (A) to (F) by means of a multi-screw extruder (twin- or three-screw) or milling by means of mill rolls to impart a shearing force of a definite value or more.

As to the shearing force at the time of using a multi-screw extruder, a specific energy W which corresponds to the shearing force and defined according to the following equation, may be in the range of 0.08 to 0.8, preferably 0.1 to 0.6:

$$W = \sqrt{3} \cdot (I - I_0) \cdot E \cdot \phi / 1000 \cdot Q$$

wherein W: specific energy (Kw Hr/Kg)

I: loaded current (A)

I_0: loaded current at the time of empty-driven screw (A)

E: voltage (V)

ϕ: power factor

Q: extruded quantity (Kg/hr)

Further, the parameters of the crosslinking conditions i.e. the quantity of the organosilane compound, the quantity of the organic radical-generator, the crosslinking temperature and the crosslinking time, are adjusted so as not to attain complete crosslinking. Whether or not a partial crosslinking to a desired extent has occurred in the composition can be judged, for example, by measuring the insolubles of partially crosslinked composition in xylene after reflux for 6 hours. The quantity of the insolubles in xylene that is a gel fraction is preferred to be 20 to 70%, preferably 30 to 60% and also to be larger by 10% or more, particularly 20% or more, than the quantity of uncrosslinked composition. Concretely, in the dynamic partial crosslinking using a twin-screw extruder, it is possible to achieve the object under the conditions of a temperature of 190° to 270°C, preferably 200° to 250°C and a retention time of 20 to 180 seconds, preferably 50 to 120 seconds. In addition, in the case where a single-screw extruder by which a definite shearing force is not obtained is used, only a product having an inferior dispersibility of the soft segment and the hard segment and also having inferior physical properties is obtained.

The dynamically partially crosslinked composition can be processed or reprocessed by means of conventional processing machines for extrusion molding, injection molding, compression molding, etc.

In the above manner, it is possible to obtain a polyolefin thermoplastic elastomer superior in heat resistance, mechanical strength, rubbery elasticity and processing fluidity.

The thus obtained elastomer is melt-extruded and cut into a suitable form or pelletized in the case of using a multi-screw extruder. A manner of cutting the melt-extrudate under water and a manner of mist-cutting the melt-extrudate while injecting water are preferred. Further, it is also possible to employ a hot-cutting manner.

The present invention will be described in more detail by way of Examples and Comparative examples, but it should not be construed to be limited thereto. The evalution methods employed in Examples and Comparative examples were carried out according to the following methods:

1) MFR: Melt Flow Rate according to JIS K 7210,

temperature: 230°C

load: 2.16 or 10 kgf

unit: g/10 min.

2) 100% elongation set

Tester: Tensilon UTM-1 type

Test piece: JIS K 7113 No. 1 test piece

Length between chacks: 115 mm

Length between bench marks: 50 mm

Tensile rate: 200 mm/min.

When the distance between the bench marks reached 100 mm, the test piece was kept for 10 minutes, followed by opening the chucks, allowing the test piece to stand still, measuring the length between the chucks and calculating the resulting elongation set according to JIS K 6301 (unit %).

3) Stress and elongation at tensile breaking point:

Tester: Strograph W 1 type

Test piece: JIS K 7113 test piece No. 1, according to JIS K 7113

Length between the chucks: 115 mm

Length between bench marks: 50 mm

Tensile rate: 50 mm/min. (unit: stress kgf/cm^2, elongation %)

4) Stress at 100% elongation:

Calculated from stress at 100% elongation at the time of measurement of 100% elongation set (unit: kgf/cm^2).

5) Flexural elastic modulus:

Tester: Tensilon STM-T-100 type,

according to JIS K 7203 (unit: kgf/cm^2)

6) Weather resistance:

Tester: Sunshinesuperlonglife weatherometer

Condition: Rain at 63°C, no rain at 83°C

Evaluated from crack occurrence time (hr).

7) Heat aging characteristics:

Tester: Gear-type aging tester

Condition: 150°C and 160°C

Evaluated from crack occurrence time (hr).

8) Immersion in hot water:

The above-mentioned physical properties after immersion in boiling water for 48 hours were evaluated.

9) Gel fraction:

This is expressed by the percentage (%) of the weight of a residue obtained by placing a sample in a metal gauze of 500 meshes, followed by reflux in xylene for 6 hours, to the weight of the sample before the test.

