FORM 1

611991

SPRUSON & FERGUSON

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

Shell Internationale Research Maatschappij B.V., a Netherlands Company, of Carel van Bylandtlaan 30, 2596 HR, The Hague, THE NETHERLANDS, hereby apply for the grant of a standard patent for an invention entitled:

Polyketone Copolymer Composition

which is described in the accompanying complete specification.

Details of basic application(s):-

Basic Applic. No:	Country:	Application Date:
8801756	GB	27 January 1988

The address for service is:-

Spruson & Ferguson
Patent Attorneys
Level 33 St Martins Tower
31 Market Street
Sydney New South Wales Australia

DATED this TWENTY FOURTH day of JANUARY 1989

Shell Internationale Research Maatschappij B.V.

By:

Registered Patent Attorney

TO: THE COMMISSIONER OF PATENTS
OUR REF: 83257
S&F CODE: 61750

5845/3

SPRUSON & FERGUSON

COMMONWEALTH OF AUSTRALIA
PATENTS ACT 1952

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

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

Polyketone copolymer composition

I, Onno Aalbers, of Carel van Bylandtlaan 30, 2596 HR The Hague, the Netherlands, do solemnly and sincerely declare as follows:-

1. I am authorised by SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., the applicant for the patent to make this declaration on its behalf.

2. The basic application~~(s)~~ as defined by Section 141 of the Act was/~~were~~ made in the United Kingdom
on 27th January, 1988
by SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.

3. Johannes Leopold Marie SYRIER, Dirk Adriaan BORGER, Johan Marie BEYEN, Antonius Augustinus BROEKHUIS, Franciscus Christiaan GROENLAND, all Netherlands nationals of Badhuisweg 3, 1031 CM Amsterdam, the Netherlands

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

The Applicant is the assignee of the actual 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 the subject of the application.

DECLARED at The Hague this 3rd day of January 1989

....
Onno Aalbers

TO: THE COMMISSIONER OF PATENTS
AUSTRALIA

(12) PATENT ABRIDGMENT (11) Document No. AU-B-28785/89
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 611991

(54) Title
POLYKETONE COPOLYMER COMPOSITION

International Patent Classification(s)
(51)[4] C08L 073/00 C08K 003/22 C08K 005/00 C08K 005/05
C08K 005/20 C08K 013/02

(21) Application No. : 28785/89 (22) Application Date : 25.01.89

(30) Priority Data

(31) Number (32) Date (33) Country
8801756 27.01.88 GB UNITED KINGDOM

(43) Publication Date : 27.07.89

(44) Publication Date of Accepted Application : 27.06.91

(71) Applicant(s)
SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.

(72) Inventor(s)
JOHANNES LEOPOLD MARIE SYRIER; DIRK ADRIAAN BORGER; JOHAN MARIE BEYEN; ANTONIUS AUGUSTINUS BROEKHUIS; FRANCISCUS CHRISTIAAN GROENLAND

(74) Attorney or Agent
SPRUSON & FERGUSON , GPO Box 3898, SYDNEY NSW 2001

(56) Prior Art Documents
AU 22852/88 C08L 73/00
AU 598662 15189/88 C08L 73/00

(57) Claim

1. Polyketone polymer composition comprising a major amount of an alternating copolymer of carbon monoxide and an olefinically unsaturated compound and a minor amount of at least one additive, characterised in that the additive(s) is/are melt-flow improving compounds selected from (a) one or more fully amidated mono- or polycarboxylic acid having from 5 to 30 carbon atoms and being optionally N-monosubstituted or N,N-disubstituted with C_{1-4} unsubstituted alkyl groups and, optionally, (b) one or more aluminium compounds of formula $Al(OX)_3$, in which X stands for a hydrogen atom or a C_{1-4} unsubstituted alkyl group.

3. A composition as claimed in claim 1 or 2, characterised in that the fully amidated carboxylic acid has the general formula R^1-C(=O)-NR^2R^3, in which R^1 is a hydrocarbyl group with from 5 to 27 carbon atoms, and R^2 and R^3 each independently are hydrogen atoms or unsubstituted alkyl groups with from 1 to 4 carbon atoms.

