APPLICATION ACCEPTED AND AMENDMENTS
ALLOWED 28-11-90

FORM 1

607015
SPRUSON & FERGUSON

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

Stamicarbon B.V., of Mijnweg 1, 6167 AC Geleen, THE NETHERLANDS, hereby apply for the grant of a standard patent for an invention entitled: 'Compositions of graft copolymers containing vinyl aromatic compounds and acrylonitrile on rubber".
which is described in the accompanying complete specification.

Details of basic application(s):-

Basic Applic. No:	Country:	Application Date:
8702602	NL	2 November 1987

The address for service is:-

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DATED this FIRST day of NOVEMBER 1988

Stamicarbon B.V.

By: M.J. Anderson

Registered Patent Attorney

TO: THE COMMISSIONER OF PATENTS
OUR REF: 76757
S&F CODE: 59400

S003327 01/11/88

AUSTRALIAN PATENT OFFICE

5845/6

Spruson & Ferguson

COMMONWEALTH OF AUSTRALIA

THE PATENTS ACT 1952

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

AUSTRALIA
CONVENTION
STANDARD
& PETTY PATENT
DECLARATION
SFP4

In support of the Convention Application made for a patent for an invention entitled:

Title of Invention: Thermoplastic Elastomer Mixture

Full name(s) and address(es) of Declarant(s)

I/~~We~~ Luc Lodewijk Maria BLEUKX

of Weertersteenweg 62, 3680 Maaseik, Belgium

do solemnly and sincerely declare as follows:—

Full name(s) of Applicant(s)

1. ~~I am/We are the applicant(s) for the~~ patent

(or, in the case of an application by a body corporate)

1. I am/~~We~~ are authorised by STAMICARBON B.V.

the applicant~~(s)~~ for the patent to make this declaration on its/~~their~~ behalf.

2. The basic application~~(s)~~ as defined by Section 141 of the Act was/~~were~~ made

Basic Country(ies): in the Netherlands

Priority Date(s): on 2 November 1987

Basic Applicant(s): by STAMICARBON B.V.

Full name(s) and address(es) of inventor(s)

3. ~~I am/We are the actual inventor(s) of the invention referred to in the basic application(s)~~

(or where a person other than the inventor is the applicant)

3. Hubertus Johannes VROOMANS
Wilhelmus Gerardus Marie BRULS
of resp. Spaanse Singel 18, 6191 GK Beek, Netherlands
Gr.Wolterhoenstr.32,6243 BE Meerssen, Netherlands
(respectively)

~~is~~/are the actual inventor(s) of the invention and the facts upon which the applicant~~(s)~~ is/~~are~~ entitled to make the application are as follows:

Set out how Applicant(s) derive title from actual inventor(s) e.g. The Applicant(s) is/are the assignee(s) of the invention from the inventor(s)

STAMICARBON B.V. is the assignee of DSM and DSM was entitled by Contract of Employment between the inventor(s) as employee(s) and DSM as employer, as a person who would be entitled to have the patent assigned to if a patent were granted upon an application made by the inventor(s).

4. The basic application~~(s)~~ referred to in paragraph 2 of this Declaration was/~~were~~ the first application~~(s)~~ made in a Convention country in respect of the invention ~~(s)~~ the subject of the application.

Declared at Geleen Neth. the Netherlands this 4th day of October 1988

L.L.M.Bleukx
Signature of Declarant(s)

SFP4 To: The Commissioner of Patents 11/81

(12) PATENT ABRIDGMENT **(11)** Document No. **AU-B-24561/88**
(19) AUSTRALIAN PATENT OFFICE **(10)** Acceptance No. **607015**

(54) Title
COMPOSITIONS OF GRAFT COPOLYMERS CONTAINING VINYL AROMATIC COMPOUNDS AND ACRYLONITRILE ON RUBBER

International Patent Classification(s)
(51)⁴ C08L 051/04 C08L 055/00 C08L 055/02 C08L 077/06
C08L 077/10

