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SPECIFICATION

THERMOPLASTIC RESIN COMPOSITION

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a thermoplastic resin composition. Particularly, the present invention relates to a thermoplastic resin composition comprising a polypropylene and an olefin copolymer rubber. This composition has superior mechanical properties such as flexural strength, thermal rigidity resistance and impact resistance and is suitably used for home electric parts, etc.

Prior Art

In recent years, a crystalline propylene-ethylene block copolymer has been used as forming materials such as home electric parts. This crystalline propylene-ethylene block copolymer has a balance among flexural modulus, heat distortion temperature and impact strength, but has a drawback such as insufficient impact strength at low temperature. It is disclosed in Japanese Patent Publication (Unexamined) Nos. Sho 53-22552(1983) and Sho 53-40045(1983) to incorporate an ethylene-propylene copolymer rubber into the crystalline



propylene-ethylene block copolymer for improving low-temperature impact strength. This composition, however, is inferior in flexural modulus and thermal properties such as heat distortion temperature and the like because of addition of the ethylene-propylene copolymer rubber. For resolving this problem, it is disclosed in, for example, Japanese Patent Publication (Unexamined) Nos. Sho 51-136735(1976) and Sho 53-64256(1978), Sho 53-64257(1978), Sho 57-55952(1982), Sho 57-207630(1982), Sho 58-17139(1983), Sho 58-111846(1983), and Sho 59-98157(1984), and Japanese Patent Publication (Examined) No. Sho 55-3374(1980) and the like, to add an inorganic filler such as calcium carbonate, barium sulfate, mica, crystalline calcium silicate, talc and the like.

Further, recently, in Japanese Patent Publication (Unexamined) Nos. Hei 5-59251(1993) and 5-230321(1993), there is proposed a resin composition improved in flexural modulus, surface hardness and the like by rising isotactic pentad fraction of propylene homopolymer portion in an ethylene-propylene block copolymer. In Japanese Patent Publication (Examined) Nos. Sho 36-11240(1961), Sho 38-2126(1963), Sho 41-21785(1966) and the like, it is proposed that impact resistance is improved by adding a vulcanized rubber to an olefinic plastics. However, as blending of the vulcanized rubber

gives a reduced flowability resulting to easy occurrence of bad appearance, there is proposed in Japanese Patent Publication (Examined) Nos. Sho 56-15740(1981) and 56-15743(1981) and the like, a composition improved in a flowability by blending a mineral oil type softening agent and a peroxide non-crosslinking type rubbery material. Further, in Japanese Patent Publication (Unexamined) No. Hei 6-145437(1994), there is proposed a material having a good balance between impact strength and rigidity.

But, recently, for use at highly thermal portion, improvement of home electric parts in thermal rigidity resistance has been required still more. However, in the conventional technic, there was a limitation in improvement of thermal rigidity resistance without damaging low-temperature impact resistance because low-temperature impact resistance and thermal rigidity resistance are antipodal properties each other.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a thermoplastic resin composition improved in a low-temperature impact strength and thermal rigidity resistance by use of a specific polypropylene.

Another object of the present invention is to

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provide a thermoplastic resin composition moreover improved in a low-temperature impact strength and thermal rigidity resistance by blending an inorganic filler to the above-thermoplastic resin composition.

The present inventors have studied about an improvement of impact resistance and thermal rigidity resistance by dispersing an olefin copolymer rubber in a polypropylene. As the result, the present inventors found that the impact resistance and thermal rigidity resistance were improved at the same time by melt-mixing a specific polypropylene with a material obtained by dynamically heat-treating a mixture of a polypropylene and an olefin copolymer rubber in the presence of an organic peroxide and crosslinking adjuvant and achieved the present invention.

According to the present invention, there is a provided a thermoplastic resin composition prepared by mixing (1) a heat-treated material obtained by dynamically heat-treating a mixture of 10 to 50 % by weight of a propylene homopolymer and/or an ethylene-propylene block copolymer(A) having 0.5 to 10g/min. of a melt index measured according to JIS-K-6758 at 230°C and 50 to 90 % by weight of an olefin copolymer rubber(B), with (2) a propylene homopolymer and/or an ethylene-propylene block copolymer (C) having 30 to 150g/min. of a melt index

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measured according to JIS-K-6758 at 230°C, whereby a final thermoplastic resin composition contains 10 to 40% by weight of the olefin copolymer rubber(B), and a thermoplastic composition prepared by blending an inorganic filler into the thermoplastic resin composition.

The present invention is explained in detail below.

DETAILED DESCRIPTION OF THE INVENTION

In the present invention, the crystalline propylene homopolymer (referred to simply as "propylene homopolymer" hereinafter) is obtained by homopolymerizing propylene with a Ziegler-Natta catalyst system. The crystalline ethylene-propylene block copolymer (referred to simply as "ethylene-propylene block copolymer" hereinafter)(A) has a propylene homopolymer portion as the first segment and propylene-ethylene random copolymer portion as the second segment. and is obtained by homopolymerizing propylene and subsequently random copolymerizing propylene and ethylene. In the present invention, these polymers can be used alone or as a mixture thereof.

A melt index measured according to JIS-K-6758 at 230°C of the polymer (A) described above is 0.5 to



10g/min. and preferably 3 to 9 g/10min. The melt index of less than 0.5 g/10min. leads to bad appearance of a shaped article because of low flowability at molding. The melt index of more than 10 g/min. leads to a decrease of mechanical property.

An ethylene content of the ethylene-propylene random copolymer portion in the ethylene-propylene block copolymer(A) preferably 20 to 70 % by weight and more preferably 25 to 60 % by weight.