8. A composition as claimed in any one of claims 1 to 7, characterised in that the aluminium compound comprises aluminium hydroxide of formula $Al(OH)_3$.

9. A composition as claimed in any one of claims 1 to 7, characterised in that the aluminium compound comprises aluminium isopropoxide of formula $Al(C_3H_7O)_3$.

611991 S & F Ref: 83257

FORM 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE:

Class   Int Class

Complete Specification Lodged:
Accepted:
Published:

Priority:

Related Art:

Name and Address of Applicant: Shell Internationale Research Maatschappij B.V.
Carel van Bylandtlaan 30
2596 HR
The Hague
THE NETHERLANDS

Address for Service: Spruson & Ferguson, Patent Attorneys
Level 33 St Martins Tower, 31 Market Street
Sydney, New South Wales, 2000, Australia

Complete Specification for the invention entitled:

Polyketone Copolymer Composition

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

5845/4

T 324

POLYKETONE COPOLYMER COMPOSITION

The present invention relates to polyketone copolymer compositions comprising certain additives. The relevant copolymers are characterized by having an alternating structure $[A-CO]_n$ in which a unit A is positioned left and right in between carbon monoxide units. A is a unit derived from an olefinically unsaturated compound. The term "copolymer" includes terpolymers in which different units A are present. As an example of suitable terpolymers reference is made to a copolymer of ethene, carbon monoxide and propene or butene. Other suitable monomers yielding a unit A are e.g. styrene, butene, octene and acrylate esters.

The relevant alternating copolymers and their methods of preparation are known per se, cf. US-A 3,694,412, EP-A 121965 and EP-A 181014. Whilst these copolymers have attractive physical and mechanical properties such as yield stress, tensile strength, impact strength and flexural modulus, their processing performance leaves room for improvement.

Extrusion of copolymer with an intrinsic viscosity, or limited viscosity number (LVN) above 2.0 dl/g (measured at 60 ^{o}C in m-cresol) is adversely affected by poor melt flow. Since copolymers with a high LVN have better physical properties, and would be very successful as fibre material and as engineering thermoplastic, this problem needs to be solved. Especially in fibre applications, i.e. fibre-reinforced compositions comprising polyketones, melt-extrusion is a critical step, even for copolymers with a low LVN.

It has been found now that the melt flow properties of the above-mentioned polyketones can be improved by incorporating certain additives selected from acid amides and aluminium-oxygen compounds. The better melt flow properties ensure that processing, such as extrusion, may be carried out more easily, with less intrinsic friction, i.e. less local heating and degradation of the polymer. It has been found too that certain additives, when used in combination, show synergy, and that other additives, which are known per se as antioxidants for other polymers, act as melt flow improver as well, when used in combination with the first mentioned amides or aluminium-oxygen compounds.

Accordingly, the invention relates to polyketone polymer composition comprising a major amount of an alternating copolymer of carbon monoxide and an olefinically unsaturated compound and a minor amount of at least one additive, characterised in that the additive(s) is/are melt-flow improving compounds selected from (a) one or more fully amidated mono- or polycarboxylic acid having from 5 to 30 carbon atoms and being optionally N-monosubstituted or N,N-disubstituted with C_{1-4} unsubstituted alkyl groups and, optionally, (b) one or more aluminium compounds of formula $Al(OX)_3$, in which X stands for a hydrogen atom or a C_{1-4} unsubstituted alkyl group.

The expression "a minor amount" will be clear to those skilled in the art. Generally it will not be necessary to employ more than a certain amount of additive to reach an acceptable performance. Suitably, from 0.01 to 5.0 %w, especially from 0.01 to 3.0 %w, of additive is used. The weight percentage relates to the global amount of melt-flow improving additive, based on the total weight of the composition.

