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- (72) Inventor; and *For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*
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(54) Title: TOUGHENED THERMOPLASTIC POLYAMIDE COMPOSITIONS

(57) Abstract: The present invention is a composition useful as an impact modifier for polyamide compositions. In one embodiment, impact modifiers of the present invention are ethylene maleic anhydride copolymers having at least 3% maleic anhydride functionality.

TITLE

TOUGHENED THERMOPLASTIC POLYAMIDE COMPOSITIONS

BACKGROUND OF THE INVENTION**Field of the Invention**

5 This invention relates to polyamide compositions, and to a process of preparing same.

Description of the Related Art

Thermoplastic resins used as plastics in engineering applications can require additives to
10 modify, that is, increase the impact resistance of said thermoplastic resins. U.S. Pat. No. 3,845,163 discloses blends of 60 to 85 weight percent polyamide and an acid-containing olefin polymer. U.S. Pat. No. 3,388,186 discloses a polyamide composition that
15 includes an ethylene-containing grafted copolymer. U.S. Pat. No. 3,465,059 similarly discloses a polyamide composition that includes an ethylene-containing grafted copolymer. U.S. Pat. No. 3,668,274 discloses polycarbonamides that have been modified with an
20 elastomeric phase and a rigid phase thermoplastic stage containing amine-reactive moieties.

Maleic anhydride grafted polyolefins (maleated polyolefins) and ethylene copolymers are widely used as impact modifiers for engineering polymers, particularly
25 for polyamide polymer resins. Maleated polyolefins can be the preferred modifiers for use with polyamide resins. U.S. Pat. No. 4,174,358 discloses copolymers of ethylene/maleic anhydride as tougheners for polyamides having a number average molecular weight of at least
30 5000. U.S. Pat. No. 5, 346,963 describes the use of maleic anhydride-grafted substantially linear ethylene polymers and blends thereof with olefin polymers and

also with non-olefin polymers such as polyamides. U.S. Pat. No. 6,008,297 describes polyamide compositions that include acid-grafted ethylene/alpha-olefin copolymers for improved low-temperature impact strength.

The use of maleated polyolefins is not trouble-free, however. There are limitations with using maleated polyolefins as impact modifiers. For example, it can be difficult to reach a high level of grafting in a maleated polyolefin. Grafting, as conventionally practiced, involves the use of a free-radical initiator. To achieve higher levels of grafting, which can be desirable, it can be necessary to include the free-radical initiator in a higher concentration. Using the initiator at higher concentrations can cause undesirable side reactions, such as crosslinking and chain scission. For this reason, grafting of maleic anhydride at a concentration of greater than 2 wt% can be difficult and troublesome. In addition, controlling the quality and consistency of maleated polyolefins - particularly those having higher concentrations of maleic anhydride grafting - can be troublesome. By-products, unreacted monomers, and crosslinking can significantly detract from the quality of maleated polyolefins at any grafting level, but this can be more of a problem particularly as the grafting level increases. Further, the cost of producing maleated polyolefins with high maleic graft levels can be substantial.

Ethylene copolymers that include reactive functional groups such as maleic anhydride can be readily obtained by a high-pressure free radical

process. However, these copolymers generally are not good impact modifiers for polyamide polymer resins.

It would be desirable to prepare an impact modifier for polyamide polymer resins that are effective tougheners for polyamide resins and do not have the problems associated with high levels of grafting in maleated polyolefins.

SUMMARY OF THE INVENTION

10 In one aspect, the present invention is a toughened polyamide composition, comprising (1) from about 50 to about 98 wt% of a polyamide polymer resin, and (2) from about 2 to about 50 wt% of an impact modifier composition comprising (a) from about 10 to about 50
15 wt% of a copolymer prepared from ethylene, a functional comonomer and optionally a third comonomer, wherein the functional comonomer is included in the range of from about 3 to about 15 wt% in the copolymer; and (b) from about 50 to about 90 wt% of an ethylene-based polymer.

