Title: THERMOPLASTIC MELT-BLENDED COMPOSITIONS

Abstract: Disclosed is a thermoplastic melt-blended composition including: A) 20 to 90 weight percent of a copolyamide resin including a 50 to 65 mol % of a first repeat unit of formula (I), b) 35 to 50 mol % of a second repeat unit selected from the group of formula (II); -C(=O)(CH2)6C(=O)NH(CH2)nNH- (II); wherein n is an integer selected from 12, 14, and 16; B) 10 to 60 wt % of at least one reinforcing agent; C) 0 to 30 wt % of at least one polymeric toughener, and D) 0 to 10 weight percent of one or more thermal stabilizer(s); wherein the weight percent of A), B), C), and D) are based on the total weight of the thermoplastic composition.
Thermoplastic Melt-blended Compositions

Field of Invention

The present invention relates to the field of thermoplastic melt-blended compositions including copolyamides derived, in part, from vegetable oils.

BACKGROUND OF INVENTION

The demand for renewable bio-based polymers having similar or better performance characteristics than petrochemical-based polymers, together with increasing fossil raw material prices, make it highly desirable to develop polyamides derived from renewable sources. Long chain dicarboxylic acids, derived from bio-based feed-stocks are used in a variety of polymer products and other applications including poly(hexamethylene decanediamide (PA 610) and poly(hexamethylene dodecanediamide) (PA 612).

There is a need to replace PA 6T/66 (55/45), which has a melting point of 290 - 310 °C, with a copolyamide that is, at least in part, renewably sourced, and having a comparable high melt temperature. At the same time, improvement in water absorption and impact resistance is desired. Needed are copolyamides made from a renewable source, having a melt point of at least 280 °C, and having improved water resistance and better impact resistance than PA 6T/66 (55/45); as well as thermoplastic melt-blended compositions including said copolyamides.

US patent application 2010/0233402 discloses a vehicular part comprising copolyamides comprising about 68 to about 82 molar percent of repeat units PA 610 or 612 and about 18 to about 32 molar percent of repeat units of PA 6T.


SUMMARY OF INVENTION

Disclosed is a thermoplastic melt-blended composition comprising:
A) 20 to 90 weight percent of a copolyamide resin comprising a) 50 to 65 mol % of a first repeat unit of formula (I),

\[ \text{I} \]

and
b) 35 to 50 mol % of a second repeat unit selected from the group consisting of formula (II)

\[-\text{C(O)(CH}_2\text{)}_n\text{C(O)NH(CH}_2\text{)}_b\text{NH-} \quad \text{(II)};\]

wherein and \(n\) is an integer selected from 12, 14, and 16; said copolyamide has a melting point, as determined with differential scanning calorimetry (DSC) at a scan rate of 10 °C/min in the first heating scan of at least 280 °C; and the mol % of repeat units are based on the total repeat units present in the copolyamide;

B) 10 to 60 wt % of at least one reinforcing agent;

C) 0 to 30 wt % of at least one polymeric toughener;

D) 0 to 10 weight percent of one or more functional additives;

wherein the weight percents of A), B), C), and D) are based on the total weight of the thermoplastic composition.

**DETAILED DESCRIPTION**

Herein melting points are as determined with differential scanning calorimetry (DSC) at a scan rate of 10 °C/min in the first heating scan, wherein the melting point is taken at the maximum of the endothermic peak, and the heat of fusion in Joules/gram (J/g) is the area within the endothermic peak.

The Copolymers disclosed herein have two or more diamide molecular repeat units. The copolymers are identified by their respective repeat units. The following list exemplifies the abbreviations used to identify monomers and repeat units in the homopolymer and copolymer polyamides (PA) disclosed herein:

- HMD: 1,6-hexamethylene diamine (or 6 when used in combination with a diacid)
- AA: Adipic acid
- T: Terephthalic acid
- 14: Tetradecanedioic acid
- 16: Hexadecanedioic acid
- 18: Octadecanedioic acid
- DDA: Decanedioic acid
- DDDA: Dodecanedioic acid
- polymer repeat unit formed from HMD and AA
- polymer repeat unit formed from HMD and DDA
polymer repeat unit formed from HMD and DDDA
polymer repeat unit formed from HMD and tetradecanedioic acid
polymer repeat unit formed from HMD and hexadecanedioic acid
polymer repeat unit formed from HMD and octadecanedioic acid
polymer repeat unit formed from HMD and T.

Note that in the art the term “6” when used alone designates a polymer repeat unit formed from \( \varepsilon \)-caprolactam. Alternatively “6” when used in combination with a diacid such as adipic acid, for instance 66, the “6” refers to HMD. In repeat units comprising a diamine and diacid, the diamine is designated first. Furthermore, when “6” is used in combination with a diamine, for instance 66, the first “6” refers to the diamine HMD, and the second “6” refers to adipic acid. Likewise, repeat units derived from other amino acids or lactams are designated as single numbers designating the number of carbon atoms.

Copolymer repeat units are separated by a slash (that is, /). For instance, poly(hexamethylene terephthalamide/hexamethylene tetradecanediamide) is abbreviated PA614/6T (35/65), and the values in brackets are the mole % repeat unit of each repeat unit in the copolymer.

One embodiment is a thermoplastic melt-blended composition comprising:

A) 20 to 90 weight percent of a copolyamide resin comprising
  a) 50 to 65 mol % and preferably 50 to 60 mol %, and 52 to 58 mol %, of a first repeat unit of formula (I),

\[
\begin{align*}
\text{C} & \quad \text{NH(CH}_2\text{)}_6\text{NH} \\
\text{O} & \quad \text{C} \\
\end{align*}
\]

(I), and

b) 35 to 50 mol % and preferably 40 to 50 mol % and 42 to 48 mol %, of a second repeat unit selected from the group consisting of formula (II)

\[
\begin{align*}
\text{-C(O)(CH}_2\text{)}_n\text{C(O)NH(CH}_2\text{)}_6\text{NH-} & \quad (\text{II}); \\
\end{align*}
\]
wherein and n is an integer selected from 12, 14, and 16; said copolyamide has a melting point, as determined with differential scanning calorimetry (DSC) at a scan rate of 10 °C/min in the first heating scan of at least 280 °C; and the mol % of repeat units are based on the total repeat units present in the copolyamide;

B) 10 to 60 wt % of at least one reinforcing agent;
C) 0 to 30 wt % of at least one polymeric toughener;
D) 0 to 10 weight percent of one or more functional additives;

wherein the weight percents of A), B), C), and D) are based on the total weight of the thermoplastic composition.

In one embodiment the copolyamide resin consists essentially of the ranges of repeat units, including the stated preferences, as disclosed above. The term “consist essentially of” means the embodiment necessarily includes the listed repeat units and is open to unlisted repeat units that do not materially affect the basic and novel properties of the invention. Herein, for instance, the term as applied to the copolyamide, means the copolyamide includes the repeat units of formula (I) and (II), and may include other repeat units in small amounts, so long as the additional repeat units do not materially affect the basic and novel properties of the invention. The basic properties of the copolyamides of this invention include a melting point of at least 280 °C; a moisture uptake of less than 2.0 weight percent when 4 mm test bars prepared from said copolyamide, and immersed in water at a test temperature of 23 °C for a test period of 100 days; and a % retention of tensile strength after the moisture uptake, as disclosed above, of at least 70 %, and preferably at least 80 %, as compared to a dry-as-molded control of identical composition.

In one embodiment of the thermoplastic melt-blended composition, the copolyamide resin consists essentially of 50 to 60 mol % of the first repeat unit of formula (I) and 40 to 50 mol % of the second repeat unit of formula (II).

In another embodiment of the thermoplastic melt-blended composition, the copolyamide resin consists essentially of 52 to 58 mol % of the first repeat unit of formula (I) and 42 to 48 mol % of the second repeat unit of formula (II).