Example 1

To (A) an ethylene-propylene-ethylidenenorbornene terpolymer having a Mooney viscosity (ML_{1+4} 100°C) of 88, an ethylene content of 74% by weight and a iodine value of 15, as a soft segment component (2.5 Kg) and (B) a crystalline ethylene-propylene block copolymer having an ethylene content of 7.5% by weight and an MFR (230°C, load 2.16 kgf) of 0.60, as a hard segment component (2.5 Kg), (the total weight of (A) and (B) being 5 Kg), were added (C) 3-methacryloxy-

propyltrimethoxysilane as an organosilane compound (100 g), (D) 2,5-di-(t-butylperoxy)hexane as an organic radical-generator (75 g), (E) white carbon (mainly SiO_2) (100 g), and Irganox 1010 (Trademark of Ciba Geigy Co., Ltd.) (5 g), BHT (5 g) and calcium stearate (5 g) each as a processing stabilizer, followed by mixing these materials with blending for 2 minutes by means of Henschel mixer or for 15 minutes by means of a tumbler mixer, melt-extruding the resulting mixture by means of a twin-screw extruder (PCM-45* manufactured by Ikegai Tekko Co., Ltd.) at 200°C, pelletizing by means of a mist cutter (PHR 100 manufactured by Ikegai Tekko Co., Ltd.), measuring the melt flow rate (MFR) of the resulting pellets, thereafter injection-molding a test piece for evaluating the physical properties, by means of an injection-molding machine (IS-100* manufactured by Toshiba Kikai Co., Ltd.) under conditions of an injection temperature of 250°C and a mold temperature of 50°C, and measuring the above-mentioned items 2) to 7). Table 1 shows the polymers of the soft segment component used, Table 2 shows the polymers of the hard segment component, Table 3 shows other components, and Table 4 shows the quantities of these components blended.

Examples 2 - 14 and Comparative examples 1 - 5

Example 1 was repeated except that the kinds and blended quantities of these components were varied to

*Trade mark

those shown in Table 4, to carry out pelletization, injection-molding of test pieces and evaluation thereof. The results are shown in Tables 5, 6 and 7.

Comparative Example 6

Example 1 was repeated except that the twin-screw extruder is replaced by a single screw extruder. The results are shown in Table 6.

B

Table 1

Kind	Type of polymer	Trade name	Name of maker	Mooney viscosity ML_{1+4} 100°C	Ethylene content (wt.%)	Amount of third component (iodine value)
A_1	Ethylene-propylene-diene terpolymer rubber	EP57P	Japan Synthetic Rubber Co.,Ltd.	24	75	-
A_2	Ethylene-propylene copolymer rubber	EP02P	Japan Synthetic Rubber Co.,Ltd.	88	74	15

Table 2

Kind	Type of polymer	Polymer composition (ethylene content wt.%)			MFR load 2.16 Kgf
		Total ethylene amount	First step ethylene amount	Second step ethylene amount	
B_1	Crystalline ethylene-propylene block copolymer	7.5	-	59	0.60
B_2	Crystalline ethylene-propylene block copolymer	11.0	-	58	2.6
B_3	Crystalline ethylene-propylene random copolymer	3.6	-	-	2.0
B_4	Crystalline ethylene-propylene block copolymer	15.5	1.5	79	2.3
B_5	Propylene homopolymer	-	-	-	0.80

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Table 3

Kind	General name	Chemical name	Trade name	Name of maker
C_1	Organosilane compound	3-Methacryloxypropyl-trimethoxysilane	Sila Ace S710	Chisso Corp.
C_2	Organosilane compound	Vinyltriethoxysilane	Sila Ace S220	Chisso Corp.
C_3	Organosilane compound	N-(2-aminoethyl)-3-aminopropyltrimethoxy-silane	Sila Ace S320	Chisso Corp.
C_4	Organosilane compound	3-Glycidoxypropyltri-methoxysilane	Sila Ace S510	Chisso Corp.
D	Organic radical-generator	2,5-Dimethyl-2,5-di-(t-butylperoxy)hexane	Perhexa 25B	Nihon Yushi Co.
E	White carbon	Silicon dioxide	AEROSIL200	Nihon Aerosil Co.
F	Extender oil	(Processing oil)	Diana process PW-380	Idemitsu Kosan Co.