In the ethylene-propylene block copolymer, a weight ratio (X) of propylene-ethylene random copolymer portion to the total block copolymer can be determined by measuring the quantity of fusion of crystal of each the propylene homopolymer portion and the total block copolymer and calculating from the following equations:

$$X=1-(\Delta Hf)_T / (\Delta Hf)_P$$

$(\Delta Hf)_T$:Quantity of heat of fusion of the total block copolymer (cal/g)

$(\Delta Hf)_P$:Quantity of heat of fusion of the propylene homopolymer portion (cal/g)

An ethylene content can be determined according to a calibration curve method measuring each absorbance of characteristic absorption of methyl group and methylene group in IR spectrum of the block copolymer formed to a pressed sheet. The ethylene content of the ethylene-



propylene copolymer portion can be determined by measuring the ethylene content of the total ethylene propylene block copolymer and calculating the following equation:

$$(C_2')_{EP} = (C_2')_T / X$$

$(C_2')_{EP}$: Ethylene content in the total block copolymer

$(C_2')_T$: Ethylene content in the propylene-ethylene random copolymer portion.

The olefinic copolymer rubber (B) used in the present invention is an ethylene- α -olefin copolymer and an ethylene- α -olefin-non-conjugated diene terpolymer. As an α -olefin, propylene, butene-1, pentene-1, hexene-1, heptene-1, octene-1 and the like are used, and among these, propylene and butene-1 are preferred.

As the non-conjugated diene, for example, a chain non-conjugated diene such as 1,4-hexadiene, 1,6-octadiene; a cyclic non-conjugated diene such as 1,4-cyclohexadiene, dicyclopentadiene, 5-vinylnorbornene, 5-ethylidene-2-norbornene; a triene such as 2,3-diisopropylidene-5-norbornene, 2-ethylidene-3-isopropylidene-5-norbornene are illustrated and among them, 1,4-hexadiene, dicyclopentadiene and 5-ethylidene-2-norbornene are preferred. As the olefinic copolymer rubber (B), 2 or more of them are not prevented to be used.



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The ethylene content of the olefinic copolymer rubber (B) is 90 to 40% by weight, an α -olefin content is 10 to 60% by weight and a non-conjugated diene content is 0 to 12% by weight. When the ethylene content exceeds 90% by weight, the ethylene component becomes much and therefore, a crystallinity appears in the copolymer rubber to decrease a low-temperature impact strength as a result. When it is less than 40% by weight, a decomposition reaction according to a peroxide is too apt to proceed and therefore, it causes a deterioration of a mechanical property and a bad appearance of a molded-article. An ethylene content is preferably 80 to 45% by weight. Besides, when a non-conjugated diene content exceeds 12% by weight, it becomes difficult to control a cross-linking reaction. It should be necessary that the olefinic copolymer rubber (B) has its Mooney viscosity at 100°C (ML₁₊₄ 100°C) of 10 to 100 and preferably 20 to 80. When the Mooney viscosity at 100°C is less than 10, a mechanical property is inferior and when it exceeds 100, a flowability is inferior to cause a bad appearance of an injection-molded article.

The ratio of the olefinic copolymer rubber(B) in 100% by weight of the mixture of the propylene homopolymer and/or the ethylene-propylene block copolymer(A) and the olefinic copolymer rubber(B) is 50



to 90% by weight and preferably 60 to 80% by weight. When it is less than 50% by weight, a decomposition reaction according to a peroxide proceeds insufficiently and it is not achieved to improve a mechanical property. When it exceeds 90% by weight, a thermoplastic property hardly appears.

The examples of the organic peroxide used in the present invention include

2,5-dimethyl-2,5-di(t-butylperoxy)hexane,

2,5-dimethyl-2,5-di(t-butylperoxy)hexine-3,

1,3-bis(t-butylperoxyisopropyl)benzene,

1,1-di(t-butylperoxy)-3,5,5-trimethylcyclohexane,

2,5-dimethyl-2,5-di(peroxybenzoyl)hexine-3,

dicumylperoxide and the like. There is particularly no restriction and it can be suitably selected according to a melt-kneading condition.

The added amount of the organic peroxide can be selected as within the range of 0.01 to 1.0% by weight per 100% by weight of (A) + (B). When it is less than 0.01% by weight, an effect of the cross-linking reaction is little and when it exceeds 1.0% by weight, it is difficult to control the cross-linking reaction.

As the cross-linking agent used in the present invention, a bismaleimide such as, for example, N,N'-m-phenylene bismaleimide and toluylene bismaleimide, a



multi-functional compound such as p-quinonedioxime, nitrobenzene, diphenylguanidine, trimethylolpropane, ethyleneglycol dimethacrylate and the like can be used. As N,N'-m-phenylene bismaleimide, for example, Sumifine BM(Registered Trade Mark)(manufactured by Sumitomo Chemical Company Ltd.), HVA-2(manufactured by E.I.Du Pont de Nemours & Company Ltd.) and the like can be used.

The added amount can be selected as within the range of 0.01 to 5.0% by weight per 100% by weight of (A) + (B). When it is less than 0.01% by weight, the effect of the cross-linking reaction hardly appears and when it exceeds 5.0% by weight, a moldability is inferior. It is preferably 0.05 to 2.0% by weight.

The heat-treated article of the present invention (in some cases, referred to as "dynamic heat-treated article") is obtained by heat-treating dynamically the propylene homopolymer and/or the ethylene-propylene block copolymer(A) and the olefinic copolymer rubber(B) in the presence of the above-mentioned organic peroxide and the cross-linking agent.

As the method heat-treating dynamically in the present invention, a melt-kneading can be performed with a well-known apparatus for kneading such as a mixing roll, a Banbury mixer, a twin screw extruder, a kneader, a continuous mixer or the like at a temperature of 160 to

280°C. In this case, it is preferred to perform in an inert gas such as nitrogen, carbon dioxide and the like.