Other embodiments are thermoplastic melt-blended compositions wherein the copolyamide resin comprises ranges of repeat units of formula (I) and (II), as disclosed above, wherein n = 12, 14 and 16, respectively.
Preferred copolyamide resins are those wherein 4 mm test bars prepared from said copolyamides, and immersed in water at a test temperature of 23 °C for a test period of 100 days, have a moisture uptake of less than 2.0 weight percent.

Preferred copolyamide resins are those wherein 4 mm test bars prepared from said copolyamides have a % retention of tensile strength after the moisture uptake, as disclosed above, of at least 70 %, and preferably at least 80 %, as compared to a dry-as-molded control of identical composition.

Preferred thermoplastic compositions have about 30 to 80 weight percent, and more preferably about 40 to 80 weight percent of copolyamide resin, based on the total weight of the thermoplastic composition.

Preferred copolyamide resins have an inherent viscosity of at least 0.8, and more preferably at least about 0.9 dl/g, measured as a 0.5% solution of copolyamide in m-cresol at 25 °C. Preferably the copolyamide resin has a melting point between 280 °C and 320 °C and, more preferably, between 285 °C and 320 °C.

The copolyamide resins are preferably prepared from aliphatic dioic acids and aliphatic diamines, at least one of which is bio-sourced or "renewable". By "bio-sourced" is meant that the primary feed-stock for preparing the dioic acid and/or diamine is a renewable biological source, for instance, vegetable matter including grains, vegetable oils, cellulose, lignin, fatty acids; and animal matter including fats, tallow, oils such as whale oil, fish oils, and the like. These bio-sources of dioic acids and aliphatic diamines have a unique characteristic in that they all possess high levels of the carbon isotope $^{14}$C; as compared to fossil or petroleum sources of the dioic acids and aliphatic diamines. This unique isotope feature remains unaffected by non-nuclear, conventional chemical modifications. Thus the $^{14}$C isotope level in bio-sourced materials provides an unalterable feature that allows any downstream products, such as polyamides; or products comprising the polyamides, to be unambiguously identified as comprising a bio-sourced material. Furthermore, the analysis of $^{14}$C isotope level in dioic acids, diamines and downstream product is sufficiently accurate to verify the percentage of bio-sourced carbon in the downstream product.

The copolyamides are prepared from aliphatic dioic acids and aliphatic diamines using conventional chemical methods as are well known in the art of

Preferred renewable copolyamides are wherein the repeat units (I) and (II) are prepared from C16 and C18 dioic acids derived from vegetable oils selected from the group consisting of soybean oil, palm oil, sunflower oil, olive oil, cotton seed oil, peanut oil and corn oil.

The thermoplastic composition may comprise 0 to about 60 weight percent of one or more reinforcement agents. In various embodiments 0.1 to about 60 weight percent, and preferably about 10 to 60 weight percent, 15 to 50 weight percent and 20 to 45 weight percent of reinforcement agent is present. The reinforcement agent may be any inorganic filler, but is preferably selected from the group consisting of calcium carbonate, glass fibers with circular cross-section, glass fibers with noncircular cross-section, glass flakes, glass beads, carbon fibers, talc, mica, wollastonite, calcined clay, kaolin, diatomite, magnesium sulfate, magnesium silicate, barium sulfate, titanium dioxide, sodium aluminum carbonate, barium ferrite, potassium titanate and mixtures thereof. Glass fibers, glass flakes, talc, and mica are preferred reinforcement agents.

The thermoplastic composition may comprise 0 to 30 weight per cent polymeric toughener. The polymeric toughener is a polymer, typically an elastomer having a melting point and/or glass transition points below 25 °C, or is rubber-like, i.e., has a heat of melting (measured by ASTM Method D3418-82) of less than about 10 J/g, more preferably less than about 5 J/g, and/or has a melting point of less than 80 °C, more preferably less than about 60 °C. Preferably the polymeric toughener has a weight average molecular weight of about 5,000 or more, more preferably about 10,000 or more, when measured by gel permeation chromatography using polyethylene standards.

The polymeric toughener can be a functionalized toughener, a nonfunctionalized toughener, or blend of the two.

A functionalized toughener has attached to it reactive functional groups which can react with the polyamide. Such functional groups are usually “attached” to the polymeric toughener by grafting small molecules onto an already existing polymer or by copolymerizing a monomer containing the desired functional group when the polymeric tougher molecules are made by copolymerization. As an example of grafting, maleic anhydride may be grafted onto a hydrocarbon rubber (such as an
ethylene/α-olefin copolymer, an α-olefin being a straight chain olefin with a terminal double bond such a propylene or 1-octene) using free radical grafting techniques. The resulting grafted polymer has carboxylic anhydride and/or carboxyl groups attached to it.

Ethylene copolymers are an example of a polymeric toughening agent wherein the functional groups are copolymerized into the polymer, for instance, a copolymer of ethylene and a (meth)acrylate monomer containing the appropriate functional group. Herein the term (meth)acrylate means the compound may be either an acrylate, a methacrylate, or a mixture of the two. Useful (meth)acrylate functional compounds include (meth)acrylic acid, 2-hydroxyethyl(meth)acrylate, glycidyl(meth)acrylate, and 2-isocyanatoethyl (meth)acrylate. In addition to ethylene and a functionalized (meth)acrylate monomer, other monomers may be copolymerized into such a polymer, such as vinyl acetate, unfunctionalized (meth)acrylate esters such as ethyl (meth)acrylate, n-butyl (meth)acrylate, i-butyl (meth)acrylate and cyclohexyl (meth)acrylate. Polymeric tougheners include those listed in U.S. Patent 4,174,358, which is hereby incorporated by reference.

Another functionalized toughener is a polymer having carboxylic acid metal salts. Such polymers may be made by grafting or by copolymerizing a carboxyl or carboxylic anhydride containing compound to attach it to the polymer. Useful materials of this sort include Surlyn® ionomers available from E. I. DuPont de Nemours & Co. Inc., Wilmington, DE 19898 USA, and the metal neutralized maleic anhydride grafted ethylene/α-olefin polymer described above. Preferred metal cations for these carboxylate salts include Zn, Li, Mg and Mn.

Polymeric tougheners useful in the invention include those selected from the group consisting of linear low density polyethylene (LLDPE) or linear low density polyethylene grafted with an unsaturated carboxylic anhydride, ethylene copolymers; ethylene/α-olefin or ethylene/α-olefin/diene copolymer grafted with an unsaturated carboxylic anhydride; core-shell polymers, and nonfunctionalized tougheners, as defined herein.

Herein the term ethylene copolymers include ethylene terpolymers and ethylene multi-polymers, i.e. having greater than three different repeat units. Ethylene copolymers useful as polymeric tougheners in the invention include those
selected from the group consisting of ethylene copolymers of the formula E/X/Y
wherein:

E is the radical formed from ethylene;

X is selected from the group consisting of radicals formed from

\[ \text{CH}_2=\text{CH}(\text{R}^1)-\text{C}(\text{O})-\text{OR}^2 \]

wherein \( R^1 \) is H, \( \text{CH}_3 \) or \( \text{C}_2\text{H}_5 \), and \( R^2 \) is an alkyl group having 1-8 carbon atoms; vinyl acetate; and mixtures thereof; wherein \( X \) comprises 0 to 50 weight % of E/X/Y copolymer;

Y is one or more radicals formed from monomers selected from the group consisting of carbon monoxide, sulfur dioxide, acrylonitrile, maleic anhydride, maleic acid diesters, (meth)acrylic acid, maleic acid, maleic acid monoesters, itaconic acid, fumaric acid, fumaric acid monoesters and potassium, sodium and zinc salts of said preceding acids, glycidyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-isocyanatoethyl (meth)acrylate and glycidyl vinyl ether; wherein \( Y \) is from 0.5 to 35 weight % of the E/X/Y copolymer, and preferably 0.5-20 weight percent of the E/X/Y copolymer, and E is the remainder weight percent and preferably comprises 40-90 weight percent of the E/X/Y copolymer.