(21) Application No. : 24561/88 (22) Application Date : 01.11.88

(30) Priority Data

(31) Number	(32) Date	(33) Country
8702602	02.11.87	NL NETHERLANDS

(43) Publication Date : 04.05.89

(44) Publication Date of Accepted Application : 21.02.91

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(56) Prior Art Documents
US 3796771
JP 56/112597

(57) Claim

1. A thermoplastic polymer mixture on the basis of a graft copolymer of a vinylaromatic compound and acrylonitrile on a rubber and a thermoplastic polymer with polar groups, characterized in that the polymer mixture consists of:

a) 5-99% wt.% of a thermoplastic polymer with polar groups;

b) 1-95% wt.% of a graft copolymer of a vinylaromatic compound and acrylonitrile on a diene rubber, on the rubber there being present monomers of a vinylaromatic compound and of a carboxy- and/or imide-containing compound in a molar ratio from 5:1 to 1:5, the carboxy- and/or imide-containing compound being in the amount of 0.1-25 wt.%.

7. A process for producing a thermoplastic polymer mixture according to any one of claims 1 to 6, characterized in that

i) a basic polymer, consisting of a copolymer of a vinylaromatic compound and acrylonitrile grafted on a diene rubber, is brought into a mixing device, where said basic polymer is brought into a melted state,

.../2

ii) to which basic polymer in a melted state monomers of a vinylaromatic compound and 0.1-25 wt.% of monomers of a carboxy- and/or imide-containing compound are added in molar ratio of 5:1 to 1:5,

iii) upon which the melt of the basic polymer and the added monomers are intensively mixed at a temperature of 180-325°C during a residence time of 1-15 minutes,

iv) after which the resulting polymer (component (b)) is mixed in an extruder with a thermoplastic polymer with polar groups (component (a)) in a molten state at a temperature between 200-250°C.

607015

S & F Ref: 76757

FORM 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE:

Class | Int Class

This document contains the amendments made under Section 49 and is correct for printing

Complete Specification Lodged:
Accepted:
Published:

Priority:

Related Art:

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Complete Specification for the invention entitled:

Compositions of graft copolymers containing vinyl aromatic compounds and acrylonitrile on rubber".

The following statement is a full description of this invention, including the best method of performing it known to me/us

5845/7

Compositions of graft copolymers containing vinyl aromatic compounds and acrylonitrile on rubber

Thermoplastic elastomer mixture on the basis of a graft copolymer of a vinylaromatic compound and acrylonitrile on a rubber and a thermoplastic polymer with polar groups.

Such a polymer mixture is already known from European patent specification No. 202214. This patent specification describes a polymer mixture on the basis of (A) a polyamide, (B) an acrylonitrile/butadiene/styrene graft copolymer and (C) a terpolymer obtained through polymerization of styrene, acrylonitrile and maleic acid anhydride. The terpolymer acts as a compatability enhancing agent.

A drawback of this polymer mixture is that the terpolymer in the mixture first has to be synthesized through polymerization. This requires additional process steps and is therefore costly.

The purpose of the invention is to provide a polymer mixture which does not have said drawback.

According to a first embodiment of this invention there is provided a thermoplastic polymer mixture on the basis of a graft copolymer of a vinylaromatic compound and acrylonitrile on a rubber and a thermoplastic polymer with polar groups, characterized in that the polymer mixture consists of:

a) 5-99% wt.% of a thermoplastic polymer with polar groups;

b) 1-95% wt.% of a graft copolymer of a vinylaromatic compound and acrylonitrile on a diene rubber, on the rubber there being present monomers of a vinylaromatic compound and of a carboxy- and/or imide-containing compound in a molar ratio from 5:1 to 1:5, the carboxy- and/or imide-containing compound being in the amount of 0.1-25 wt.%.

