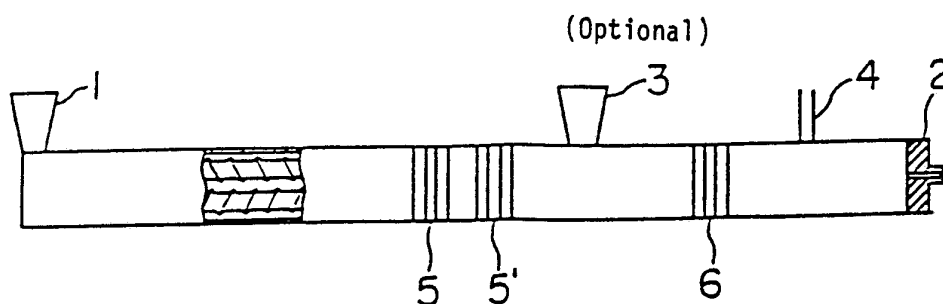




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(54) Title: POLYMER COMPOSITION AND PROCESS FOR PRODUCING THE SAME



(57) Abstract

A polymer composition which comprises a polyamide resin, rubber, unsaturated carboxylic-acid modified rubber, and, optionally, a glass fiber filler, said polyamide resin forming the continuous matrix phase and said rubber forming the uniformly dispersed domain phase having an average diameter of 0.1-5 μm , and process for preparation in a twin-screw extruder. The polymer composition is suitable for use as mechanical, automotive, and electrical parts and building materials formed by injection molding and extrusion molding.

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Title of the Invention

POLYMER COMPOSITION AND PROCESS FOR PRODUCING THE SAME

Technical Field

The present invention relates to a polymer composition
5 composed mainly of a polyamide resin and rubber, particularly
a [fiber-reinforced] polymer composition composed mainly of a
polyamide resin and rubber, optionally fiber reinforced,
having balanced superior mechanical properties, heat
resistance, impact resistance, and moldability, and also to a
10 process for producing the same.

Background Art

Polyamide resins are light in weight and superior in
mechanical properties, heat resistance, wear resistance, and
chemical resistance. Among the most popular polyamide resins
15 are nylon-6 and nylon-66 which are superior especially in
strength and heat resistance.

Despite the superior mechanical strength, heat
resistance, and long-term durability, the moldings of
polyamide resin have a disadvantage that they do not have
20 sufficient impact resistance.

The characteristic properties in which polyamide resins
are lacking are usually possessed by rubber.

There is disclosed in Japanese Patent Laid-open No.
6693/1975 a rubber-reinforced polyamide composed of (A)
25 polyamide resin, (B) crosslinked elastomer having epoxy and

oxy functional groups, and (C) fine particle filler (with the ratio of component (A) to component (B) being 100:6 to 100:70 by weight). In this rubber-reinforced polyamide, said polyamide resin forms the continuous phase and said elastomer
5 forms the dispersion phase, with the two phases forming an interface in which the amide group of the polyamide resin and the epoxy and oxy functional groups of the elastomer chemically bond each other. A disadvantage of this rubber-reinforced polyamide is that it does not have the
10 well-balanced mechanical strength, heat resistance, impact resistance, and moldability because it is composed of polyamide resin and modified elastomer, which are excessively compatible with each other, and hence it has the equalized properties of the two constituents.

15 There is also disclosed in Japanese Patent Laid-open No. 165952/1980 a polyamide composition which is composed of (A) 50-99 parts by weight of polyamide resin and (B) 50-1 parts by weight of modified polyolefin or modified polyolefin elastomer formed by adding 0.001-10 mol% of at least one
20 compound selected from the group consisting of alicyclic carboxylic acid having a cis-type double bond in the ring and a functional derivative thereof to a polyolefin or polyolefin elastomer. Further, there is disclosed a composition which is composed of said polyamide composition and an unmodified
25 polyolefin. In one embodiment glass fiber is also included.

The polyamide composition disclosed in Japanese Patent

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Laid-open No. 165952/1980 does not have the well-balanced mechanical properties, heat resistance, impact resistance, and moldability because of the excessive compatibility of the polyamide resin and modified polyolefin.

5 It is an object of the present invention to provide a polymer composition which has well-balanced heat resistance and impact resistance, with the polyamide resin exhibiting its characteristic properties, especially heat distortion resistance, and the rubber exhibiting its good impact
10 resistance.

It is another object of the present invention to provide a process for producing such a polymer composition.

Summary Of The Invention

In order to achieve the above-mentioned objects, the
15 present inventors carried out a series of researches which led to the finding that it is possible to obtain a polymer composition which exhibits well-balanced mechanical strength, heat resistance, impact resistance, and moldability while retaining the good heat distortion temperature of polyamide
20 resin and the good impact resistance of rubber, if a polyamide resin is incorporated with a rubber and an unsaturated carboxylic acid-modified rubber so as to form a specific morphology in which the rubber uniformly disperses as the domain phase having a specific diameter in the matrix
25 phase of the polyamide resin. The present invention was completed based on this finding.