In the present invention, it is preferred in the dynamic heat-treated article not to use a mineral oilic softener used for the improvement of a flowability and an appearance in an usual thermoplastic elastomer. A mineral oilic softener is not suitable to the object of the present invention owing to the deterioration of a rigidity and a thermal resistance.

The propylene homopolymer and/or the ethylene-propylene block copolymer (C) used for the present invention blended with the dynamic heat-treated article is a crystalline homopolymer of propylene (referred to simply as "homopolymer of propylene " hereinafter), or a crystalline ethylene-propylene block copolymer (referred to simply as "ethylene-propylene block copolymer" hereinafter), namely, the one obtained by copolymerizing ethylene and propylene after homopolymerizing propylene. these may be used alone or as a mixture thereof.

An ethylene content of an ethylene-propylene copolymer portion in the ethylene-propylene block copolymer (C) should be 20 to 70% by weight and preferably 25 to 60% by weight. An isotactic pentad fraction of a propylene homopolymer portion is needed to be 0.98 or more. When it is less than 0.98, it is

difficult to obtain a rigidity and a thermal resistance necessary for the object of the present invention.

A melt index of the propylene homopolymer portion is needed to be 30 to 150g/10min. When it is less than 30g/10min., a flowability is low and when it exceeds 150g/10min., it causes the deterioration of a mechanical property. Besides, a propylene homopolymer portion in the ethylene-propylene block copolymer (C) can be obtained by taking out from a polymerization vessel after homopolymerizing propylene at the polymerization. The propylene homopolymer portion means both the propylene homopolymer and the propylene homopolymer portion of the ethylene-propylene block copolymer (C).

An isotactic pentad fraction mentioned hereby is an isotactic chain in five monomer units of a crystalline polypropylene molecular chain measured by using a method published in Macromolecules, vol.6, 925(1973) by A.Zambelli et al, that is, ^{13}C -NMR, and in other words, a propylene monomer unit ratio being the center of a chain wherein five propylene monomer units are meso-bonded successively. However, concerning an ascription of NMR absorption peak, it is to be performed in accordance with Macromolecules, Vol.8, 687(1975) published thereafter. In the concrete, an isotactic-pentad ratio is measured as an area ratio of a mmmmm peak to total absorption peaks

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of ^{13}C -NMR spectrum. An isotactic pentad ratio of CRM No. M19-14 Polypropylene PP/MWD/2 of NATIONAL PHYSICAL LABORATORY in U. K. measured according to this method was 0.944.

In the present invention, concerning a method blending the heat-treated article, and the propylene homopolymer and/or ethylene-propylene block copolymer (C), they can also be melt-kneaded with a well-known kneading machine in like manner as the case of the fore-mentioned dynamic heat-treated article. The melt-kneading may be divided into two steps and may be carried out using a multi-step feeding type biaxial melt-kneading machine in one step.

The content of the olefinic copolymer rubber (B) in the thermoplastic resin composition of the present invention thus obtained should be 10 to 40% by weight. When it is less than 10% by weight, a low-temperature impact strength is inferior and when it exceeds 40% by weight, a flowability is inferior to cause a bad appearance of a molded-article. It is preferably 12 to 30% by weight.

In the present invention, further, a rigidity and a thermal resistance can be improved by adding the inorganic fillers (D) to the above-mentioned thermoplastic resin composition comprising (A), (B) and



(c). The added amount of the inorganic fillers (D) is 5 to 40% by weight to (A) to (D). When it is less than 5% by weight, an effect improving a rigidity and a thermal resistance is little and when it exceeds 40% by weight, a flowability deteriorates.

As the inorganic fillers (D) used, ones improving a rigidity and a thermal resistance may be good, and for example, calcium carbonate, barium sulfate, a mica, a crystalline calcium silicate, a talc, a glass fiber and the like are illustrated. Particularly, a talc and a glass fiber are preferred.

As a talc, one having an average particle size of 1 to $5\mu\text{m}$ is preferred. When the average particle size is less than $1\mu\text{m}$, problems such as a re-coagulation, a bad dispersion and the like tend to appear. When the average particle size is more than $5\mu\text{m}$, an effect improving a rigidity and a thermal resistance tends to smaller degree. As a glass fiber, a chopped glass having a fiber diameter of 4 to $13\mu\text{m}$ treated with a silane-coupling agent is preferably used.

In the present invention, the fore-mentioned kneading apparatus can be similarly used for blending the inorganic fillers (D) and a method blending (D) after obtaining the above-mentioned thermoplastic resin composition comprising (A) to (c) in advance, or a method

blending (D) simultaneously when (C) is blended to the heat-treated article of (A) and (B) or the like can be adopted. Usually, a method adding and blending simultaneously (C) and (D) to the heat-treated article of (A) and (B) is adopted.

Further, the thermoplastic resin composition relating to the present invention may contain thermal stabilizers, nucleating agents, ultra violet absorbers, lubricating agents, antistatic agents, flame retardants, pigments, dyes, other polymers and the like so long as the object of the present invention is not damaged.

EXAMPLES

Examples of the present invention are illustrated as follows but the present invention is not limited thereto.

The measurement methods of physical properties in the Examples and the specification of the kneading apparatus are as follows:.

(1) Melt index (MI) was performed according to a method prescribed in JIS-K-6758. A measurement temperature was 230°C and it was measured under a load of 2.16kg.

(2) Bending test was measured according to a method prescribed in JIS-K-7203. A test piece (a thickness of 6.4mm) molded by injection-molding was used and a flexural modulus was evaluated under conditions of span

length of 100mm and a loading speed of 2.0mm/min.. A measurement temperature was 23°C.

(3) Izod impact strength was measured according to a method prescribed in JIS-K-7110. A test piece (a thickness of 6.4mm) molded by injection-molding was used and a notched impact strength of test piece notched after the molding was evaluated. A measurement temperature was 23°C unless remarking. In other case except the temperature, a measurement was performed after modulating a state for 2 hours in a constant temperature bath at a fixed temperature.

