



US 20100029819A1

(19) **United States**(12) **Patent Application Publication**
PALMER et al.(10) **Pub. No.: US 2010/0029819 A1**(43) **Pub. Date: Feb. 4, 2010**(54) **HEAT RESISTANT MOLDED OR EXTRUDED
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(US)(21) Appl. No.: **12/512,109**(22) Filed: **Jul. 30, 2009****Related U.S. Application Data**(60) Provisional application No. 61/137,345, filed on Jul.
30, 2008.**Publication Classification**(51) **Int. Cl.**
C08K 5/053 (2006.01)(52) **U.S. Cl.** **524/387**(57) **ABSTRACT**

Disclosed is a molded or extruded thermoplastic article having high heat stability over at least 500 hours at least 170° C. including a thermoplastic composition including a thermoplastic resin; one or more polyhydric alcohols having more than two hydroxyl groups and a having a number average molecular weight (M_n) of less than 2000; one or more reinforcement agents; and optionally, a polymeric toughener; wherein 4 mm test bars prepared from said thermoplastic composition, and exposed at a test temperature at 170° C. for a test period of 500 hours, have, on average, a retention of tensile strength of at least 50 percent, as compared with that of an unexposed control of identical composition and shape. Further disclosed is a molded or extruded thermoplastic article, including a thermoplastic polyamide composition, wherein 4 mm test bars of said thermoplastic polyamide composition, when exposed at 210° C. for a test period of 500 hours, have a retention of tensile strength of at least 70 percent.

HEAT RESISTANT MOLDED OR EXTRUDED THERMOPLASTIC ARTICLES

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority of U.S. Provisional Application No. 61/137,345, filed on 30 Jul. 2008 and currently pending.

FIELD OF THE INVENTION

[0002] The present invention relates to the field of molded and extruded thermoplastic articles having improved long-term high temperature aging characteristics.

BACKGROUND OF THE INVENTION

[0003] High temperature resins based on polyamides and polyesters possess desirable chemical resistance, processability and heat resistance. This makes them particularly well suited for demanding high performance automotive and electrical/electronics applications. There is a current and general desire in the automotive field to have high temperature resistant structures since temperatures higher than 150° C., even higher than 200° C., are often reached in underhood areas of automobiles. When plastic parts are exposed to such high temperatures for a prolonged period, such as in automotive under-the-hood applications or in electrical/electronics applications, the mechanical properties generally tend to decrease due to the thermo-oxidation of the polymer. This phenomenon is called heat aging.

[0004] In an attempt to improve heat aging characteristics, it has been the conventional practice to add heat stabilizers (also referred as antioxidants) to thermoplastic compositions comprising polyester or polyamide resins. Examples of such heat stabilizers include hindered phenol antioxidants, amine antioxidants and phosphorus-based antioxidants. For polyester compositions, phenolic antioxidants optionally combined with phosphorus based synergist are conventionally used. For polyamide compositions, three types of heat stabilizers are conventionally used to retain the mechanical properties of the composition upon exposure to high temperatures. One is the use of phenolic antioxidants optionally combined with a phosphorus based synergist as previously mentioned, the use of aromatic amines optionally combined with a phosphorus based synergist and the third one is the use of copper salts and derivatives. Phenolic antioxidants are known to improve the mechanical/physical properties of the thermoplastic composition up to an aging temperature of 120° C.

[0005] U.S. Pat. No. 5,965,652 discloses a thermally stable polyamide molding composition containing colloidal copper formed in situ. However, the disclosed compositions exhibit retention of impact strength only for a heat aging at 140° C.

[0006] GB patent 839,067 discloses a polyamide composition comprising a copper salt and a halide of a strong organic base. However, the disclosed compositions exhibit improved bending heat stability performance only for a heat aging at 170° C.

[0007] Existing technologies lead not only to a poor improvement of long-term heat aging resistance, but also the improved heat aging characteristics are insufficient for more demanding applications involving exposure to higher temperatures such as for example in automotive under-the-hood applications and in electrical/electronics applications.

[0008] US 2006/0155034 and US 2008/0146718 patent publications disclose polyamide compositions comprising a metal powder as thermal stabilizer with a fibrous reinforcing agent. Disclosed compositions exhibit improved mechanical properties such as tensile strength and elongation at break upon long-term heat aging at 215° C. However, such metal powders are not only expensive but they are also highly unstable because they are prone to spontaneous combustion. [0009] EP 1041109 discloses a polyamide composition comprising a polyamide resin, a polyhydric alcohol having a melting point of 150 to 280° C., that has good fluidity and mechanical strength and is useful in injection welding techniques.

[0010] Unfortunately, with the existing technologies, molded articles based on polyamide or polyester compositions either suffer from an unacceptable deterioration of their mechanical properties upon long-term high temperature exposure or they are very expensive due to the use of high-cost heat stabilizers.

[0011] There remains a need for low-cost polyamide and polyester compositions that are suitable for manufacturing articles and that exhibit good mechanical properties after long-term high temperature exposure.

SUMMARY OF THE INVENTION

[0012] There is disclosed and claimed herein a molded or extruded thermoplastic article comprising a thermoplastic composition comprising:

[0013] (a) a thermoplastic resin selected from the group consisting of polyamides, polyesters, and mixtures thereof;

[0014] (b) 0.25 to 15 weight percent of one or more polyhydric alcohols having more than two hydroxyl groups and a having a number average molecular weight (M_n) of less than 2000;

[0015] (c) 10 to about 60 weight percent of one or more reinforcement agents; and

[0016] (d) 0 to 50 weight percent of a polymeric toughener comprising a reactive functional group and/or a metal salt of a carboxylic acid;

wherein all weight percentages are based on the total weight of the thermoplastic composition and wherein 4 mm test bars prepared from said thermoplastic composition, and exposed at a test temperature of 170° C. for a test period of 500 hours, in an atmosphere of air, and tested according to ISO 527-2/1A, have, on average, a retention of tensile strength of at least 50 percent, as compared with that of an unexposed control of identical composition and shape.

[0017] Further disclosed is a molded or extruded thermoplastic article, as disclosed above, wherein said thermoplastic resin comprises a polyamide resin and wherein molded 4 mm test bars prepared from said thermoplastic composition, and exposed at a test temperature at 210° C. for a test period of 500 hours, in an atmosphere of air, and tested according to ISO 527-2/1A, have, on average, a retention of tensile strength of at least 70 percent, as compared with that of an unexposed control of identical composition and shape.

DETAILED DESCRIPTION OF THE INVENTION

[0018] For the purposes of the description, unless otherwise specified, "high-temperature" means a temperature at or higher than 170° C., preferably at or higher than 210° C., and most preferably at or higher than 230° C.

[0019] In the present invention, unless otherwise specified, “long-term” refers to an aging period equal or longer than 500 hrs, preferably equal or longer than 1000 hrs.

[0020] As used herein, the term “high heat stability”, as applied to the thermoplastic composition disclosed herein or to an article made from the composition, refers to the retention of physical properties (for instance, tensile strength) of 4 mm thick molded test bars consisting of the polyamide composition that are exposed to air oven aging (AOA) conditions at a test temperature at 170° C. for a test period of at least 500 h, in an atmosphere of air, and then tested according to ISO 527-2/1A method. The physical properties of the test bars are compared to that of unexposed controls that have identical composition and shape, and are expressed in terms of “% retention”. In another preferred embodiment the test temperature is at 210° C., the test period is at 500 hours and the exposed test bars have a % retention of tensile strength of at least 70%. Herein “high heat stability” means that said molded test bars, on average, meet or exceed a retention for tensile strength of 50% when exposed at a test temperature at 170° C. for a test period of at least 500 h. Compositions exhibiting a higher retention of physical properties for a given exposure temperature and time period have better heat stability.

[0021] The terms “at 170° C.” and “at 210° C.” refer to the nominal temperature of the environment to which the test bars are exposed; with the understanding that the actual temperature may vary by $\pm 2^\circ$ C. from the nominal test temperature.

[0022] The term “(meth)acrylate” is meant to include acrylate esters and methacrylate esters.

[0023] Herein melting points and glass transitions 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 glass transition, if evident, is considered the mid-point of the change in enthalpy.

[0024] The resin composition used in the present invention comprises a thermoplastic resin selected from the group consisting of polyamides, polyesters, and mixtures thereof. A preferred thermoplastic resin is a polyamide resin. Another preferred thermoplastic resin is a polyester resin.

[0025] Polyamides are condensation products of one or more dicarboxylic acids and one or more diamines, and/or one or more aminocarboxylic acids, and/or ring-opening polymerization products of one or more cyclic lactams. Suitable cyclic lactams are caprolactam and laurolactam. Polyamides may be fully aliphatic or semi-aromatic.

[0026] Fully aliphatic polyamides used in the resin composition of the present invention are formed from aliphatic and alicyclic monomers such as diamines, dicarboxylic acids, lactams, aminocarboxylic acids, and their reactive equivalents. A suitable aminocarboxylic acid is 11-aminododecanoic acid. Suitable lactams are caprolactam and laurolactam. In the context of this invention, the term “fully aliphatic polyamide” also refers to copolymers derived from two or more such monomers and blends of two or more fully aliphatic polyamides. Linear, branched, and cyclic monomers may be used.

[0027] Carboxylic acid monomers comprised in the fully aliphatic polyamides include, but are not limited to aliphatic carboxylic acids, such as for example adipic acid (C6), pimelic acid (C7), suberic acid (C8), azelaic acid (C9), decanedioic acid (C10), dodecanedioic acid (C12), tridecanedioic acid (C13), tetradecanedioic acid (C14), and pen-

tadecanedioic acid (C15). Diamines can be chosen among diamines having four or more carbon atoms, including, but not limited to tetramethylene diamine, hexamethylene diamine, octamethylene diamine, decamethylene diamine, dodecamethylene diamine, 2-methylpentamethylene diamine, 2-ethyltetramethylene diamine, 2-methyloctamethylenediamine; trimethylhexamethylenediamine, meta-xylylene diamine, and/or mixtures thereof.