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Accordingly, the gist of the present invention resides in a polymer composition which comprises a polyamide resin, rubber, unsaturated carboxylic-acid modified rubber, and, optionally, a glass fiber filler said polyamide resin forming
5 the continuous matrix phase and said rubber forming the uniformly dispersed domain phase having an average diameter of 0.1-5 μm .

The polymer composition is produced by a process which comprises feeding said polyamide resin, rubber, and
10 unsaturated carboxylic acid-modified rubber to a twin-screw extruder provided with a hopper, vacuum vent, and die outlet (arranged consecutively) and having a length-to-diameter ratio (L/D) of 25 and above through said hopper, intensively mixing said components in at least one set of a first
15 kneading zone constructed of consecutive four or more kneading discs having an L/D of 1/4 to 1/8 before said components reach the point of L/D 15 downstream from said hopper, and intensively mixing said components again in at least one set of a second kneading zone constructed of
20 consecutive four or more kneading discs having an L/D of 1/4 to 1/8 before said components reach the point short of said vacuum vent and beyond the point of L/D 15 downstream from said hopper. A second hopper, to be used for the addition of glass fiber should be included at the point L/D 15-20
25 downstream from the first hopper, but upstream of the vacuum vent. The glass fiber is thus added after the intensive mixing in the first kneading zone causes a temperature rise

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to 280°-320°C just upstream of the second hopper.

This application is combined from Ja241,586/88 and Ja241,587/88. The specification has been combined. Claims need to be sorted out and U.S. formatting requirements met.

5 Brief Description of the Drawings

Fig. 1 is a partial schematic sectional view showing an example of the twin-screw extruder used for producing the fiber-reinforced polymer composition of the present invention according to the process of the present invention.

10 Fig. 2 is a partial enlarged view showing the kneading zone of the twin-screw extruder used for the process of the present invention.

Fig. 3 is a sectional view showing a pair of kneading discs.

- 15 1 . . . First hopper
2 . . . Die
3 . . . Second hopper (optional)
4 . . . Vent
5, 5' . . . First kneading zone
6 . . . Second kneading zone
10, 11 . . . Screws
12, 12' . . . Kneading discs
20 13, 13' . . . Projecting parts
14, 14' . . . Circumferential parts
15, 15' . . . Spline grooves
N . . . Kneading zone
T . . . Seal ring
S, S' . . . Screw

Description Of The Preferred Embodiments

25 The polyamide resin used in the present invention includes polyamide resins formed from an aliphatic, alicyclic, or aromatic diamine (such as hexamethylene diamine, decamethylene diamine, dodecamethylene diamine,

2,2,4- or 2,4,4-trimethylhexamethylene diamine, 1,3- or
1,4-bis(aminomethyl)cyclohexane,
bis(p-aminocyclohexylmethane), and m- or p-xylylene diamine)
and an aliphatic, alicyclic, or aromatic dicarboxylic acid
5 (such as adipic acid, suberic acid, sebacic acid, cyclohexane
dicarboxylic acid, terephthalic acid, and isophthalic acid);
polyamide resins formed from an aminocarboxylic acid (such as
6-aminocaproic acid, 11-aminoundecanoic acid, and 12
aminododecanoic acid); polyamide resins formed from a lactam
10 (such as ϵ -caprolactam and ω -dodecalactam); copolymer
polyamide resins composed of the above-mentioned components;
and mixtures of these polyamide resins. Typical examples of
the polyamide resin include nylon-6, nylon-66, nylon-610,
nylon-9, nylon-6/66, nylon-66/610, nylon-6/11, nylon-6/12,
15 nylon-12, and nylon-46. Preferable among them are nylon-6
and nylon-66.

These polyamides are not specifically limited in
molecular weight. Usually, they should preferably have a
relative viscosity η_r (measured in 98% sulfuric acid
20 according to JIS K6810) of 1.0 and above. Those having a
relative viscosity of 2.0 and above are preferable because of
their high mechanical strength.

The rubber used in the present invention includes
natural rubber, ethylene-propylene rubber (EPR),
25 ethylene-propylene-diene rubber (EPDM), ethylene-butene
rubber (EBR), butadiene rubber (BR), isoprene rubber (IR),
styrene-butadiene rubber (SBR), nitrile-butadiene rubber

(NBR), chloroprene rubber (CR), butyl rubber (IIR), hydrogenated styrene-butadiene block copolymer rubber (SEBS), polyisobutylene rubber, acrylic rubber, etc.

Preferable among these rubbers are ethylene-butene
5 rubber (EBR), ethylene-propylene rubber (EPR), and hydrogenated styrene-butadiene block copolymer rubber (SEBS). When used as the rubber component, these rubbers impart superior impact resistance to the polymer composition.