(4) Rockwell hardness

Rockwell hardness was measured according to a method prescribed in JIS-K-7202. A test piece (a thickness of 6.4mm) molded by injection-molding was used and evaluated by using a steel ball of R. A value was represented by a R scale.

(5) Heat distortion temperature

Heat distortion temperature was measured according to a method prescribed in JIS-K-7207. A test piece (a thickness of 6.4mm) molded by injection-molding was used and a temperature wherein the test piece formed a bending of 0.254mm when a temperature was elevated at a rate of 2°C/min. under a fiber stress of 4.6kgf/cm².

(6) Banbury mixer

MIXTRON BB-16 MIXER having 2 wings-type rotor and a chamber volume of 17.7 l manufactured by Kobe Steel Works Ltd. was used.

(7) Twin screw kneading extruder

TEX-44SS-30W-2V (a different-direction rotor type) having two screws of 44mm × 30L/D manufactured by Nippon Steel Works Ltd. was used.

In Examples and Comparative Examples illustrated as follows, various materials abbreviated in Tables 1 and 2, that is, the following ones are used.

PP: Propylene homopolymer

BC: Ethylene-propylene block copolymer rubber

EPR: Ethylene-propylene copolymer rubber

EBR: Ethylene-butene-1 copolymer rubber

EPDM: Ethylene-propylene-non-conjugated diene terpolymer rubber

TALC: Talc

PO: Organic peroxide

2,5-dimethyl-2,5-di(t-butylperoxy)hexane

BM: Cross-linking agent

N,N'-m-phenylene bismaleimide

Example 1

30% by weight of a propylene homopolymer (PP-1) having an isotactic pentad fraction of a propylene homopolymer portion of 0.97 and a melt index of 8g/10min.

and 70% by weight of an ethylene-propylene-non-conjugated diene terpolymer rubber (EPDM-1) having a propylene content of 50% by weight, 5-ethylidene-2-norbornene of the non-conjugated diene of 5.3% by weight and a Mooney viscosity at 100°C of 43 were melt-kneaded in the presence of 0.04% by weight of 2,5-dimethyl-2,5-di(t-butylperoxy)hexane and 0.5% by weight of N,N'-m-phenylene bismaleimide with a Banbury mixer in an adiabatic state for 10 minutes and successively, passed through a roll to be pelletized with a sheet cutter (hereinafter, named as MB or MB pellets)(the first step).

Next, after 44% by weight of a propylene homopolymer (PP-3) having an isotactic pentad fraction of a propylene homopolymer portion of 0.98 and a melt index of 77g/10min., 36% by weight of an ethylene-propylene block copolymer (BC) having an ethylene-propylene copolymer portion content of 16.7% by weight and a melt index of 12g/10min. and 20% by weight of the MB pellets prepared in the first step were homogeneously blended with various kinds of stabilizers, they were pelletized with a twin-axial kneading extruder at 200°C (the second step) and test pieces were prepared with an injection-molding machine to be evaluated. MB and the compositions of homogeneous mixtures (compounds) were shown in Table 2 for reference. The results are shown in Table 4.

Examples 2 to 9

MB of the materials in Table 1 and the compositions in Table 2 were melt-kneaded with a Banbury mixer in an adiabatic state for 10 minutes and successively, passed through a roll to be pelletized with a sheet cutter and named as MB(the first step). The compounds of the compositions in Table 2 containing the MB pellets were pelletized with a twin-axial kneading extruder at 200°C (the second step) and test pieces were prepared with an injection-molding machine to be evaluated. The results are shown in Table 4.

Comparative Examples 1 to 5

Compounds of the materials in Table 1 and the compositions in Table 3 were pelletized in like manner as the second step of Example 1 and test pieces were prepared to be evaluated. The results are shown in Table 4.

Comparative Examples 6 to 12

Compounds of the materials in Table 1 and the compositions in Table 3 were pelletized in like manner as the second step of Example 1 and test pieces were prepared to be evaluated. The results are shown in Table 5 in combination with Examples 2 and 6 for reference.

Example 10 and Comparative Examples 13 and 14

MB of the materials in Table 1 and the compositions

in Table 4 were melt-kneaded with a Banbury mixer in an adiabatic state for 10 minutes and successively, passed through a roll to be pelletized with a sheet cutter and named as MB(the first step). The compounds of the compositions in Table 4 containing the MB pellets were pelletized with a twin-axial kneading extruder at 200°C (the second step) and test pieces were prepared with an injection-molding machine to be evaluated. The results are shown in Table 6 in combination with Example 2 for reference.

Table 1

Sample		MI(230°C)(g/10min.)		Isotactic pentad fraction	Ethylene-propylene copolymer portion	
		Total	PP portion of BC		Content 1 (wt%)	Content 2 (wt%)
Polypropylene	PP-1	8	—	0.97	—	—
	PP-2	7	—	0.99	—	—
	PP-3	77	—	0.98	—	—
	PP-4	68	—	0.99	—	—
	PP-5	30	—	0.98	—	—
	BC	12	35	0.98	16.7	36.5
				(PP portion)		
Sample		ML ₁₊₄ 100°C		α -olefin content	Nonconjugated diene content (wt%)	
Rubber	EPR	52		27(propylene)	—	
	EBR	48		17(butene-1)	—	
	EPDM-1	43		50(propylene)	5.3 (EN)	
	EPDM-2	88		28(propylene)	7.2 (EN)	

PP:Propylene homopolymer BC:Ethylene-propylene block copolymer EPR:Ethylene-propylene copolymer rubber EBR:Ethylene-butene-1 copolymer rubber EPDM:Ethylene-propylene-nonconjugated terpolymer rubber EN:5-Ethylidene-2-norbornene Content 1:Content of ethylene propylene copolymer portion Content 2:Ethylene content in ethylene propylene copolymer portion