It is preferred that the functionalized toughener contain a minimum of about

0.5, more preferably 1.0, very preferably about 2.5 weight percent of repeat units
and/or grafted molecules containing functional groups or carboxylate salts (including
the metal), and a maximum of about 15, more preferably about 13, and very
preferably about 10 weight percent of monomers containing functional groups or
carboxylate salts (including the metal). It is to be understood than any preferred
minimum amount may be combined with any preferred maximum amount to form a
preferred range. There may be more than one type of functional monomer present
in the polymeric toughener, and/or more than one polymeric toughener. In one
embodiment the polymeric toughener comprises about 2.5 to about 10 weight
percent of repeat units and/or grafted molecules containing functional groups or
carboxylate salts (including the metal).

It has been found that often the toughness of the composition is increased by
increasing the amount of functionalized toughener and/or the amount of functional
groups and/or metal carboxylate groups. However, these amounts should preferably
not be increased to the point that the composition may crosslink (thermoset).
especially before the final part shape is attained, and/or the first to melt tougheners may crosslink each other. Increasing these amounts may also increase the melt viscosity, and the melt viscosity should also preferably not be increased so much that molding is made difficult.

Nonfunctionalized tougheners may also be present in addition to a functionalized toughener. Nonfunctionalized tougheners include polymers such as ethylene/α-olefin/diene (EPDM) rubber, polyolefins including polyethylene (PE) and polypropylene, and ethylene/α-olefin (EP) rubbers such as ethylene/1-octene copolymer, and the like such as those commercial copolymers under the ENGAGE® brand from Dow Chemical, Midland Michigan. Other nonfunctional tougheners include the styrene-containing polymers including acrylonitrile-styrene copolymer, acrylonitrile-butadiene-styrene copolymer, styrene-isoprene-styrene copolymer, styrene-hydrogenated isoprene-styrene copolymer, styrene-butadiene-styrene copolymer, styrene-hydrogenated butadiene-styrene copolymer, styrenic block copolymer, (are not the above listed polymers block or random polymers?) polystyrene. For example, acrylonitrile-butadiene-styrene, or ABS, is a terpolymer made by polymerizing styrene and acrylonitrile in the presence of polybutadiene. The proportions can vary from 15 to 35% acrylonitrile, 5 to 30% butadiene and 40 to 60% styrene. The result is a long chain of polybutadiene criss-crossed with shorter chains of poly(styrene acrylonitrile).

Other polymeric tougheners useful in the invention are having a (vinyl aromatic comonomer) core comprising an ethylene copolymer as disclosed above, the core optionally cross-linked and optionally containing a vinyl aromatic comonomer, for instance styrene; and a shell comprising another polymer that may include polymethyl methacrylate and optionally contain functional groups including epoxy, or amine. The core-shell polymer may be made up of multiple layers, prepared by a multi-stage, sequential polymerization technique of the type described in US4180529. Each successive stage is polymerized in the presence of the previously polymerized stages. Thus, each layer is polymerized as a layer on top of the immediately preceding stage.

When used, the minimum amount of polymeric toughener is 0.5, preferably 2, and more preferably about 8 weight percent of the melt-blended thermoplastic composition, while the maximum amount of polymeric toughener is about 30 weight
percent, preferably about 25 weight percent. It is to be understood that any minimum amount may be combined with any maximum amount to form a preferred weight range.

Useful polymeric tougheners include:

(a) A copolymer of ethylene, glycidyl (meth)acrylate, and optionally one or more (meth)acrylate esters.

(b) An ethylene/α-olefin or ethylene/α-olefin/diene (EPDM) copolymer grafted with an unsaturated carboxylic anhydride such as maleic anhydride.

(c) A copolymer of ethylene, 2-isocyanatoethyl (meth)acrylate, and optionally one or more (meth)acrylate esters.

(d) a copolymer of ethylene and acrylic acid reacted with a Zn, Li, Mg or Mn compound to form the corresponding ionomer.

The thermoplastic composition may include 0 to 10 weight percent of one or more functional additives. Functional additives are materials that provide a specific function known in the art of thermoplastic melt-blend compositions. Such additives can be added according to the desired properties of the resulting material, and the control of these amounts versus the desired properties is within the knowledge of the skilled artisan. Functional additives include those selected from the group consisting of thermal stabilizers, plasticizers, colorants, lubricants, and mold release agents.

The thermoplastic composition may include a thermal stabilizer selected from the group consisting of polyhydric alcohols having more than two hydroxyl groups and having a number average molecular weight ($M_n$) of less than 2000; one or more polyhydroxy polymer(s) having a number average molecular weight of at least 2000 and selected from the group consisting of ethylene/vinyl alcohol copolymer and poly(vinyl alcohol); organic stabilizer(s) selected from the group consisting of secondary aryl amines and hindered amine light stabilizers (HALS), hindered phenols and mixtures of these; copper salts; and mixtures these.

The thermoplastic composition may comprise 0 to 10 weight percent, and preferably 0.1 to 10 weight per cent, of one or more polyhydric alcohols having more than two hydroxyl groups and having a number average molecular weight ($M_n$) of less than 2000 or less than 2000 as determined for polymeric materials with gel permeation chromatography (GPC).

Polyhydric alcohols may be selected from aliphatic hydroxylic compounds containing more than two hydroxyl groups, aliphatic-cycloaliphatic compounds
containing more than two hydroxyl groups, cycloaliphatic compounds containing more than two hydroxyl groups, aromatic and saccharides.

Preferred polyhydric alcohols include those having a pair of hydroxyl groups which are attached to respective carbon atoms which are separated one from another by at least one atom. Especially preferred polyhydric alcohols are those in which a pair of hydroxyl groups is attached to respective carbon atoms which are separated one from another by a single carbon atom.

Preferably, the polyhydric alcohol used in the thermoplastic composition is pentaerythritol, dipentaerythritol, tripentaerythritol, di-trimethylolpropane, D-mannitol, D-sorbitol and xylitol. More preferably, the polyhydric alcohol used is dipentaerythritol and/or tripentaerythritol. A most preferred polyhydric alcohol is dipentaerythritol.

In various embodiments the content of said polyhydric alcohol in the thermoplastic composition is 0.25 to 10 weight percent, preferably 0.25 to 8 weight percent, and more preferably 0.25 to 5, and 1 to 4 weight percent.

The thermoplastic composition may comprise 0.1 to 10 weight percent of at least one polyhydroxy polymer having a number average molecular weight (Mn) of at least 2000, selected from the group consisting of ethylene/vinyl alcohol copolymers; as determined for polymeric materials with gel permeation chromatography (GPC).

Preferably the polyhydroxy polymer has a Mn of 5000 to 50,000.

In one embodiment the polyhydroxy polymer is an ethylene/vinyl alcohol copolymer (EVOH). The EVOH may have a vinyl alcohol repeat content of 10 to 90 mol % and preferably 30 to 80 mol %, 40 to 75 mol %, 50 to 75 mol %, and 50 to 60 mol %, wherein the remainder mol % is ethylene. A suitable EVOH for the thermoplastic composition is Soarnol® A or D copolymer available from Nippon Gosei (Tokyo, Japan) and EVAL® copolymers available from Kuraray, Tokyo, Japan.

The thermoplastic composition may comprise 1 to 10 weight percent; and preferably 1 to 7 weight percent and more preferably 2 to 7 weight percent polyhydroxy polymer based on the total weight of the thermoplastic polyamide composition.

The thermoplastic composition may comprise 0 to 3 weight percent of one or more organic co-stabilizer(s) having a 10% weight loss temperature, as determined by thermogravimetric analysis (TGA), of greater than 30 °C below the melting point of the polyamide resin, if a melting point is present, or at least 250 °C if said melting
point is not present, selected from the group consisting of secondary aryl amines, hindered phenols and hindered amine light stabilizers (HALS), and mixtures thereof.