The modified rubber used in the present invention is
10 one which is formed by modifying a rubber with an unsaturated carboxylic acid or an anhydride thereof. Examples of the unsaturated carboxylic acid or anhydride thereof include monocarboxylic acid (such as acrylic acid and methacrylic acid), dicarboxylic acid (such as maleic acid, fumaric acid,
15 and itaconic acid), and dicarboxylic acid anhydride (such as maleic anhydride and itaconic anhydride). Preferable among them are dicarboxylic acids and anhydrides thereof.

The rubber to be modified with the unsaturated carboxylic acid or anhydride thereof includes those rubbers
20 enumerated above. Preferred rubbers are ethylene-butene rubber (EBR), ethylene-propylene rubber (EPR), and hydrogenated styrene-butadiene block copolymer (SEBS). When used as the rubber component of the modified rubber, these rubbers impart superior impact resistance to the polymer
25 composition.

The modified rubber should preferably contain the unsaturated carboxylic acid or derivative thereof in an amount of 0.01-15 wt%. With an amount less than 0.01 wt%,

the modified rubber does not sufficiently improve the compatibility of the polyamide resin and rubber. With an amount in excess of 15 wt%, the modified rubber lowers the compatibility of the rubber.

- 5 The modified rubber can be produced by either the melt-mixing method or the solution method. In the former case, a rubber, unsaturated carboxylic acid (or anhydride thereof) for modification, and catalyst are heated, melted, and mixed at 150-250°C in an extruder or twin-screw kneader.
- 10 In the latter case, the above-mentioned starting materials are dissolved in an organic solvent such as xylene and the reaction is carried out at 80-140°C with stirring. In either case, the catalyst is an ordinary catalyst for radical polymerization. The catalyst includes peroxides (such as
- 15 benzoyl peroxide, lauroyl peroxide, di-t-butyl peroxide, acetyl peroxide, t-butyl peroxybenzoic acid, dicumyl peroxide, peroxybenzoic acid, peroxyacetic acid, t-butyl peroxyphthalate, and 2,5-dimethyl-2,5-di-t-butyl peroxyhexyne) and diazo compounds (such as azobisisobutyronitrile). The
- 20 catalyst should be used in an amount of 1-100 parts by weight for 100 parts by weight of the unsaturated carboxylic acid or anhydride thereof for modification.

 The polymer composition of the present invention is not specifically limited in the amount of the polyamide resin and

25 rubber component. For the polyamide resin to form the continuous matrix phase and for the rubber to form the uniformly dispersed domain phase, thereby imparting good heat

distortion resistance and impact resistance, the polymer composition should contain the polyamide resin in an amount of 30-90 wt%, preferably 50-70 wt%, of the total amount of the rubber components (rubber plus modified rubber) and also
5 contain the rubber plus modified rubber in an amount of 10-70 wt%, preferably 30-50 wt%.

The amount of the modified rubber should be related with the amount of the terminal amine in the polyamide resin so that the rubber forms the domain which has a desired
10 diameter. In other words, the amount of the modified rubber in the polymer composition should be adjusted so that a molar ratio of 10-1000 is established between the number of moles of the terminal amine and the number of moles of the carboxylic acid group in the modified rubber. With an
15 amine/carboxylic acid molar ratio smaller than 10, the compatibility is so high that the rubber forms the domain having an excessively small diameter. This lowers the heat resistance of the polymer composition. With an amine/carboxylic acid molar ratio in excess of 1000, the
20 modified rubber does not sufficiently improve the compatibility, resulting in a polymer composition having low mechanical strength. The preferred molar ratio is 20-200. Thus the content of the modified rubber should be 0.1-20 wt%, preferably 0.5-10 wt%, which meet the above-mentioned
25 requirements.

The fiber-reinforced polymer composition of the present invention should contain glass fiber in an amount of 10-50

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parts by weight for 100 parts by weight of the total amount of the composition excluding glass fiber. With glass fiber in an amount less than 10 parts by weight, the fiber-reinforced polymer composition does not have satisfactory heat resistance and mechanical strength. With glass fiber in an amount in excess of 50 parts by weight, the fiber-reinforced polymer composition is so poor in moldability that it cannot be produced easily. A preferred content of glass fiber is 15-40 parts by weight. The glass fiber should preferably be in the form of chopped strand or roving, having a fiber diameter of 5-15 μm . In addition, surface-treated glass fiber is desirable for the improved adhesion to the polyamide resin.

The polymer composition of the present invention is characterized by that the polyamide resin forms the continuous matrix phase and the rubber forms the domain phase having an average diameter of 0.1-5 μm . If the polyamide resin does not form the continuous matrix phase or if the rubber does not form the domain phase having an average diameter smaller than 0.1 μm , the resulting polymer composition will be very poor in heat distortion resistance. If the rubber forms the domain phase having average diameter larger than 5 μm , the resulting polymer composition will be very poor in mechanical properties such as tensile strength, flexural modulus, and impact strength.