Table 2

	M B (wt%)							Compound (wt%)							
	PP-1	PP-2	EPDM-1	PIB	OIL	PO	BM	PP-3	PP-4	PP-5	BC	MB	EPR	EBR	EPDM-2 TALC
Example 1	30	-	70	-	-	0.04	0.5	44	-	-	36	20	-	-	-
2	-	30	70	-	-	0.04	0.5	44	-	-	36	20	-	-	-
3	30	-	70	-	-	0.02	0.4	-	49	-	30	21	-	-	-
4	30	-	70	-	-	0.02	0.4	-	29	-	30	21	-	-	20
5	30	-	70	-	-	0.02	0.5	-	24	-	36	20	-	-	20
6	-	30	70	-	-	0.04	0.5	24	-	-	36	20	-	-	20
7	30	-	70	-	-	0.02	0.4	-	29	-	30	21	-	-	20
8	30	-	70	-	-	0.04	0.5	-	29	-	30	21	-	-	20
9	-	30	70	-	-	0.04	0.5	-	24	-	36	20	-	-	20
10	-	30	70	-	-	0.2	0.5	44	-	-	36	20	-	-	-

TALC: Talc (JR-39 manufactured by Nihon Talc Co. Ltd.)

PIB : Polyisobutylene (Exxon Vistanex L-100)

OIL : Parafinic process oil

PO : 2,5-dimethyl-2,5-di(t-butylperoxy)hexane

BM : N,N'-m-phenylene bismaleimide

Table 3

	M B (wt%)							Compound (wt%)							
	PP-1	PP-2	EPDM-1	PIB	OIL	PO	BM	PP-3	PP-4	PP-5	BC	MB	EPR	EBR	EPDM-2 TALC
Comparative								50	-	-	36	-	14	-	-
Example 1	-	-	-	-	-	-	-	50	-	-	36	-	-	14	-
2	-	-	-	-	-	-	-	50	-	-	36	-	-	-	14
3	-	-	-	-	-	-	-	42	-	-	22	-	-	-	16 20
4	-	-	-	-	-	-	-	-	42	-	22	-	6	8	2 20
5	-	-	-	-	-	-	-	38	-	-	36	26	-	-	-
6	-	23	54	-	23	0.04	0.5	41	-	-	36	23	-	-	-
7	15	-	54	8	23	0.3	0.5	-	-	71	-	29	-	-	-
8	-	30	70	-	-	0.04	0.5	-	-	68	-	32	-	-	-
9	15	-	54	8	23	0.3	0.5	24	-	-	36	20	-	-	20
10	-	23	54	-	23	0.04	0.5	-	-	51	-	29	-	-	20
11	-	30	70	-	-	0.04	0.5	-	-	48	-	32	-	-	20
12	15	-	54	8	23	0.3	0.5	44	-	-	36	20	-	-	-
13	-	30	70	-	-	-	0.5	44	-	-	36	20	-	-	-
14	-	30	70	-	-	0.01	0.5								

Table 4

	M I	Specific gravity	Flexural modulus	Izod Impact 23°C -30°C		HDT	Roackwell hardness
Unit	g/10min.		kg/cm ²	kg · cm/cm		°C	R scale
Example	1	20	0.902	11500	17 4.6	114	80
	2	20	0.902	11500	14 4.5	113	81
	3	16	0.902	12100	12 4.1	115	83
	4	8	1.034	22800	21 4.1	137	73
	5	8	1.038	23500	27 4.1	141	73
	6	11	1.035	23100	22 4.0	140	75
	7	9	1.039	24200	21 3.8	141	74
	8	8	1.036	22700	31 4.1	139	75
	9	11	1.039	24200	24 3.7	142	77
Comparative							
Example	1	26	0.900	12400	7.3 2.6	111	86
	2	26	0.904	13400	6.8 2.0	116	89
	3	25	0.902	13300	5.9 2.7	113	88
	4	17	1.035	23500	7.6 2.9	137	78
	5	19	1.040	26700	7.1 2.3	145	85

Table 5

	M I	Specific gravity	Flexural modulus	Izod Impact 23°C -30°C	HDT	Roackwell hardness
Unit	g/10min.		kg/cm ²	kg · cm/cm	°C	R scale
Example 2	20	0.902	11500	14 4.5	113	81
6	11	1.035	23100	22 4.0	140	75
Comparative						
Example 6	28	0.902	9700	12 3.3	107	89
7	28	0.902	10100	20 4.1	107	66
8	12	0.899	9300	17 4.4	108	63
9	20	0.900	7400	19 4.3	98	30
10	14	1.040	21000	13 3.0	134	66
11	8	1.034	20300	20 4.0	131	58
12	12	1.035	17900	25 4.2	121	25

Table 6

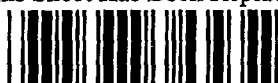
	M I	Specif ic gravit y	Flexural modulus	Izod Impact 23°C -30°C	HDT	Roackwell hardness
Unit	g/10min.		kg/cm ²	kg · cm/cm	°C	R scale
Example 2	20	0.902	11500	14 4.5	113	81
10	21	0.902	11500	14 4.5	111	81
Comparative						
Example 13	23	0.901	11900	9 3.1	109	85
14	20	0.902	11900	13 3.3	105	84

According to the present invention, there are provided a thermoplastic resin composition comprising a heat-treated composition (1) obtained by dynamically heat-treating a specific polypropylene and an olefin copolymer rubber in the presence of an organic peroxide and a crosslinking agent and a specified polypropylene (2), and further, a composition prepared by incorporating an inorganic filler into the above-described thermoplastic resin composition. These compositions are superior in mechanical properties, particularly, for example, flexural modulus, thermal rigidity resistance and impact resistance, and can be suitably used for home electric parts and the like.