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TABLE 4

Example or Comp. ex.	Soft segment		Hard Segment		Organosilane compound		Organic radical-generator D wt.%	White carbon E wt.%	Extender oil F wt. %
	Kind	Blended amount wt.%	Kind	Blended amount wt.%	Kind	Blended amount wt.%			
Ex. 1	A_1	50	B_1	50	C_1	2.0	1.5	2.0	-
Ex. 2	A_1	50	B_1	50	C_1	2.0	1.5	-	-
Ex. 3	A_2	50	B_2	50	C_1	2.0	1.5	2.0	-
Ex. 4	A_2	50	B_2	50	C_1	2.0	1.5	-	-
Ex. 5	A_1	50	B_1	50	C_2	2.0	1.5	2.0	-
Ex. 6	A_1	50	B_1	50	C_3	2.0	1.5	2.0	-
Ex. 7	A_1	50	B_1	50	C_4	2.0	1.5	2.0	-
Ex. 8	A_1	50	B_1	50	C_1	0.5	1.5	2.0	-
Ex. 9	A_1	50	B_3	50	C_1	2.0	1.5	2.0	-
Ex. 10	A_1	50	B_4	50	C_1	2.0	1.5	2.0	-
Ex. 11	A_1	50	B_1	50	C_1	2.0	0.3	2.0	-
Ex. 12	A_1	50	B_1	50	C_1	2.0	1.0	2.0	-
Ex. 13	A_1	50	B_1	50	C_1	2.0	1.5	2.0	25
Ex. 14	A_1	50	B_1	50	C_1	2.0	1.5	2.0	45
Ex. 15	A_1	60	B_1	40	C_1	2.0	1.5	2.0	-
Ex. 16	A_1	80	B_1	20	C_1	2.0	1.5	2.0	-
Comp. Ex. 1	A_1	50	B_1	50	-	-	-	-	-

Note: The sum of soft segment and hard segment is 100 wt.%

TABLE 4 (continued)

Example or Comp. ex.	Soft segment		Hard Segment		Organosilane compound		Organic radical-generator D wt.%	White carbon E wt.%	Extender oil F wt. %
	Kind	Blended amount wt.%	Kind	Blended amount wt.%	Kind	Blended amount wt.%			
Comp. Ex. 2	A_1	50	B_1	50	-	-	1.5	-	-
Comp. Ex. 3	A_2	50	B_2	50	-	-	-	-	-
Comp. Ex. 4	A_2	50	B_2	50	-	-	1.5	-	-
Comp. Ex. 5	A_1	50	B_5	50	C_1	2.0	1.5	2.0	-

Note: The sum of soft segment and hard segment is 100 wt.%

Table 5

Example or Comp. ex.	MFR g/10 min. load 10 Kgf	100% Elongation set %	Stress at tensile breaking point Kgf/cm^2	Elongation at tensile breaking point %	Stress at 100% Elongation Kgf/cm^2	Flexural modulus Kgf/cm^2
Ex. 1	18	42	180 <	450 <	94	2240
Ex. 2	17	45	150 <	450 <	85	2120
Ex. 3	5.4	37	103	340	76	1480
Ex. 4	4.8	34	115	360	75	1220
Ex. 5	149	41	127	335	87	2330
Ex. 6	98	43	148	390	90	2540
Ex. 7	350	40	106	275	84	2340
Ex. 8	258	46	105	140	78	3240
Ex. 9	34	44	146 <	450 <	77	2030
Ex. 10	4.2	42	180 <	450 <	90	2360
Ex. 11	0.24	45	144 <	450 <	109	2380
Ex. 12	2.1	42	176 <	450 <	96	2350

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Table 5 (continued)

Example or Comp. ex.	MFR g/10 min. load 10 Kgf	100% Elongation set %	Stress at tensile breaking point Kgf/cm^2	Elongation at tensile breaking point %	Stress at 100% elongation Kgf/cm^2	Flexural modulus Kgf/cm^2
Ex. 13	30	20	112	330	65	1300
Ex. 14	462	13	53	190	44	580
Ex. 15	2.1	32	162	390	-	1360
Ex. 16	0.1 >	10	55	220	-	220
Comp. ex. 1	5.1	48	146	360	133	3340
Comp. ex. 2	274	broken	86	149	broken	2560
Comp. ex. 3	31	49	112	490	112	2990
Comp. ex. 4	254	41	69	520	63	1530
Comp. ex. 5	76	51	185 <	450 <	99	3190