As acid amides may be used various amides of mono or poly-, especially di-, carboxylic acids. Examples of suitable amides are thus the bis-amides of dicarboxylic acids such as succinic, maleic or terephthalic acid,

RLEW1173y

but preferred are the amides of aliphatic monoacids having relatively long carbon chains. However, benzamide and derivatives give good results as well. Thus, preferably the acid amide has the general formula R^1-C(=O)-NR^2R^3, in which R^1 is an optionally substituted hydrocarbyl group with from 5 to 27 carbon atoms, and R^2 and R^3 each independently are hydrogen atoms or alkyl groups with from 1 to 4 carbon atoms. In particular, R^1 is selected from optionally substituted aliphatic groups having 10 to 27 carbon atoms and optionally substituted phenyl groups, and R^1 is especially an alkyl group or an olefinically unsaturated hydrocarbyl group, such as linoleic acid amide. More preferably, R^1 represents a group of formula $H-(CH_2)_x-CH=CH-(CH_2)_y-$ or of formula $H-(CH_2)_{x+y+2}-$, the sum of x and y being 8 to 25.

Suitable examples of the latter class are unsaturated alkyl amides such as oleic acid amide (x+y=7) and particularly erucamide (x=8 and y=11), or saturated alkyl amides such as lauric acid amide (x+y=9), myristyl amide (x+y=11), palmityl amide (x+y=13), stearyl amide (x+y=15) or montanyl amide (x+y=25).

Most preferred additives are those in which R^2 and R^3 are hydrogen atoms or methyl groups, especially those in which both are hydrogen.

The aluminium compounds suitable in the present compositions are either aluminium hydroxide of formula $Al(OH)_3$, in its various known forms such as with or without crystal water, in dry or gel form, or even mixed with other aluminium oxygen compounds, such as in natural boehmite or diaspore or in (hydrated)trioxide, or they are alkoxide compounds of formula $Al(OX)_3$, e.g. aluminium ethoxide, propoxide or isopropoxide.

Especially suitable is the hydroxide also called natural bayerite, of formula $Al_2O_3.3H_2O$ (which can be thought of as $2Al(OH)_3$ molecules). Natural gibbsite or hydrargilite having the same molecular formula may be used as well. Another very suitable compound is aluminium isopropoxide of formula $Al(OC_3H_7)_3$, especially when the processing time can be kept shorter than about 15 minutes - longer periods sometimes destabilize the composition.

It has been found that when using aluminium compounds as melt flow improvers, an unexpected synergistic effect is obtained by the co-addition of an aromatic amine known per se as an antioxidant, such as bis(7-phenyl-p-cumenyl)amine. Other suitable aromatic amines are mentioned in Applicant's (yet not published) EP-88.200742.

It has also been found that very advantageous results are obtained, in general, when next to the melt flow improving additives of the invention, an anti-oxidant additive is present, in a minor amount, of e.g. 0.01-3.0 %w. Very suitable anti-oxidant additives have been found to be the sterically hindered phenolic compounds, which are commercially available, e.g. under the trademarks "Irganox" or "Ionol". Preferably the sterically hindered phenolic compound is selected from 2,5-dialkylphenols, from esters of a straight chain alcohol and a hydroxy,alkylphenyl-substituted carboxylic acid, from diesters of a polyoxyalkylene glycol and a hydroxy,alkylphenyl-substituted carboxylic acid, from 1,2-bis(acetyl)hydrazines in which the acetyl group carries a hydroxy,alkylphenyl substituent, and from alpha-N,omega-N-bis(acetyl)diamines in which the acetyl group carries a hydroxy,alkylphenyl substituent.

MNS

Preferred copolymers are those having a LVN of at least 1.4 dl/g, better still, at least 2.1 dl/g. Other preferred groups of copolymers are CO/ethene copolymers and ethene/CO/propene terpolymers.

The compositions of this invention can be processed into articles of manufacture such as fibres, films, laminates, tubes, piping and articles having an intricate shape by conventional processing techniques such as melt-spinning, extrusion, and co-extrusion, injection moulding and compression moulding.