[0028] The semi-aromatic polyamide is a homopolymer, a copolymer, a terpolymer or more advanced polymers formed from monomers containing aromatic groups. One or more aromatic carboxylic acids may be terephthalate or a mixture of terephthalate with one or more other carboxylic acids, such as isophthalic acid, phthalic acid, 2-methyl terephthalic acid and naphthalic acid. In addition, the one or more aromatic carboxylic acids may be mixed with one or more aliphatic dicarboxylic acids, as disclosed above. Alternatively, an aromatic diamine such as meta-xylylene diamine (MXD) can be used to provide a semi-aromatic polyamide, an example of which is MXD6, a homopolymer comprising MXD and adipic acid.

[0029] Preferred polyamides disclosed herein are homopolymers or copolymers wherein the term copolymer refers to polyamides that have two or more amide and/or diamide molecular repeat units. The homopolymers and copolymers are identified by their respective repeat units. For copolymers disclosed herein, the repeat units are listed in decreasing order of mole % repeat units present in the copolymer. The following list exemplifies the abbreviations used to identify monomers and repeat units in the homopolymer and copolymer polyamides (PA):

[0030] HMD hexamethylene diamine (or 6 when used in combination with a diacid)

[0031] T Terephthalic acid

[0032] AA Adipic acid

[0033] DMD Decamethylenediamine

[0034] 6 ϵ -Caprolactam

[0035] DDA Decanedioic acid

[0036] DDDA Dodecanedioic acid

[0037] I Isophthalic acid

[0038] MXD meta-xylylene diamine

[0039] TMD 1,4-tetramethylene diamine

[0040] 4T polymer repeat unit formed from TMD and T

[0041] 6T polymer repeat unit formed from HMD and T

[0042] DT polymer repeat unit formed from 2-MPMD and T

[0043] MXD6 polymer repeat unit formed from MXD and AA

[0044] 66 polymer repeat unit formed from HMD and AA

[0045] 10T polymer repeat unit formed from DMD and T

[0046] 410 polymer repeat unit formed from TMD and DDA

[0047] 510 polymer repeat unit formed from 1,5-pentanediamine and DDA

[0048] 610 polymer repeat unit formed from HMD and DDA

[0049] 612 polymer repeat unit formed from HMD and DDDA

[0050] 6 polymer repeat unit formed from ϵ -caprolactam

[0051] 11 polymer repeat unit formed from 11-aminoundecanoic acid

[0052] 12 polymer repeat unit formed from 12-aminododecanoic acid

[0053] Note that in the art the term “6” when used alone designates a polymer repeat unit formed from ϵ -caprolactam. Alternatively “6” when used in combination with a diacid such as T, for instance 6T, 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. In one embodiment the polyamide composition comprises a one or more polyamides selected from the group consisting of

[0054] Group (I) polyamides having a melting point of less than 210° C., and comprising an aliphatic or semi-aromatic polyamide selected from the group consisting of poly(pentamethylene decanediamide) (PA510), poly(pentamethylene dodecanediamide) (PA512), poly(ϵ -caprolactam/hexamethylene hexanediamide) (PA6/66), poly(ϵ -caprolactam/hexamethylene decanediamide) (PA6/610), poly(ϵ -caprolactam/hexamethylene dodecanediamide) (PA6/612), poly(hexamethylene tridecanediamide) (PA613), poly(hexamethylene pentadecanediamide) (PA615), poly(ϵ -caprolactam/tetramethylene terephthalamide) (PA6/4T), poly(ϵ -caprolactam/hexamethylene terephthalamide) (PA6/6T), poly(ϵ -caprolactam/decamethylene terephthalamide) (PA6/10T), poly(ϵ -caprolactam/dodecamethylene terephthalamide) (PA6/12T), poly(hexamethylene decanediamide/hexamethylene terephthalamide) (PA610/6T), poly(hexamethylene dodecanediamide/hexamethylene terephthalamide) (PA612/6T), poly(hexamethylene tetradecanediamide/hexamethylene terephthalamide) (PA614/6T), poly(ϵ -caprolactam/hexamethylene isophthalamide/hexamethylene terephthalamide) (PA6/61/6T), poly(ϵ -caprolactam/hexamethylene hexanediamide/hexamethylene decanediamide) (PA6/66/610), poly(ϵ -caprolactam/hexamethylene hexanediamide/hexamethylene decanediamide) (PA6/66/612), poly(ϵ -caprolactam/hexamethylene hexanediamide/hexamethylene decanediamide/hexamethylene dodecanediamide) (PA6/66/610/612), poly(2-methylpentamethylene hexanediamide/hexamethylene hexanediamide/hexamethylene terephthalamide) (PA D6/66//6T), poly(2-methylpentamethylene hexanediamide/hexamethylene hexanediamide/) (PA D6/66), poly(decamethylene decanediamide) (PA1010), poly(decamethylene dodecanediamide) (PA1012), poly(decamethylene decanediamide/decamethylene terephthalamide) (PA1010/10T) poly(decamethylene decanediamide/dodecamethylene decanediamide/decamethylene terephthalamide/dodecamethylene terephthalamide) (PA1010/1210/10T/12T), poly(11-aminoundecanamide) (PA11), poly(11-aminoundecanamide/tetramethylene terephthalamide) (PA11/4T), poly(11-aminoundecanamide/hexamethylene terephthalamide) (PA11/6T), poly(11-aminoundecanamide/decamethylene terephthalamide) (PA11/10T), poly(11-aminoundecanamide/dodecamethylene terephthalamide) (PA11/12T), poly(12-aminododecanamide) (PA12), poly(12-aminododecanamide/tetramethylene terephthalamide) (PA12/4T), poly(12-aminododecanamide/hexamethylene terephthalamide) (PA12/6T), poly(12-aminodode-

canamide/decamethylene terephthalamide) (PA12/10T) poly(dodecamethylene dodecanediamide) (PA1212), and poly(dodecamethylene dodecanediamide/dodecamethylene dodecanediamide/dodecamethylene terephthalamide)) (PA1212/12T);

[0055] Group (II) polyamides having a melting point of at least 210° C., and comprising an aliphatic polyamide selected from the group consisting of poly(tetramethylene hexanediamide) (PA46), poly(ϵ -caprolactam) (PA 6), poly(hexamethylene hexanediamide/(ϵ -caprolactam/)) (PA 66/6) poly(hexamethylene hexanediamide) (PA 66), poly(hexamethylene hexanediamide/hexamethylene decanediamide) (PA66/610), poly(hexamethylene hexanediamide/hexamethylene dodecanediamide) (PA66/612), poly(hexamethylene hexanediamide/decamethylene decanediamide) (PA66/1010), poly(hexamethylene decanediamide) (PA610), poly(hexamethylene dodecanediamide) (PA612), poly(hexamethylene tetradecanediamide) (PA614), poly(hexamethylene hexadecanediamide) (PA616), and poly(tetramethylene hexanediamide/2-methylpentamethylene hexanediamide) (PA46/D6);

[0056] Group (III) polyamides having a melting point of at least 210° C., and comprising

[0057] (aa) about 20 to about 35 mole percent semi-aromatic repeat units derived from monomers selected from one or more of the group consisting of:

[0058] (i) aromatic dicarboxylic acids having 8 to 20 carbon atoms and aliphatic diamines having 4 to 20 carbon atoms; and

[0059] (bb) about 65 to about 80 mole percent aliphatic repeat units derived from monomers selected from one or more of the group consisting of:

[0060] (ii) an aliphatic dicarboxylic acid having 6 to 20 carbon atoms and said aliphatic diamine having 4 to 20 carbon atoms; and

[0061] (iii) a lactam and/or aminocarboxylic acid having 4 to 20 carbon atoms;

[0062] Group (IV) polyamides comprising

[0063] (cc) about 50 to about 95 mole percent semi-aromatic repeat units derived from monomers selected from one or more of the group consisting of:

[0064] (i) aromatic dicarboxylic acids having 8 to 20 carbon atoms and aliphatic diamines having 4 to 20 carbon atoms; and

[0065] (dd) about 5 to about 50 mole percent aliphatic repeat units derived from monomers selected from one or more of the group consisting of:

[0066] (ii) an aliphatic dicarboxylic acid having 6 to 20 carbon atoms and said aliphatic diamine having 4 to 20 carbon atoms; and

[0067] (iii) a lactam and/or aminocarboxylic acid having 4 to 20 carbon atoms;

[0068] Group (V) polyamides having a melting point of at least 260° C., comprising

[0069] (ee) greater than 95 mole percent semiaromatic repeat units derived from monomers selected from one or more of the group consisting of:

[0070] (i) aromatic dicarboxylic acids having 8 to 20 carbon atoms and aliphatic diamines having 4 to 20 carbon atoms; and

[0071] (ff) less than 5 mole percent aliphatic repeat units derived from monomers selected from one or more of the group consisting of:

[0072] (ii) an aliphatic dicarboxylic acid having 6 to 20 carbon atoms and said aliphatic diamine having 4 to 20 carbon atoms;

[0073] (iii) a lactam and/or aminocarboxylic acid having 4 to 20 carbon atoms; and

[0074] Group (VI) polyamides having no melting point, and selected from the group consisting of poly(hexamethylene isophthalamide/hexamethylene terephthalamide) (61/6T) and poly(hexamethylene isophthalamide/hexamethylene terephthalamide/hexamethylene hexanediamide) (61/6T/66).

[0075] Group (I) polyamides may have semiaromatic repeat units to the extent that the melting point is less than 210° C. and generally the semiaromatic polyamides of the group have less than 40 mole percent semiaromatic repeat units. Semiaromatic repeat units are defined as those derived from monomers selected from one or more of the group consisting of: aromatic dicarboxylic acids having 8 to 20 carbon atoms and aliphatic diamines having 4 to 20 carbon atoms.

[0076] Another embodiment is a molded or extruded thermoplastic article wherein said polyamide resin is selected from Group (III) polyamides selected from the group consisting of poly(tetramethylene hexanediamide/tetramethylene terephthalamide) (PA46/4T), poly(tetramethylene hexanediamide/hexamethylene terephthalamide) (PA46/6T), poly(tetramethylene hexanediamide/2-methylpentamethylene hexanediamide/decamethylene terephthalamide) (PA46/D6/10T), poly(hexamethylene hexanediamide/hexamethylene terephthalamide) (PA66/6T), poly(hexamethylene hexanediamide/hexamethylene isophthalamide/hexamethylene terephthalamide) (PA66/61/6T), and poly(hexamethylene hexanediamide/2-methylpentamethylene hexanediamide/hexamethylene terephthalamide) (PA66/D6/6T); and a most preferred Group (III) polyamide is PA 66/6T.