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Table 6

Example or Comp. ex.	Granulation conditions				Gel fraction %	MFR g/10min. load 10 Kgf	100% elongation set %	Stress at tensile breaking point Kgf/cm^2	Elongation at tensile breaking point %	Stress at 100% elongation Kg/cm^2	Flexural elastic modulus Kgf/cm^2
	Name of extruder	Extrusion temp. °C	Extruded amount Kg/hr	Specific energy $Kw.hr/_{Kg}$							
Ex.1	Ikegai PCM-45	200	27	0.24	59	18	42	180 <	450 <	94	2240
Comp. ex.4	Ikegai PCM-45	200	26	0.25	18	254	41	69	520	63	1530
Comp. ex.6	Toshiba SE-65 type	230	27	0.07	19	17	broken	195	90	broken	3100

Ikegai PCM-45: twin-screw extender

Toshiba SE-65 type: single-screw extruder

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Table 7

Item	Example or Comparative example	Deterioration time (hr)			
		Example 1	Comparative example 2	Example 3	Comparative exampple 4
Weather resistance	63°C, rain	300	280	420	280
	83°C, no rain	130	120	220	120
Heat aging characteristics	150°C	9	8	11	8
	160°C	3	2	5	0.5

As seen from Table 6, in the case of Comparative example 6 where the same blend as in Example 1 was melt-extruded by means of a single-screw extruder, the specific energy and the gel fraction is so lower than those in Example 1 that the rubbery properties (100% elongation set) are deficient.

Examples 15 and 16

The components excluding the extender oil among those in Table 4 were blended in the same manner as in Example 1, followed by melt-extruding the resulting blend by means of a twin-screw extruder (PCM-45 manufactured by Ikegai Tekko Co., Ltd.) at 200°C, while injecting an extender oil in a definite quantity through an injection port by means of a pump to obtain pellets of compositions of Examples 15 and 16. Injection molding of test pieces and their evaluations were carried out in the same manner as in Example 1.

As seen from Examples 1-4 and Comparative examples 1-4, the composition of the present invention has been improved in the elongation set and flexural elasticity as compared with simple blend product or product cross-linked with organic peroxide.

As seen from Examples, 1, 9 and 10 and Comparative example 5, when a crystalline ethylene-propylene block copolymer or a crystalline ethylene-propylene random copolymer is used as the hard segment, the elongation set and flexural elasticity are improved.

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As seen from Examples 1, 15 and 16, when the quantities of the hard segment and the soft segment blended are in the definite ranges, it is possible to achieve the effectiveness of the present invention.

As seen from Examples 1, 3, 5, 6 and 7 and Comparative examples 1 to 4, the effect of improving the physical properties due to the organosilane compound is evident, and in particular, the improvement effect of 3-methacryloxypropyltrimethoxysilane is notable.

From Examples 1 and 8, the effect of the quantity of the organosilane compound blended is evident, and from Examples 1, 11 and 12, the effect of the quantity of the organic peroxide blended is evident.

As seen from comparison of Examples 13, 14 and 1, the improvement effects of the fluidity in the processing, elongation set and flexural elasticity due to the blending of the processing oil is notable.

With a material obtained by immersing the test piece of Example 1 in hot water for 48 hours and a material obtained by immersing the test piece of Example 2 in hot water for 48 hours, change in the crosslinking due to water with lapse of time was observed. The results are shown in Table 8. The former case is referred to Example 1', and the latter case, Example 2'.

As seen from the results of Table 8, change in MFR is less when white carbon is used. Further, the product obtained by using white carbon formed no blocks due to coagulation processed easily.

Table 8

Example or Compar. ex.	MFR g/10 min. load 10 Kgf	100% elongation set %	Stress at tensile breaking point Kgf/cm^2	Elongation at tensile breaking point %	Stress at 100% elongation Kgf/cm^2	Flexural elastic modulus Kgf/cm^2
Example 1	18	42	180 <	450 <	94	2240
Example 1'	6.2	35	167	275	106	2610
Example 2	17	45	150 <	450 <	85	2120
Example 2'	0.22	38	171	300	102	2440

Note: The molded products of Example 1' and Example 2' are samples obtained by subjecting the molded products of Example 1 and Example 2 to immersion in hot water, respectively.