For the purposes of this invention, TGA weight loss will be determined according to ASTM D 3850-94, using a heating rate of 10 °C/min, in air purge stream, with an appropriate flow rate of 0.8 mL/second. The one or more co-stabilizer(s) preferably has a 10% weight loss temperature, as determined by TGA, of at least 270 °C, and more preferably 290 °C, 320 °C, and 340 °C, and most preferably at least 350 °C.

The one or more co-stabilizers preferably are present from 0.1 to 3 weight percent, more preferably 0.2 to 1.2 weight percent; or more preferably from 0.5 to 1.0 weight percent, based on the total weight of the thermoplastic composition.

By secondary aryl amine is meant an amine compound that contains two carbon radicals chemically bound to a nitrogen atom where at least one, and preferably both carbon radicals, are aromatic. Preferably, at least one of the aromatic radicals, such as, for example, a phenyl, naphthyl or heteroaromatic group, is substituted with at least one substituent, preferably containing 1 to about 20 carbon atoms.

Examples of suitable secondary aryl amines include 4,4′-di(α,α-dimethylbenzyl)diphenylamine available commercially as Naugard 445 from Uniroyal Chemical Company, Middlebury, Conn.; the secondary aryl amine condensation product of the reaction of diphenylamine with acetone, available commercially as Aminox from Uniroyal Chemical Company; and para-(paratoluenesulfonylamido)diphenylamine also available from Uniroyal Chemical Company as Naugard SA. Other suitable secondary aryl amines include N,N′-di-(2-naphthyl)-p-phenylenediamine, available from ICI Rubber Chemicals, Calcutta, India. Other suitable secondary aryl amines include 4,4′-bis(α,α′-tertiaryoctyl)diphenylamine, 4,4′-bis(α-methylbenzhydryl)diphenylamine, and others from EP 0509282 B1.

The hindered amine light stabilizers (HALS) may be one or more hindered amine type light stabilizers (HALS). HALS are compounds of the following general formulas and combinations thereof:
In these formulas, R₁ up to and including R₅ are independent substituents. Examples of suitable substituents are hydrogen, ether groups, ester groups, amine groups, amide groups, alkyl groups, alkenyl groups, alkynyl groups, aralkyl groups, cycloalkyl groups and aryl groups, in which the substituents in turn may contain functional groups; examples of functional groups are alcohols, ketones, anhydrides, imines, siloxanes, ethers, carboxyl groups, aldehydes, esters, amides, imides, amines, nitriles, ethers, urethanes and any combination thereof. A hindered amine light stabilizer may also form part of a polymer or oligomer.

Preferably, the HALS is a compound derived from a substituted piperidine compound, in particular any compound derived from an alkyl-substituted piperidyl, piperidinyl or piperazinone compound, and substituted alkoxy piperidinyl compounds. Examples of such compounds are: 2,2,6,6-tetramethyl-4-piperidone; 2,2,6,6-tetramethyl-4-piperidinol; bis-(1,2,2,6,6-pentamethyl piperidyl)-(3',5'-di-tert-butyl-4'-hydroxy benzyl) butyl malonate; di-(2,2,6,6-tetramethyl-4-piperidyl) sebacate (Tinuvin® 770, MW 481); oligomer of N-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-piperidinol and succinic acid (Tinuvin® 622); oligomer of cyanuric acid and N,N-di(2,2,6,6-tetramethyl-4-piperidyl)-hexamethylene diamine; bis-(2,2,6,6-tetramethyl-4-piperidinyl) succinate; bis-(1-octyloxy-2,2,6,6-tetramethyl-4-piperidinyl) sebacate (Tinuvin® 123); bis-(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate (Tinuvin® 765); Tinuvin® 144; Tinuvin® XT850; tetrakis-(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butane tetracarboxylate; N,N'-bis-(2,2,6,6-tetramethyl-4-piperidyl)-hexane-1,6-diamine (Chimasorb® T5); N-butyl-2,2,6,6-tetramethyl-4-piperidinamine; 2,2'-([(2,2,6,6-tetramethyl-piperidinyl)-imino]-bis-[ethanol]; poly(6-morpholine-S-triazine-
2,4-diyl(2,2,6,6-tetramethyl-4-piperidinyl)-iminohexamethylene-(2,2,6,6-tetramethyl-4-piperidinyl)-imino) (Cyasorb® UV 3346); 5-(2,2,6,6-tetramethyl-4-piperidinyl)-2-cyclo-undecyl-oxazole (Hostavin® N20); 1,1’-(1,2-ethane-di-yl)-bis-(3,3’,5,5’-tetramethyl-piperazinone); 8-acetyl-3-doxyec-7,7,9,9-tetramethyl-1,3,8-triazaspiro(4,5)decane-2, 4-dione; polymethylpropyl-3-oxy-[4(2,2,6,6-tetramethyl-piperidinyl)siloxane (Uvasil® 299); 1,2,3,4-butane-tetracarboxylic acid-1,2,3-tris(1,2,2,6,6-pentamethyl-4-piperidinyl)-4-tridecylester; copolymer of alphamethylstyrene-N-(2,2,6,6-tetramethyl-4-piperidinyl) maleimide and N-stearyl maleimide; 1,2,3,4-butanetetracarboxylic acid, polymer with beta,beta,beta’,beta’-tetramethyl-2,4,8,10-tetraoxaspiro[5.5]undecane-3,9-diethanol, 1,2,2,6,6-pentamethyl-4-piperidinyl ester (Mark® LA63); 2,4,8,10-tetraoxaspiro[5.5]undecane-3,9-diethanol, beta,beta,beta’,beta’-tetramethyl-polymer with 1,2,3,4-butanetetracarboxylic acid, 2,2,6,6-tetramethyl-4-piperidinyl ester (Mark® LA68); D-glucitol, 1,3:2,4-bis-O-(2,2,6,6-tetramethyl-4-piperidinylidene)-(HALS 7); oligomer of 7-oxy-3,20-diazadispiro[5.1.11.2]-heneicosan-21-one-2,2,4,4-tetramethyl-20-(oxiranylmethyl) (Hostavin® N30); propanedioic acid, [(4-methoxyphenyl)methylene]-.bis(1,2,2,6,6-pentamethyl-4-piperidinyl) ester (Sanduvar® PR 31); formamide, N,N'-1,6-hexanediylbis[N-(2,2,6,6-tetramethyl-4-piperidinylidene) (Uvinul® 4050H); 1,3,5-triazine-2,4,6-triamine, N,N’-[1,2-ethanediylbis [[[(4,6- bis[butyl](1,2,2,6,6-pentamethyl-4-piperidinyl)arnimo]-1,3,5-triazine-2-yl] imino]-3,1-propanediyl]]-bis[N,N’-dibutyl-N’,N’-bis(1,2,2,6,6-pentamethyl-4-piperidinyl) (Chimassorb® 119 MW 2286); poly[[6-{(1,1,3,333-tetramethylbutyl) amino]-1,3,5-triazine-2,4-diyl][[(2,2,6,6-tetramethyl-4-peperidinyl)-imino] -1,6-hexanediyl [[(2,2,6,6-tetramethyl-4-piperidinyl)imino]] (Chimassorb® 944 MW 2000-3000); 1,5-dioxaspiro(5.5) 25 undecane 3,3-dicarboxylic acid, bis(2,2,6,6-tetramethyl-4-peridinyl) ester (Cyasorb® UV-500); 1,5-dioxaspiro (5.5) undecane 3,3-dicarboxylic acid, bis (1,2,2,6,6-pentamethyl-4-peridinyl-N-amino-oxamide; 4-acryloyloxy-1,2,2,6,6-pentamethyl-4-piperidine. 1,5,8,12-tetraakis[2’,4’-bis(1”,2”,2”,6”,6”-pentamethyl-4”-piperidinyl(butyl)amino)-1’,3’,5’-triazine-6’-yl]-1,5,8,12- tetraazadodecane; HALS PB-41 (Clariant Hungenue S. A.); Nylostab® S-EED (Clariant Hungenue S. A.); 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)-pyrrollidin-2,5-dione; Uvasor® HA88; 1,1’-(1,2-ethane-di-yl)-bis-(3,3’,5,5’-tetra-methyl-piperazinone) (Good-rite® 3034); 1,1’’-(1,3,5-triazine-2,4,6-triytris ((cyclohexylimino)-2,1- ethanediyl)tris(3,3,5,5-tetramethylpiperazinone) (Good-rite®
3150) and 1,1"-(1,3,5-triazine-2,4,6-triyl)tris(cyclohexylimino)-2,1-ethanediyl)tris(3,3,4,5,5-tetramethylpiperazinone) (Good-rite® 3159). (Tinuvin® and Chimassorb® materials are available from Ciba Specialty Chemicals; Cyasorb® materials are available from Cytec Technology Corp.; Uvasil® materials are available from Great Lakes Chemical Corp.; Saduvor®, Hostavin®, and Nylostat® materials are available from Clariant Corp.; Uvinul® materials are available from BASF; Uvasorb® materials are available from Partecipazioni Industriali; and Good-rite® materials are available from B.F. Goodrich Co. Mark® materials are available from Asahi Denka Co.)