The additives used in this invention do not only improve the flow of the relevant CO/olefin co- and terpolymers, but also render the co- and terpolymer less prone to polymer degradation during melt-processing. Both improvements are unexpected.

Thus they render processable certain types of polyketones which were hardly processable before the present invention.

EXAMPLE 1

Copolymer compositions comprising ethene/propene/carbon monoxide copolymer having a LVN of 1.8 dl/g and a crystalline melting point 226°C, and being thermostabilized with a mixture of 0.3 %w 2,6-di-t.butyl-4-methylphenol and 0.6 %w of the n-octadecyl ester of 3-(3,5-di-t.butyl-4-hydroxyphenyl)propanoic acid, were extruded at 240°C with a 5.00 kg load through a die with a 2.096 mm diameter orifice. By varying the position of the piston in the barrel (internal barrel diameter 9.55 mm) the residence time of the composition in the barrel was varied. Melt flow index (MFI) versus residence time is set out in the Table below. The reference composition (a) and the composition of this invention (b) comprised no and 0.1 %w erucamide, respectively.

TABLE 1

Residence time, min

	8		10		12	
	a	b	a	b	a	b
MFI (g/10 min)	2.2	7.9	1.7	5.8	1.4	3.9

EXAMPLE 2

In a commercial L/D 28 twin-screw extruder comprising a crammer-feeder and venting-section, and having a screw diameter of 0.6 m, extrusion tests were performed.

A reference ethene/CO/propene terpolymer composition having a crystalline melting point of 218 °C, a LVN of 2.27 dl/g, and a bulk density of 122 kg/m^3 was extruded in the absence of additives of the invention. The die of the extruder got clogged and blocked within a few minutes. Further extrusion was impossible.

An ethene/CO/propene terpolymer composition having a crystalline melting point of 212 °C, a LVN of 2.12 dl/g, and a bulk density of 77 kg/m^3 was extruded with 0.1 %w erucamide. The extrusion continued for more than 2 hours without any problem. This clearly demonstrates the remarkable improvement of melt flow of samples with erucamide over compositions, without such additive.

EXAMPLE 3

A polyketone terpolymer comprising ethene, propene and carbon monoxide, having a LVN of 1.40 dl/g (measured at 60 °C in m-cresol), a crystalline melting point of 220 °C, and a bulk density of 110 g/ml was converted into a granulate on a short screw extruder.

Samples with various amides were prepared in the same way as in Example 1, i.e. by means of a roller mixer, running at low speed for 6 hours. The melt stability was measured using a commercial torque rheometer under standard conditions, as in Example 1. The results are presented in Table 2.

TABLE 2

Additive (%w)	Initial melt torque (Nm)	Max. Torque (Nm)	Time to max. torque (min)
None	4.7	32.2	10
-duplo-	4.5	30.7	13
Erucamide (0.5)	3.9	25.6	45
-duplo-	3.7	23.1	55
Erucamide (1.0)	4.1	?	>120
-duplo-	4.0	?	>120
-triplo-	3.8	?	>120
Laurylamide (1.0)	3.3	22.0	100
-duplo-	3.3	19.2	100
Stearylamide (0.5)	3.3	26.2	26
-duplo-	3.2	28.1	24
Stearylamide (1.0)	2.2	?	>100
-duplo-	2.8	16.0	200
Benzamide (1.0)	3.9	25.0	110
-duplo-	4.6	24.0	120

The maximum torque for several samples according to the invention is not given, as most experiments lasted only 120 minutes per sample. When looking at the time for the first signs of cross-linking to occur, a similar trend as for the time to maximum torque was observed. All amides observed acted as a stabilizer, and acceptable results appear to be obtainable using concentrations of about 1 %w.

EXAMPLE 4

The experiment of Example 3 was repeated using aluminium-based additives, also in combination with amides. The results are given in Table 3.