For the purpose of property improvement, the polymer composition of the present invention may be incorporated with

additives such as inorganic filler, heat stabilizer, antioxidant, photostabilizer, flame retardant, plasticizer, antistatic agent, mold release, blowing agent, nucleating agent, and the like.

5 The polymer composition of the present invention is produced in the manner explained below.

The mixing of the components is accomplished by using a twin-screw extruder which meets the following requirements.

- (a) It should have a first hopper, a vacuum vent, and a die
10 outlet arranged consecutively and also have a length to diameter ratio (L/D) of 25 and above. A second hopper arranged consecutively after the first hopper is suitable where fiber-reinforced polymer compositions are desired.
- 15(b) It should have at least one set of a first kneading zone constructed of consecutive four or more kneading discs having an L/D of 1/4 to 1/8 which is used for intensively mixing the polyamide resin and rubber components before they reach the point of L/D 15
20 downstream from the hopper. This first kneading zone is installed upstream from the second hopper where included.
- (c) It should have at least one set of a second kneading zone (constructed of consecutive four or more kneading
25 discs as mentioned above) which is used for intensively mixing the polyamide resin and rubber components again before they reach the vacuum vent.

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The requirement (a) is supplemented below. The hopper is intended for feeding the polyamide resin, rubber, and modified rubber. The second hopper is intended for feeding glass fiber. The vacuum vent is intended for eliminating the low-molecular weight components which occur during the mixing of the polyamide resin and rubber components. The die outlet is intended for extruding the mixed composition in the form of strand.

The requirement (b) is supplemented below. The first kneading zone is intended for intensively mixing the polyamide resin and rubber components. If necessary, a plurality of kneading zones may be installed. Each unit of the first kneading zone should preferably be composed of four or more, especially 4 to 16 consecutive kneading discs having an L/D of 1/4 to 1/8. Each pair of the kneading discs is fixed to two screw shafts such that they rotate as the screws rotate. Each kneading disc has a cam-like shape, so that the distance between paired kneading discs varies as the kneading discs rotate. This exerts intensive mixing on the polyamide resin and rubber components which pass through the space between them.

The requirement (c) is supplemented below. The second kneading zone is intended for intensively mixing the polyamide resin and rubber components again, optionally with the glass fiber. It is constructed substantially the same way as the first kneading zone.

The twin-screw extruder having the above-mentioned

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features is constructed as shown in Fig. 1. According to the preferred structure, it should have:

- (1) a length-to-diameter ratio (L/D) of 25 and above;
- (2) a hopper 1 through which the polyamide resin and rubber
5 components are fed;
- (3) a die 2 from which the resulting polymer composition is extruded;
- (4) an optional second hopper 3 for glass fiber feeding,
which is installed at the point of L/D 15-20 downstream
10 from said first hopper;
- (5) a vacuum vent 4 installed between said hopper 1 and said die 2, or between said hopper 3 and said die 2 where said hopper 3 is included;
- (6) at least one set (two sets in the example shown) of a
15 first kneading zone 5, 5' installed at the point before L/D 15 downstream from said hopper 1, but upstream of said hopper 3 where included;
- (7) at least one set of a second kneading zone 5 installed at the point before said vacuum vent 3, but downstream
20 of said hopper 3 where included; and it should perform the mixing under the following conditions.
- (8) the temperature of the polyamide resin and rubber should be 250-300°C during mixing in the twin-screw extruder and at the die outlet, in the case in which
25 glass fiber is not added;
- (9) and, when glass fiber is to be added, the temperature of the polyamide resin and rubber components should be

280-320°C during mixing in the section L/D 3.5-7.5 upstream from said second hopper; the temperature of the polyamide resin and rubber components should be 260-290°C during mixing in the other sections; and, the
5 temperature of the polyamide resin and rubber components should be 250-290°C at the die outlet.

The twin-screw extruder should have an L/D ratio of 25 and above. With an L/D ratio smaller than 25, the extruder cannot perform complete mixing. A preferred L/D ratio is 25
10 to 35.

The first hopper 1, the optional second hopper 3, the vacuum vent 4, and the die 2 may be of the known structure.

For compositions of the invention not fiber-reinforced, the vacuum vent 4 should be installed a distance equivalent
15 to an L/D 15-20 away from the hopper 1. If the distance between the two is smaller than L/D 15, the extruder does not perform complete mixing and the vacuum vent does not fully produce its effect. If the distance is larger than an L/D
20, the extruder is liable to vent-up.

20 For fiber reinforced compositions of the invention, the distance between the second hopper 3 and the die 2 should be L/D 5-20. With a distance shorter than L/D 5, the mixing of the polyamide resin and rubber components is incomplete. With a distance longer than L/D 20, the polyamide resin and
25 rubber components become deteriorated and glass fiber is broken. The distance between the first hopper 1 and the second hopper 3 should be L/D 15-20.