[0077] Another embodiment is a molded or extruded thermoplastic article wherein said polyamide resin is selected from Group (IV) polyamides selected from the group consisting of poly(tetramethylene terephthalamide/hexamethylene hexanediamide) (PA4T/66), poly(tetramethylene terephthalamide/ε-caprolactam) (PA4T/6), poly(tetramethylene terephthalamide/hexamethylene dodecanediamide) (PA4T/612), poly(tetramethylene terephthalamide/2-methylpentamethylene hexanediamide/hexamethylene hexanediamide) (PA4T/D6/66), poly(hexamethylene terephthalamide/2-methylpentamethylene terephthalamide/hexamethylene hexanediamide) (PA6T/DT/66), poly(hexamethylene terephthalamide/hexamethylene hexanediamide) (PA6T/66), poly(hexamethylene terephthalamide/hexamethylene decanediamide) (PA6T/610), poly(hexamethylene terephthalamide/hexamethylene tetradecanediamide) (PA6T/614), poly(nonamethylene terephthalamide/nonamethylene decanediamide) (PA9T/910), poly(nonamethylene terephthalamide/nonamethylene dodecanediamide) (PA9T/912), poly(nonamethylene terephthalamide/11-aminoundecanamide) (PA9T/11), poly(nonamethylene terephthalamide/12-aminododecanamide) (PA9T/12), poly(decamethylene terephthalamide/11-aminoundecanamide) (PA 10T/11), poly(decamethylene terephthalamide/12-aminododecanamide) (PA10T/12), poly(decamethylene terephthalamide/decamethylene decanediamide) (PA10T/1010), poly(decamethylene terephthalamide/decamethylene dodecanediamide) (PA10T/1012), poly(decamethylene terephthalamide/tetramethylene hexanediamide) (PA10T/46), poly(decamethylene

terephthalamide/ε-caprolactam) (PA10T/6), poly(decamethylene terephthalamide/hexamethylene hexanediamide) (PA10T/66), poly(dodecamethylene terephthalamide/dodecamethylene dodecanediamide) (PA12T/1212), poly(dodecamethylene terephthalamide/ε-caprolactam) (PA12T/6), and poly(dodecamethylene terephthalamide/hexamethylene hexanediamide) (PA12T/66); and a most preferred Group (IV) polyamide is PA6T/66.

[0078] Another embodiment is a molded or extruded thermoplastic article wherein said polyamide resin is selected from Group (V) polyamides selected from the group consisting of poly(tetramethylene terephthalamide/2-methylpentamethylene terephthalamide) PA4T/DT, poly(tetramethylene terephthalamide/hexamethylene terephthalamide) PA4T/6T, poly(tetramethylene terephthalamide/decamethylene terephthalamide) PA4T/10T, poly(tetramethylene terephthalamide/dodecamethylene terephthalamide) PA4T/12T, poly(tetramethylene terephthalamide/2-methylpentamethylene terephthalamide/hexamethylene terephthalamide) (PA4T/DT/6T), poly(tetramethylene terephthalamide/hexamethylene terephthalamide/2-methylpentamethylene terephthalamide) (PA4T/6T/DT), poly(hexamethylene terephthalamide/2-methylpentamethylene terephthalamide) (PA6T/DT), poly(hexamethylene hexanediamide/hexamethylene isophthalamide) (PA 6T/61), poly(hexamethylene terephthalamide/decamethylene terephthalamide) PA6T/10T, poly(hexamethylene terephthalamide/dodecamethylene terephthalamide) (PA6T/12T), poly(hexamethylene terephthalamide/2-methylpentamethylene terephthalamide/poly(decamethylene terephthalamide) (PA6T/DT/10T), poly(hexamethylene terephthalamide/decamethylene terephthalamide) (PA6T/10T/12T), poly(decamethylene terephthalamide) (PA10T), poly(decamethylene terephthalamide/tetramethylene terephthalamide) (PA10T/4T), poly(decamethylene terephthalamide/2-methylpentamethylene terephthalamide) (PA10T/DT), poly(decamethylene terephthalamide/dodecamethylene terephthalamide) (PA10T/12T), poly(decamethylene terephthalamide/2-methylpentamethylene terephthalamide) (PA10T/DT/12T), poly(dodecamethylene terephthalamide) (PA12T), poly(dodecamethylene terephthalamide)/tetramethylene terephthalamide) (PA12T/4T), poly(dodecamethylene terephthalamide/hexamethylene terephthalamide) PA12T/6T, poly(dodecamethylene terephthalamide)/decamethylene terephthalamide) (PA12T/10T), and poly(dodecamethylene terephthalamide/2-methylpentamethylene terephthalamide) (PA12T/DT); and a most preferred Group (V) Polyamide is PA6T/DT.

[0079] In various embodiments the polyamide is a Group (I) Polyamide, Group (II) Polyamide, Group (III) Polyamide, Group (IV) Polyamide, Group (V) Polyamide or Group (VI) Polyamide, respectively.

[0080] The polyamides may also be blends of two or more polyamides. Preferred blends include those selected from the group consisting of Group (I) and Group (II) Polyamides; Group (I) and Group (III) Polyamide, Group (I) and Group (VI) Polyamides, Group (II) and Group (III) Polyamides, Group (II) and Group (IV) Polyamides, Group (II) and Group (V) Polyamides, Group (II) and Group (VI) Polyamides, Group (III) and Group (VI) Polyamides, and Group (IV) and Group (V) Polyamides.

[0081] A preferred blend includes Group (II) and (V) Polyamides, and a specific preferred blend includes poly(hex-

amethylene hexanediamide) (PA 66) and poly(hexamethylene terephthalamide/2-methylpentamethylene terephthalamide) (PA 6T/DT).

[0082] Another preferred blend includes Group (II) and Group (III) Polyamides and a specific preferred blend includes poly(ϵ -caprolactam) (PA6) and poly(hexamethylene hexanediamide/hexamethylene terephthalamide (PA66/6T).

[0083] Another embodiment is a molded or extruded thermoplastic article comprising a thermoplastic polyamide composition as disclosed above, wherein molded 4 mm test bars prepared from said polyamide composition, and exposed at a test temperature at 210° C. for a test period of 500 hours, in an atmosphere of air, and tested according to ISO 527-2/1A, have, on average, a retention of tensile strength of at least 70 percent, as compared with that of an unexposed control of identical composition and shape. Thermoplastic polyamide compositions meeting these test requirements are referred to as "meeting the requirements of AOA 210° C./500 hours testing."

[0084] The thermoplastic polyamide compositions meeting the requirements of AOA 210° C./500 hours testing comprise one or more polyamide resins wherein said polyamide resin comprises a one or more polyamides independently selected from the groups consisting of Group (II) Polyamides, Group (III) Polyamides, Group (IV) polyamides, Group (V) Polyamides and Group (VI) Polyamides, as disclosed above.

[0085] In various embodiments thermoplastic polyamide compositions meeting the requirements of AOA 210° C./500 hours are Group (II) Polyamides, Group (III) Polyamides, Group (IV) Polyamides, Group (V) Polyamides and Group (VI) Polyamides, respectively.

[0086] A further preferred embodiment is the molded or extruded thermoplastic article wherein said polyamide resin is selected from Group (V) Polyamides and wherein said test temperature is at least 230° C. for a test period of at least 500 hours and said retention of tensile strength is at least 60%, and more preferably at least 70%, 80% and 90%.

[0087] The molded or extruded thermoplastic article may comprise a polyester as the thermoplastic resin. Polyesters that are useful are typically derived from one or more dicarboxylic acids (where herein the term "dicarboxylic acid" also refers to dicarboxylic acid derivatives such as esters) and one or more diols. In preferred polyesters the dicarboxylic acids comprise one or more of terephthalic acid, isophthalic acid, and 2,6-naphthalene dicarboxylic acid, and the diol component comprises one or more of $\text{HO}(\text{CH}_2)_n\text{OH}$ (I); 1,4-cyclohexanedimethanol; and $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_m\text{CH}_2\text{CH}_2\text{OH}$ (II); wherein n is an integer of 2 to 12, and m on average is 1 to 4. Other dicarboxylic acids that may be used to form the thermoplastic polyester include decandioic acid, dodecanedioic acid, and adipic acids. Hydroxycarboxylic acids such as hydroxybenzoic acid may be used as comonomers. Preferably, the polyester used in the resin composition according to the present invention is selected from poly(ethylene terephthalate) (PET), poly(trimethylene terephthalate) (PTT), poly(1,4-butylene terephthalate) (PBT), poly(ethylene 2,6-naphthoate) (PEN), and poly(1,4-cyclohexyldimethylene terephthalate) (PCT), and copolymers and blends of the same.

[0088] The molded or extruded thermoplastic article comprises 0.25 to 15 weight percent of one or more polyhydric alcohols having more than two hydroxyl groups and a number average molecular weight (M_n) of less than 2000, as determined for polymeric materials with gel permeation chromatography (GPC)

[0089] 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.

[0090] An aliphatic chain in the polyhydric alcohol can include not only carbon atoms but also one or more hetero atoms which may be selected, for example, from nitrogen, oxygen and sulphur atoms. A cycloaliphatic ring present in the polyhydric alcohol can be monocyclic or part of a bicyclic or polycyclic ring system and may be carbocyclic or heterocyclic. A heterocyclic ring present in the polyhydric alcohol can be monocyclic or part of a bicyclic or polycyclic ring system and may include one or more hetero atoms which may be selected, for example, from nitrogen, oxygen and sulphur atoms. The one or more polyhydric alcohols may contain one or more substituents, such as ether, carboxylic acid, carboxylic acid amide or carboxylic acid ester groups.