Other specific HALS are selected from the group consisting or di-(2,2,6,6-tetramethyl-4-piperidyl) sebacate (Tinuvin® 770, MW 481) Nylostat® S-EEED (Clariant Hungingue S. A.); 1,3,5-triazine-2,4,6-triamine, N,N"-[1,2-ethanediyl]bis[[[4,6- bis[butyl(1,2,2,6,6-pentamethyl-4-piperidinyl)amino]-1,3,5-triazine-2-yl] imino]3,1-propanediyl]]-bis[N',N"-dibutyl-N',N"-bis(1,2,2,6,6- pentamethyl-4-piperidinyl) (Chimassorb® 119 MW 2286) ; and poly[[6-[(1,1,3,33-tetramethylbutyl) amino]-1,3,5-triazine-2,4-diyll][(2,2,6,6-tetramethyl-4-piperidinyl)-imino] -1,6-hexanediyl [(2,2,6,6-tetramethyl-4-piperidinyl)imino]] (Chimassorb® 944 MW 2000-3000).

Mixtures of secondary aryl amines and HALS may be used. A preferred embodiment comprises at least two co-stabilizers, at least one selected from the secondary aryl amines; and at least one selected from the group of HALS, as disclosed above, wherein the total weight percent of the mixture of co-stabilizers is at least 0.5 wt percent, and preferably at least 0.9 weight percent.

Mixtures of polyhydric alcohols, secondary aryl amines, and HALS may be used. A preferred embodiment includes at least one polyhydric alcohol and at least one secondary aryl amine.

The thermoplastic composition may comprise about 0.1 to at or about 1 weight per cent, or more preferably from at or about 0.1 to at or about 0.7 weight percent, based on the total weight of the polyamide composition, of copper salts. Copper halides are mainly used, for example CuI, CuBr, Cu acetate and Cu naphthenate. Cu halides in combination with alkali halides such as KI, KBr or LiBr may be used. Copper salts in combination with at least one other stabilizer selected from the group consisting of polyhydric alcohols, polyhydric polymers, secondary aryl amines and HALS; as disclosed above, may be used as thermal stabilizers.
Herein the thermoplastic composition is a mixture by melt-blending, in which all polymeric ingredients are adequately mixed, and all non-polymeric ingredients are adequately dispersed in a polymer matrix. Any melt-blending method may be used for mixing polymeric ingredients and non-polymeric ingredients of the present invention. For example, polymeric ingredients and non-polymeric ingredients may be fed into a melt mixer, such as single screw extruder or twin screw extruder, agitator, single screw or twin screw kneader, or Banbury mixer, and the addition step may be addition of all ingredients at once or gradual addition in batches. When the polymeric ingredient and non-polymeric ingredient are gradually added in batches, a part of the polymeric ingredients and/or non-polymeric ingredients is first added, and then is melt-mixed with the remaining polymeric ingredients and non-polymeric ingredients that are subsequently added, until an adequately mixed composition is obtained. If a reinforcing filler presents a long physical shape (for example, a long glass fiber), drawing extrusion molding may be used to prepare a reinforced composition.

In another embodiment 4 mm thick test bars prepared from the thermoplastic melt-blended composition, and immersed in water at a test temperature of 23 °C for a test period of 100 days, have a moisture uptake of less than 1.5 weight percent.

In another embodiment 4 mm thick test bars prepared from said composition, exposed at a test temperature of 120 °C, a test pressure of 2 atm, for 500 hours; have a tensile strength retention of greater than 50 %, preferably greater than 55 % and more preferably greater than 60 %, as compared to a dry-as-molded (DAM) control of identical composition.

Methods for Characterization of Copolyamide Resins

**Melting point**

Herein melting points were as determined with DSC at a scan rate of 10 °C/min in the first heating scan, wherein the melting point is taken at the maximum of the endothermic peak.

**Inherent Viscosity**

Inherent viscosity (IV) was measured on a 0.5% solution of copolyamide in m-cresol at 25 °C.

**Water absorption measurement:**

The water absorption measurement was carried out by determining the increase in water uptake of injection molded bars upon immersion in water at 23 °C.
for 100 days. The test bars used were tensile bars with a thickness of 4 mm and a
width of 10 mm. The bars were taken out from the vacuum sealed bags, weighed
and immediately immersed in water bath maintained at 23 °C. The specimens were
immersed in water for 100 days. After that, they were withdrawn, surface wiped and
recorded the weights. The percentage increase in weight was calculated as per
ASTM D570-98. All the test bars were tested immediately for physical properties.

Physical properties measurement

ISO 527-1A injection molded bars were molded with a mold temperature of
80 °C and melt temperature of 310 °C.

Tensile properties at 23 °C were measured as per ASTM D638 specification
using an Instron tensile tester model 4469. Measurements were made on ISO 527-
1A injection molded bars. The crosshead speed was 50 mm/min.

Flex strength was measured according to ISO 178 using 3-point bending.
Measurements were made on ISO 527-1A injection molded bars.

Notched izod was measured according to ISO 180 with ISO 527-1A injection
molded bars.

Materials

Tetradecanedioic acid having a melting point of 125 – 128 °C was obtained
from Cathay Biotechenechnology, Shanghai, China.

Hexadecanedioic acid refers to a material having a nominal melting point of
124 – 126 °C, obtained from Cathay Biotechenechnology, Shanghai, China.

Octadecanedioic acid refers to Emerox 118, having a melting point of 128-
130 °C, obtained from Emery Oleochemicals LLC, Ohio, US.

PA 6T/66 refers Zytel® HTN502HNC010copolyamide, made from terephthalic
acid, adipic acid, and hexamethylenediamine; wherein the two acids are used in a
55:45 molar ratio; having a melting point of about 310 °C and an inherent viscosity
(IV), according to ASTM D2857 method, typically about 1.07, available from E.I.
DuPont de Nemours and Company, Wilmington, Delaware, USA.

Glass Fiber C refers to CPIC 301HP refers to CPIC 301HP chopped glass
fiber available from Chongqing Polycomp International Corp., Chongqing, China.

Cu heat stabilizer refers to a mixture of 7 parts of potassium iodide and 1 part
of copper iodide in 0.5 part of a stearate wax binder.