According to a second embodiment of this invention there is provided a process for producing a thermoplastic polymer mixture according to the first embodiment characterized in that:

i) a basic polymer, consisting of a copolymer of a vinylaromatic compound and acrylonitrile grafted on a diene rubber, is brought into a mixing device, where said basic polymer is brought into a melted state,

ii) to which basic polymer in a melted state monomers of a vinylaromatic compound and 0.1-25 wt.% of monomers of a carboxy- and/or imide-containing compound are added in molar ratio of 5:1 to 1:5,

iii) upon which the melt of the basic polymer and the added monomers are intensively mixed at a temperature of 180-325°C during a residence time of 1-15 minutes,

iv) after which the resulting polymer (component (b)) is mixed in an extruder with a thermoplastic polymer with polar groups (component (a)) in a molten state at a temperature between 200-250°C.

Surprisingly, it has been found that the polymer mixture according to the invention possesses an optimum balance of properties, while moreover the graft copolymer of component (b) is very easy to synthesize. Surprisingly is also the good compatability of the used components. A homogeneous blend is obtained.

The polymer mixture according to the invention preferably contains:

a) 20-90 wt.% of a thermoplastic polymer with polar groups;

b) 10-80 wt.% of a polymer obtained by polymerizing 40-80 wt.% of a mixture of
  - 10-40 wt.% acrylonitrile;
  - 60-90 wt.% of a vinylaromatic compound;
  - 0-20 wt.% of a third monomer;

in the presence of 20-60 wt.% of a rubber, upon which the polymer obtained by polymerization is brought into a melted state, to which 0.1-25 wt.% monomers of a vinylaromatic compound and of a carboxy- and/or imide-containing compound are added in a molar ratio of 1 : 5 to 5 : 1 and at a temperature of 180°C-325°C.

As such the addition of monomers to a polymer in the melted phase is known in the art. In US-A-3.862.265 the addition is described of maleic anhydride and styrene to polyolefins, polybutadiene and butadiene-styrene rubbers in an extruder. DE-A-2943 657 describes the addition of maleic anhydride to a styrene-butadiene block copolymer in an extruder. In the side chains the resulting polymers from said patent specifications only have separate maleic anhydride and/or styrene units. The polymer according to ~~the invention~~ component (b) distinguishes itself from these in that, in additon to these separate units, the polymer also has α-methylstyrene and/or styrene-acrylonitrile copolymers in the side chains so that, when used as compatibilizer in a mixture, also an improvement of the properties of the mixture is achieved, in addition to a higher degree of crosslinking.

NL-A-7102312 describes a process for the preparation of a carboxyl-containing polymer which is prepared by reaction above 120°C of a mixture of styrene and maleic anhydride with a polymer containing active hydrogen atoms. No indication is given of the good compatibility between the obtained polymer and polymers with polar groups.

Component (b) in the polymer mixture according to the invention thus consists of a polymerized basic polymer built up from a diene rubber with one or more copolymers in the side chains, which is processed in the melt with a vinylaromatic compound and with a carboxy- and/or imide-containing compound.

The basic polymer used is preferably an acrylonitrile-styrene-butadiene rubber (ABS), an acrylonitrile-styrene-acrylate rubber (ASA) or an ethylene-propylene-diene rubber, polymerized with styrene and acrylonitrile (AES). More particularly the basic polymer is ABS.

The basic polymer can be synthesized in the manner known in the art, for instance by means of mass polymerization, emulsion polymerization, suspension polymerization or mass-suspension polymerization.

Suitable as vinylaromatic compound in the preparation of the basic polymer are styrene, α-methylstyrene, or derivatives thereof substituted on the aromatic ring. Suitable substituents are alkyl groups, chlorine or bromine. It is possible to use mixtures of two or more vinylaromatic compounds. Acrylonitrile can be replaced in whole or in part by methacrylonitrile.

In addition to the vinylaromatic compound and acrylonitrile one or more other monomers can be used in the preparation of the basic ~~monomer~~ polymer. Of particular importance in this connection are the acrylates, for instance methylmethacrylate and/or ethylacrylate.