The distance between the second hopper 3 and the vacuum vent 4 should be L/D 2.5-10. With a distance shorter than L/D 2.5, the sizing agent of the glass fiber does not melt and the sufficient venting effect is not produced. With a distance longer than L/D 10, there is a possibility of vent-up.

The first kneading zone 5, 5' and the second kneading zone 6 each should have a length equivalent to an L/D 1 to 4. The requirement is met by forming the kneading zone from four and more consecutive kneading discs each having a length equivalent to an L/D $1/4$ to $1/8$.

Both the first and second kneading zones have a structure as shown in Fig. 2. The kneading zone N is formed by a plurality of kneading discs 12, 12', ... installed somewhere along the two screws 10, 11. The kneading zone lies between the screw zones S and S'. In the kneading zone N, the kneading discs 12, 12', ... are paired and fixed to the two screws. Fig. 3 is a sectional view of a pair of kneading discs 12, 12'. The individual kneading discs 12, 12' have a cam-like peripheral composed of projecting parts 13, 13' and circumferential parts 14, 14'. A pair of kneading discs are fixed to the screw shafts (not shown) by means of spline grooves 15, 15' such that the projecting parts 13, 13' and the circumferential parts 12, 12' face each other. Because of this arrangement, the distance between the paired kneading discs 12, 12' greatly increases and decreases as the screws

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rotate. This exerts by far more intensive mixing to the polyamide resin and rubber components (or a mixture of the polyamide resin, rubber, and glass fiber) passing through the kneading discs than the screws do, as the kneading discs 12, 5 12' ... are arranged consecutively with the plural pieces. Incidentally, the structure shown in Fig. 2 has the transition section (seal ring) T downstream from the kneading zone N so that the compound being mixed does not move forward easily beyond the kneading zone.

10 The extruder should have at least one set, preferably two sets, of the first kneading zone and at least one set of the second kneading zone.

If the first kneading zone 5, 5' does not exist or does not have the sufficient length, the extruder does not 15 perform the complete mixing of the polyamide resin and rubber components and hence does not plasticize them sufficiently.

With the second kneading zone 6 shorter than L/D 1 and for compositions not fiber-reinforced, the extruder will yield a polymer composition in which the rubber domain has 20 uneven particle diameters. For fiber-reinforced compositions, if the second kneading zone 6 is shorter than L/D 1, the polyamide resin and rubber components are cooled as the glass fiber is fed. This presents the smooth mixing of glass fiber, causing surge (pulsation) and hindering 25 production.

In the case where there are two or more sets of the first kneading zone 5, 5', its forward end is located L/D

5-15 downstream from the hopper 1 and its total length is equivalent to L/D 2-8. In the case where there are two or more sets of the second kneading zone 6, its forward end is located L/D 15-20 downstream from the hopper 1 and its total
5 length is equivalent to L/D 1-4.

For compositions not fiber-reinforced, the polyamide resin and rubber should be kept at 250-300°C during their mixing; otherwise, the desired morphology is not obtained. With an excessively high mixing temperature, the polyamide
10 resin and rubber become deteriorated and do not exhibit their performance.

For fiber-reinforced compositions, the temperature of the polyamide resin and rubber components should be 280-320°C in the section which is L/D 3.5-7.5 upstream from the second
15 hopper 3; otherwise, the mixing of glass fiber is hindered and surge is liable to occur. With an excessively high mixing temperature, the polyamide resin and rubber components become deteriorated and do not exhibit their performance. The temperature of the polyamide resin and rubber components
20 should be 260-290°C in other sections. The temperature of the polyamide resin and rubber components should be 250-290°C at the die outlet.

According to the process of the present invention, the polyamide resin and rubber components are fed to the first
25 hopper 1 of the above-mentioned twin-screw extruder and are mixed by the two screws running at a rate of 100-300 rpm. Glass fiber, where desired, is fed to the second hopper 3,

and mixed under the same conditions. The mixed compound is extruded through the die outlet 2 in the form of strand. The strand is easily pelletized by a strand cutter.

Both the polymer composition and fiber-reinforced composition produced by the above-mentioned twin-screw extruder can be formed into a desired shape by ordinary injection molding.

Function of the Invention

As mentioned above, the polymer composition of the present invention has such a morphology that the polyamide resin forms the continuous matrix phase or the polyamide resin constitutes the skeleton of the composition. Therefore, the polymer composition has high heat distortion resistance.

According to the present invention, the rubber component forms the domain having an average diameter larger than $0.1\ \mu\text{m}$ so that the rubber component does not become excessively compatible with the polyamide resin. This is important for the polyamide resin skeleton to retain its heat resistance. If the rubber component forms the domain having an average diameter larger than $5\ \mu\text{m}$, the surface of the domain is cracked by external stress, which causes the composition to decrease in mechanical properties.