[0091] Examples of polyhydric alcohol containing more than two hydroxyl groups include, without limitation, triols, such as glycerol, trimethylolpropane, 2,3-di-(2'-hydroxyethyl)-cyclohexan-1-ol, hexane-1,2,6-triol, 1,1,1-tris-(hydroxymethyl)ethane, 3-(2'-hydroxyethoxy)-propane-1,2-diol, 3-(2'-hydroxypropoxy)-propane-1,2-diol, 2-(2'-hydroxyethoxy)-hexane-1,2-diol, 6-(2'-hydroxypropoxy)-hexane-1,2-diol, 1,1,1-tris-[(2'-hydroxyethoxy)-methyl]-ethane, 1,1,1-tris-[(2'-hydroxypropoxy)-methyl]-propane, 1,1,1-tris-(4'-hydroxyphenyl)-ethane, 1,1,1-tris-(hydroxyphenyl)-propane, 1,1,3-tris-(dihydroxy-3-methylphenyl)-propane, 1,1,4-tris-(dihydroxyphenyl)-butane, 1,1,5-tris-(hydroxyphenyl)-3-methylpentane, di-trimethylolpropane, trimethylolpropane ethoxylates, or trimethylolpropane propoxylates; polyols such as pentaerythritol, dipentaerythritol, and tripentaerythritol; and saccharides, such as cyclodextrin, D-mannose, glucose, galactose, sucrose, fructose, xylose, arabinose, D-mannitol, D-sorbitol, D-or L-arabitol, xylitol, iditol, talitol, allitol, altritol, guilitol, erythritol, threitol, and D-gulonic- γ -lactone; and the like.

[0092] 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.

[0093] 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.

[0094] In various embodiments the content of said polyhydric alcohol in the thermoplastic composition is 0.25-15 weight percent, preferably 0.25-8 weight percent, more preferably 0.25-5 weight percent. In polyamides, most preferably 1-4 weight percent; in polyesters most preferably 0.25 to 1.5 weight percent, based on the total weight of said thermoplastic composition.

[0095] The molded or extruded thermoplastic article comprises 10 to about 60 weight percent, and preferably about 12.5 to 55 weight percent and 15 to 50 weight percent, of one or more reinforcement agents. The reinforcement agent may be any filler, but is preferably selected from the group con-

sisting calcium carbonate, glass fibers with circular and non-circular 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.

[0096] Glass fibers with noncircular cross-section refer to glass fiber having a cross section having a major axis lying perpendicular to a longitudinal direction of the glass fiber and corresponding to the longest linear distance in the cross section. The non-circular cross section has a minor axis corresponding to the longest linear distance in the cross section in a direction perpendicular to the major axis. The non-circular cross section of the fiber may have a variety of shapes including a cocoon-type (figure-eight) shape, a rectangular shape; an elliptical shape; a roughly triangular shape; a polygonal shape; and an oblong shape. As will be understood by those skilled in the art, the cross section may have other shapes. The ratio of the length of the major axis to that of the minor axis is preferably between about 1.5:1 and about 6:1. The ratio is more preferably between about 2:1 and 5:1 and yet more preferably between about 3:1 to about 4:1. Suitable glass fiber are disclosed in EP 0 190 001 and EP 0 196 194.

[0097] The molded or extruded thermoplastic article, optionally, comprises 0 to 50 weight percent of a polymeric toughener comprising a reactive functional group and/or a metal salt of a carboxylic acid. In one embodiment the molded or extruded thermoplastic article comprises 2 to 20 weight percent polymeric toughener selected from the group consisting of: a copolymer of ethylene, glycidyl (meth)acrylate, and optionally one or more (meth)acrylate esters; an ethylene α -olefin or ethylene/ α -olefin/diene copolymer grafted with an unsaturated carboxylic anhydride; a copolymer of ethylene, 2-isocyanatoethyl (meth)acrylate, and optionally one or more (meth)acrylate esters; and a copolymer of ethylene and acrylic acid reacted with a Zn, Li, Mg or Mn compound to form the corresponding ionomer.

[0098] In the present invention, the polymer composition of the present invention may also comprise other additives commonly used in the art, such other heat stabilizers or antioxidants referred to as "co-stabilizers", antistatic agents, blowing agents, lubricants, plasticizers, and colorant and pigments.

[0099] Co-stabilizers include copper stabilizers, secondary aryl amines, hindered amine light stabilizers (HALS), hindered phenols, and mixtures thereof.

[0100] A significant advantage of the molded or extruded thermoplastic articles of the invention is that high thermal stability is provided without the use of conventional copper heat stabilizers. Copper heat stabilizers tend to act as corrosive agents over long periods of time at elevated temperatures; and in some environments actually cause degradation of semiaromatic polymers. Thus, another embodiment is molded or extruded thermoplastic article wherein said thermoplastic resin is a polyamide and said thermoplastic composition comprises less than 25 ppm copper as determined with atomic absorption spectroscopy.

[0101] 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 ingredi-

ents 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.

[0102] The thermoplastic composition having a polyhydric alcohol having two or more hydroxyl groups, as disclosed above, is useful in increasing long-term thermal stability at high temperatures of molded or extruded articles made therefrom. The long-term heat stability of the articles can be assessed by exposure (air oven ageing) of 4 mm thick test samples at various test temperatures in an oven for various test periods of time. The oven test temperatures for the composition disclosed herein include 170° C. and 500 hours test periods; 210° C. and 500 hours test periods; and 230° C. and 500 hours test periods. The test samples, after air oven ageing, are tested for tensile strength and elongation to break, according to ISO 527-2/1A test method; and compared with unexposed controls having identical composition and shape, that are dry as molded (DAM). The comparison with the DAM controls provides the retention of tensile strength and/or retention of elongation to break, and thus the various compositions can be assessed as to long-term heat stability performance.

[0103] In various embodiments the thermoplastic composition has an AOA 170° C./500 hours retention of tensile strength of at least 50% and preferably at least 60, 70, 80, and 90%, based upon comparison with DAM non-exposed controls.

[0104] In various embodiments the thermoplastic polyamide composition has an AOA 210° C./500 hours retention of tensile strength of at least 70% and preferably at least 70, 80, and 90%, based upon comparison with DAM non-exposed controls.

[0105] In another aspect, the present invention relates a use of the above disclosed thermoplastic compositions for high temperature applications.

[0106] In another aspect, the present invention relates to a method for manufacturing an article by shaping the thermoplastic composition of the invention. Examples of articles are films or laminates, automotive parts or engine parts or electrical/electronics parts. By "shaping", it is meant any shaping technique, such as for example extrusion, injection moulding, thermoform moulding, compression moulding or blow moulding. Preferably, the article is shaped by injection moulding or blow moulding.

[0107] The molded or extruded thermoplastic articles disclosed herein may have application in many vehicular components that meet one or more of the following requirements: high impact requirements; significant weight reduction (over conventional metals, for instance); resistance to high temperature; resistance to oil environment; resistance to chemical agents such as coolants; and noise reduction allowing more compact and integrated design. Specific molded or extruded thermoplastic articles are selected from the group consisting of charge air coolers (CAC); cylinder head covers (CHC); oil

pans; engine cooling systems, including thermostat and heater housings and coolant pumps; exhaust systems including mufflers and housings for catalytic converters; air intake manifolds (AIM); and timing chain belt front covers. As an illustrative example of desired mechanical resistance against long-term high temperature exposure, a charge air cooler can be mentioned. A charge air cooler is a part of the radiator of a vehicle that improves engine combustion efficiency. Charge air coolers reduce the charge air temperature and increase the density of the air after compression in the turbocharger thus allowing more air to enter into the cylinders to improve engine efficiency. Since the temperature of the incoming air can be more than 200° C. when it enters the charge air cooler, it is required that this part be made out of a composition maintaining good mechanical properties under high temperatures for an extended period of time.

[0108] The present invention is further illustrated by the following examples. It should be understood that the following examples are for illustration purposes only, and are not used to limit the present invention thereto.

EXAMPLES

Materials

[0109] In the Examples and Comparative Examples:

[0110] PA66 refers to an aliphatic polyamide made of 1,6-hexanedioic acid and 1,6-hexamethylenediamine having an relative viscosity in the range of 46-51 and a melting point of about 263° C., commercially available from E.I. DuPont de Nemours and Company, Wilmington, Del., USA under the trademark Zytel® 101NC010.

[0111] PA6-1 refers to Durethan B29 poly(ε-caprolactam) available from Lanxess Germany.

[0112] PA6-2 refers to Ultramid® B27 poly(ε-caprolactam) available from BASF, USA.

[0113] PA6T/DT refers HTN501 NC010, a copolyamide of terephthalic acid, hexamethylenediamine, and 2-methyl-pentamethylenediamine having an inherent viscosity (IV), according to ASTM D2857 method, in the range of 0.8 to 0.95 (typically 0.88) and a melting point of about 300° C., and available from E.I. DuPont de Nemours and Company, Wilmington, Del., USA.

[0114] PA 6T/66 refers HTN502 NC010, a copolyamide 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 ca. 310° C., having an inherent viscosity (IV), according to ASTM D2857 method, in the range of 0.9 to 1.0 (typically 0.96) available from E.I. DuPont de Nemours and Company, Wilmington, Del., USA.

[0115] PBT refers to Crastin® 6003 poly(1,4-butylene terephthalate) having a melt flow rate (MFR) from 77 to 97 g/10 min (measured according to ISO1133, 250° C., 2.16 kg) available from E.I. DuPont de Nemours and Company, Wilmington, Del., USA

[0116] PE refers to pentaerythritol that was from Perstorp Speciality Chemicals AB, Perstorp, Sweden.

[0117] DPE refers to dipentaerythritol that was from Perstorp Speciality Chemicals AB, Perstorp, Sweden as Di-Penta 93.

[0118] TPE refers to tripentaerythritol that was from Sigma Aldrich Co., Milwaukee Wis.

[0119] Sorbitol was from Sigma Aldrich Co., Milwaukee Wis.

[0120] DI-TMP refers to di-trimethylolpropane that was from Perstorp Speciality Chemicals AB, Perstorp, Sweden.

[0121] Glass fibers A 4.5 mm length chopped glass fibers, refers to OCV 983, available from Owens Corning Vetrotex, France.

[0122] Glass Fiber B refers to PPG 3660 chopped glass fiber available from PPG Industries, Pittsburgh, Pa.

[0123] Glass Fiber C refers to OCV 952 chopped glass fiber available from Owens Corning Vetrotex, France.

[0124] Glass Fiber D refers to PPG 3540 chopped glass fiber available from PPG Industries, Pittsburgh, Pa.

[0125] Black Pigment A refers to 40 wt % nigrosine black pigment concentrate in a PA66 carrier.

[0126] 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.

[0127] Vestowax A01535 was available from Evonik Industries, Germany.