The rubber used in the preparation of the basic polymer may in principle be any diene rubber.

Preference is given to the use of polybutadiene-homopolymers or butadiene-copolymers with a butadiene content of 60-90 wt.%. When other dienes, for instance isoprene, or the lower alkyl esters of acrylic acid, are used as comonomers, the butadiene content of the rubber can be reduced to 30 wt.% without any adverse effect on the properties of the basic polymer.

In the polymerization the customary auxiliaries are used, such as chain length regulators, emulsifiers (emulsion polymerization) and compounds supplying free radicals.

Depending on the application of the polymer mixture, it is possible also in the polymerization of component (b) to use two or more butadiene homopolymers which differ from each other in particle size. The particle size (d_{50}) must then be smaller than 0.3 μ, respectively larger than 0.35 μ. Such a polymer is described in

EP-A-116 330. When such a polymer has been processed in the melt with a vinylaromatic compound and with a carboxy- and/or imide-containing substance, it is highly suitable to be used as impact modifier.

The vinylaromatic compound added to the melt of the basic polymer in a mixing device is styrene and/or α-methylstyrene. The carboxy- and/or imide-containing compound is chosen from organic acids and/or anhydrides, imides or combinations hereof, for instance maleic anhydride, citraconic acid, itaconic acid, maleimide, N-phenylmaleimide and semi-acid amides. It is possible also, in addition to styrene, to add maleic anhydride together with a primary amine, so as to promote during the mixing the formation of a semi-acid amide.

The choice of the carboxy- and/or imide-containing compound to be added is determined by the application. Thus maleic anhydride and/or maleimide will be added to the polymer if it is used as compatibilizer in a mixture with a polyamide or a polyester. Preference is given to maleic anhydride.

The monomers of the vinylaromatic compound and the carboxy-and/or imide-containing group are added in a molar ratio of 5 : 1 to 1 : 5, preferably 2 : 1 to 1 : 2. Component (b) in the polymer mixture according to the invention must contain 0.1-25 wt.% of the carboxy- and/or imide-containing compound.

Component (b) preferably contains 1-20 wt.% of the carboxy- and/or imide-containing compound, more particularly 1-10 wt.%.

The addition of the monomers to the basic polymer can be done in a manner described in US-A-3862265. It is important for the monomers to be added to the melt of the basic polymer while intensive mixing takes place. It is not necessary in the process to use a solvent and/or a radical catalyst. It has been found, however, that the addition of a solvent, particularly a polar solvent, for instance acetone, methylethylketone and/or an initiator, particularly a peroxide or an azo compound, increases the grafting rate, as well as the rate of conversion.

The polymer according to component (b) is prepared by injecting monomers of styrene and/or α-methylstyrene and monomers of a carboxy- and/or imide-containing compound in a molar ratio of 5 : 1 to

1 : 5 at a temperature of 180¤C-325¤C into a mixing device, the basic polymer being present in the mixing device in a melted state, in which process the polymer has been obtained by polymerizing 40-80 wt.% of a mixture of:

- 10-40 wt.% acrylonitrile;
- 60-90 wt.% styrene and α-methylstyrene;
- 0-20 wt.% of one or more monomers; in the presence of 60-20 wt.% of a diene rubber.

Preferably the monomers are added to a polar solvent at room temperature and this mixture is injected to the melt of the basic polymers.

The temperature in the mixing device is preferably 190-300¤C, more particularly 200-250¤C.

It is important for the monomers to be added at the place where the basic polymer is present in the melt, so that the grafting, during intensive mixing, can take place at once.

To the extruder can be supplied also, in addition to a solvent and a radical initiator, the usual auxiliaries, for instance an anti-oxidant.