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With regard to Comparative examples 1 and 2 and Example 1, test pieces of 10 mm × 5 mm × 1 mm were prepared by means of an injection molding machine, followed by measuring the loss tangents (tan δ) thereof within a temperature region of -150° to +165°C by means of a dynamic viscoelasticity-measuring apparatus (DMA 983 type manufactured by Dupont Co., Ltd., resonant frequency mode, temperature-raising rate 5°C/min.). The following peaks were observed: a peak based on the γ-transition of polyethylene (a large portion of ethylene part of ethylene-propylene block copolymer or ethylene-propylene (diene) copolymer) in the vicinity of -100°C, a peak based on the glass transition of ethylene-propylene (diene) copolymer in the vicinity of -20°C and a peak based on glass transition of polypropylene in the vicinity of room temperature. When Comparative examples 1 and 2 and Example 1 are compared, it was observed that the peak intensities in the vicinity of -20°C increase in the order of 0.087 (Comparative example 1), 0.118 (Comparative example 2) and 0.127 (Example 1), and to the contrary the peak intensities in the vicinity of room temperature decrease in this order. In the cases of Comparative example 3 and Example 3, too, the same tendency was observed.

In view of the above facts, it is evident that the composition according to the present invention has been more improved in the elastomeric properties due to the crosslinking.

According to the present invention, it is possible to provide a polyolefin thermoplastic elastomer composition having superior rubbery elasticity and mechanical properties, superior processing fluidity e.g. for injection molding, extrusion molding, etc. of thick products, and superior workability.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for producing a polyolefin thermoplastic elastomer composition, comprising the steps of:

forming a blend of

(a) 50 to 80% by weight of a soft segment component selected from the group comprising an ethylene-propylene copolymer rubber and an ethylene-propylene-diene terpolymer;

(b) 50 to 20% by weight of a hard segment selected from the group comprising a crystalline ethylene-propylene block copolymer having an ethylene content of at least 5% by weight and a melt flow index of 0.5 to 30 g/10 minutes, and a crystalline ethylene-propylene random copolymer having an ethylene content of at least 1.5% by weight and a melt flow index of 0.5 to 30 g/10 minutes, based upon 100 parts by weight of the total of (a) and (b);

(c) 0.3 to 5 parts by weight of an organosilane;

(d) 0.1 to 3 parts by weight of an organic radical generator exhibiting a half-life period for one minute at a temperature of 170^{o}C or higher;

(e) 0 to 100 parts by weight of an extender oil; and

(f) 0 to 5 parts by weight of white carbon;

followed by subjecting the resulting blend to

dynamic partial crosslinking carried out by using a twin-screw extruder under the conditions of a temperature of 190°C to 270°C and a retention time of 20 to 180 seconds in said extruder so that the residue in xylene after reflux for 6 hours is in the range of 20 to 70% by weight in the resultant partially crosslinked composition, a specific energy W of 0.08 to 0.8, expressed by the formula:

$$W = \sqrt{3} \cdot (I-I_o) \cdot E \cdot \Phi/1000 \cdot Q$$

wherein

W = specific energy (Kwhr/Kg),

I = loaded current (A),

I_o = loaded current at the time of empty-driven screw (A),

E = voltage (v),

Φ = power factor, and

Q = extruded quantity (Kg/hr).

2. A process for producing a polyolefin thermoplastic elastomer composition according to claim 1, wherein the quantity of said white carbon blended is 0.3 to 5 parts by weight based upon 100 parts by weight of the total of said (a) and (b).

3. A process for producing a polyolefin thermoplastic elastomer composition according to claim 1, wherein said organosilane is expressed by the formula $RR'SiX_2$, wherein R represents vinyl group, chloro group, amino group, mercapto

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group, glycidoxy group or methacryloxy group, X represents methoxy or ethoxy group, and R′ represents R or X.

4. A process for producing a polyolefin thermoplastic elastomer composition according to claim 3, wherein said organosilane is at least one compound selected from vinyltrimethoxysilane, vinyltriethoxysilane, 3-aminopropyltriethoxysilane, n-(2-aminoethyl)-3-aminopropyltrimethoxysilane, 3-glycydoxypropyltrimethoxysilane, 3-chloropropyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane and 3-mercaptopropyltrimethoxysilane.

5. A process for producing a polyolefin thermoplastic elastomer composition according to claim 1, wherein said organic radical-generator is at least one compound selected from di-t-butylperoxydiisopropylbenzene, 2,5-dimethyl-2,5-di-(t-butylperoxy)hexane and dicumyl peroxide.