[0128] Irganox® 1010 stabilizer was available from Ciba Speciality Chemicals Inc, Switzerland.

[0129] Irganox® 1098 stabilizer was available from Ciba Speciality Chemicals Inc, Switzerland.

[0130] Irgafos® 12 stabilizer refers to phosphite heat stabilizer Ciba Speciality Chemicals Inc, Switzerland.

[0131] Acrawax® C lubricant refers to N,Ni-ethylene bis-stearamide from Lonza Chemical Co.

[0132] SHP refers to sodium dihydrogen phosphate from Sigma-Aldrich GmbH.

[0133] Fusabond® EP 1021 is a copolymer of ethylene and maleic anhydride mono ester, available from E.I. DuPont de Nemours and Company, Wilmington, Del., USA.

[0134] DER 732 Epoxy is a liquid epoxy resin available from Dow Chemical, Midland, Mich.

[0135] Polyamide A refers to PA66/6T (75/25 molar ratio repeat units) with amine ends approximately 50 meq/kg that was provided according to the following procedure: Polyamide 66 salt solution (3928 lbs. of a 51.7 percent by weight with a pH of 8.1) and 2926 lbs of a 25.2% by weight of polyamide 6T salt solution with a pH of 7.6 were charged into an autoclave with 100 g of a conventional antifoam agent, 20g of sodium hypophosphite, 220g of sodium bicarbonate, 2476 g of 80% HMD solution in water, and 1584 g of glacial acetic. The solution was then heated while the pressure was allowed to rise to 265 psia at which point, steam was vented to maintain the pressure at 265 psia and heating was continued until the temperature of the batch reached 250° C. The pressure was then reduced slowly to 6 psia, while the batch temperature was allowed to further rise to 280-290° C. The pressure was then held at 6 psia and the temperature was held at 280-290° C. for 20 minutes. Finally, the polymer melt was extruded into strands, cooled, and cut into pellets. The resulting polyamide 66/6T is referred to herein as Polyamide A having a melting point of about 268±1° C., relative viscosity (according to ASTM D-789 method) of 42±2; NH₂ ends of 43±2 meq/kg and COOH ends of 88±5 meq/kg.

[0136] Polyamide B refers to PA66/6T (75/25 molar ratio repeat units) with high amine ends, that is, at least 70 meq/kg, that was provided according to the following procedure:

Polyamide 66/6T salt solution (214.25 lbs. of a 39.70 percent by weight) was prepared from hexamethylenediamine, 1,6-adipic acid, and terephthalic acid in water, where the molar ratio of 1,6-adipic acid to terephthalic acid is 75:25. The salt solution had a pH of 8.20±0.05 and was charged into an autoclave with 3.5 g of a 10 percent by weight solution of a

conventional antifoam agent in water, 0.7 g of sodium hypophosphite, 7.7 g of sodium bicarbonate, 237.5 g of 80% HMD solution in water, and 15 g of glacial acetic acid. The solution was then heated while the pressure was allowed to rise to 265 psia at which point, steam was vented to maintain the pressure at 265 psia and heating was continued until the temperature of the batch reached 255° C. The pressure was then reduced slowly to 10 psia, while the batch temperature was allowed to further rise to 275-285° C. The pressure was then held at 10 psia and the temperature was held at 275-285° C. for 20 minutes. Finally, the polymer melt was extruded into strands, cooled, and cut into pellets. The resulting polyamide 66/6T is referred to herein as Polyamide B having a melting point of about 269±1° C.; relative viscosity (according to ASTM D-789 method) of 44±2, NH₂ ends of 88±2 meg/kg and COOH ends of 51±5 meg/kg.

Methods

[0137] Compounding Method A

[0138] Examples 1-14 and comparative examples C-1-C-7 were prepared by melt blending the ingredients listed in the Tables in a 40 mm twin screw extruder (Berstorff ZE40) operating at about 280° C. using a screw speed of about 300 rpm, a throughput of 110 kg/hour. The glass fibers were added to the melt through a screw side feeder. Ingredient quantities shown in the Tables are given in weight percent on the basis of the total weight of the thermoplastic composition.

[0139] The compounded mixture was extruded in the form of laces or strands, cooled in a water bath, chopped into granules and placed into sealed aluminum lined bags in order to prevent moisture pick up. The cooling and cutting conditions were adjusted to ensure that the materials were kept below 0.15 wt % of moisture level.

[0140] Compounding Method B

[0141] Examples 15, 16 and Comparative Example C-8 were prepared by melt blending the ingredients listed in the Table 9 in a 40 mm twin screw extruder (Berstorff ZE40) operating at a processing set temperature of barrel and die of 250° C. and a melt temperature of about 290° C. Extrusion and chopping was as described in Method A; with the exception that before molding, the samples were pre-dried to less than 0.04 wt % moisture.

[0142] Compounding Method C

[0143] Examples 17-22 and Comparative Examples C-9-C-11 were prepared by melt blending the ingredients listed in the Tables in a 30 mm twin screw extruder (ZSK 30 by Coperion) operating at about 310° C. barrel setting using a screw speed of about 300 rpm, a throughput of 13.6 kg/hour and a melt temperature measured by hand of about 355° C. The glass fibers were added to the melt through a screw side feeder. Ingredient quantities shown in the Tables are given in weight percent on the basis of the total weight of the thermoplastic composition. Extrusion and chopping was as described in Method A.

[0144] Physical Properties Measurement

[0145] 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 as listed:

[0146] Examples 1-14 and Comparative Examples C-1-C-7: mold temperature was 100° C., melt temperature was 295-300° C.;

[0147] Examples 15-16 and C-8: PBT mold temperature was 80° C., melt temperature was about 250° C.

[0148] Examples 17-22 and C-11: mold temperature for PA 6T/6D was 145-150° C.; mold temperature for PA 6T/66 was 90-100° C.; and melt temperature was 325-330° C. for both resins.

[0149] 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). Tensile Modulus was measured at 1 mm/min.

[0150] Air Oven Ageing (AOA)

[0151] The test specimens were heat aged in a re-circulating air ovens (Heraeus type UT6060) according to the procedure detailed in ISO 2578. At various heat aging times, the test specimens were removed from the oven, allowed to cool to room temperature and sealed into aluminum lined bags until ready for testing. The tensile mechanical properties were then measured according to ISO 527 using a Zwick tensile instrument. The average values obtained from 5 specimens are given in the Tables.

[0152] Retention of E-modulus, stress at break and strain at break corresponds to the percentage of the E-modulus, stress at break and strain at break after heat aging for 500 hours 1000 hours in comparison with the value of the specimens non-heat-aged control specimens considered as being 100%.

Example 1 and 2 and C-1

[0153] Compositions of Examples 1, 2 and Comparative Example C-1 are listed in Table 1 for PA66 compositions. Tensile properties after AOA at 210° C. at 500 h and 1000 h, and non-heat-aged control are listed in Table 2. Table 3 lists the retention of physical properties of the AOA samples as compared with the non-aged controls. Higher values of mechanical tensile properties (E-modulus, tensile strength, stress at yield) mean better mechanical properties.

TABLE 1

Formulation	Example No.		
	C-1	1	2
PA66	69.7	68.2	66.7
Glass fiber A	30.0	30.0	30.0
Cu Heat stabilizer	0.3	0.3	0.3
DPE	—	1.5	3.0

TABLE 2

	Example No.		
	C-1	1	2
Tensile modulus at 23° C. (MPa)			
non-heat-aged	9731	9881	10200
heat aging at 210° C. for 500 hours	9543	10047	10322
heat aging at 210° C. for 1000 hours	9360	9786	10002
Tensile Strength at break at 23° C. (MPa)			
non-heat-aged	206	214	213
heat aging at 210° C. for 500 hours	161	191	211
heat aging at 210° C. for 1000 hours	121	165	202
Elongation at break at 23° C. (MPa)			
DAM	3.5	3.6	3.1
heat aging at 210° C. for 500 hours	2.0	2.5	2.9
heat aging at 210° C. for 1000 hours	1.5	2.1	2.7

TABLE 3

	Example No.		
	C-1	1	2
Retention of Tensile modulus at 23° C.			
non-heat-aged (MPa)	100% (9731)	100% (9881)	100% (10200)
heat aging at 210° C. for 500 hours	98.1%	101.7%	101.2%
heat aging at 210° C. for 1000 hours	96.2%	99.0%	98.1%
Retention of Tensile Strength at 23° C.			
non-heat-aged (MPa)	100% (206)	100% (214)	100% (213)
heat aging at 210° C. for 500 hours	78.2%	89.3%	99.1%
heat aging at 210° C. for 1000 hours	58.7%	77.1%	94.8%

polyamide composition comprising 3 wt % of a polyhydric alcohol (Example 2) exhibited a surprising and unexpected 1.5 to 2 fold increase of the retention of tensile strength and elongation at break upon a 1000 hours heat aging.

Examples 3-5 and Comparative Examples C-2-C-3

[0155] Compositions of Examples 3-5 and Comparative Example C-2 and C-3 are listed in Table 4 for PA66 compositions. Tensile properties after AOA at 210° C. at 500 h and 1000 h, and non-heat-aged control; and retention of physical properties; are listed in Table 4.

[0156] As shown in Table 4, the comparative examples containing no copper stabilizer (C-2); or only copper stabilizer (C-3), showed poor retention of tensile strength under AOA conditions. Example 4 containing, only DPE as a thermal stabilizer, showed much better retention of tensile strength than the conventional copper stabilized system (C-3).