20

DETAILED DESCRIPTION OF THE INVENTION

In one embodiment, the present invention is a composition useful as an impact modifier for polyamide polymer compositions. The composition comprises as one
25 component a maleated polyolefin which is a copolymer of ethylene and maleic anhydride, or its functional equivalent. Such equivalents include derivatives of maleic anhydride such as maleic acid and/or salts thereof, maleic acid diesters, maleic acid monoesters,
30 itaconic acid, fumaric acid, fumaric acid monoester, or mixtures of any of these. Maleated polyolefins also include E/X/Y terpolymers, wherein: E is ethylene; X is

a monomer selected from the group consisting of vinyl acetate, (meth)acrylic acid, and/or derivatives thereof; and Y is maleic anhydride or its functional equivalent. Examples of monomers suitable for inclusion as component X are: (Meth)acrylic acid derivatives include acids, salts, esters, anhydrides, or other acid derivatives that are known to one of ordinary skill in the chemical arts. Methyl acrylate and butyl acrylate are also examples of acrylate monomers suitable for inclusion as component X. Suitable as Y components are: Maleic diesters or monoesters (maleic half-esters) include esters of C1 - C4 alcohols, such as, for example, methyl, ethyl, n-propyl, isopropyl, and n-butyl alcohols. Preferably the maleated polyolefin includes maleic anhydride, maleic acid diesters, and/or maleic acid half-esters. More preferably the maleated polyolefin includes maleic anhydride and/or maleic acid half-esters.

Maleated polyolefins useful herein are obtained by a high pressure free radical polymerization process. A high pressure process suitable for use in the practice of the present invention is described, for example, in U.S. Pat. No. 4,351,931.

The modifier composition comprises as a second component an ethylene-based polymer (base resin). The base resin can be: high density polyethylenes (HDPE); low density polyethylenes (LDPE); linear low density polyethylenes (LLDPE); ultra low density polyethylenes (ULDPE); copolymers of ethylene and alpha-olefin monomer using a metallocene catalyst (metallocene polyethylenes, or MPE); ethylene/propylene copolymers;

or terpolymers such as ethylene/propylene/diene monomer (EPDM).

Suitable base resins can include ethylene copolymers obtained from copolymerization of ethylene
5 with a polar monomer. Such suitable copolymers include: ethylene acrylate copolymers and ethylene vinyl acetate copolymers, including ethylene acrylic acid copolymers, ethylene methacrylic acid copolymers, salts derivable from ethylene acrylic and/or
10 methacrylic acid copolymers, ethylene acrylic ester copolymers, ethylene methacrylic ester copolymers, and/or mixtures of any of these.

Preferably, the base resin is a soft polymer. More preferably, the base resin is MPE, LLDPE, and
15 ethylene copolymers of ethylene and acrylate. Most preferably, the base resin is selected from either MPE or ethylene copolymers of ethylene and acrylate. In a particularly preferred embodiment, where ethylene copolymers are included, the ethylene copolymer is of
20 the type that is prepared in a tubular reactor, according to the procedure described in the article "High Flexibility EMA Made from High Pressure Tubular Process" (Annual Technical Conference - Society of Plastics Engineers (2002), 60th(Vol. 2), 1832-1836).

25 Without being held to theory, MPE can be preferred in the practice of the present invention because of its substantially linear structure and narrow molecular weight distribution of MPE. MPE technology is capable of making lower density MPE with high flexibility and
30 low crystallinity, which can be desirable as the second component of this invention.

MPE technology is described in, for example, U. S. Patent No. 5,272,236; U.S. Patent No. 5,278,272, U.S. Patent No. 5,507,475, U.S. Patent No. 5,264,405, and U.S. Patent No. 5,240,894.

5 The modifier composition can include from about 10 to about 50 wt%, based on the total weight of the modifier composition, of the ethylene maleic anhydride copolymer, or its functional equivalent. Preferably, the modifier includes from about 10 to about 45 wt% of
10 the maleated polyolefin, more preferably the composition includes from about 15 to about 40 wt% of the maleated polyolefin, and most preferably from about 20 to about 35 wt% of the maleated polyolefin.

 The modifier can include from about 50 to about 90
15 wt% of the ethylene-based polymer, based on the total weight of the modifier composition. Preferably the modifier includes from about 55 to about 90 wt%, more preferably from about 60 to about 85 wt%, and most preferably from about 70 to about 85 wt% of the
20 ethylene-based polymer.

 A modifier composition of the present invention is particularly useful for improving the impact resistance of polyamide compositions that include the modifier compositions of the present invention. Without being
25 held to theory, it is believed that the anhydride functionality aids in dispersing the polymer modifier in the polymer matrix. In addition, it is believed that the anhydride functionality assists in enhancing the interfacial adhesion between the modifier and the
30 polymer matrix. Modifier compositions of the present invention can include a higher concentration of grafted anhydride functionality, which can enhance the

effectiveness of the modifier composition as a polyamide toughener, without detracting from the other desirable characteristics of the modified polyamide composition.