WHAT IS CLAIMED IS:

1. A thermoplastic resin composition prepared by mixing a heat-treated material (1) obtained by dynamically heat-treating a mixture of 10 to 50% by weight of a crystalline propylene homopolymer and/or a crystalline ethylene-propylene block copolymer(A) having a melt index measured according to JIS-K-6758 at 230°C of 0.5 to 10g/min. and 50 to 90% by weight of an olefinic copolymer rubber (B) in the presence of an organic peroxide and a crosslinking agent, with a crystalline propylene homopolymer and/or a crystalline ethylene-

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propylene block copolymer (C)(2) having a melt index measured according to JIS-K-6758 at 230°C of a propylene homopolymer portion of 30 to 150g/min. and an isotactic pentad fraction of a propylene homopolymer portion of 0.98 or more whereby a final thermoplastic resin composition contains 10 to 40% by weight of the olefinic copolymer rubber(B).

2. A thermoplastic resin composition according to claim 1, wherein the olefinic copolymer rubber (B) is an ethylene- α -olefin copolymer or an ethylene- α -olefin-non-conjugated diene terpolymer having an ethylene content of 90 to 40% by weight, an α -olefin content of 10 to 60% by weight and a non-conjugated diene content of 0 to 12% by weight and its Mooney viscosity (ML₁₊₄ 100°C) is 10 to 100.

3. A thermoplastic resin composition according to claim 2, wherein the α -olefin is propylene or butene-1.

4. A thermoplastic resin composition according claim 1, wherein an added amount of the organic peroxide is 0.01 to 1.0% by weight based on the total of the propylene homopolymer and/or an ethylene-propylene block copolymer(A) and the olefinic copolymer rubber(B).

5. A thermoplastic resin composition according claim 1, wherein an added amount of the crosslinking agent is 0.01 to 5.0% by weight based on the total of the





crystalline propylene homopolymer and/or the crystalline ethylene-propylene block copolymer(A) and the olefinic copolymer rubber(B).

6. A thermoplastic resin composition according to claim 1, wherein a mixture of the crystalline propylene homopolymer and/or the crystalline ethylene-propylene block copolymer (A) and the olefinic copolymer rubber (B) contain 20 to 40% by weight and 60 to 80% by weight based on the mixture, respectively.

7. A thermoplastic resin composition according to claim 1, wherein 5 to 40% by weight of an inorganic filler (D) is blended to 95 to 60% by weight of the thermoplastic resin composition.

8. A thermoplastic resin composition according claim 2, wherein 5 to 40% by weight of an inorganic filler (D) is blended to 95 to 60% by weight of the thermoplastic resin composition.

9. A thermoplastic resin composition according claim 3, wherein 5 to 40% by weight of an inorganic filler (D) is blended to 95 to 60% by weight of the thermoplastic resin composition.

10. A thermoplastic resin composition according to claim 4, wherein wherein 5 to 40% by weight of an inorganic filler (D) is blended to 95 to 60% by weight of the thermoplastic resin composition.



ABSTRACT OF THE DISCLOSURE

THERMOPLASTIC RESIN COMPOSITION

A thermoplastic resin composition comprising a heat-treated composition (1) obtained by heat-treating dynamically a specific polypropylene and an olefin copolymer rubber in the presence of an organic peroxide and a crosslinking agent and a specified polypropylene (2), and further, a composition prepared by incorporating an inorganic filler into the above-described thermoplastic resin composition.

These compositions are superior in mechanical properties such as flexural modulus, thermal rigidity, resistance and impact resistance, and can be suitably used for home electric parts and the like.

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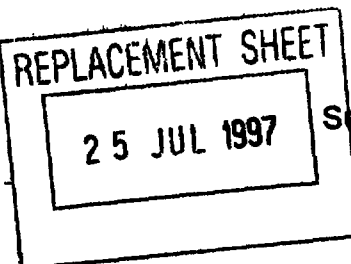
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propylene-ethylene block copolymer for improving low-temperature impact strength. This composition, however, is inferior in flexural modulus and thermal properties such as heat distortion temperature and the like because of addition of the ethylene-
5 propylene copolymer rubber. For resolving this problem, it is disclosed in, for example, Japanese Patent Publication (Unexamined) Nos. Sho 51-136735 (1976) and Sho 53-64256 (1978), Sho 53-64257 (1978), Sho 57-55952 (1982), Sho 57-207630 (1982), Sho 58-17139 (1983), Sho 58-111846 (1983), and Sho 59-98157
10 (1984), and Japanese Patent Publication (Examined) No. Sho 55-3374 (1980) and the like, to add an inorganic filler such as calcium carbonate, barium sulfate, mica, crystalline calcium silicate, talc and the like.

Further, recently, in Japanese Patent Publication
15 (Unexamined) Nos. Hei 5-59251 (1993) and 5-230321 (1993), there is proposed a resin composition improved in flexural modulus, surface hardness and the like by rising isotactic pentad fraction of propylene homopolymer portion in an ethylene-propylene block copolymer. In Japanese Patent Publication
20 (Examined) Nos. Sho 36-11240 (1961), Sho 38-2126 (1963), Sho 41-21785 (1966) and the like, it is proposed that impact resistance is improved by adding a vulcanized rubber to an olefinic plastics. However, as blending of the vulcanized rubber



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provide a thermoplastic resin composition moreover improved in a low-temperature impact strength and thermal rigidity resistance by blending an inorganic filler to the above-thermoplastic resin composition.

5 The present inventors have studied about an improvement of impact resistance and thermal rigidity resistance by dispersing an olefin copolymer rubber in a polypropylene. As the result, the present inventors found that the impact resistance and thermal rigidity resistance were improved at the same time by
10 melt-mixing a specific polypropylene with a material obtained by dynamically heat-treating a mixture of a polypropylene and an olefin copolymer rubber in the presence of an organic peroxide and crosslinking adjuvant and achieved the present invention.