TABLE 4

	Example				
	C-2	C-3	3	4	5
PA66	70.00	69.70	68.95	67.00	66.70
Glass fiber A	30.00	30.00	30.00	30.00	30.00
Cu Heat stabilizer		0.30	0.30		0.30
DPE			0.75	3.00	3.00
Tensile properties DAM					
Tensile Modulus [MPa]	9385.0	9502.0	9706.0	9872.0	9888.0
Tensile Strength [MPa]	199.8	204.2	208.2	198.0	196.5
Elongation @ Break [%]	3.9	3.8	3.7	3.0	2.9
Tensile properties 500 h at 210° C.					
Tensile Modulus [MPa]	9810	10530	10618	10824	10930
Tensile Strength [MPa]	94.2	155.8	179.6	212.2	207.2
retention Tensile Strength (%)	47.2	76.3	86.2	107.2	105.4
Elongation @ Break [%]	1.2	1.8	2.2	3.2	2.8
Tensile properties 1000 h at 210° C.					
Tensile Modulus [MPa]	5123	8837	10146	10645	10931
Tensile Strength [MPa]	12.8	74.4	115.7	168.1	178.1
% retention Tensile Strength	6.4%	36.4%	55.6%	84.9%	90.6%
Elongation @ Break [%]	0.3	1.1	1.5	2.1	2.1

TABLE 3-continued

	Example No.		
	C-1	1	2
Retention of Elongation at break at 23° C.			
non-heat-aged (MPa)	100% (3.5)	100% (3.6)	100% (3.1)
heat aging at 210° C. for 500 hours	57.1%	69.4%	93.5%
heat aging at 210° C. for 1000 hours	42.9%	58.3%	87.1%

[0154] As shown in Table 3, the comparative example comprising only a conventional copper heat stabilizer (C-1) showed poor retention of the mechanical properties, e.g. the retention of elongation at break upon a 1000 hours heat aging value was only 42.9%. In contrast, the Examples 1 and 2 according to the present invention exhibited retention of elongation at break values of 58.3 and 87.1%. For example, the

Examples 6-9

[0157] PA66 compositions of Examples 6-10 with a variety of polyhydric alcohols and Comparative Example C-3 are listed in Table 5. Tensile properties after AOA at 210° C. at 500 h and 1000 h, and tensile properties of non-heat-aged control; and retention of physical properties; are listed in Table 5. All the examples showed greater than 80% retention of tensile strength, after 500 hours AOA at 210° C. These results are comparable to or better than the conventional copper stabilizer (C-3).

Examples 10 and C-4

[0158] PA6 compositions of Examples 10 and Comparative Example C-4 are listed in Table 6. Tensile properties after AOA at 210° C. at 500 h and 1000 h; tensile properties of non-heat-aged control; and retention of physical properties; are listed in Table 6. After 1000 hours AOA at 210° C., Example 10 showed greater than 100% retention of tensile strength, whereas C-4 with copper stabilizer showed only about 52% retention of tensile strength.

TABLE 5

	Example				
	C-3	6	7	8	9
PA66	69.70	66.70	66.70	66.70	66.70
Glass fiber A	30.00	30.00	30.00	30.00	30.00
Cu Heat stabilizer	0.30	0.30	0.30	0.30	0.30
PE		3.0			
TPE			3.00		
Sorbitol				3.00	
Di-TMP					3.00
Tensile properties DAM					
Tensile Modulus [MPa]	9502.0	9804.0	10058.0	9890.0	9522.0
Tensile Strength [MPa]	204.2	196.1	211.3	195.8	201.8
Elongation @ Break [%]	3.8	2.7	3.2	2.7	3.5
Tensile properties 500 h at 210° C.					
Tensile Modulus [MPa]	10530	10749	10955	10856	10991
Tensile Strength [MPa]	155.8	190.8	200.2	167.8	191.6
retention Tensile Strength (%)	76.3	97.3	94.7	85.7	95.0
Elongation @ Break [%]	1.8	2.3	2.5	1.9	2.4
Tensile properties 1000 h at 210° C.					
Tensile Modulus [MPa]	8837	10719	10810	10502	10844
Tensile Strength [MPa]	74.4	155.8	162.0	118.8	170.4
retention Tensile Strength (%)	36.4	79.4	76.7	60.7	84.4
Elongation @ Break [%]	1.1	1.8	1.8	1.3	2.0

TABLE 6

	Example	
	C-4	10
PA6-1	69.70	66.70
Glass fiber A	30.00	30.00
Cu Heat stabilizer	0.30	0.30
DPE		3.00
Tensile properties DAM		
Tensile Modulus [MPa]	9286.0	9298.0
Tensile Strength [MPa]	186.6	186.8
Elongation @ Break [%]	4.3	3.9
Tensile properties 500 h at 210° C.		
Tensile Modulus [MPa]	11552	11364
Tensile Strength [MPa]	158.3	206.9

TABLE 6-continued

	Example	
	C-4	10
Retention Tensile Strength (%)	84.8	110.8
Elongation @ Break [%]	1.7	3.0
Tensile properties 1000 h at 210° C.		
Tensile Modulus [MPa]	11030	11304
Tensile Strength [MPa]	98.0	207.1
Retention Tensile Strength (%)	52.5	110.9
Elongation @ Break [%]	1.0	3.3

TABLE 7

	Example					
	C-5	11	C-6	12	C-7	13
PA66	68.85	67.80				
Polyamide A (66/6T)			68.85	67.80		
Polyamide B (66/6T)					68.85	67.80
Glass Fiber B	30.00	30.00	30.00	30.00	30.00	30.00
Black Pigment A	0.70	0.70	0.70	0.70	0.70	0.70
Cu Heat stabilizer	0.45		0.45		0.45	
DPE		1.50		1.50		1.50
Tensile properties DAM						
Tensile Modulus [MPa]	9747.0	9811.0	8791.0	8848.0	9207.7	8631.0
Tensile Strength [MPa]	207.8	205.2	198.6	189.1	196.1	187.2
Elongation @ Break [%]	3.8	3.4	3.7	3.2	5.5	3.4

TABLE 7-continued

	Example					
	C-5	11	C-6	12	C-7	13
Tensile properties 500 h at 210° C.						
Tensile Modulus [MPa]	9558.0	9028.0	8353.0	8549.0	8377.0	8355.0
Tensile Strength [MPa]	160.7	210.0	148.0	198.5	151.3	202.0
Retention Tensile Strength [%]	77.3%	102.3%	74.5%	105.0%	77.1%	107.9%
Elongation @ Break [%]	2.0	3.3	1.9	3.4	2.0	3.8
Tensile properties 1000 h at 210° C.						
Tensile Modulus [MPa]	7353	9700	9142	9392	9404	9310
Tensile Strength [MPa]	62.0	127.0	86.0	152.0	101.0	165
Retention Tensile Strength [%]	29.8%	61.9%	43.3%	80.4%	51.5%	88.1%
Elongation @ Break [%]	1.1	1.8	1.1	2.1	1.2	2.4

Examples 11-13 and C-5-C-7

[0159] Compositions of Examples 11-13 and C-5-C-7 are listed in Table 7. Examples 12 and C-6 show the heat ageing performance of PA66/6T (75/25 molar ratio) having a number of amine ends of about 45 meq/Kg. Examples 13 and C-7 show the heat ageing performance of PA66/6T (75/25 molar ratio) having a number of amine ends of about 88 meq/Kg. Tensile properties after AOA at 210° C. at 500 h and 1000 h, and tensile properties of non-heat-aged control; and retention of physical properties; are listed in Table 7. The Examples show that the presence of DPE at 1.5 wt % level provides significant improvement in retention of tensile strength, and especially at 1000 h and 210° C., as compared to the comparative examples having the conventional copper stabilizer. Furthermore Example 13, having amine ends at 88 meq/Kg exhibits unexpectedly higher % retention of tensile strength in heat ageing at 1000 h and 210° C., than Example 12 (amine ends 45 meq/Kg) and Example 11 (PA66 having NH₂ ends in the 45-50 meq/Kg range).

Example 14

[0160] This Example illustrates the unexpected and surprising results provided a blend of Group (II) polyamide (PA6) with Group (III) polyamide (PA66/6T) having high amine ends (88 meq/Kg). Example 14, listed in Table 8, contains PA66/6T and 5 wt % PA6, and has a 98.6% retention of tensile strength after AOA at 1000 h and 210° C., compared with Example 13 containing PA66/6T alone, which shows 88.1% retention of tensile strength under the same conditions. This indicates that blends of polyamides can have significantly improved properties over that of the base polyamide comprising the major fraction of the blend. The PA6 composition of Example 10 shows 110.9% retention of tensile strength under the same conditions.

TABLE 8

	Example 14
Polyamide B (66/6T)	57.81
PA6-2	5.00
Glass Fiber A	35.00
Black Pigment A	0.69
DPE	1.50

TABLE 8-continued

	Example 14
Tensile properties DAM	
Tensile Modulus [MPa]	11300
Tensile Strength [MPa]	208
Elongation @ Break [%]	3.4
Tensile properties 500 h at 210° C.	
Tensile Modulus [MPa]	11425
Tensile Strength [MPa]	227
Retention Tensile Strength (%)	109.1
Elongation @ Break [%]	3.5
Tensile properties 1000 h at 210° C.	
Tensile Modulus [MPa]	11418
Tensile Strength [MPa]	205
Retention Tensile Strength (%)	98.6
Elongation @ Break [%]	2.7

Example 15-16 and Comparative Example C-8

[0161] These Examples, listed in Table 9, illustrate the results provided with poly(butylene terephthalate) (PBT) stabilized with DPE. The Tensile properties after 1000 h AOA at 180° C. show 93 and 104% retention of Tensile strength for Examples 15 and 16, respectively, versus an 80% retention for the Comparative Example C-8 lacking DPE.

Examples 17-21 and Comparative Examples C-9 and C-10

[0162] Examples 17-21 illustrate the use of a Group (V) Polyamide, in the form of PA6T/DT, in combination with polyhdric alcohols in heat ageing. Tensile properties after AOA at 210° C. at 500 h and 1000 h; AOA at 230° C. at 500 h and 1000 h; tensile properties of non-heat-aged DAM control (0 hours); and retention of physical properties; are listed in Table 10. The Examples show a surprising and unexpected improvement in % retention of tensile strength as compared to a composition with no thermal stabilizer (C-9) or a composition with the conventional copper thermal stabilizer (C-10) at both temperatures.