5 In another embodiment, the present invention is a polyamide composition comprising the modifier of this invention. The polyamide can be any that is commercially available, such as for example nylon 6, nylon 66, nylon 612, nylon 11 or nylon 12. Various
10 nylon grades can be purchased commercially from E.I. DuPont de Nemours & Company. Alternatively, methods for preparing polyamides suitable for use in the present invention are known and conventional. For example, suitable polyamides can be prepared according
15 to methods described in U.S. Pat. Nos. 2,071,250; U.S. Pat. Nos. 2,130,523; U.S. Pat. Nos. 3,393,210. The polyamide compositions of the present invention can include from about 50 to about 98 wt%, based on the weight of the total polyamide composition, of
20 polyamide. Preferably the polyamide composition includes from about 60 to about 98 wt% polyamide, more preferably from about 70 to about 98 wt% polyamide, most preferably from about 80 to about 98 wt% polyamide.

25 The modifier is included in the polyamide composition in the range of from about 2 to about 50 wt% of the total polyamide composition. Preferably the modifier is included in an amount of from about 2 to about 40 wt%, more preferably from about 2 to about 30
30 wt%, and most preferably from about 2 to about 20 wt% of the total polyamide.

The modifier composition and/or the polyamide composition can include optional components, so long as they do not interfere with the basic and novel characteristics of the polyamide composition of the present invention. For example, components that interfere with the interfacial adhesion between the modifier and the polyamide polymer matrix, or detract from the strength or quality of the polyamide polymer composition, or add substantial costs to the manufacture of the presently claimed polyamide composition, or are otherwise deleterious to the toughness or impact resistance of the polyamide composition are considered to interfere with some of the basic characteristics of the presently claimed invention. Other characteristics that were not exemplified above may nonetheless still be considered basic and/or novel to the presently claimed invention. For example, color, smell, appearance, feel, safety in handling or using, are considered basic characteristics of the present invention. Any added component that interferes with these characteristics, whether mentioned above or not, can be excluded from the composition claimed herein. Any optional components, whether or not contemplated herein, that negatively effect the basic novelty of the present invention can be excluded from the claimed invention.

EXAMPLES

The following examples are illustrations of the present invention, and not intended to limit the scope of the present invention in any way.

Examples:

Preparing blends

The Examples samples in table I and table II were
5 prepared by melt blending using a twin screw extruder
with a mixing screw, using a melt temperature of
between 280-300 C for the samples in table I, and using
a melt temperature of between 260-280 C for the samples
listed in Table II.

10

Test Procedures

Melt flow index (MI) is measured using ASTM D-1238
using a 2160 gram weight, and measured at 190 C.

15

Izod impact was measured using ASTM D-256 using
injection molded specimens. The molded bars were 5
inches long, 1/2 inch wide and 1/8 inch thick. The
bars were cut in half and notches made 1 1/4 inches
20 from the gate (near gate, listed in table as gate) and
3 3/4 inches from the gate (far from gate, listed in
the table as far) because of possible orientation
during molding, the impact results can be different
from the two locations, as can be seen from the data in
25 Table 1 and table 2.

Tensile strength was measured using ASTM D-638 using
injection molded bars.

Materials used in Table 1

5 Nylon 66 employed is a commercial nylon 66, Zytel 101,
available from Du Pont Co.

MPE employed is a commercial Engage 8100 with a density
of 0.87 g/cc and a melt flow index of 1.0, available
from DuPont Dow Co.

10

EMA employed is a commercial copolymer of ethylene and
methyl acrylate with 24 weight percent of methyl
acrylate and a melt flow index of 2.0, available from
Du Pont Co.

15

E/MAME(a) and E/MAME(b) are copolymers of ethylene and
ethyl hydrogen maleate(MAME), prepared in a pilot plant
unit. E/MAME(a) contains about 6 weight percent of
MAME with a melt flow index of 30; E/MAME(b) contains
20 about 8 weight percent of MAME with a melt flow index
of 30.

E/MAA/MAME is a terpolymer of ethylene, methacrylic
acid (11 weight percent) and ethyl hydrogen maleate(6
25 weight percent) with a melt flow index of 90, prepared
in a pilot plant unit.

Materials used in Table II

30 The nylon 6 samples employed are Ultramide B3 and
Ultramide B35, both available from BASF. LLDPE
employed is a commercial resin with a density of 0.91

g/cc and a melt flow index of 1.0, available from Exxon Co. MPE, and both E/MAME(a) and E/MAME(b) are described above.