TABLE 3

Additive (%w)	Initial torque (Nm)	Max. torque (Nm)	Time to first crosslink (min)	Time to max. torque (min)
None	4.6	32	3	12
Bayerite (0.2)	1.9	21	10	200
Stearylamide (0.5)	3.0	27	3	26
Stearylamide/-bayerite (0.2/0.2)	2.8	22	>5	270

It appears that the time during which the polymer may be processed is prolonged from 12 minutes (using no additive) to 26 or 200 minutes using a single additive, and to 270 minutes using them in combination. Especially the latter, synergistic result is unexpected.

EXAMPLE 5

A number of compositions was prepared starting from an ethene/propene/carbon monoxide terpolymer having a LVN (measured at 60 $^{\circ}C$ in m-cresol) of 2.85 dl/g, a bulk density of 0.290 g/ml and a melting point of 213 $^{\circ}C$. Their recipes are shown below in Table 4.

TABLE 4

Sample:	a*	b*	A	B	C	D	E	F
%w of								
bayerite	-	-	-	1.5	1.5	1.5	-	-
$Al(O\text{-}iPr)_3$	-	-	-	-	-	-	0.3	0.3
"MD 1024"	0.7	0.7	0.65	0.65	0.65	0.65	0.65	0.65
"245"	-	-	0.65	0.65	0.65	0.65	0.65	0.65
"445"	-	-	0.4	-	0.4	0.4	-	0.4

* sample a was dried before extrusion, sample b was not.

In these compositions, "MD 1024" stands for 1,2-bis(3-(4-hydroxy-3,5-di-t.butylphenyl)propanoyl)-hydrazine, "245" stands for the diester of tris(oxyethylene)glycol and 3-(4-hydroxy-3-methyl-5-t.butylphenyl)propanoic acid, and "445" stands for bis(7-phenyl-p-cumenyl)amine. Typically, the additives were suspended in methanol (e.g. 5-7 kg of methanol per 10 kg of terpolymer) and added to the polyketone, followed by drying at 60 °C for approximately 16 hours. The difference between samples C and D resides in the amount of methanol in which the additives were suspended, prior to their addition to the terpolymer: 5 kg and 7 kg, respectively, on 10 kg of terpolymer.

Analysis of the samples A-F showed that of all additives the amounts were lower than would be expected, which could be due to loss of filtrate during the blending in of the additives.

TABLE 5

Actual compositions

Sample	A	B	C	D	E	F
%w of:						
bayerite	-	0.702	0.3	0.234	-	-
$Al(O\text{-}iPr)_3$	-	-	-	-	0.255	0.2025
"MD 1024"	0.22	0.21	0.26	0.23	0.31	0.30
"245"	0.22	0.24	0.26	0.27	0.27	0.25
"445"	0.20	-	0.21	0.21	-	0.21

Each sample was tested for its melt flow properties, its viscosity behaviour, and so on. The melt index of the samples was assessed using standard methods as in Example 1. The results are given below in Table 6.

TABLE 6

Sample	a	b	A	B	C	D	E	F
viscosity (kPa.s)	8.1	9.2	4.1	3.8	3.3	3.5	4.3	4.5
melting point (^{o}C)	272	265	267	269	267	274	267	267
initial MI at 240 ^{o}C (g/10 min)	–	–	1.3	1.8	1.9	1.9	2.1	1.9
initial MI at 260 ^{o}C (g/10 min)	–	–	1.8	3.0	2.6	4.1	2.5	3.0
initial MI at 280 ^{o}C (g/10 min)	–	–	2.0	5.2	5.6	8.1	3.6	5.5
flexural modulus (ASTM D 790, GPa)	–	–	1.63	1.59	1.57	1.62	1.74	1.69
Extrusion performance (visual)*	-1	-2	0	-0.5	+1	+1	0	+1

* scale assessing melt fracture and fouling properties, wherein -2 is very bad and +1 is very good

The claims defining the invention are as follows:

1. Polyketone polymer composition comprising a major amount of an alternating copolymer of carbon monoxide and an olefinically unsaturated compound and a minor amount of at least one additive, characterised in that the additive(s) is/are melt-flow improving compounds selected from (a) one or more fully amidated mono- or polycarboxylic acid having from 5 to 30 carbon atoms and being optionally N-monosubstituted or N,N-disubstituted with C_{1-4} unsubstituted alkyl groups and, optionally, (b) one or more aluminium compounds of formula $Al(OX)_3$, in which X stands for a hydrogen atom or a C_{1-4} unsubstituted alkyl group.