TABLE 9

	Example		
	C-8	15	16
Composition (wt %)			
PBT	69.20	68.70	67.70
Glass Fiber C	30.00	30.00	30.00
Irganox 1010	0.30	0.30	0.30
Vestowax AO 1535	0.50	0.50	0.50
DPE		0.50	1.50
Tensile properties DAM			
Tensile Modulus [MPa]	9718.0	9858.0	10105.0
Tensile Strength [MPa]	147.2	151.1	139.8
Elongation @ Break [%]	2.8	2.5	1.9

TABLE 9-continued

	Example		
	C-8	15	16
Tensile properties 500 h at 180° C.			
Tensile Modulus [MPa]	9399.0	10296.0	10096.0
Tensile Strength [MPa]	157.6	158.8	158.8
Retention Tensile Strength (%)	107.1	105.1	113.6
Elongation @ Break [%]	2.5	2.1	2.0
Tensile properties 1000 h at 180° C.			
Tensile Modulus [MPa]	9999.0	10065.0	10665.0
Tensile Strength [MPa]	118.2	140.9	145.3
Retention Tensile Strength (%)	80.3%	93.2%	103.9%
Elongation @ Break [%]	1.5	1.7	1.7

TABLE 10

	Example						
	C-9	C-10	17	18	19	20	21
PA6T/DT	64.75	64.05	63.25	61.75	62.75	63.75	61.75
DPE			1.5	3			
TPE					2	1	3
Cu heat stabilizer		0.7					
Wax OP	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Glass Fiber D	35	35	35	35	35	35	35
AOA 210° C.							
TS (MPa) 0 h	225	223	214	212	218	218	215
TS (MPa) 500 h	115	141	218	218	220	186	213
TS (MPa) 1000 h	98	130	210	208	210	152	207
500 h TS Retention (%)	51	63	102	103	101	85	99
1000 h TS Retention (%)	44	58	98	98	96	70	96
El (%) 0 h	2.3	2.4	2.2	2.2	2.2	2.2	2.2
El (%) 500 h	1.2	1.4	2.2	2.2	2.2	1.8	2.2
El (%) 1000 h	0.9	1.3	2.1	2.1	2.1	1.5	2.1
500 h El Retention (%)	52	58	100	100	100	82	100
1000 h El Retention (%)	39	54	95	95	95	68	95
AOA 230° C.							
TS (MPa) 0 h	225	223	214	212	218	218	215
TS (MPa) 500 h	75	125	135	172	158	135	177
TS (MPa) 1000 h	20	91	115	156	142	128	152
500 h TS Retention (%)	33	56	63	81	72	62	82
1000 h TS Retention (%)	9	41	54	74	65	59	71
El (%) 0 h	2.3	2.4	2.2	2.2	2.2	2.2	2.2
El (%) 500 h	0.8	1.1	1.3	1.8	1.7	1.2	1.7
El (%) 1000 h	0.3	0.8	1.2	1.7	1.4	1.1	1.5
500 h El Retention (%)	35	46	59	82	77	55	77
1000 h El Retention (%)	13	33	55	77	64	50	68

TS = tensile strength

EL = elongation to break

Examples 22 and Comparative Examples C-11

[0163] Examples 22 and C-11 illustrate the use of a Group (IV) Polyamide, in the form of PA6T/66, in combination with polyhydric alcohols in heat ageing. AOA at 210° C. 1000 h show 87% retention of tensile strength for Example 22, versus a 62% retention for a copper stabilized composition lacking DPE.

TABLE 11

	Example	
	C-11	22
<u>Composition (wt %)</u>		
PA 6T/66	64.35	62.75
DPE		2.00
Wax OP	0.25	0.25
Copper heat stabilizer	0.40	
Glass Fiber D	35.00	35.00
<u>AOA 210° C.</u>		
TS (MPa) 0 h	202	202
TS (MPa) 500 h	135	185
TS (MPa) 1000 h	126	176
500 hrs TS Retention (%)	67	92
1000 hrs TS Retention (%)	62	87
EI (%) 0 h	2.2	2.1
EI (%) 500 h	1.4	1.9
EI (%) 1000 h	1.2	1.8
500 hrs EI Retention (%)	64	90
1000 hrs EI Retention (%)	55	86
<u>AOA 230° C.</u>		
TS (MPa) 0 h	202	202
TS (MPa) 500 h	131	162
TS (MPa) 1000 h	100	148
500 hrs TS Retention (%)	65	80
1000 hrs TS Retention (%)	50	73
EI (%) 0 h	2.2	2.1
EI (%) 500 h	1.4	1.8
EI (%) 1000 h	1.0	1.5
500 hrs EI Retention (%)	64	86
1000 hrs EI Retention (%)	45	71

TS = tensile strength

EI = elongation to break

Examples 23 and Comparative Examples C-12

[0164] Examples 23 and C-12 illustrate a toughened blend of Group (II) and Group (V) Polyamide, in the form of PA66 and PA6T/DT, respectively, in combination with TPE polyhydric alcohol in heat ageing. AOA at 220° C. 1008 h show 110% retention of tensile strength for Example 23, versus 63% retention for C-12 having no TPE present.

TABLE 12

	Example	
	C-12	23
PA6T/DT	47.11	44.11
PA66	20	20
Fusabond® EP1021	13	13
Glass Fiber B	17.5	17.5
Black Pigment B	1	1
DER 732 Epoxy	0.5	0.5
SHP	0.04	0.04
Irganox® 1010	0.25	0.25
Irganox® 1098	0.2	0.2

TABLE 12-continued

	Example	
	C-12	23
Irgafos 12	0.2	0.2
Acrawax	0.2	0.2
TPE		3
<u>AOA 200° C.</u>		
TS (MPa) 0 h	121	124
TS (MPa) 504 h	77.36	122
TS (MPa) 1008 h	78.42	129.6
504 hrs TS Retention (%)	64.04	98.15
1008 hrs TS Retention (%)	64.92	104.26
<u>AOA 220° C.</u>		
TS (MPa) 0 h	121	124
TS (MPa) 504 h	88.65	133.4
TS (MPa) 1008 h	76.64	137.4
504 hrs TS Retention (%)	73.39	107.32
1008 hrs TS Retention (%)	63.44	110.54

[0165] The Examples illustrate that polyhydric alcohols added to polyamide and/or polyester compositions are an economically viable solution to the current need of having articles that are highly heat resistant upon long-term exposure in comparison with conventional heat stabilizers that lead either to poor heat aging resistant compositions or expensive ones.

We claim:

1. A molded or extruded thermoplastic article comprising a thermoplastic composition comprising

- a thermoplastic resin selected from the group consisting of polyamides, polyesters, and mixtures thereof;
- 0.25 to 15 weight percent of one or more polyhydric alcohols having more than two hydroxyl groups and a having a number average molecular weight (M_n) of less than 2000;
- 10 to about 60 weight percent of one or more reinforcement agents; and
- 0 to 50 weight percent of a polymeric toughener comprising a reactive functional group and/or a metal salt of a carboxylic acid;

wherein all weight percentages are based on the total weight of the thermoplastic composition and wherein 4 mm test bars prepared from said thermoplastic composition, and exposed at a test temperature of 170° C. for a test period of 500 hours, in an atmosphere of air, and tested according to ISO 527-2/1A, have, on average, a retention of tensile strength of at least 50 percent, as compared with that of an unexposed control of identical composition and shape.

2. The molded or extruded thermoplastic article of claim 1 wherein said thermoplastic resin is a polyamide resin comprising one or more polyamides independently selected from the group consisting of

Group (I) polyamides having said melting point of less than 210° C., comprising an aliphatic or semiaromatic polyamide selected from the group poly(pentamethylene decanediamide) (PA510), poly(pentamethylene dodecanediamide) (PA512), poly(ϵ -caprolactam/hexamethylene hexanediamide) (PA6/66), poly(ϵ -caprolactam/hexamethylene decanediamide) (PA6/610), poly(ϵ -caprolactam/hexamethylene dodecanediamide) (PA6/612), poly(hexamethylene tridecanediamide) (PA613), poly(hexamethylene pentadecanediamide) (PA615),

poly(ϵ -caprolactam/tetramethylene terephthalamide) (PA6/4T), poly(ϵ -caprolactam/hexamethylene terephthalamide) (PA6/6T), poly(ϵ -caprolactam/decamethylene terephthalamide) (PA6/10T), poly(ϵ -caprolactam/dodecamethylene terephthalamide) (PA6/12T), poly(hexamethylene decanediamide/hexamethylene terephthalamide) (PA6 10/6T), poly(hexamethylene dodecanediamide/hexamethylene terephthalamide) (PA612/6T), poly(hexamethylene tetradecanediamide/hexamethylene terephthalamide) (PA614/6T), poly(ϵ -caprolactam/hexamethylene isophthalamide/hexamethylene terephthalamide) (PA6/6I/6T), poly(ϵ -caprolactam/hexamethylene hexanediamide/hexamethylene decanediamide) (PA6/66/610), poly(ϵ -caprolactam/hexamethylene hexanediamide/hexamethylene dodecanediamide) (PA6/66/612), poly(ϵ -caprolactam/hexamethylene hexanediamide/hexamethylene decanediamide/hexamethylene dodecanediamide) (PA6/66/610/612), poly(2-methylpentamethylene hexanediamide/hexamethylene hexanediamide/hexamethylene terephthalamide) (PA D6/66/6T), poly(2-methylpentamethylene hexanediamide/hexamethylene hexanediamide) (PA D6/66), poly(decamethylene decanediamide) (PA1010), poly(decamethylene dodecanediamide) (PA1012), poly(decamethylene decanediamide/decamethylene terephthalamide) (PA1010/10T) poly(decamethylene decanediamide/dodecamethylene decanediamide/decamethylene terephthalamide/dodecamethylene terephthalamide) (PA1010/1210/10T/12T), poly(11-aminoundecanamide) (PA11), poly(11-aminoundecanamide/tetramethylene terephthalamide) (PA11/4T), poly(11-aminoundecanamide/hexamethylene terephthalamide) (PA11/6T), poly(11-aminoundecanamide/decamethylene terephthalamide) (PA11/10T), poly(11-aminoundecanamide/dodecamethylene terephthalamide) (PA11/12T), poly(12-aminododecanamide) (PA12), poly(12-aminododecanamide/tetramethylene terephthalamide) (PA12/4T), poly(12-aminododecanamide/hexamethylene terephthalamide) (PA12/6T), poly(12-aminododecanamide/decamethylene terephthalamide) (PA12/10T) poly(dodecamethylene dodecanediamide) (PA1212), and poly(dodecamethylene dodecanediamide/dodecamethylene dodecanediamide/dodecamethylene terephthalamide)) (PA1212/12T);