PED 191 refers to oxidized polyethylene wax available from Clariant Corp.,
Charlotte, NC.
Synthesis of Copolyamide Resins for Examples and Comparative Examples

Resin Examples R1, R3 and R4

The ingredients listed in Table 1 were weighed into 14 inch long 1 inch diameter stainless steel tubes that were capped on one end. Four tubes were run at the same time for each Example. A pressure controller was connected to each tube. The four tubes were initially heated to 130 °C, at atmospheric pressure, with a sand bath to purge air from the tubes with steam. The pressure controllers were set for 320 psi and the tubes were heated to 280 °C in about 60 minutes. Steam began venting from the tubes during the heating to 280 °C. After reaching 280 °C, the pressure in each of the tubes was reduced from 320 psi to atmospheric over 45 minutes while increasing the temperature to 325 °C. The tubes were heated for an additional 30 minutes at atmospheric pressure and 325 °C before cooling. When the tubes were cool, they were opened and the polymer was removed as a solid plug.

Resin Comparative Example RC4

Resin Comparative Example RC4 was prepared in an identical manner to Resin Example R1 described above except: after reaching 280 °C, the pressure in each of the tubes was reduced from 320 psi to atmospheric over 60 minutes while increasing the temperature to 330 °C. The tubes were heated for an additional 30 minutes at atmospheric pressure and 330 °C before cooling.

Table 1 Ingredients used in Resin Examples R1, R3 and R4, and Resin Comparative Example RC4

<table>
<thead>
<tr>
<th>Resin Examples and Comparative Examples</th>
<th>tetradecanedioic acid (g)</th>
<th>terephthalic acid (g)</th>
<th>78% hexamethylenediamine in water (g)</th>
<th>Water (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>11.04</td>
<td>7.10</td>
<td>12.94</td>
<td>25</td>
</tr>
<tr>
<td>R3</td>
<td>9.12</td>
<td>8.80</td>
<td>13.35</td>
<td>25</td>
</tr>
<tr>
<td>R4</td>
<td>8.11</td>
<td>9.69</td>
<td>13.57</td>
<td>25</td>
</tr>
<tr>
<td>RC4</td>
<td>7.07</td>
<td>10.61</td>
<td>13.80</td>
<td>25</td>
</tr>
</tbody>
</table>

Resin Example R2

Preparation of PA614/6T (45/55)

Salt Preparation: A 10L autoclave was charged with tetradecanedioic acid (1342 g), terephthalic acid (1055 g), an aqueous solution containing 76 weight % of hexamethylene diamine (HMD) (1774 g), an aqueous solution containing 28 weight
percent acetic acid (30 g), an aqueous solution containing 1 weight percent sodium hypophosphite (66 g), an aqueous solution containing 1 weight percent Carbowax 8000 (10 g), and water (2330 g).

Polymerization process conditions: The autoclave agitator was set to 5 rpm and the contents were purged with nitrogen at 10 psi for 10 minutes. The agitator was then set to 50 rpm, the pressure control valve was set to 2.41 MPa (350 psi), and the autoclave was heated. The pressure was allowed to rise to 2.41 MPa at which point steam was vented to maintain the pressure at 2.41 Mpa. The temperature of the contents was allowed to rise to 290 °C. The pressure was then reduced to 0 psig over about 45 minutes. During this time, the temperature of the contents rose to 315 °C. The autoclave pressure was reduced to 5 psia by applying vacuum and held there for approximately 20 minutes. The autoclave was then pressurized with 50 psi nitrogen and the molten polymer was extruded into strands, quenched with cold water and cut into pellets.

The polyamide obtained had an inherent viscosity (IV) of 1.09 dL/g. The polymer had a melting point of 288 °C.

Resin Example R5

Preparation of PA616/6T (45/55).
A 10L autoclave was charged with hexadecanedioic acid (1432 g), terephthalic acid (1015 g), an aqueous solution containing 76 weight % of hexamethylene diamine (HMD) (1708 g), an aqueous solution containing 28 weight percent acetic acid (30 g), an aqueous solution containing 1 weight percent sodium hypophosphite (66 g), an aqueous solution containing 1 weight percent Carbowax 8000 (10 g), and water (2330 g). Polymerization process conditions were the same as described earlier for Resin Example R2. The polyamide obtained had an IV of 1.10 dL/g. The polymer had a melting point of 300 °C.

Resin Example R6

Preparation of PA618/6T 45/55.
A 10L autoclave was charged with octadecanedioic acid (1515 g), terephthalic acid (978 g), an aqueous solution containing 76 weight % of hexamethylene diamine (HMD) (1646 g), an aqueous solution containing 28 weight percent acetic acid (30 g), an aqueous solution containing 1 weight percent sodium hypophosphite (66 g), an aqueous solution containing 1 weight percent Carbowax 8000 (10 g), and water (2360 g). Polymerization process conditions were the same as described earlier for
Resin Example R2 except that the finish temperature was 320 °C. The polyamide obtained had an IV of 0.98 d/l/g. The polymer had a melting point of 301 °C.

Resin Comparative Example RC1

Preparation of PA614/6T 85/15

A 10L autoclave was charged with tetradecanoedioic acid (2374 g), terephthalic acid (269 g), an aqueous solution containing 76 weight % of hexamethylene diamine (HMD) (1667 g), an aqueous solution containing 28 weight percent acetic acid (21 g), an aqueous solution containing 1 weight percent sodium hypophosphite (66 g), an aqueous solution containing 1 weight percent Carbowax 8000 (10 g), and water (2190 g). Polymerization process conditions were the mostly the same as described earlier for Resin Example R2 except that the reactor pressure was 1.72 MPa and the finish temperature was 260 °C. The polyamide obtained had an IV of 1.09 d/l/g. The polymer had a melting point of 199 °C.

Resin Comparative Example RC2

Preparation of PA614/6T 75/25

A 10L autoclave was charged with tetradecanoedioic acid (2150 g), terephthalic acid (461 g), an aqueous solution containing 76 weight % of hexamethylene diamine (HMD) (1711 g), an aqueous solution containing 28 weight percent acetic acid (21 g), an aqueous solution containing 1 weight percent sodium hypophosphite (66 g), an aqueous solution containing 1 weight percent Carbowax 8000 (10 g), and water (2180 g). Polymerization process conditions were the mostly the same as described earlier for Resin Example R2 except that the reactor pressure was 1.72 MPa and the finish temperature was 260 °C. The polyamide obtained had an IV of 1.13 d/l/g. The polymer had a melting point of 192 °C.

Resin Comparative Example RC3

Preparation of PA614/6T 60/40

A 10L autoclave was charged with tetradecanoedioic acid (1790 g), terephthalic acid (767 g), an aqueous solution containing 76 weight % of hexamethylene diamine (HMD) (1728 g), an aqueous solution containing 28 weight percent acetic acid (21 g), an aqueous solution containing 1 weight percent sodium hypophosphite (66 g), an aqueous solution containing 1 weight percent Carbowax 8000 (10 g), and water (2230 g). Polymerization process conditions were the mostly the same as described earlier for Resin Example R2 except that the reactor pressure was 2.07 MPa and the
finish temperature was 285 °C. The polyamide obtained had an IV of 1.11 dl/g. The polymer had a melting point of 266 °C.

Resin Comparative Example RC5

Preparation of PA616/6T 85/15

A 10L autoclave was charged with hexadecanedioic acid (2263 g), terephthalic acid (232 g), an aqueous solution containing 76 weight % of hexamethylene diamine (HMD) (1431 g), an aqueous solution containing 28 weight percent acetic acid (21 g), an aqueous solution containing 1 weight percent sodium hypophosphite (66 g), an aqueous solution containing 1 weight percent Carbowax 8000 (10 g), and water (2575 g). Polymerization process conditions were the mostly the same as described earlier for Resin Example R2 except that the reactor pressure was 1.72 MPa and the finish temperature was 260 °C. The polyamide obtained had an IV of 1.14 dl/g. The polymer had a melting point of 187 °C.