According to the present invention, there is provided a
15 thermoplastic resin composition prepared by a process comprising mixing:

(1) a heat-treated material obtained by dynamically heat-treating a mixture of 10 to 50% by weight of a crystalline propylene homopolymer and/or a crystalline ethylene-propylene
20 block copolymer (A) having a melt index measured according to JIS-K-6758 at 230°C of 0.5 to 10g/10 min. and 50 to 90% by weight of an olefinic copolymer rubber (B) in the presence of an organic peroxide and a crosslinking agent; with

(2) a crystalline propylene homopolymer and/or a
25 crystalline ethylene-propylene block copolymer comprising a propylene homopolymer portion and an ethylene-propylene random copolymer portion, (C), wherein the crystalline propylene homopolymer and/or propylene homopolymer portion of the crystalline ethylene-propylene copolymer have a melt index
30 measured according to JIS-K-6758 at 230°C of 30 to 150g/10 min.

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and an isotactic pentad fraction of 0.98 or more,

and wherein the final thermoplastic resin composition contains 10 to 40% by weight of the olefinic copolymer rubber (B).

5 The present invention is explained in detail below.

DETAILED DESCRIPTION OF THE INVENTION

In the present invention, the crystalline propylene
10 homopolymer (referred to simply as "propylene homopolymer" hereinafter) (A) is obtained by homopolymerizing propylene with a Ziegler-Natta catalyst system. The crystalline ethylene-propylene block copolymer (referred to simply as "ethylene-propylene block copolymer" hereinafter) (A) has a propylene
15 homopolymer portion as the first segment and propylene-ethylene random copolymer portion as the second segment, and is obtained by homopolymerizing propylene and subsequently random copolymerizing propylene and ethylene. In the present invention, these polymers can be used alone or as a mixture
20 thereof.

A melt index measured according to JIS-K-6758 at 230°C of the polymer (A) described above is 0.5 to

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10g/10 min. and preferably 3 to 9 g/10 min. The melt index of less than 0.5 g/10min. leads to bad appearance of a shaped article because of low flowability at molding. The melt index of more than 10 g/10 min. leads to a decrease of mechanical
5 property.

An ethylene content of the ethylene-propylene random copolymer portion in the ethylene-propylene block copolymer (A) preferably 20 to 70% by weight and more preferably 25 to 60% by weight.

10 In the ethylene-propylene block copolymer, a weight ratio (X) of propylene-ethylene random copolymer portion to the total block copolymer can be determined by measuring the heat of fusion of crystals of each of the propylene homopolymer portion and the total block copolymer and calculating from the following
15 equations:

$$X = 1 - (\Delta H_f)_T / (\Delta H_f)_P$$

(ΔH_f)_T: Quantity of heat of fusion of the total block copolymer (cal/g)

(ΔH_f)_P: Quantity of heat of fusion of the propylene homopolymer
20 portion (cal/g)

An ethylene content can be determined according to a calibration curve method measuring each absorbance of characteristic absorption of methyl group and methylene group in IR spectrum of the block copolymer formed to a pressed sheet.
25 The ethylene content of the ethylene-

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propylene copolymer portion can be determined by measuring the ethylene content of the total ethylene propylene block copolymer and calculating the following equation:

$$(C_2')_{EP} = (C_2')_T / X$$

5 $(C_2')_{EP}$: Ethylene content in the total block copolymer (% by weight)

$(C_2')_T$: Ethylene content in the propylene-ethylene random copolymer portion (% by weight).

The olefinic copolymer rubber (B) used in the present
10 invention is preferably selected from an ethylene- α -olefin copolymer and an ethylene- α -olefin-non-conjugated diene or triene terpolymer. As the α -olefin, propylene, butene-1, pentene-1, hexene-1, heptene-1, octene-1 and the like are used, and among these, propylene and butene-1 are preferred.

15 As the non-conjugated diene, for example, a chain non-conjugated diene such as 1,4-hexadiene, 1,6-octadiene; a cyclic non-conjugated diene such as 1,4-cyclohexadiene, dicyclopentadiene, 5-vinyl-2-norbornene, 5-ethylidene-2-norbornene; a triene such as 2,3-diisopropylidene-5-norbornene,
20 2-ethylidene-3-isopropylidene-5-norbornene are illustrated and among them, 1,4-hexadiene, dicyclopentadiene and 5-ethylidene-2-norbornene are preferred. As the olefinic copolymer rubber (B), 2 or more of them are not prevented to be used.

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The ethylene content of the olefinic copolymer rubber (B) is 90 to 40% by weight, an α -olefin content is 10 to 60% by weight and a non-conjugated diene content is 0 to 12% by weight. When the ethylene content exceeds 90% by weight, the ethylene component becomes much and therefore, a crystallinity appears in the copolymer rubber to decrease a low-temperature impact strength as a result. When it is less than 40% by weight, a decomposition reaction according to a peroxide is too apt to proceed and therefore, it causes a deterioration of a mechanical property and a bad appearance of a molded-article. An ethylene content is preferably 80 to 45% by weight. Besides, when a non-conjugated diene content exceeds 12% by weight, it becomes difficult to control a cross-linking reaction. It should be necessary that the olefinic copolymer rubber (B) has a Mooney viscosity at 100°C (ML1+4 100°C) of 10 to 100 and preferably 20 to 80. When the Mooney viscosity at 100°C is less than 10, a mechanical property is inferior and when it exceeds 100, a flowability is inferior to cause a bad appearance of an injection-molded article.