2. A composition as claimed in claim 1, characterised in that it comprises from 0.01 to 3.0 %w of additive.

3. A composition as claimed in claim 1 or 2, characterised in that the fully amidated carboxylic acid has the general formula $R^1-C(=O)-NR^2R^3$, in which R^1 is a hydrocarbyl group with from 5 to 27 carbon atoms, and R^2 and R^3 each independently are hydrogen atoms or unsubstituted alkyl groups with from 1 to 4 carbon atoms.

4. A composition as claimed in claim 3, characterised in that R^1 is selected from unsubstituted aliphatic groups having 10 to 27 carbon atoms and phenyl groups.

5. A composition as claimed in claim 4, characterised in that R^1 is an alkyl group or an olefinically unsaturated hydrocarbyl group.

6. A composition as claimed in claim 5, characterised in that R^1 represents a group of formula $H-(CH_2)_x-CH=CH-(CH_2)_y-$ or of formula $H-(CH_2)_{x+y+2}-$, the sum of x and y being 8 to 25.

7. A composition as claimed in any one of claims 3 to 6, characterised in that R^2 and R^3 are hydrogen.

8. A composition as claimed in any one of claims 1 to 7, characterised in that the aluminium compound comprises aluminium hydroxide of formula $Al(OH)_3$.

9. A composition as claimed in any one of claims 1 to 7, characterised in that the aluminium compound comprises aluminium isopropoxide of formula $Al(C_3H_7O)_3$.

10. A composition as claimed in claim 8 or 9, characterised in that it comprises as an additional additive an aromatic amine.

11. A composition as claimed in claim 10, characterised in that the additional additive is bis(7-phenyl-p-cumenyl)amine.

RLE:1173y

12. A composition as claimed in any one of claims 1 to 11, characterised in that it comprises at least both a fully amidated carboxylic acid ~~an acid amide~~ and an aluminium compound.

13. A composition as claimed in any one of claims 1 to 12, characterised in that it comprises as an additional additive a sterically hindered phenolic compound.

14. A composition as claimed in claim 13, characterised in that the sterically hindered phenolic compound is selected from 2,5-dialkylphenols, from esters of a straight chain alcohol and a hydroxy, alkylphenyl-substituted carboxylic acid, from diesters of a polyoxyalkylene glycol and a hydroxy, alkylphenyl-substituted carboxylic acid, from 1,2-bis(acetyl)-hydrazines in which the acetyl group carries a hydroxy, alkylphenyl substituent, and from alpha-N,omega-N-bis(acetyl)-diamines in which the acetyl group carries a hydroxy,-alkylphenyl substituent.

15. A composition as claimed in any one of claims 1 to 14, characterised in that it comprises as the copolymer a copolymer of carbon monoxide and ethene.

16. A composition as claimed in any one of claims 1 to 14, characterised in that it comprises as the copolymer a copolymer of carbon monoxide, ethene and propene.

17. A composition as claimed in claim 3, characterised in that it comprises from 0.01 to 3.0 %w of an additive having the general formula R^1-C(=O)-NR^2R^3 in which R^1 is an optionally substituted hydrocarbyl group with 12 to 26 carbon atoms.

18. Polyketone polymer composition, substantially as hereinbefore described with reference to any one of the Examples but excluding any comparative examples therein.

19. A process for preparing polyketone polymer composition, substantially as hereinbefore described with reference to any one of the Examples but excluding any comparative example therein.

DATED this ELEVENTH day of DECEMBER 1990
Shell International Research Maatschappij B.V.

Patent Attorneys for the Applicant
SPRUSON & FERGUSON

MNS KXW:1173y