According to the process of the present invention, the polyamide resin and rubber components, with optionally added glass fiber, are mixed using a twin-screw extruder provided with a first kneading zone and a second kneading zone. The

extruder performs intensive mixing in a stable manner. The intensive mixing uniformly disperses the difficultly compatible rubber into the polyamide, so that the resulting composition has improved mechanical strength and heat
5 resistance.

Examples

The invention will be described in more detail with reference to the following examples.

Examples 1 to 18 of Table 1

10 A polyamide resin, rubber, and modified rubber were dry-blended using a high-speed mixer according to the formulation shown in Table 1. The resulting dry blend was fed to the hopper of a twin-screw extruder having the structure specified below.

15 Screw diameter: 45 mm

L/D ratio: 28

Position of vacuum vent: L/D 5.5 upstream from the die

First kneading zone:

Number: 1

20 Position: L/D 2-3.5 and L/D 5-6.5 downstream from the hopper

Size of kneading disc: $L/D = 1/4$

Number of kneading discs: 6

Second kneading zone:

25 Number: 1

Position: L/D 7 upstream from the die

Size of kneading disc: $L/D = 1/4$

Number of kneading discs: 4

The resin temperature in the twin-screw extruder was as follows:

270°C in Examples 1 to 12, 15, and 16

5 250°C in Examples 13 and 14

290°C in Examples 17 and 18

The twin-screw extruder was run at a screw speed of 200 rpm and the resulting composition was pelletized. After drying, the pellets of the composition were made into test
10 pieces by injection molding and the test pieces were tested as follows:

- (1) MFR according to JIS K7210, at 275°C under a load of 2160 g.
- (2) Heat distortion temperature according to JIS K7207. A
15 test piece (simple beam) measuring 110 x 4 x 12.7 mm is heated at a constant rate (2°C/min) under a fixed load (4.6 kg/cm²) and the temperature at which the test piece is bent as much as a prescribed amount (0.25 mm) is recorded.
- 20 (3) Tensile strength at 23°C according to JIS K7113.
- (4) Flexural modulus at 23°C according to JIS K7203.
- (5) Izod impact strength at 23°C and -40°C according to JIS K7110.

The results are shown in Table 1.

Examples 1 to 18 of Table 2

A polyamide resin, rubber, and modified rubber were dry-blended using a high-speed mixer according to the formulation shown in Table 2. The resulting dry blend was
5 fed to the main hopper of a twin-screw extruder as shown in Fig. 1. Glass fiber (chopped strand having an average diameter of 13 μm and an average length of 3 mm) was fed to the second hopper according to the formulation shown in Table 2.

10 The extruder had the same structure specified for the examples of Table 1 except for the additional inclusion of a second hopper. Configuration differences are specified below.

Position of second hopper: L/D 10 upstream from the die

15 The temperature of the polyamide resin and rubber components in the twin-screw extruder was as follows:

In the section L/D 3.5-7.5 upstream from the second hopper:

290°C in Examples 1 to 12, 15, and 16

280°C in Examples 13 and 14

20 310°C in Examples 17 and 18

In other sections L/D 7.5-25:

270°C in Examples 1 to 12, 15, and 16

250°C in Examples 13 and 14

290°C in Examples 17 and 18

25 The twin-screw extruder was run at a screw speed of 200 rpm and the resulting composition was pelletized and tested as done for the examples of Table 1. Additional tensile strength and flexural modulus measurements were taken as noted.

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(1) Tensile strength at 23°C and 140°C according to JIS
K7113.

(2) Flexural modulus at 23°C and 140°C according to JIS
K7203.

5 The results are shown in Table 3.

Notes to Tables 1 and 2

- (1) The amount of the polyamide resin, rubber, and modified rubber is expressed in terms of wt% on the basis of the total amount of the resin and rubber components. The amount of glass fiber (Table 2) is expressed in terms of wt% on the basis of the total amount of the composition.
- (2) "Amiran CM3001N", made by Toray Industries Inc., containing 0.034 milliequivalents/g of terminal amino group measured according to Korshak-Zamyatona method (back titration method) (Chem. Abs. 40, 4665, '46, ib. 42, 6152, '48)
- (3) "A1030BRT", made by Unitica Ltd., containing 0.042 milliequivalents/g of terminal amino group measured according to Korshak-Zamyatona method (as mentioned in (2) above).
- (4) "Unitica Nylon-46", made by Unitica Ltd., containing 0.026 milliequivalents/g of terminal amino group measured according to Korshak-Zamyatona method (as mentioned in (2) above).
- (5) "Tafmer A4085", made by Mitsui Petrochemical Industry Co., Ltd.
- (6) "Tafmer P0180", made by Mitsui Petrochemical Industry Co., Ltd.
- (7) "Kraton G1652", made by Shell Chemical Co., Ltd.
- (8) Polyisobutylene, "Vistanex MML-80", made by Esso Chemical Co., Ltd.