Resin Comparative Example RC6

Preparation of PA616/6T 75/25

Salt Preparation and polymerization: A 10L autoclave was charged with hexadecanedioic acid (2061 g), terephthalic acid (399 g), an aqueous solution containing 76 weight % of hexamethylene diamine (HMD) (1477 g), an aqueous solution containing 28 weight percent acetic acid (21 g), an aqueous solution containing 1 weight percent sodium hypophosphite (66 g), an aqueous solution containing 1 weight percent Carbowax 8000 (10 g), and water (2560 g). Polymerization process conditions were the mostly the same as described earlier for Resin Example R2 except that the reactor pressure was 1.72 MPa and the finish temperature was 260 °C. The polyamide obtained had an IV of 1.07 dl/g. The polymer had a melting point of 188 °C.

Resin Comparative Example RC7

Preparation of PA616/6T 70/30

A 10L autoclave was charged with hexadecanedioic acid (1955 g), terephthalic acid (486 g), an aqueous solution containing 76 weight % of hexamethylene diamine (HMD) (1501 g), an aqueous solution containing 28 weight percent acetic acid (21 g), an aqueous solution containing 1 weight percent sodium hypophosphite (66 g), an aqueous solution containing 1 weight percent Carbowax 8000 (10 g), and water (2560 g). Polymerization process conditions were the mostly the same as described earlier for Resin Example R2 except that the reactor pressure
was 1.72 MPa and the finish temperature was 260 °C. The polyamide obtained had an IV of 1.04 dl/g. The polymer had a melting point of 188 °C.

Preparation of PA618/6T 85/15

A 10L autoclave was charged with octadecanedioic acid (2339 g), terephthalic acid (218 g), an aqueous solution containing 76 weight % of hexamethylene diamine (HMD) (1338 g), an aqueous solution containing 1 weight percent sodium hypophosphite (66 g), an aqueous solution containing 1 weight percent Carbowax 8000 (10 g), and water (2610 g). Polymerization process conditions were the mostly the same as described earlier for Resin Example R2 except that the reactor pressure was 1.72 MPa and the finish temperature was 260 °C. The polyamide obtained had an IV of 1.04 dl/g. The polymer had a melting point of 185 °C.

Preparation of PA618/6T 75/25

A 10L autoclave was charged with octadecanedioic acid (2142 g), terephthalic acid (377 g), an aqueous solution containing 76 weight % of hexamethylene diamine (HMD) (1398 g), an aqueous solution containing 28 weight percent acetic acid (21 g), an aqueous solution containing 1 weight percent sodium hypophosphite (66 g), an aqueous solution containing 1 weight percent Carbowax 8000 (10 g), and water (2570 g). Polymerization process conditions were the mostly the same as described earlier for Resin Example R2 except that the reactor pressure was 1.72 MPa and the finish temperature was 260 °C. The polyamide obtained had an IV of 0.87 dl/g. The polymer had a melting point of 184 °C.
### Table 2 DSC data of PA614/6T Resin Compositions

<table>
<thead>
<tr>
<th>Composition (mole%)</th>
<th>RC1</th>
<th>RC2</th>
<th>RC3</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>R4</th>
<th>RC4</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA 614/6T 85/15</td>
<td>199.1</td>
<td>192.1</td>
<td>266.4</td>
<td>283</td>
<td>288.0</td>
<td>307.6</td>
<td>316.9</td>
<td>327.2</td>
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<tr>
<td>PA 614/6T 75/25</td>
<td>57.5</td>
<td>51.0</td>
<td>14.4</td>
<td>38.9</td>
<td>43.4</td>
<td>41.4</td>
<td>52.9</td>
<td>47.8</td>
</tr>
</tbody>
</table>

### Table 3 DSC data of PA616/6T and 618/6T Resin Compositions

<table>
<thead>
<tr>
<th>Composition (mole%)</th>
<th>RC5</th>
<th>RC6</th>
<th>RC7</th>
<th>R5</th>
<th>RC8</th>
<th>RC9</th>
<th>R6</th>
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</thead>
<tbody>
<tr>
<td>PA 616/6T 85/15</td>
<td>187</td>
<td>187.6</td>
<td>186.7</td>
<td>300.2</td>
<td>184.8</td>
<td>183.9</td>
<td>301.4</td>
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<tr>
<td>PA 616/6T 70/30</td>
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<td>28.1</td>
<td>23.2</td>
<td>52.5</td>
<td>74.2</td>
<td>30.4</td>
</tr>
<tr>
<td>PA 618/6T 45/55</td>
<td>52.5</td>
<td>74.2</td>
<td>30.4</td>
<td>38.7</td>
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Table 4 Physical Properties of Copolyamide Resin Compositions

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<th>RC10</th>
<th>R2</th>
<th>R5</th>
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<tbody>
<tr>
<td>Polymer composition</td>
<td>PA6T/66 55/45</td>
<td>PA6T/614 55/45</td>
<td>PA6T/616 55/45</td>
</tr>
<tr>
<td>Polymer wt %</td>
<td>100</td>
<td>100</td>
<td>100</td>
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<tr>
<td>Melt point (1st heat)</td>
<td>313</td>
<td>288</td>
<td>300</td>
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<tr>
<td>Freeze point</td>
<td>272</td>
<td>243</td>
<td>245</td>
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<tr>
<td>Heat of fusion (1st heat)</td>
<td>60</td>
<td>43</td>
<td>53</td>
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<tr>
<td>Physical Properties DAM</td>
<td></td>
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</tr>
<tr>
<td>Notched izod (kJ/m(^2))</td>
<td>5.3</td>
<td>4.2</td>
<td>4.3</td>
</tr>
<tr>
<td>Flex Strength (MPa)</td>
<td>128</td>
<td>102</td>
<td>97</td>
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<tr>
<td>Tensile Strength at 23 °C (MPa) (break)</td>
<td>93</td>
<td>70</td>
<td>51</td>
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<td>Tensile Modulus (Mpa)</td>
<td>2971</td>
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<td>Elongation at 23 °C (%)</td>
<td>4.4</td>
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Physical properties after immersion in water at 23 °C for 100 days

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<tr>
<td>% moisture intake</td>
<td>2.9</td>
<td>1.8</td>
<td>1.8</td>
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<tr>
<td>Tensile Strength at 23 °C (MPa) (break)</td>
<td>58</td>
<td>58</td>
<td>46</td>
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<tr>
<td>Tensile Modulus (Mpa)</td>
<td>2322</td>
<td>2168</td>
<td>2055</td>
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<tr>
<td>Elongation at 23 °C (%)</td>
<td>3.8</td>
<td>4.8</td>
<td>3.3</td>
</tr>
<tr>
<td>% Retention of tensile strength (Mpa) after moisture uptake</td>
<td>62</td>
<td>83</td>
<td>90</td>
</tr>
<tr>
<td>% Retention of tensile modulus (Mpa) after moisture uptake</td>
<td>78</td>
<td>91</td>
<td>89</td>
</tr>
</tbody>
</table>
Methods for Reinforced Compounded Compositions

All compounded resin compositions were prepared by melt blending the ingredients listed in the Table 5 in a 26 mm twin screw extruder operating with barrels heated at 300°C and a polymer melt of about 340°C using a screw speed of about 300 rpm and a throughput of 14 kg/hour. The glass fibers were added to the melt through a screw side feeder. Ingredient quantities shown in the Table are given in weight percent on the basis of the total weight of the thermoplastic composition. The compounded mixture was extruded in the form of laces or strands, cooled in a water bath and chopped into granules.

Physical properties measurement

Mechanical tensile properties, i.e. E-modulus, stress at break (Tensile strength) and strain at break (elongation at break) were measured according to ISO 527-2/1A. Measurements were made on injection molded ISO tensile bar with a mold temperature of 80°C and a melt temperature of 310°C.