A solvent, for instance acetone, is added in a weight ratio of 5 : 1 to 1 : 20, preferably 2 : 1 to 1 : 10, to the monomers to be added. A radical catalyst, for instance dialkylperoxides, diacylperoxides, diacrylperoxides, organic peracids, organic peracid esters, alkylhydroperoxides and azo compounds, is added in an amount of 0.01 to 0.5 wt.% calculated on the basic polymer. A highly suitable anti-oxidant is Irganox 1076^{R}, Irganox 1010^{R} or di-tert.-butyl-p-cresol.

The residence time in the mixing device is preferably 1 to 15 minutes. Any non-converted monomers and the solvent can be removed in the usual manner, for instance by degassing. The polymer according to the invention can subsequently be granulated or be processed to form a moulding compound.

The mixing device in which the monomers are added to the basic polymer is, for instance, a batch kneader or a single or twin-screw extruder. The mixing device is preferably a single or twin-screw extruder. After the mixing device a static mixer may yet have been placed, so that an extension of the residence time is possible.

The polymer ~~mixture~~ according to component (b) ~~the invention~~ is suitable to be mixed, in amounts of 5-95 wt.%, preferably 10-80 wt.%, more particularly 40-60 wt.%, with a polymer which contains polar groups. Examples of such polymers are: polycarbonates, polyacetals, vinylaromatic polymers, polyamides, polyesters, polyvinylchloride polymers or mixtures of these polymers. The polymer according to ~~the invention~~ component (b) is then mixed with the above-mentioned polymers in an extruder in a manner known in the art. Preference is given to Polyamide.

Polyamides are understood to comprise the conventional polyamide resins known under the name of nylons, including the aliphatic polylactams, such as polycaprolactam and nylon 6.

The polyamides are obtained by polycondensation of aliphatic, alicyclic and aromatic diamines and dicarboxylic acids or by anionic polymerization of lactams, for instance poly-ε-caprolactame. With these, polyamides can be obtained, such as nylon 4,6, nylon 6,6, nylon 6,10, nylon 9, nylon 11, nylon 12, nylon 6/6,6, nylon 6,6/6,10 and nylon 6/11.

To the polymer mixture according to the invention the usual additives can be added, for instance glass, stabilizers, lubricants and the organic and inorganic fillers and reinforcing agents, etc.

The invention is further elucidated with the following examples without being limited thereto.

Examples I-III

ABS, with a rubber content of 40 wt.% calculated on the SAN phase, 27 wt.% acrylonitrile were supplied to a ZSK 30 D twin-screw extruder (speed 150 rpm, temperature 210¤C). The throughput rate was 4 kg/hour.

To the ABS melt were added by injection, styrene (S), maleic anhydride (MA) and acetone in a ratio of 2/2/1. The polymer obtained was cooled, dried and granulated. The resulting granulate was processed on an Arburg-1 injection-moulding machine to form test plates.

Of the resulting plates the Izod (according to ISO 180, 23¤C) and the HDT (according to ASTM D 648) were determined.

The results are shown in table 1.

TABLE 1

Example	Injection S/MA/Acetone ml/min	MA incorporation % (wt)	Izod	HDT
I	3.4	2.4	40	87
II	6.8	4.0	42	87
III	10.2	4.5	42	88

Example IV-VII

A mixture is prepared using:

- a polyamide, Ultramid B^{3} ^{R}, BASF
- the component of example I.

The components were supplied to a Berstoff 25 extruder. Throughput rate was 7 kg/h, temperature 220-245°C.

Results are shown in table 2.

TABLE 2

Example	PA	Comp. ex. I	Izod notched	
	wt.%	wt.%	23°C	0°C
IV	40	60	80	17
V	45	55	75	18
VI	50	50	73	23
VII	55	45	59	21

Comparative example A

A mixture of unmodified ABS (rubber content 40 wt.%, and wt.% Acrylonitrile of the SAN-phase) and polyamide (Ultramid B3 ^{R}) was prepared as described in example V.