(9) Maleic acid anhydride

(10) "MA03FT-2", made by Asahi Fiberglass Co., Ltd.

Comparative Examples 1 to 5 of Tables 3 and 4

The same procedures as in Example 1 of Table 1 (for
5 Table 3) and Example 1 of Table 2 (for Table 4) were repeated
except that the materials and formulations were changed as
shown in Tables 3 and 4. The results are shown in those
Tables 3 and 4.

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Note to Tables 3 and 4

(1), (2), (5), (6), and (9): same as in Table 1.

(10) J-215, made by Tonen Sekiyukagaku K. K.

5 It is noted from Tables 1 and 3 that the composition of the present invention has good impact resistance and heat resistance because the rubber forms the uniformly dispersed domain having a diameter in the range of 0.1 to 5 μm in the nylon matrix phase. In contrast to the examples of Table 101, the compositions in the Comparative Examples of Table 3 (which have the rubber or polypropylene domain outside the specified range or contain no modified-rubber) are poor in heat distortion resistance and impact resistance.

 It is noted from Tables 2 and 4 that the 15 fiber-reinforced composition of the present invention also has good impact resistance and heat resistance because of the rubber forming the uniformly dispersed domain having a diameter in the range of 0.1 to 5 μm in the nylon matrix phase. In contrast to the examples of Table 2, the 20 composition in Comparative Example 1 of Table 4 (which contains polypropylene in place of rubber), the compositions in Comparative Examples 2 and 4 (which have the rubber domain outside the range specified above), and the compositions in Comparative Examples 3 and 5 (which do not contain the 25 modified rubber) are poor in heat distortion resistance and impact resistance.

Effect of the invention

As mentioned above, the polymer composition pertaining to the present invention has the well-balanced heat distortion resistance, impact resistance, tensile strength, and moldability, because it contains an unsaturated carboxylic acid-modified rubber which promotes the compatibility of polyamide resins and rubbers and it also has the morphology characterized in that the rubber having an average diameter in a specific range is uniformly dispersed in the polyamide resin matrix phase. It has an additional advantage that the production cost is reduced on account of the comparatively high content of polyolefin.

The compositions of the present invention are suitable for use as mechanical, automotive, and electrical parts and building materials formed by injection molding and extrusion molding.

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CLAIMS:

(1) A polymer composition which comprises a polyamide resin, rubber, and unsaturated carboxylic-acid modified rubber, said polyamide resin forming the continuous matrix phase and said rubber forming the uniformly dispersed domain phase having an average diameter of 0.1-5 μm .

(2) A polymer composition as claimed in Claim 1, wherein the ratio of the number of moles of the terminal amine in said polyamide resin to the number of moles of the carboxylic acid group in said unsaturated carboxylic acid-modified rubber is 10-1000.

(3) A polymer composition as claimed in Claim 1, wherein the amount of said polyamide resin is 30-90 wt% and the total amount of said rubber and said unsaturated carboxylic acid-modified rubber is 10-70 wt%.

(4) A polymer composition as claimed in Claim 2, wherein the amount of said polyamide resin is 30-90 wt% and the total amount of said rubber and said unsaturated carboxylic acid-modified rubber is 10-70 wt%.

(5) A polymer composition as claimed in any of Claims 1 to 4, wherein said rubber and the rubber component in said unsaturated carboxylic acid-modified rubber are both ethylene-butene rubber, ethylene-propylene rubber, or hydrogenated styrene-butadiene-block copolymer rubber.

(6) A polymer composition as claimed in Claim 3, which additionally comprises 10-50 parts by weight of glass fiber for 100 parts by weight of the total amount of the composition.

(7) A polymer composition as claimed in Claim 6, wherein the ratio of the number of moles of the terminal amine in said polyamide resin to the number of moles of the carboxylic acid group in said unsaturated carboxylic acid-modified rubber is 10-1000.

(8) A polymer composition as claimed in Claims 6 or 7, wherein said rubber and the rubber component in said unsaturated carboxylic acid-modified rubber are both ethylene-butene rubber, ethylene-propylene rubber, or hydrogenated styrene-butadiene-block copolymer rubber.

(9) A process for producing a polymer composition containing a polyamide resin, rubber, and unsaturated carboxylic acid-modified rubber, said process comprising feeding said polyamide resin, rubber, and unsaturated carboxylic acid-modified rubber to a twin-screw extruder provided with a hopper, vacuum vent, and die outlet (arranged consecutively) and having a length-to-diameter ratio (L/D) of 25 and above through said hopper, intensively mixing said components in at least one set of a first kneading zone constructed of consecutive four or more kneading discs having an L/D of 1/4 to 1/8 before said components reach the point of L/D 15 downstream from said hopper, and intensively mixing said components again in at least one set of a second kneading zone constructed of consecutive four or more kneading discs having an L/D of 1/4 to 1/8 before said components reach the point short of said vacuum vent and beyond the point of L/D 15 downstream from said hopper.