The ratio of the olefinic copolymer rubber (B) in 100% by weight of the mixture of the propylene homopolymer and/or the ethylene-propylene block copolymer (A) and the olefinic copolymer rubber (B) is 50

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to 90% by weight and preferably 60 to 80% by weight. When it is less than 50% by weight, a decomposition reaction according to a peroxide proceeds insufficiently and it is not achieved to improve a mechanical property. When it exceeds 90% by weight, 5 a thermoplastic property hardly appears.

The examples of the organic peroxide used in the present invention include

2,5-dimethyl-2,5-di(t-butylperoxy)hexane,
2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3,
10 1,3-bis(t-butylperoxyisopropyl)benzene,
1,1-di(t-butylperoxy)-3,5,5-trimethylcyclohexane,
2,5-dimethyl-2,5-di(peroxybenzoyl)hexyne-3,
dicumylperoxide and the like. There is particularly no
restriction and it can be suitably selected according to a melt-
15 kneading condition.

The added amount of the organic peroxide can be selected as within the range of 0.01 to 1.0% by weight per 100% by weight of (A) + (B). When it is less than 0.01% by weight, an effect of the cross-linking reaction is little and when it exceeds 1.0% by 20 weight, it is difficult to control the cross-linking reaction.

As the cross-linking agent used in the present invention, a bismaleimide such as, for example, N,N'-m-phenylene bismaleimide and toluylene bismaleimide, a

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of ^{13}C -NMR spectrum. An isotactic pentad ratio of CRM No. M19-14 Polypropylene PP/MWD/2 of NATIONAL PHYSICAL LABORATORY in U.K. measured according to this method was 0.944.

In the present invention, concerning a method blending the
5 heat-treated article, and the propylene homopolymer and/or ethylene-propylene block copolymer (C), they can also be melt-kneaded with a well-known kneading machine in like manner as the case of the forementioned dynamic heat-treated article. The melt-kneading may be divided into two steps and may be carried
10 out using a multi-step feeding type biaxial melt-kneading machine in one step.

The content of the olefinic copolymer rubber (B) in the thermoplastic resin composition of the present invention thus obtained should be 10 to 40% by weight. When it is less than
15 10% by weight, a low-temperature impact strength is inferior and when it exceeds 40% by weight, a flowability is inferior to cause a bad appearance of a molded-article. It is preferably 12 to 30% by weight.

In the present invention, further, a rigidity and a thermal
20 resistance can be improved by adding the inorganic fillers (D) to the above-mentioned thermoplastic resin composition comprising (A), (B) and

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WHAT IS CLAIMED IS:

1. A thermoplastic resin composition prepared by a process comprising mixing:
- 5 (1) a heat-treated material obtained by dynamically heat-treating a mixture of 10 to 50% by weight of a crystalline propylene homopolymer and/or a crystalline ethylene-propylene block copolymer (A) having a melt index measured according to JIS-K-6758 at 230°C of 0.5 to 10g/10 min. and 50 to 90% by weight of an olefinic copolymer rubber (B) in the presence of an organic peroxide and a crosslinking agent; with
- (2) a crystalline propylene homopolymer and/or a crystalline ethylene-propylene block copolymer comprising a propylene homopolymer portion and an ethylene-propylene random
- 15 copolymer portion, (C), wherein the crystalline propylene homopolymer and/or propylene homopolymer portion of the crystalline ethylene-propylene copolymer have a melt index measured according to JIS-K-6758 at 230°C of 30 to 150g/10 min. and an isotactic pentad fraction of 0.98 or more,
- 20 and wherein the final thermoplastic resin composition contains 10 to 40% by weight of the olefinic copolymer rubber (B).
2. A thermoplastic resin composition according to claim 1,
- 25 wherein the olefinic copolymer rubber (B) is an ethylene- α -olefin copolymer or an ethylene- α -olefin-non-conjugated diene terpolymer having an ethylene content of 40 to 90% by weight, an α -olefin content of 10 to 60% by weight and a non-conjugated diene content of 0 to 12% by weight and a Mooney viscosity
- 30 (ML1+4 100°C) of 10 to 100.
3. A thermoplastic resin composition according to claim 2, wherein the α -olefin is propylene or butene-1.
- 35 4. A thermoplastic resin composition according to claim 1, wherein the organic peroxide is added in an amount of 0.01 to 1.0% by weight based on the total weight of the crystalline



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propylene homopolymer and/or ethylene-propylene block copolymer (A) and the olefinic copolymer rubber (B).

5. A thermoplastic resin composition according to claim 1,
5 wherein the crosslinking agent is added in an amount of 0.01 to 5.0% by weight based on the total weight of the crystalline propylene homopolymer and/or crystalline ethylene-propylene block copolymer (A) and the olefinic copolymer rubber (B).
- 10 6. A thermoplastic resin composition according to claim 1, wherein said heat-treated material is obtained by dynamically heat-treating a mixture of 20 to 40% by weight of the crystalline propylene homopolymer and/or crystalline ethylene-propylene block copolymer (A) and 60 to 80% by weight of the
15 olefinic copolymer rubber (B).
7. A thermoplastic resin composition according to claim 1, wherein an inorganic filler (D) is blended to the thermoplastic resin composition in an amount of 5 to 40% by weight based on
20 the total weight of (A), (B), (C) and (D).
8. A thermoplastic resin composition according to claim 2, wherein an inorganic filler (D) is blended to the thermoplastic resin composition in an amount of 5 to 40% by weight based on
25 the total weight of (A), (B), (C) and (D).
9. A thermoplastic resin composition according to claim 3, wherein an inorganic filler (D) is blended to the thermoplastic resin composition in an amount of 5 to 40% by weight based on
30 the total weight of (A), (B), (C) and (D).
10. A thermoplastic resin composition according to claim 4, wherein an inorganic filler (D) is blended to the thermoplastic resin composition in an amount of 5 to 40% by weight based on
35 the total weight of (A), (B), (C) and (D).
11. A shaped article comprising a thermoplastic resin composition according to claim 1.



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