ABS : 55 wt.%

PA : 45 wt.%

Izod notched: 4.5.

Comparative example B/C

ABS and polyamide (same components as example E) and a copolymer of styrene/maleic anhydride (SMA, maleic anhydride content 14 wt.%, mole weight 200.000) were mixed as described in example V.

Results in table 3.

TABLE 3

ex.	ABS	PA	SMA	Izod notched
	wt.%	wt.%	wt.%	23¤C
B	50	35	15	5.7
C	55	40	5	6

The claims defining the invention are as follows:

1. A thermoplastic polymer mixture on the basis of a graft copolymer of a vinylaromatic compound and acrylonitrile on a rubber and a thermoplastic polymer with polar groups, characterized in that the polymer mixture consists of:

a) 5-99% wt.% of a thermoplastic polymer with polar groups;

b) 1-95% wt.% of a graft copolymer of a vinylaromatic compound and acrylonitrile on a diene rubber, on the rubber there being present monomers of a vinylaromatic compound and of a carboxy- and/or imide-containing compound in a molar ratio from 5:1 to 1:5, the carboxy- and/or imide-containing compound being in the amount of 0.1-25 wt.%.

2. The thermoplastic polymer mixture according to claim 1, characterized in that the polymer mixture consists of:

a) 20-90 wt.% of a thermoplastic polymer with polar groups, and

b) 10-80 wt.% of a polymer mixture which has been obtained by polymerizing 40-80 wt.% of a mixture of

- 10-40 wt.% acrylonitrile;
- 60-90 wt.% of a vinylaromatic compound;
- 0-20 wt.% of a third monomer,

in the presence of 20-60 wt.% of a rubber, upon which the resulting basic polymer is brought into a melted state, to which 0.1-25 wt.% monomers of a vinylaromatic compound and of a carboxy- and/or imide-containing compound are added in a molar ratio of 5:1 to 1:5, and at a temperature of 180°C-325°C.

3. The thermoplastic polymer mixture according to claim 1 or claim 2 characterized in that component (b) contains 1-20 wt.% monomers of a vinylaromatic compound and of a carboxy- and/or imide-containing compound.

4. The thermoplastic polymer mixture according to any one of claims 1 to 3, characterized in that the vinylaromatic compound is styrene and/or α-methylstyrene.

5. The thermoplastic polymer mixture according to any one of claims 1 to 4, characterized in that the carboxy- and/or imide-containing compound is chosen from maleic anhydride, itaconic acid, citraconic acid, N-phenylmaleimide, maleimide and/or a semi-acid amide.

6. The thermoplastic polymer mixture according to any one of claims 1 to 5, characterized in that the polymer with polar groups is a polyamide.

7. A process for producing a thermoplastic polymer mixture according to any one of claims 1 to 6, characterized in that

i) a basic polymer, consisting of a copolymer of a vinylaromatic compound and acrylonitrile grafted on a diene rubber, is brought into a mixing device, where said basic polymer is brought into a melted state,

ii) to which basic polymer in a melted state monomers of a vinylaromatic compound and 0.1-25 wt.% of monomers of a carboxy- and/or imide-containing compound are added in molar ratio of 5:1 to 1:5,

iii) upon which the melt of the basic polymer and the added monomers are intensively mixed at a temperature of 180-325°C during a residence time of 1-15 minutes,

iv) after which the resulting polymer (component (b)) is mixed in an extruder with a thermoplastic polymer with polar groups (component (a)) in a molten state at a temperature between 200-250°C.

8. A thermoplastic polymer according to claim 1 and substantially as hereinbefore described with reference to any one of the Examples I-VII.

9. A process according to claim 7, substantially as hereinbefore described with reference to any one of the Examples I-VII.

10. A thermoplastic polymer when prepared by the process of claim 7 or claim 9.

DATED this TWENTY-SECOND day of NOVEMBER 1990
Stamicarbon B.V.

Patent Attorneys for the Applicant
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LMM/388Z