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(10) A process for producing a fiber-reinforced polymer composition containing a polyamide resin, rubber, and unsaturated carboxylic acid-modified rubber, said process comprising feeding said polyamide resin, rubber, and unsaturated carboxylic acid-modified rubber to a twin-screw extruder provided with a first hopper and a second hopper, a vacuum vent, and a die outlet (arranged consecutively) and having a length-to-diameter ratio (L/D) of 25 and above through said first hopper, intensively mixing said components in at least one set of a first kneading zone constructed of consecutive four or more kneading discs having an L/D of 1/4 to 1/8 before said components reach said second hopper, thereby raising the temperature of the polyamide resin and rubber components to 280-320°C at the point upstream from the second hopper, feeding glass fiber to the extruder through said second hopper, and intensively mixing said polyamide resin, rubber components, and glass fiber in at least one set of a second kneading zone constructed of consecutive four or more kneading discs having an L/D of 1/4 to 1/8 before said components reach the point short of said vacuum vent.

(11) A process as claimed in Claim 10, wherein the temperature of the polyamide resin and rubber components is kept at 280-320°C at the point of L/D 3.5-7.5 upstream from said second hopper and the temperature of the polyamide resin and rubber components is kept at 260-290°C at the other points.

FIG.1

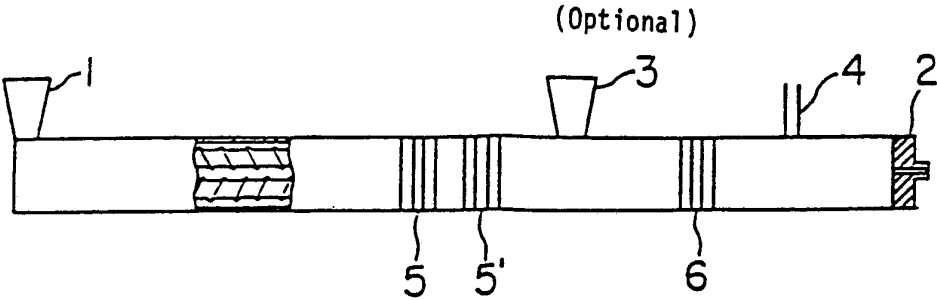


FIG.2

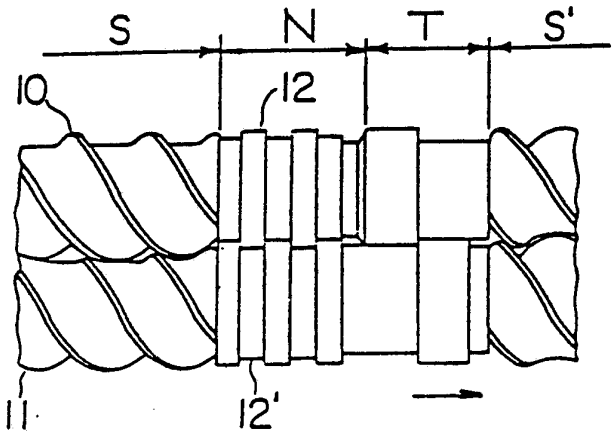
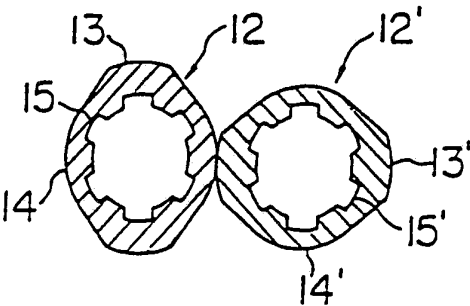


FIG.3



INTERNATIONAL SEARCH REPORT

International Application No. PCT/US89/04158

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁴ C08L 77/00 US CL. 524/504, 505, 514, 515; 525/66, 179		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
US CL.	524/504, 505, 514, 515 525/66, 179	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X Y	US, A, 4,485,214 OCHIAI ET AL 27 NOVEMBER 1984 (see column 2, lines 24-34; column 4, lines 59-62; column 6, lines 7-12; column 7, lines 25-59; column 12, lines 11-18)	1-4, 6, 7 9-11
Y	US, A, 4,757,112 PHADKE 12 JULY 1988	1-11
P, X	US, A, 4,803,247 ALTMAN ET AL 7 FEBRUARY 1989	1-4, 6, 7, 9-11
P, X	US, A, 4,849,471 SAITO ET AL 18 JULY 1989	1-11
P, Y	US, A, 4,851,473 DUNPHY 25 JULY 1989	1-4, 6, 7, 9-11
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
27 NOVEMBER 1989		18 DEC 1989
International Searching Authority		Signature of Authorized Officer
ISA/US		ANA L. CARRILLO