6. A process for producing a polyolefin thermoplastic elastomer composition according to claim 1, wherein said soft segment component is an ethylene-propylene copolymer rubber having a Mooney viscosity ML_{1+4} (100°C) of 10 to 100 and a propylene content of 20 to 50% by weight, or an ethylene-propylene-diene terpolymer having a Mooney viscosity ML_{1+4} (100°C) of 10 to 110, using as the third component diene to be copolymerized, any one of ethylidene, norbornene and 1,4-hexadiene, and having a iodine value

(degree of unsaturation) of 16 or less.

7. A process for producing a polyolefin thermoplastic elastomer composition comprising the steps of:

forming a blend of

(a) 50 to 80% by weight of a soft segment component selected from the group comprising an ethylene-propylene copolymer rubber and an ethylene-propylene-diene terpolymer;

(b) 50 to 20% by weight of a hard segment selected from the group comprising a crystalline ethylene-propylene block copolymer obtained by copolymerizing ethylene with propylene at two stages, in the first stage of which an ethylene-propylene copolymer having an ethylene content of 0 to 5% by weight is formed so as to occupy 20 to 95% by weight of the total quantity polymerized, and in the second stage of which an ethylene-propylene copolymer having an ethylene content of 50 to 85% by weight is formed so as to occupy 80 to 5% by weight of the total quantity polymerized, said crystalline ethylene-propylene block copolymer having an ethylene content of at least 5% by weight and a melt flow index of 0.5 to 30 g/10 minutes, and a crystalline ethylene-propylene random copolymer having an ethylene content of at least 1.5% by weight and a melt flow index of 0.5 to 30 g/10 minutes, based upon 100 parts by weight of the total of (a) and (b);

(c) 0.3 to 5 parts by weight of an organosilane;

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(d) 0.1 to 3 parts by weight of an organic radical generator exhibiting a half-life period for one minute at a temperature of 170°C or higher;

(e) 0 to 100 parts by weight of an extender oil; and

(f) 0 to 5 parts by weight of white carbon;

followed by subjecting the resulting blend to dynamic partial crosslinking carried out by means of a twin-screw extruder so as to give a specific energy W, of 0.08 to 0.8, expressed by the following formula:

$$W = \sqrt{3} \cdot (I-I_o) \cdot E \cdot \Phi/1000 \cdot Q$$

wherein

W = specific energy (Kwhr/Kg),

I_o = loaded current at the time of empty-driven screw (A),

I = loaded current (A),

E = voltage (v),

Φ = power factor, and

Q = extruded quantity (Kg/hr).

8. A process for producing a polyolefin thermoplastic elastomer composition according to claim 1, wherein said extender oil is at least one compound selected from paraffin, naphthene or aromatic compounds.

9. A process for producing a polyolefin thermoplastic elastomer composition, comprising the steps of:

forming a blend of

(a) 50 to 80% by weight of a soft segment component selected from the group comprising an ethylene-propylene copolymer rubber and an ethylene-propylene-diene terpolymer;

(b) 50 to 20% by weight of a hard segment selected from the group comprising a crystalline ethylene-propylene block copolymer having an ethylene content of at least 5% by weight and a melt flow index of 0.5 to 30 g/10 minutes, and a crystalline ethylene-propylene random copolymer having an ethylene content of at least 1.5% by weight and a melt flow index of 0.5 to 30 g/10 minutes, based upon 100 parts by weight of the total of (a) and (b);

(c) 0.3 to 5 parts by weight of an organosilane;

(d) 0.1 to 3 parts by weight of an organic radical-generator exhibiting a half-life period for one minute at a temperature of 170°C or higher;

(e) 0 to 100 parts by weight of an extender oil; and

(f) 0.3 to 5 five parts by weight of white carbon;

followed by subjecting the resulting blend to dynamic partial crosslinking carried out by means of a twin-screw extruder so as to give a specific energy W of 0.08 to 0.8, expressed by the following formula:

$$W = \sqrt{3} \cdot (I - I_o) \cdot E \cdot \Phi/1000 \cdot Q$$

wherein

W = specific energy (Kwhr/Kg),

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I = loaded current (A),

I_o = loaded current at the time of empty-driven screw (A),

E = voltage (v),

Φ = power factor, and

Q = extruded quantity (Kg/hr).