The thickness of the test specimens was 4 mm and a width of 10 mm according to ISO 527/1A at a testing speed of 5 mm/min (tensile strength and elongation). Test specimens used for air oven ageing were 2 mm thick and a width of 10 mm.

Air Oven Ageing (AOA)

The test specimens were heat aged in a re-circulating air oven at 230°C. At various heat aging times, the test specimens were removed from the oven and allowed to cool to room temperature under vacuum in a vacuum oven. The tensile mechanical properties were then measured according to ISO 527. The average values obtained from 5 specimens are given in the Tables. Retention of tensile strength corresponds to the percentage of the tensile strength after heat aging for 500 hours and 1000 hours in comparison with the value of the specimens non-heat-aged control specimens considered as being 100%.

Hydrolysis Resistance (120°C, 2 atm)

Test bars were conditioned in an autoclave at 120°C and 2 atmospheres steam pressure, and 100% relative humidity for preset times. Tensile strengths were measured on the conditioned test bars and the results were compared to the properties of the unconditioned bars. The average values obtained from 5 specimens are given in the Table. Retention of tensile strength corresponds to the percentage of the tensile strength after hydrolysis at 120°C and 2 atmospheres.
steam pressure for 500 hours in comparison with the tensile strength of untreated controls of identical composition considered as being 100%.

Table 5 lists the physical properties of the thermoplastic compositions in Examples 1 and 2 versus those of a conventional PA 6T/66 thermoplastic composition (C1). Notably, the Examples have improved tensile strength retention after hydrolysis testing and substantially improved AOA tensile strength retention versus the conventional PA 6T/66 thermoplastic composition.
<table>
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<th>Example</th>
<th>C1</th>
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<tr>
<td>Polymer Composition</td>
<td>6T/66</td>
<td>614/8T</td>
<td>616/6T</td>
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<tr>
<td></td>
<td>55/45</td>
<td>45/55</td>
<td>45/55</td>
</tr>
<tr>
<td>Polymer wt%</td>
<td>64.35</td>
<td>64.35</td>
<td>64.35</td>
</tr>
<tr>
<td>Cu heat stabilizer</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
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<td>PED 191</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>Glass Fiber C</td>
<td>35</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>Physical properties-DAM at 23 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EI (%)</td>
<td>2.98</td>
<td>3.69</td>
<td>3.71</td>
</tr>
<tr>
<td>Notched izod (KJ/m2)</td>
<td>12</td>
<td>15.7</td>
<td>15.7</td>
</tr>
<tr>
<td>Hydrolysis 120 °C, 2 atm</td>
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<td></td>
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<tr>
<td>TS (MPa) 0 h</td>
<td>230</td>
<td>219</td>
<td>207</td>
</tr>
<tr>
<td>TS (MPa) 100 h</td>
<td>125</td>
<td>126</td>
<td>134</td>
</tr>
<tr>
<td>TS (MPa) 500 h</td>
<td>120</td>
<td>124</td>
<td>126</td>
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<tr>
<td>500 hr TS Retention (%)</td>
<td>52</td>
<td>57</td>
<td>61</td>
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<tr>
<td>AOA 230 °C</td>
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<tr>
<td>TS (MPa) 0 h</td>
<td>216</td>
<td>200</td>
<td>198</td>
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<tr>
<td>TS (MPa) 500 h</td>
<td>110</td>
<td>119</td>
<td>111</td>
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<tr>
<td>TS (MPa) 1000 h</td>
<td>47</td>
<td>83</td>
<td>80</td>
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<tr>
<td>500 h TS Retention (%)</td>
<td>51</td>
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<td>56</td>
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<tr>
<td>1000 h TS Retention (%)</td>
<td>22</td>
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<td>Physical properties at 23 °C, DAM</td>
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<td>TS (MPa) (break)</td>
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<td>223</td>
<td>216</td>
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<td>Tensile Modulus (Mpa)</td>
<td>5531</td>
<td>5615</td>
<td>4946</td>
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<tr>
<td>Elongation (%)</td>
<td>4.7</td>
<td>5.5</td>
<td>5.7</td>
</tr>
<tr>
<td>Physical properties after immersion in water, 23 °C, 100 days</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>% moisture uptake</td>
<td>2.42</td>
<td>1.31</td>
<td>1.24</td>
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<td>TS at 23 °C (Mpa)</td>
<td>166</td>
<td>173</td>
<td>167</td>
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<td>Tensile Modulus (Mpa)</td>
<td>4287</td>
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<td>4065</td>
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<tr>
<td>Elongation at 23 °C (%)</td>
<td>4.7</td>
<td>5.6</td>
<td>6.0</td>
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<tr>
<td>% Retention of TS</td>
<td>73</td>
<td>77</td>
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<td>% Retention of tensile modulus</td>
<td>78</td>
<td>72</td>
<td>82</td>
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CLAIMS

We Claim:

1. A thermoplastic melt-blended composition comprising:
   A) 20 to 90 weight percent of a copolyamide resin comprising:
      a) 50 to 65 mol % of a first repeat unit of formula (I),

      \[
      \text{C} - \text{O} - \text{C} - \text{NH(CH}_2\text{)}_6\text{NH} -
      \]  
      (I), and

      b) 35 to 50 mol % of a second repeat unit selected from the group consisting
      of formula (II)

      \[
      -\text{C(}\text{O})(\text{CH}_2)_n\text{C(}\text{O})\text{NH(CH}_2\text{)}_6\text{NH}-
      \]  
      (II);

   wherein and \( n \) is an integer selected from 12, 14, and 16; said copolyamide has a
   melting point, as determined with differential scanning calorimetry (DSC) at a scan
   rate of 10 °C/min in the first heating scan of at least 280 °C; and the mol % of repeat
   units are based on the total repeat units present in the copolyamide;

   B) 10 to 60 wt % of at least one reinforcing agent;
   C) 0 to 30 wt % of at least one polymeric toughener;
   D) 0 to 10 weight percent of one or more functional additives;

2. The thermoplastic melt-blended composition of claim 1 wherein the
   copolyamide resin consists essentially of 50 to 60 mol % of a first repeat unit
   of formula (I) and 40 to 50 mol % of a second repeat unit selected from the
   group consisting of formula (II).

3. The thermoplastic melt-blended composition of claim 1 wherein \( n = 12 \).

4. The thermoplastic melt-blended composition of claim 1 wherein \( n = 14 \).

5. The thermoplastic melt-blended composition of claim 1 wherein \( n = 16 \).

6. The thermoplastic melt-blended composition of claim 1 wherein 4 mm test bars
   prepared from said composition, and immersed in water at a test temperature of 23
°C for a test period of 100 days, have a moisture uptake of less than 1.5 weight percent.

7. The thermoplastic melt-blended composition of claim 1 wherein 4 mm thick test bars prepared from said composition, exposed at a test temperature of 120 °C, a test pressure of 2 atm, for 500 hours; have a tensile strength retention of greater than 50% as compared to a dry-as-molded control of identical composition.

8. The thermoplastic melt-blended composition of claim 1 wherein the reinforcing agent is glass fiber.
**INTERNATIONAL SEARCH REPORT**

**International application No**
PCT/US2013/068622

**A. CLASSIFICATION OF SUBJECT MATTER**

<table>
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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)

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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 practicable, search terms used)

EPO-Internal, BIOSIS, COMPENDEX, INSPEC, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
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<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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| | Further documents are listed in the continuation of Box C. | See patent family annex. |

**Date of the actual completion of the international search**
30 January 2014

**Date of mailing of the international search report**
06/02/2014

**Name and mailing address of the ISA/European Patent Office, P.B. 5018 Patentlaan 2 NL-2280 HV Rijswijk**
Tel. (+31-70) 340-3040, Fax: (+31-70) 340-3016

<table>
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Form PCT/ISA/210 (second sheet) (April 2005)
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