Table I
Toughened Nylon 66

5

	Modifier		Notched Izod Impact			Tensile Strength
	Ethylene Copolymer	Functional Copolymer	R. T. (ft-lbs)	0°C (ft-lbs)	- 20°C (ft-lbs)	R.T.(kpsi)
	(wt.%)	(wt.%)	(gate/far)	(gate/far)	(gate/far)	
C1	control		0.8			8.6
			0.8			
C2	MPE		0.8	0.7	0.6	7.4
	(20%)		0.8	0.6	0.4	
Ex. 1	MPE	E/MAME(a)	14.7	2.9	2.1	
	(15%)	(5%)	18	10	2.6	
Ex. 2	MPE	E/MAA/MAME	3.3	1.9	1.6	7.9
	(15%)	(5%)	15.3	2	1.4	
Ex. 3	MPE	E/MAME(b)	17.2	13.7	4.4	
	(15%)	(5%)	21.2	16.8	5.6	
C3	EMA		1.63	1.2	0.8	
	(20%)		3.2	1.7	0.9	
Ex. 4	EMA	E/MAA/MAME	14	3.6	2.4	
	(15%)	(5%)	19.1	5.6	2.2	
Ex. 5	EMA	E/MAME(b)	7	3.2	2	
	(15%)	(5%)	16.2	4.8	1.9	

Table II
Toughened Nylon 6

	Nylon 6	Modifier		Notched Izod Impact			Tensile Strength
		Ethylene Copolymer	Functional Copolymer	R. T. (ft-lbs)	0°C (ft-lbs)	- 20°C (ft-lbs)	R.T.(kpsi)
		(wt.%)	(wt.%)	(gate/far)	(gate/far)	(gate/far)	
C4	Ultramide B35	control		0.9	1	0.9	9.3
				0.9	0.9	0.7	
C5	Ultramide B35	MPE		1.6	1	0.9	6.7
		(20%)		1.5	0.9	0.7	
Ex. 6	Ultramide B35	MPE	E/MAA/MAME	18.3	11.3	3	8.3
		(15%)	(5%)	12.7	4.4	3	
Ex. 7	Ultramide B35	MPE	E/MAME(b)	26.8	20.7	7.9	
		(15%)	(5%)	22.5	21.9	8.3	
Ex. 8	Ultramide B35	MPE	E/MAME(b)	24.8	21.4	5.5	
		(17.5%)	(2.5%)	21.3	20	5	
Ex. 9	Ultramide B3	MPE	E/MAME(b)	7.7	2.9	1.9	
		(15%)	(5%)	11.8	9.1	2.4	
Ex. 10	Ultramide B3	MPE	E/MAME(a)	11.9	9.59	3.5	
		(15%)	(5%)	14.3	13.4	3.3	
C6	Ultramide B35	EMA		2.6	1.7	0.9	
		(20%)		2.7	1.5	0.9	
Ex. 11	Ultramide B35	EMA	E/MAME(a)	14	7.6	2.5	
		(15%)	(5%)	14.7	5	2.4	
Ex. 12	Ultramide B35	EMA	E/MAME(b)	19.3	12.7	2.6	
		(15%)	(5%)	13	7.3	2.4	
Ex. 13	Ultramide B35	EMA	E/MAME(b)	14.2	3.7	2.3	
		(17.5%)	(2.5%)	10.9	3.2	2.3	
Ex. 14	Ultramide B3	EMA	E/MAA/MAME	4.8	3.5	NA	
		(15%)	(5%)	7.7	3.1	NA	
Ex. 15	Ultramide B3	EMA	E/MAME(b)	8.5	3.1	NA	
		(15%)	(5%)	9.4	3.3	NA	
Ex. 16	Ultramide B3	LLDPE	E/MAME(a)	3.5	3.5	2.9	
		(15%)	(5%)	9.2	3.8	2.8	

5

CLAIMS:

What is claimed is:

1. A toughened polyamide composition,
5 comprising: (1) from about 50 to about 98 wt% of a polyamide polymer resin; and (2) from about 2 to about 50 wt% of an impact modifier composition comprising (a) from about 10 wt% to about 50 wt% of a copolymer prepared from ethylene and a functional comonomer,
10 wherein the copolymer comprises from about 3 wt% to about 15 wt% of the functional comonomer, and (b) from about 50 wt% to about 90 wt% of an ethylene-based polymer (base resin).
2. The polyamide composition of Claim 1 wherein
15 the impact modifier is included in an amount of from about 5 wt% to about 45 wt%.
3. The polyamide composition of Claim 2 wherein the impact modifier is included in an amount of from about 5 wt% to about 30 wt%.
- 20 4. The polyamide composition of Claim 3 wherein the impact modifier is included in an amount of from about 5 wt% to about 20 wt%.
5. The polyamide composition of Claim 4 wherein the functional comonomer is maleic anhydride or its
25 functional equivalent.
6. The polyamide composition of Claim 5 wherein the functional equivalent is an equivalent selected from the group consisting of: maleic acid and/or salts thereof; maleic acid diesters; maleic acid monoesters;
30 itaconic acid; fumaric acid; fumaric acid monoesters; and mixtures of any of these.
7. The polyamide composition of Claim 6 wherein the functional equivalent is a maleic acid half-ester.

8. The polyamide composition of Claim 7 wherein the functional comonomer is maleic anhydride.

9. The polyamide composition of Claim 8 wherein the base resin comprises a polymer selected from
5 polymers in the group consisting of: high density polyethylenes (HDPE); low density polyethylenes (LDPE); linear low density polyethylenes (LLDPE); ultra low density polyethylenes (ULDPE); metallocene polyethylenes (MPE); ethylene/propylene copolymers;
10 terpolymers such as ethylene/propylene/diene monomer (EPDM); copolymers obtained from copolymerization of ethylene with a polar monomer; or mixtures of any of these.

10. The polyamide composition of Claim 9 wherein
15 the ethylene polar monomer copolymer is selected from the group consisting of: ethylene acrylate copolymers and ethylene vinyl acetate copolymers, including ethylene acrylic acid copolymers, ethylene methacrylic acid copolymers, salts derivable from ethylene acrylic
20 and/or methacrylic acid copolymers, ethylene acrylic ester copolymers, ethylene methacrylic ester copolymers, and/or mixtures of any of these.

11. The polyamide composition of Claim 10 wherein the ethylene copolymer is an ethylene acrylate
25 copolymer or an ethylene vinyl acetate copolymer.

12. The polyamide composition of Claim 11 wherein the ethylene copolymer is an ethylene acrylate copolymer.

13. The polyamide composition of Claim 12 wherein
30 the polyamide is included in an amount of from about 60 wt% to about 98 wt% based on the total weight of the polyamide composition.

14. The polyamide composition wherein the polyamide is included in an amount of from about 70 wt% to about 98 wt%.

5 15. The polyamide composition wherein the polyamide is included in an amount of from about 80 wt% to about 98 wt%.

10 16. An article obtained from a polyamide composition wherein the polyamide composition comprises: (1) from about 50 to about 98 wt% of a polyamide polymer resin; and (2) from about 2 to about 50 wt% of an impact modifier composition comprising (a) from about 10 wt% to about 50 wt% of a copolymer prepared from ethylene and a functional comonomer, wherein the copolymer comprises from about 3 wt% to 15 about 15 wt% of the functional comonomer, and (b) from about 50 wt% to about 90 wt% of an ethylene-based polymer.

17. The article of Claim 16 wherein the article is suitable for use in: household appliances; 20 automobiles; tools; sports equipment; personal protective equipment; sports wear; and/or electronic equipment.

25 18. The polyamide composition of Claim 4 wherein component (a) is an E/X/Y terpolymer wherein: E is ethylene; X is a monomer selected from the group consisting of vinyl acetate, (meth)acrylic acid, and/or derivatives thereof; and Y is maleic anhydride or its functional equivalent.

30 19. The polyamide composition of Claim 18 wherein X is (meth)acrylic acid and/or derivatives thereof.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/16353

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C08L77/00 C08L23/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 859 137 A (CHOU RICHARD TIEN-HUA) 12 January 1999 (1999-01-12) column 3, line 29 - line 34; claims 1-9 ---	1-19
X	WO 98 41576 A (QIU CHUNHAI ;VALTION TEKNILLINEN (FI); KOMPPA VEIKKO (FI); SIVOLA) 24 September 1998 (1998-09-24) claims 1-15 ---	1-19
X	US 4 849 476 A (MASHITA KENTARO ET AL) 18 July 1989 (1989-07-18) column 1, line 6 - line 15; claims 1-5 -----	1-19

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International Application No
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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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