Group (II) polyamides having said melting point of at least 210° C., comprising an aliphatic polyamide selected from the group consisting of poly(tetramethylene hexanediamide) (PA46), poly(ϵ -caprolactam) (PA 6), poly(hexamethylene hexanediamide/(ϵ -caprolactam/)) (PA 66/6) poly(hexamethylene hexanediamide) (PA 66), poly(hexamethylene hexanediamide/hexamethylene decanediamide) (PA66/610), poly(hexamethylene hexanediamide/hexamethylene dodecanediamide) (PA66/612), poly(hexamethylene hexanediamide/decamethylene decanediamide) (PA66/1010), poly(hexamethylene decanediamide) (PA612), poly(hexamethylene tetradecanediamide) (PA614), poly(hexamethylene hexadecanediamide) (PA616), and poly(tetramethylene hexanediamide/2-methylpentamethylene hexanediamide) (PA46/D6);

Group (III) polyamides having said melting point of at least 210° C., comprising

(aa) about 20 to about 35 mole percent semiaromatic repeat units derived from monomers selected from one or more of the group consisting of:

(i) aromatic dicarboxylic acids having 8 to 20 carbon atoms and aliphatic diamines having 4 to 20 carbon atoms; and

(bb) about 65 to about 80 mole percent aliphatic repeat units derived from monomers selected from one or more of the group consisting of:

(ii) an aliphatic dicarboxylic acid having 6 to 20 carbon atoms and said aliphatic diamine having 4 to 20 carbon atoms; and

(iii) a lactam and/or aminocarboxylic acid having 4 to 20 carbon atoms; and

(iv) mixtures thereof;

Group (IV) polyamides comprising

(cc) about 50 to about 95 mole percent semiaromatic repeat units derived from monomers selected from one or more of the group consisting of:

(j) aromatic dicarboxylic acids having 8 to 20 carbon atoms and aliphatic diamines having 4 to 20 carbon atoms; and

(dd) about 5 to about 50 mole percent aliphatic repeat units derived from monomers selected from one or more of the group consisting of:

(ii) an aliphatic dicarboxylic acid having 6 to 20 carbon atoms and said aliphatic diamine having 4 to 20 carbon atoms;

(iii) a lactam and/or aminocarboxylic acid having 4 to 20 carbon atoms; and

(iv) mixtures thereof;

Group (V) polyamides having said melting point of at least 260° C., comprising

(ee) greater than 95 mole percent semiaromatic repeat units derived from monomers selected from one or more of the group consisting of:

(j) aromatic dicarboxylic acids having 8 to 20 carbon atoms and aliphatic diamines having 4 to 20 carbon atoms; and

(ff) less than 5 mole percent aliphatic repeat units derived from monomers selected from one or more of the group consisting of:

(ii) an aliphatic dicarboxylic acid having 6 to 20 carbon atoms and said aliphatic diamine having 4 to 20 carbon atoms;

(iii) a lactam and/or aminocarboxylic acid having 4 to 20 carbon atoms; and

(iv) mixtures thereof; and

Group (VI) polyamides having no melting point selected from the group consisting of poly(hexamethylene isophthalamide/hexamethylene terephthalamide) (6I/6T) and poly(hexamethylene isophthalamide/hexamethylene terephthalamide/hexamethylene hexanediamide) (6I/6T/66).

3. The molded or extruded thermoplastic article of claim 2 wherein said polyamide resin comprises a blend of two or more polyamides selected from the group consisting of Group (I) and Group (II) Polyamides; Group (I) and Group (III) Polyamide, Group (I) and Group (VI) Polyamides, Group (II) and Group (III) Polyamides, Group (II) and Group (IV) Polyamides, Group (II) and Group (V) Polyamides, Group (II) and Group (VI) Polyamides, Group (III) and Group (VI) Polyamides, and Group (IV) and Group (V) Polyamides.

4. The molded or extruded thermoplastic article of claim 2 wherein said polyamide resin comprises a blend of Group (II) and (V) Polyamides.

5. The molded or extruded thermoplastic article of claim 2 wherein said polyamide resin comprises a blend of (II) and Group (III) Polyamides.

6. The molded or extruded thermoplastic article of claim 1 wherein the thermoplastic material is a polyester selected from the group consisting of poly(ethylene terephthalate), poly(trimethylene terephthalate), poly(1,4-butylene terephthalate), poly(ethylene 2,6-naphthoate), and poly(1,4-cyclohexyldimethylene terephthalate), and copolymers and blends of the same.

7. The molded or extruded thermoplastic article of claim 1 wherein the polyhydric alcohol is selected from the group consisting of pentaerythritol, dipentaerythritol, tripentaerythritol, di-trimethylolpropane, D-mannitol, D-sorbitol and xylytol.

8. The molded or extruded thermoplastic article of claim 1 wherein said thermoplastic resin is a polyamide and said thermoplastic composition comprises less than 25 ppm copper as determined with atomic absorption spectroscopy.

9. The molded or extruded thermoplastic article of claim 1 selected from the group consisting of charge air coolers; cylinder head covers; oil pans; engine cooling systems, thermostat and heater housings, coolant pumps, mufflers, housings for catalytic converters; air intake manifolds; and timing chain belt front covers.

10. A molded or extruded thermoplastic article comprising a thermoplastic polyamide comprising

- (a) a polyamide resin;
- (b) 0.25 to 15 weight percent of one or more polyhydric alcohols having more than two hydroxyl groups and a having a number average molecular weight (M_n) of less than 2000;
- (c) 10 to about 60 weight percent of one or more reinforcement agents; and
- (d) 0 to 50 weight percent of a polymeric toughener comprising a reactive functional group and/or a metal salt of a carboxylic acid;

wherein all weight percentages are based on the total weight of the thermoplastic composition and wherein 4 mm test bars prepared from said thermoplastic composition, and exposed at a test temperature at 210° C. for a test period of 500 hours, in an atmosphere of air, and tested according to ISO 527-2/1A, have, on average, a retention of tensile strength of at least 70 percent, as compared with that of an unexposed control of identical composition and shape.

11. The molded or extruded thermoplastic article of claim 10 wherein said thermoplastic resin is a polyamide resin comprising one or more polyamides independently selected from the group consisting of

Group (II) polyamides having a melting point of at least 210° C., and comprising an aliphatic polyamide selected from the group consisting of poly(tetramethylene hexanediamide) (PA46), poly(ϵ -caprolactam) (PA 6), poly(hexamethylene hexanediamide/ ϵ -caprolactam/) (PA 66/6) poly(hexamethylene hexanediamide) (PA 66), poly(hexamethylene hexanediamide/hexamethylene decanediamide) (PA66/610), poly(hexamethylene hexanediamide/hexamethylene dodecanediamide) (PA66/612), poly(hexamethylene hexanediamide/decamethylene decanediamide) (PA66/1010), poly(hexamethylene decanediamide) (PA610), poly(hexamethylene dode-

canediamide) (PA612), poly(hexamethylene tetradecanediamide) (PA614), poly(hexamethylene hexadecanediamide) (PA616), and poly(tetramethylene hexanediamide/2-methylpentamethylene hexanediamide) (PA46/D6);

Group (III) polyamides having a melting point of at least 210° C., and comprising

(aa) about 20 to about 35 mole percent semiaromatic repeat units derived from monomers selected from one or more of the group consisting of:

(i) aromatic dicarboxylic acids having 8 to 20 carbon atoms and aliphatic diamines having 4 to 20 carbon atoms; and

(bb) about 65 to about 80 mole percent aliphatic repeat units derived from monomers selected from one or more of the group consisting of:

(ii) an aliphatic dicarboxylic acid having 6 to 20 carbon atoms and said aliphatic diamine having 4 to 20 carbon atoms; and

(iii) a lactam and/or aminocarboxylic acid having 4 to 20 carbon atoms;

Group (IV) polyamides comprising

(cc) about 50 to about 95 mole percent semiaromatic repeat units derived from monomers selected from one or more of the group consisting of:

(i) aromatic dicarboxylic acids having 8 to 20 carbon atoms and aliphatic diamines having 4 to 20 carbon atoms; and

(dd) about 5 to about 50 mole percent aliphatic repeat units derived from monomers selected from one or more of the group consisting of:

(ii) an aliphatic dicarboxylic acid having 6 to 20 carbon atoms and said aliphatic diamine having 4 to 20 carbon atoms;

(iii) a lactam and/or aminocarboxylic acid having 4 to 20 carbon atoms; and

(iv) mixtures thereof;

Group (V) polyamides having a melting point of at least 260° C., and comprising

(ee) greater than 95 mole percent semiaromatic repeat units derived from monomers selected from one or more of the group consisting of:

(i) aromatic dicarboxylic acids having 8 to 20 carbon atoms and aliphatic diamines having 4 to 20 carbon atoms; and

(ff) less than 5 mole percent aliphatic repeat units derived from monomers selected from one or more of the group consisting of:

(ii) an aliphatic dicarboxylic acid having 6 to 20 carbon atoms and said aliphatic diamine having 4 to 20 carbon atoms;

(iii) a lactam and/or aminocarboxylic acid having 4 to 20 carbon atoms; and

Group (VI) polyamides having no melting point, and selected from the group consisting of poly(hexamethylene isophthalamide/hexamethylene terephthalamide) (6I/6T) and poly(hexamethylene isophthalamide/hexamethylene terephthalamide/hexamethylene hexanediamide) (6I/6T/66).

12. The molded or extruded thermoplastic article of claim 11 wherein said polyamide resin comprises a blend of two or more polyamides selected from the group consisting of Group (II) and Group (III) Polyamides, Group (II) and Group (IV) Polyamides, Group (II) and Group (V) Polyamides,

Group (II) and Group (VI) Polyamides, Group (III) and Group (VI) Polyamides, and Group (IV) and Group (V) Polyamides.

13. The molded or extruded thermoplastic article of claim **10** wherein the polyhydric alcohol is selected from the group consisting of pentaerythritol, dipentaerythritol, tripentaerythritol, di-trimethylolpropane, D-mannitol, D-sorbitol and xylytol.

14. The molded or extruded thermoplastic article of claim **10** wherein said thermoplastic resin is a polyamide and said

thermoplastic composition comprises less than 25 ppm copper as determined with atomic absorption spectroscopy.

15. The molded or extruded thermoplastic article of claim **10** selected from the group consisting of charge air coolers; cylinder head covers; oil pans; engine cooling systems, thermostat and heater housings, coolant pumps, mufflers, housings for catalytic converters; air intake manifolds; and timing chain belt front covers.

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